Metalation-induced Micelle Formation of a Block Copolymer in Non-selective Solvent

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Abstract. Metalation-induced micelle formation of polystyrene-block-poly[4-(2-aminoethyl amino)styrene] (PS-\(b\)-PDAES) with Cu\(^{2+}\) in THF, which is a good solvent for both PS and PDAES blocks, was investigated. The PS-\(b\)-PDAES makes dissolution of CuCl\(_2\) into THF up to \(1.0 \times 10^{-4}\) mol/L (ca. 1/50 molar against diamine unit of PDAES) possible. Small-angle X-ray scattering measurements for THF solution of PS-\(b\)-PDAES with Cu\(^{2+}\) showed PS-\(b\)-PDAES forms spherical particle with 30 nm of core diameter, although PS-\(b\)-PDAES in THF without Cu\(^{2+}\) forms a Gaussian coil with 2.8 nm of the radius of gyration. Therefore, it was concluded that the micellar aggregation of PS-\(b\)-PDAES in THF by adding Cu\(^{2+}\) was induced by metalation of diamine units of PDAES and Cu\(^{2+}\).

1. Introduction

Block copolymers composed of dissimilar blocks can form polymeric micelles with core-shell architecture in a selective solvent [1]. The formation of polymeric micelles is based on van der Walls interactions among the solventphobic blocks in block copolymers. Hence, the cores of polymeric micelles are mainly composed of solventphobic blocks in the block copolymers. The solventphobicity of selective blocks in block copolymers can be induced by external stimuli, such as pH, temperature, and pressure [2-4].

It has been well known that strong and multiple interactions, such as hydrogen bonding, electrostatic attractive interaction, and metalation with metal ion, between a polymer and the other moieties cause drastic changes in solubility of the polymer for a solvent [5-7]. Therefore, introducing such a strong interaction into one block of block copolymers should induce micelle formation of the block copolymers even in a good solvent for all blocks [8].

It has been well known that diamine derivatives can form complex with heavy metal ions, such as Cu\(^{2+}\) [9,10]. Therefore, solubility of a polymer having diamine groups for a good solvent should be drastically changed by metalation with Cu\(^{2+}\) ions. Consequently, a block copolymer containing the diamine groups in one block should form polymeric micelle having the solventphobic core composed of complex of the polymer having diamine units and Cu\(^{2+}\) via metalation between diamine units and Cu\(^{2+}\) ions in a good solvent for all block of the block copolymer under consideration. Thus, in this study, we investigated metalation-induced micelle formation of the block copolymer composed of polystyrene (PS) and poly[4-(2aminoethylamino)styrene] (PDAES) chelating with Cu\(^{2+}\) in tetrahydrofuran (THF), which is a good solvent for both PS and PDAES.
2. Experimental section

2.1. Synthesis of PS-b-PDAES and Preparation of Solution

The 4-(2-aminoethyl amino)styrene (DAES) is synthesized by reaction between p-chloromethyl styrene and 1,2-diamino ethane. The PS-b-PDAES was synthesized by sequential nitroxide-mediated radical polymerization (NMRP) technique using TEMPO as a stable radical. First of all, PS was synthesized by NMRP of styrene at 125 °C under N₂ atmosphere. Using the resulting PS (M_n = 4.8 x 10³, M_w = 5.0 x 10³ determined by GPC calibrated by the standard PS) as a macroinitiator, DAES was polymerized under same condition. Fig. 1 shows the structure and molecular weight of the resulting PS-b-PDAES. The M_n and M_w of PS-b-PDAES were determined by GPC calibrated by standard PS and ¹H-NMR.

The resulting PS-b-PDAES was dissolved in THF at 2.0 mg/mL (5.2 x 10⁻³ mol/L of diamine unit). For the THF solution, desired amount of CuCl₂ was added and dispersed with ultrasonicator.

2.2. Measurements

For THF solutions of PS-b-PDAES containing Cu²⁺, dynamic light scattering (DLS), UV-Vis spectra, and small-angle X-ray scattering (SAXS) measurements were performed. DLS measurements were performed at 25 °C at 90° scattering angle with He-Ne gas laser (633 nm) using an Otuka Electronics DLS-7000 photometer. UV-Vis absorption measurements were performed using a JASCO D-10 photometer. UV-Vis spectra, and small-angle X-ray scattering (SAXS) measurements were performed. DLS measurements were performed at 25 °C at 90° scattering angle with He-Ne gas laser (633 nm) using an Otuka Electronics DLS-7000 photometer. UV-Vis absorption measurements were performed using a JASCO UV-2000 spectrophotometer. For THF solutions of PS-b-PDAES containing Cu²⁺, the absorbance of visible light was measured after filtration. Absorbance is linearly increasing with increasing Cu²⁺ up to 1.0 x 10⁻⁴ mol/L for 2.0 mg/mL THF solution of PS-b-PDAES (5.2 x 10⁻³ mol/L of diamine unit). Therefore the saturation concentration of Cu²⁺ in

Fig. 2. Plot of absorbance of visible light at 615 nm against added amount of Cu²⁺ for THF solution of PS-b-PDAES at 2.0 ml/mL.

