Polymer Cononsolvency Explored using Soft X-Ray Absorption Spectroscopy

The cononsolvency mechanism of poly(*N*-isopropylacrylamide) (PNIPAM), dissolving in pure methanol and water but being insoluble in aqueous methanol solutions, was investigated from the molecular interactions of the C=O groups in PNIPAM with solvent molecules using oxygen K-edge X-ray absorption spectroscopy. The inner-shell spectra of PNIPAM in solutions were calculated using snapshots from the molecular dynamics simulations and evaluated the energy shifts of the C=O π* peaks of PNIPAM. These results proposed that the cononsolvency emerges from the aggregation of PNIPAM owing to the hydrophobic interactions with methanol clusters in solutions, leading to the collapse of the hydrophobic hydration of PNIPAM.

Poly(*N*-isopropylacrylamide) (PNIPAM) is a stimuli-responsive polymer that is sensitive to various chemical environments. PNIPAM is dissolved in pure methanol (MeOH) and H_2O at 25°C but is insoluble in MeOH-H_2O mixtures at the same temperature, which is known as cononsolvency [1]. Understanding the cononsolvency mechanism is important for comprehending the phase transition dynamics of biomolecules, including protein folding, DNA packing, and interchain complexation. In this study, the cononsolvency mechanism of PNIPAM in aqueous MeOH solutions were investigated from the molecular interactions of the C=O groups in PNIPAM with solvent MeOH and H_2O molecules using the energy shifts of the C=O π* peaks of PNIPAM in the O K-edge X-ray absorption spectroscopy (XAS) [2].

The experiments were performed at soft X-ray beamline BL-7A. The XAS spectra were measured using a transmission-type liquid cell, whose details were described previously [3, 4]. The liquid cell was placed at an ambient pressure condition of helium gas, which was separated using a small Si_3N_4 membrane from the beamline under an ultrahigh vacuum condition. In the liquid cell, a liquid layer was sandwiched between two Si_3N_4 membranes and the thickness of the liquid layer was precisely controlled from 20 nm to 40 μm by adjusting the helium pressure for obtaining appropriate absorbance of soft X-rays. Liquid samples were introduced to the liquid cell using a syringe pump. The XAS spectra were obtained using the Beer-Lambert law, $\ln(I_0/I)$, where I_0 and I were the transmission signals of the bare Si_3N_4 membranes and liquid samples confined by the Si_3N_4 membranes, respectively.

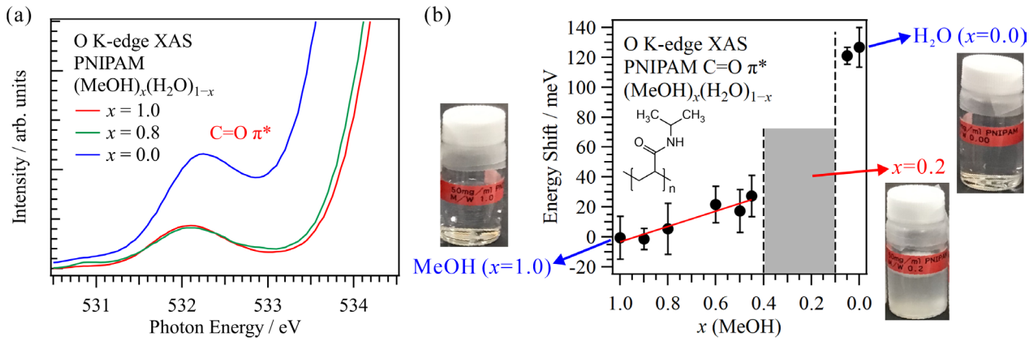

Figure 1: (a) O K-edge XAS spectra of PNIPAM in $(MeOH)_x(H_2O)_{1-x}$ solutions. **(b)** Energy shift of the C=O π* peak in PNIPAM as a function of MeOH molar fraction from pure MeOH. The middle concentration region denotes cononsolvency, where PNIPAM is insoluble at x = 0.2 and is dissolvable in pure MeOH (x = 1.0) and pure H_2O (x = 0.0), as shown in the photos.

