

Lower Critical Solution Temperature Behavior of Aqueous Polymer Solution Observed by Soft X-ray Absorption Spectroscopy

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1 Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) is a stimuli-responsive polymer that is sensitive to various chemical environments, especially in temperature dependence. It is well known that the aqueous PNIPAM solution shows a lower critical solution temperature behavior, where it is dissolvable in solutions at low temperatures and is insoluble at high temperatures [1]. In this study, the molecular interactions of the C=O group in PNIPAM with solvent H₂O molecules at the low temperature regions were investigated using oxygen K-edge X-ray absorption spectroscopy (XAS) for discussing the mechanism of the lower critical solution temperature behavior of aqueous PNIPAM solutions.

2 Experiment

The XAS experiments were performed at the soft X-ray beamline BL-13A. The O K-edge XAS spectra of aqueous PNIPAM solutions were measured using a transmission-type liquid cell, whose details were described previously [2, 3]. The liquid cell consists of two Si₃N₄ membranes with the thickness of 100 nm, and the thickness of the liquid layer was precisely controlled from 20 nm to 40 μm for obtaining the appropriate absorbance of soft X-rays. The XAS spectra were obtained using the Beer-Lambert law, $\ln(I_0/I)$, where I_0 and I are the transmission signals of the bare Si₃N₄ membranes and the liquid samples confined by the Si₃N₄ membranes, respectively. Temperature is controlled using a chiller system and is precisely measured using a Pt100 resistance temperature detector, which is directly connected to the liquid cell.

3 Results and Discussion

In the O K-edge XAS spectra, the C=O π* peaks (532 eV) in PNIPAM polymers can be observed in aqueous solutions by separating from solvent H₂O molecules, whose first peaks are around 535 eV [4]. Figure 1 shows O K-edge XAS spectra of aqueous PNIPAM solutions at different temperatures. Note that the measurement temperature from 25.8 to 30.5 °C is the low temperature region, where PNIPAM is dissolved in aqueous solutions. The C=O π* peaks of PNIPAM polymers were observed around 532 eV. The pre-edge peaks of liquid H₂O were

observed around 535 eV. The C=O π* peaks of PNIPAM consist of two spectral contributions. By increasing the liquid temperature, the intensities of the C=O π* peaks at the low energy sides are increased, resulting the lower energy shifts of the C=O π* peaks of PNIPAM. The pre-edge peaks of liquid H₂O show lower energy shifts by increasing the liquid temperature.

The energy shifts of the C=O π* peaks of PNIPAM reflect the molecular interactions of the C=O group of PNIPAM with solvent H₂O molecules. The energy shifts of the pre-edge peaks of liquid H₂O reflect the hydrogen bonds between H₂O molecules. Thus, the precise analyses of these energy shifts would be useful for discussing the mechanism of the lower critical solution temperature behavior of aqueous PNIPAM solutions. In the present status, the molecular dynamics simulations and inner-shell calculations are performed for relating the energy shifts of the XAS peaks with the molecular interactions in aqueous PNIPAM solutions at different temperatures.

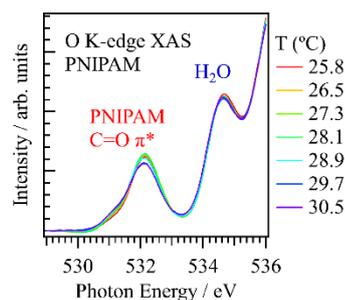


Fig. 1: O K-edge XAS spectra of aqueous PNIPAM solution at different temperatures.

References

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