3. Results and discussion

Fig. 2 shows plot of absorbance at 615 nm for PS-b-PDAES solutions against added Cu²⁺. When Cu²⁺ was added larger than 1.0 x 10⁻³ mol/L for the 2.0 ml/mL THF solution of PS-b-PDAES, CuCl₂ was not perfectly dispersed in the solution. Therefore, for the solution with [Cu²⁺]>1.0 mol/L, UV-Vis spectra were measured after filtration. Absorbance is linearly increasing with increasing Cu²⁺ up to 1.0 x 10⁻⁴ mol/L for 2.0 mg/mL THF solution of PS-b-PDAES (5.2 x 10⁻³ mol/L of diamine unit). Therefore the saturation concentration of Cu²⁺ in
THF containing 2.0 mg/mL of PS-b-PDAES is estimated as $1.0 \times 10^{-4}$ mol/L although Cu$^{2+}$ is scarcely dissolved in THF without PS-b-PDAES. This result indicates that the dissolution of Cu$^{2+}$ into THF solution is induced by metalation between diamine-unit of PDAES and Cu$^{2+}$. Consequently, it should be expected that micelle formation of PS-b-PDAES is induced by the metalation in THF solution. To confirm the micelle formation of PS-b-PDAES in THF, SAXS measurements are carried out.

Fig. 3 shows SAXS profiles from THF solutions of PS-b-PDAES at 2.0 mg/mL containing $1.0 \times 10^{-4}$ mol/L of Cu$^{2+}$. $I(q)$ of PS-b-PDAES/Cu$^{2+}$ shows $q^{-4}$ dependence, although that of $I(q)$ of PS-b-PDAES without shows $q^{-2}$ dependence. The $q^{-4}$ and $q^{-2}$ dependences of $I(q)$ characterize the scattering from sharp interface (Porod’s law) and Gaussian coil, respectively. Therefore, PS-b-PDAES in THF without Cu$^{2+}$ behaves like a homopolymer in a good solvent. The SAXS profile of PS-b-PDAES in THF without Cu$^{2+}$ is well fitted with the scattering profile calculated for Gaussian coil of 2.8 nm radius of gyration ($R_g$). On the other hand, the SAXS profile of PS-b-PDAES in THF containing Cu$^{2+}$ shows good agreement with theoretical scattering curve calculated for solid sphere with 15.0 nm radius ($R$) using the following equation.

$$I(q) \propto \left[\frac{3\{\sin(qR) - qR\cos(qR)\}}{(qR)^3}\right]^2 \tag{1}$$

Taking into account the polydispersity as a Gaussian distribution and using standard deviation $\sigma=4 (\sigma R=0.27)$, the fitting analyses have been successfully done. In this case, the polymeric micelle should form core-shell structure having solventphobic core composed of complex of PDAES with Cu$^{2+}$ and shell of the mixture of PS and THF. When the polymeric micelle takes core-shell structure, the SAXS profile of the micelle should be expressed by the profile calculated for the core-shell model given by the following equation [13].

$$I(q) \propto \left[(\rho_c - \rho_s)v_i f_i(q) + (\rho_p - \rho_s)v_i f_i(q)\right]^2$$

$$f_i(q) = \left[\frac{3\{\sin(qR_i) - qR_i\cos(qR_i)\}}{(qR_i)^3}\right] \tag{2}$$
Here, $R_c$ and $R_s$ are radii of core and overall micelle; $\rho_c$, $\rho_s$, and $\rho_0$ are electron densities of core, shell, and solvent, respectively. In this case, $\rho_c - \rho_s$ should be much higher than $\rho_s - \rho_0$. Therefore, the second term of equation (2) can be ignored. Thus, it is considered that the SAXS profile from PS-$b$-PDAES/Cu$^{2+}$ shows good agreement with the theoretical scattering profile calculated for simple hard sphere model. Consequently, the PS-$b$-PDAES/Cu$^{2+}$ micelle should have the solventphobic PDAES/Cu$^{2+}$ core with 15 nm radius. According to dynamic light scattering measurements, radius of overall PS-$b$-PDAES/Cu$^{2+}$ micelle is estimated to 26 nm. Using these results, we can derive the conclusion schematically represented in Fig. 4 for mechanism of formation of PS-$b$-PDAES micelle in THF solution by metalation of diamine units of PDAES with Cu$^{2+}$.

![Schematic representation of mechanism of micelle formation of PS-b-PDAES with Cu$^{2+}$ in THF solution.](image)

**Fig. 4.** Schematic representation of mechanism of micelle formation of PS-$b$-PDAES with Cu$^{2+}$ in THF solution.

4. Acknowledgement

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