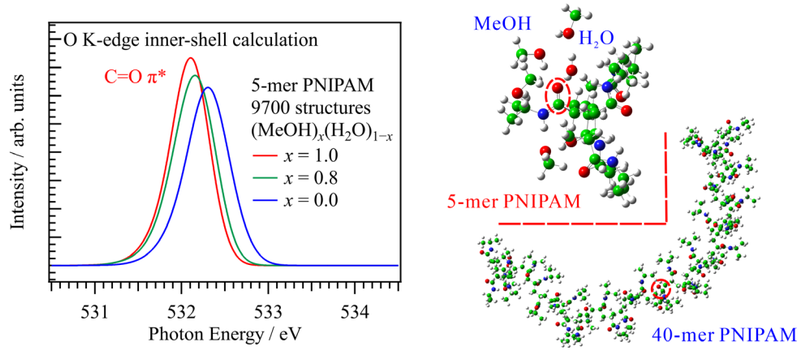

Figure 2: O K-edge inner-shell spectra of the 5-mer PNIPAM chains, including solvent MeOH and H_2O molecules, which were extracted from the 40-mer PNIPAM chains in $(MeOH)_x(H_2O)_{1-x}$ solutions obtained by the MD simulations, as shown in the inset.

Figure 1(a) shows the O K-edge XAS spectra of PNIPAM with the concentration of 50 mg/mL in $(MeOH)_x(H_2O)_{1-x}$ solutions at 25 °C. The C=O π* peaks of PNIPAM (532 eV) were separately observed from the strong absorbance of solvent MeOH and H_2O molecules above 535 eV. **Figure 1(b)** shows the energy shift of the C=O π* peak in PNIPAM as a function of MeOH molar fraction from pure MeOH. The C=O π* peaks were not observed at 0.4 > x > 0.1, denoting the cononsolvency region. By increasing the H_2O molar fraction in the MeOH-rich region (x > 0.4), the C=O π* peaks show higher energy shifts from that of pure MeOH (x = 1.0). In contrast, in the H_2O-rich region (0.1 > x), the C=O π* peaks show notably higher energy shifts, especially the higher energy shifts by 127 meV in pure H_2O (x = 0.0). It means that the molecular interactions of PNIPAM with solvent molecules in pure H_2O are significantly different from those in pure MeOH at the microscopic scale although these dissolution behaviors are identical on the macroscopic scale.

For discussing the origin of the energy shift of the C=O π* peak in PNIPAM, the O K-edge inner-shell calculations of PNIPAM in solutions were performed [5]. Molecular structures of 40-mer PNIPAM chain with 10000 solvent MeOH and H_2O molecules were obtained using the molecular dynamics (MD) simulations. **Figure 2** shows the O K-edge inner-shell spectra of the 5-mer PNIPAM chains, including second coordination shells of solvent MeOH and H_2O molecules, which were obtained by averaging 9700 inner-shell spectra of the polymer structures extracted from the 40-mer PNIPAM chains in the snapshots from the MD simulations. The calculated energy shifts of the C=O π* peaks in PNIPAM well reproduced the XAS experiments shown in **Fig. 1** and reflected the structural changes of the polymer chains, the substitutions of the hydrogen bonds of the C=O groups in PNIPAM from MeOH to H_2O molecules, and the increase in the coordination numbers of solvent molecules with the C=O groups. These results proposed that PNIPAM in pure H_2O forms rounded structures with the hydrophobic hydration of the isopropyl group in PNIPAM, whereas PNIPAM in pure MeOH shows linear structures. The cononsolvency emerges from the aggregation of PNIPAM owing to the hydrophobic interactions with MeOH clusters in solutions, leading to the collapse of the hydrophobic hydration of PNIPAM.

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BEAMLINE

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