Microanalysis of a Polymer droplet by Optical Tweezers Combined Confocal Raman Microspectroscopy: Molecular Weight Dependence

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Poly(*N*-isopropylacrylamide) (PNIPAM), which is a representative thermoresponsive polymer, is homogeneously dissolved in water at room temperature. Above a lower critical solution temperature (LCST) at 32 °C, the solution exhibits a phase separation with a formation of polymer-rich domains due to dehydration and aggregation of the polymer chains (grobule). Studies on the phase separation of PNIPAM systems have a deep history. However, in spite of a huge number of data accumulated, fundamental aspects of the phase separation still remain somewhat ambiguous. Because, it has been rather difficult to analyze each micro-domains that continuously fluctuate in a solution. For addressing the issue, we recently developed a Raman microspectroscopy technique combined with laser trapping technique [1]. It enables us to produce, fix, and chemically analyze a single polymer-rich domain. In the present study, we investigated molecular weight dependence of the polymer concentration in the domain using it.

We synthesized atactic PNIPAMs with different molecular weights (*m.w.* = 64000, 95000, 180000) by free radical polymerization. PNIPAM was dissolved in ultrapure water (2.0~20 wt%). We prepared a correction curve of Raman intensity versus PNIPAM concentration and used it for the following microspectroscopy. A near-infrared (NIR) laser (λ= 1064 nm) was used for the formation and trapping of a single polymer-rich domain, and a visible laser (λ= 532 nm) was used for Raman excitation of it.

Focusing a 1064 nm laser beam into a sample solution (2.0 wt%), a single polymer-rich domain was successfully formed owing to a photothermal effect (water was heated by 1064 nm irradiation) and an optical force (Figure 1) [2]. Phase separation was induced by temperature elevation at the focal point. Simultaneously, the polymer-rich domains were assembled and trapped by an optical force at the focus. We obtained Raman spectra of the domains with varying *m.w.* Vibrational bands of C-H stretching of PNIPAM chains appeared in 2800~3050 cm^{-1},while vibrational bands of O-H stretching of H_2O appeared in 3100~3800 cm^{-1} (Figure 2). As compared with a spectrum of sample solution (before irradiation), for the spectra of the domain, C-H band intensity increased because of assembling of polymer chains, and O-H band intensity decreased because of dehydration. The relative intensity ratio of these C-H and O-H bands directly reflects the polymer concentration in the domain. Using the
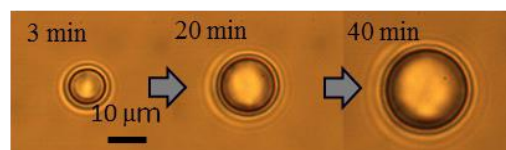

Figure 1. Time course of microscopic images of the polymer rich domain formed by optical tweezers.

correction curve, we can determine polymer concentration of the domain. Figure 3 shows the molecular weight dependence of the polymer concentration in the domain. It was ranging from 60 to 70 wt%, indicating the polymer-rich domain contains a large amount of water. The polymer concentration decreased with the increase of molecular weight. Spectral analysis of O-H band showed that the water molecules involved in the domain bound to polymer chains.

We demonstrated that the polymer concentration in the domain depended on molecular weight. This result will be useful for gaining a deeper insight into the phase separation behaviors.
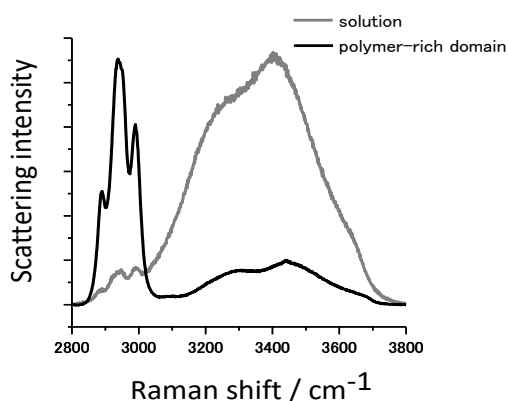

Figure 2. Raman spectra of the polymer rich domain formed by optical tweezers (black line) and that of the PNIPAM aqueous solution(gray line).
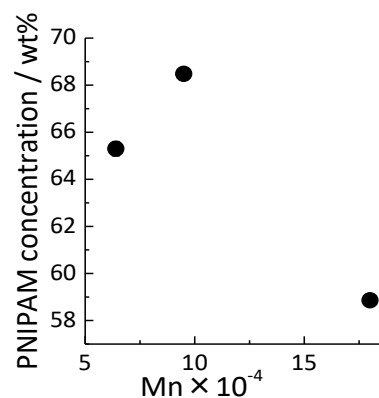

Figure 3. Molecular weight dependence of polymer concentration in the polymer rich domain.

References:

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