

# Cononsolvency of Poly(*N*-isopropylacrylamide) in Aqueous Methanol Solutions Probed by Oxygen K-Edge X-ray Absorption Spectroscopy

Masanari NAGASAKA,<sup>1,2,\*</sup> Fumitoshi KUMAKI,<sup>3</sup> Yifeng YAO,<sup>4</sup> Jun-ichi ADACHI,<sup>3,5</sup> and Kenji MOCHIZUKI<sup>4</sup>

<sup>1</sup> Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

<sup>2</sup> Molecular Science Program, Graduate Institute for Advanced Studies, SOKENDAI, Myodaiji, Okazaki 444-8585, Japan

<sup>3</sup> Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

<sup>4</sup> Department of Chemistry, Zhejiang University, Hangzhou, 310028, P. R. China

<sup>5</sup> Materials Structure Science Program, Graduate Institute for Advanced Studies, SOKENDAI, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

## 1 Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) is dissolved in pure methanol (MeOH) and H<sub>2</sub>O at 25 °C but is insoluble in MeOH-H<sub>2</sub>O mixtures at the same temperature, which is known as cononsolvency [1]. Although the cononsolvency mechanism of PNIPAM has been investigated in several experimental and theoretical studies [2, 3], this mechanism is still unknown because the molecular interactions of PNIPAM with MeOH and H<sub>2</sub>O have not been fully understood yet. In this study, we investigated the molecular interactions of the C=O group in PNIPAM with MeOH and H<sub>2</sub>O from the energy shifts of the C=O  $\pi^*$  peaks in the O K-edge X-ray absorption spectroscopy (XAS) of PNIPAM along with molecular dynamics simulations and inner-shell calculations [4].

## 2 Experiment

The XAS experiments were performed at the soft X-ray beamline BL-7A. The details of the transmission-type liquid cell for XAS has been described previously [5, 6]. The liquid cell was placed at ambient pressure conditions of helium gas, where a liquid layer was sandwiched between two Si<sub>3</sub>N<sub>4</sub> membranes with a thickness of 100 nm. The thickness of the liquid was controlled by adjusting the helium pressure around the liquid cell. 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 Si<sub>3</sub>N<sub>4</sub> membranes and liquid samples confined by the Si<sub>3</sub>N<sub>4</sub> membranes, respectively. Liquid samples were exchanged using a syringe pump.

## 3 Results and Discussion

Figure 1 shows the O K-edge XAS spectra of PNIPAM with the concentration of 50 mg/mL in aqueous MeOH solutions (MeOH)<sub>*x*</sub>(H<sub>2</sub>O)<sub>1-*x*</sub> with different molar fractions at 25 °C. The C=O  $\pi^*$  peaks of PNIPAM were observed at approximately 532 eV, and the strong absorbances of solvent MeOH and H<sub>2</sub>O were observed at the higher energy side. The C=O  $\pi^*$  peaks were not observed at  $x = 0.4$  and  $x = 0.2$  because the concentrations of PNIPAM are

below the detection limit due to the formation of PNIPAM aggregates.

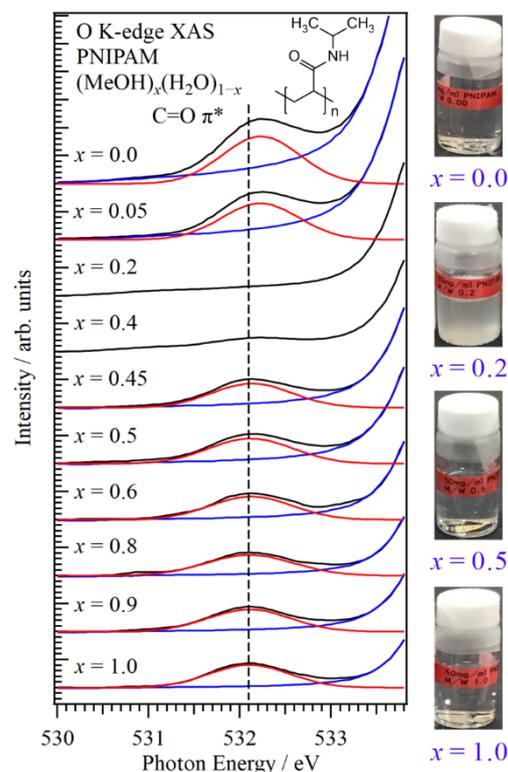


Fig. 1: O K-edge XAS spectra of PNIPAM in aqueous MeOH solutions at different molar fractions. The photos of PNIPAM in aqueous MeOH solutions are shown.

By increasing the H<sub>2</sub>O molar fraction in the MeOH-rich region ( $x > 0.4$ ), the C=O  $\pi^*$  peaks exhibited higher energy shifts compared to that of pure MeOH ( $x = 1.0$ ). The highest energy shift corresponding to the C=O  $\pi^*$  peak at  $x = 0.45$  was 27 meV. On the contrary, in the H<sub>2</sub>O-rich region ( $0.1 > x$ ), notably higher energy shifts were recorded for the C=O  $\pi^*$  peaks; specifically, the energy shift of the C=O  $\pi^*$  peak in pure H<sub>2</sub>O ( $x = 0.0$ ) was 127 meV.

The inner-shell calculations proposed that the higher energy shift of the C=O  $\pi^*$  peak in the MeOH-rich region ( $x > 0.4$ ) by increasing the H<sub>2</sub>O molar fraction was derived from the simple substitution of the HB structure of the C=O group in PNIPAM from MeOH to H<sub>2</sub>O. The extremely higher energy shift of the C=O  $\pi^*$  peak in pure H<sub>2</sub>O from pure MeOH was due to the increase of the interaction between polymer units, indicating PNIPAM in pure H<sub>2</sub>O is the rounded structure with the hydrophobic hydration of the isopropyl group in PNIPAM. Although PNIPAM is dissolved in pure MeOH and H<sub>2</sub>O, this study proposes that PNIPAM forms rounded structures in pure H<sub>2</sub>O, whereas it forms chain structures in pure MeOH. At  $0.4 > x > 0.1$ , the hydrophobic hydration of PNIPAM is interrupted by the addition of MeOH, whereas the hydrophobic interaction of PNIPAM with MeOH is enhanced. The polymer units of PNIPAM aggregated via the MeOH hydrophobic clusters, emerging the cononsolvency.

#### References

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\* nagasaka@ims.ac.jp