Molecular Mechanism Underlying the Heat-Induced Phase Separation and Crystallization of Poly(2-isopropyl-2-oxazoline) in Water

Yukiteru Katsumoto,[*,†] *Aki Tsuchiizu*,[†] *XingPing Qui*,[‡] *and Françoise Winnik*[‡]

[†]Graduate School of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526, Japan

[‡]Department of Chemistry and Faculty of Pharmacy, University of Montreal, CP 6128 Succursale Centre Ville, Montreal, QC H3C 3J7, Canada

Poly(2-isopropyl-2-oxazoline) (PiPrOx) in water shows a characteristic thermo-responsive behavior, in which precipitation and crystallization irreversibly occurs around the cloud point temperature (T_c) under a certain condition. To reveal the physical background of this phenomenon at molecular level is a challenging subject in the polymer science. We demonstrate how the vibrational spectroscopy techniques combined with molecular orbital (MO) calculations is useful for investigate the molecular origin of the irreversible process of phase separation and crystallization of PiPrOx in water. The thermally induced spectral variations suggest that the dehydration of PiPrOx gradually occurs as the temperature goes up from one phase region. On the other hand, the temporal spectral changes observed above T_c indicate that the conformational change occurs in the polymer backbone. The simultaneous changes in hydration and conformation are owing to the irreversible thermo-responsive behavior of PiPrOx.

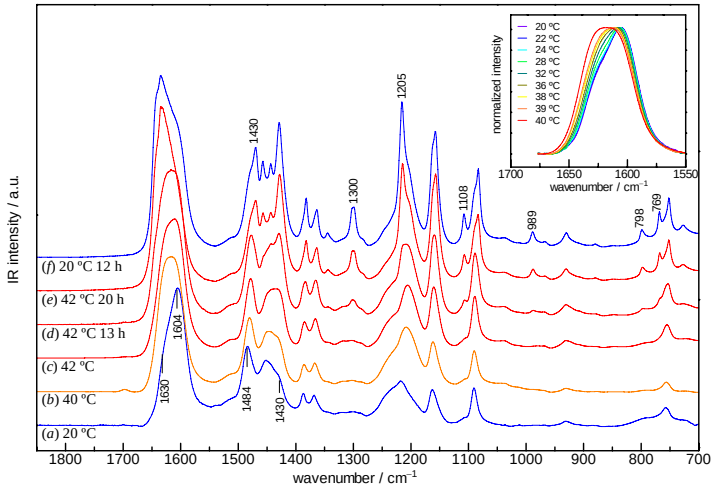

Fig. 1. Temperature and time dependence of IR spectra of PiPrOx in D_2O. The spectra after subtraction of D_2O are shown. The spectrum is measured (a) at 20 °C, (b) at 40 °C, (c) at 42 °C, (d) after incubation for 13 hours at 42 °C, (e) after incubation for 24 hours at 42 °C. The spectrum (f) is obtained from the solution recooled to 20 °C and incubated for 12 hours after the incubation at 42 °C. The inset represents the temperature dependence of the $\nu_{C=O}$ band in water after the baseline correction.