Anomalous Small-angle X-ray Scattering Study on Aggregation of a Block Copolymer in a Selective Solvent

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Abstract. Anomalous small-angle X-ray Scattering (ASAXS) analysis for poly(4-vinylphenol)-b-poly(4-bromostyrene) (PVPh-b-PBrS) in N,N',N'-tetramethyl ethylenediamine (TMEDA) solution was examined. The ASAXS measurements, executed at three different energies, provided the separation of the scattering of the Br atoms from whole system. The energy-dependent term in the SAXS profile, which is corresponding to the form factor of PBrS domain, sufficiently agree with the SAXS profile calculated for hard sphere with 41 nm radius. Therefore, the PBrS chains assemble into spherical core with 41 nm radius in TMEDA solution.

1. Introduction

Anomalous small-angle X-ray scattering (ASAXS) using absorption edge of a specific element is expected to be a powerful tool for analysis of internal structure of multiphase system because ASAXS reveals the localization of atoms or molecules in a surrounding media [1-4]. The basis of the ASAXS method is the energy-dependence of the scattering factors of the atoms, which show a remarkable change with the energy of incident X-ray in the vicinity of the absorption edge of the targeted atom [5]. Up to now, ASAXS has mainly been applied to inorganic or metallic materials because the absorption edges of the elements contained in these materials could easily be reached. On the other hand, ASAXS has hardly been used for polymer systems. For polymer systems, ASAXS using K-edge of bromine is expected to be useful because sufficient amount of Br atoms as ASAXS probe can be easily introduced into organic molecules through C-Br covalent bond and the range of energy of incident X-ray requested in ASAXS measurements near Br K-edge is available in general synchrotron light source [6]. Therefore, to achieve ASAXS method using K-edge of Br for polymer systems is of great importance for detail structural analyses of polymer materials.

Thus, in this study, we try to apply ASAXS method near the K-edge of Br atom to analysis of the internal structure of block copolymer composed of poly(4-vinylphenol) (PVPh) and poly(4-bromostyrene) (PBrS) in N,N',N'-tetramethylethylenediamine (TMEDA), which is a selective solvent and cross-linking agent through hydrogen bonds for PVPh. In this system, structural analysis
for dispersed particle composed of PBrS by normal SAXS method is prevented by network of PVPh-TMEDA matrix. Therefore, ASAXS in the vicinity of K-edge of Br for this system is expected to remove the scattering from matrix and reveal the structure of PBrS domain.

2. Experimental Section

2.1. Synthesis of PVPh-b-PBrS and Preparation of Solution

Poly(4-t-butoxystyrene)-b-poly(4-bromostyrene) (PtBS-b-PBrS) diblock copolymer was synthesized by sequential nitroxide-mediated radical polymerization (NMRP) by using TEMPO and AIBN (Scheme 1). PtBS-b-PBrS was converted to poly(4-vinylstyrene)-b-poly(4-bromostyrene) (PVPh-b-PBrS) added excess of trifluoroacetyl (TFA) in THF containing excess amount of trifluoroacetic acid at room temperature. Table 1 shows molecular characteristics of PBrS and PVPh-b-PBrS. The resulting PVPh-b-PBrS was dissolved in TMEDA at 50 mg mL\(^{-1}\). Here, TMEDA is the good solvent only for PVPh and forms cross-linking network with PVPh through hydrogen bond between tertiary amino groups and PVPh [7]. In addition, in this system, PBrS forms homogeneously dispersed spherical domains.

2.2. ASAXS measurement

Anomalous Small-angle X-ray Scattering (ASAXS) measurements were carried out at BL40B2 SPring-8, Japan. A 30 cm x 30 cm imaging plate detector (Rigaku R-AXIS VII) was placed 4.0 m away from the sample position. To obtain the SAXS data with high S/N ratio, a bespoke vacuum sample chamber was used. The measured SAXS intensities were corrected to an absolute scale using the absolute scattering intensities of the water [8]. The exact position of the K-edge of Br in the PVPh-b-PBrS was determined by the measurements of X-ray transmission. The imaginary part of the anomalous scattering factor, \(f''\), is proportional to the absorption coefficient and is converted to \(f'\) through the Kramers-Kronig (K-K) transform. Figure 1 shows \(f'\) and \(f''\) for PVPh-b-PBrS in TMEDA. The measurement provided 13.384 keV of the absorption edge of Br. Thus, the ASAXS measurements were performed at 13.473, 13.433, and 13.383 keV of the incident X-ray energy.

3. Results and Discussion

The energy-dependence of SAXS intensity \(I(q,E)\) can be written in the following form:

\[
\begin{array}{c|c|c|c|c|c|c|c}
\hline
E/keV & f' & f'' \\
\hline
13.473 & -2.44 & 0.19 \\
13.483 & -0.421 & 0.189 \\
13.283 & -0.271 & 0.188 \\
\hline
\end{array}
\]
where $I(q)$ is Br contribution of the scattering amplitude, $U(q)$ is the non-resonant term of the scattering amplitude, $S(q)$ is the structure factor. In dilute concentration, $S(q)$ can be regarded as 1. In equation (1), scattered intensity can be divided into three terms, a resonant term, a non-resonant term and a cross-term, and the energy dependence of the scattered factor of bromine contains anomalous dispersion coefficients $f'(E)$ and $f''(E)$. Figure 2 shows energy-dependence of SAXS profiles of PVPh-$b$-PBrS in TMEDA. SAXS intensity is decreased with increasing the energy of incident X-ray due to the energy dependence of $f'$ of PBrS. This result suggests that ASAXS analysis can be applied to the PVPh-$b$-PBrS system. In lowest $q$-region, $I(q)$ shows strong $q$ dependence. The steep slopes in the SAXS profiles should be caused by network structure composed of PVPh and TMEDA. Therefore, they should be included in $I'(q)$ in equation (1). By using equation (1), the difference of two scattering curves, measured at two different energies, is given by the following equation:

$$
\Delta I(q, E_1, E_2) = 2[I'(q, E_1) - I'(q, E_2)]U(q)V(q) + [f'^2(E_1) - f'^2(E_2) + f''^2(E_1) - f''^2(E_2)]V^2(q)
$$

(2)

According to equation (2), $I'(q)$ and $U^2(q)$ can be removed in the $\Delta I(q, E_1, E_2)$. Figure 3 shows $\Delta I(q, E_1, E_2)$ profiles for PVPh-$b$-PBrS. In this figure, steep slopes in the lowest $q$ region is disappeared. Therefore, as mentioned above, the strong $q$ dependence in the lowest $q$ region in Figure 2 reflects the $I'(q)$ contribution in SAXS profiles. Although $I'(q)$ and $U^2(q)$ can be removed as shown in Figure 3 by equation (2), the cross-term of $U(q)$ and $V(q)$ is still remained. To analyze structure of PBrS domains, the cross-term must be removed from the SAXS profiles. The cross-term in equation (2) can be removed by further difference between $\Delta I(q, E_1, E_2)$ and $\Delta I(q, E_1, E_3)$ as the following equation.

$$
V^2(q) = \frac{1}{K} \left[ \frac{\Delta I(q, E_1, E_3)}{f'(q, E_1) - f'(q, E_2)} - \frac{\Delta I(q, E_1, E_3)}{f'(q, E_1) - f'(q, E_3)} \right]
$$

(3)
\[ K = f'(q, E_2) - f'(q, E_1) + \frac{f''(q, E_1) - f''(q, E_2)}{f'(q, E_1) - f'(q, E_2)} - \frac{f''(q, E_1) - f''(q, E_3)}{f'(q, E_1) - f'(q, E_3)} \] (4)

Figure 4 shows the \( V^2(q) \) obtained from \( \Delta I(q, E_1, E_2) \) and \( \Delta I(q, E_1, E_3) \) by using equations (3) and (4). As mentioned above, the \( V^2(q) \) is corresponding to the form factor of PBrS domain because Br atoms are included only in PBrS domains. In \( q > 0.3 \text{ nm}^{-1} \), \( I(q) \) shows \( q^{-4} \) dependence, that means the PBrS domains have sharp interfaces. The \( V^2(q) \) can be fitted with the form factor calculated for the hard sphere with 41 nm radius given in the following equation.

\[ P(q) = \left[ \frac{3\sin(qR) - qR\cos(qR)}{(qR)^3} \right]^2 \] (5)

where \( R \) is radius of the spherical particle. Therefore, PBrS domains form spherical shape with 41 nm radius and with sharp interface against matrix. In addition, we can clearly observe bump around \( q = 0.5 \text{ nm}^{-1} \). Using the core-shell model with 41 nm micelle radius and 8.5 nm core radius. In this model, electron density of shell is lower than that of core. This result should be caused by slight dissolution of TMEDA or PVPh in the outer layer of PBrS core.

4. Conclusion

ASAXS measurements near the K edge of Br for PVPh-\( b \)-PBrS in TMEDA reveal that PBrS domains form core-shell sphere (\( R=41 \) nm) with sharp interface in the cross-linked network of PVPh and TMEDA. Therefore, PVPh or TMEDA should partially dissolve in the outer layer of PBrS core. Thus, ASAXS analysis makes detail analysis of morphology of dispersed phase and inside of dispersed domains in a multiphase polymer system possible.

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