A Laser T-jump Study on the Phase Separation Dynamics of Poly(N-isopropylacrylamide) Copolymerized with Hydrophilic Monomer

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Poly(*N*-isopropylacrylamide) (polyNIPAM) , which is a representative thermoresponsive polymer, exhibits coil-to-globule phase transition followed by phase separation upon temperature elevation above the lower critical solution temperature (LCST). We have studied dynamics and kinetics of such phase separation behaviors of polyNIPAM using our laser temperature-jump (T-jump) technique, by which we can determine time constants of the phase separation with high accuracy.

Fig.1 Chemical structure of poly(NIPAM-*co*-DMA).

In our previous works, we reported that the phase separation dynamics of polyNIPAM depended on molecular weight, polymer concentration, and stereoregularity of the polymer chain.[1-3] In these studies, we reported that phase separation dynamics was closely related to a hydrophobic-hydrophilic balance in a polymer chain.

Here, we focused on an effect of copolymerization of NIPAM with a hydrophilic comonomer, *N,N*-dimethylacrylamide (DMA), to the phase separation dynamics. Although DMA has an analogous chemical structure to NIPAM, it has a more hydrophilic character than NIPAM. The purpose of this study is to clarify the effect of the hydrophilic comonomer on the phase separation dynamics.

We synthesized poly (NIPAM-*co*-DMA) (Fig.1) with DMA molar fraction (x_{DMA}) of 0 to 0.26 by free radical copolymerization. For T-jump technique, an aqueous solution of each copolymer (0.20 ~ 10 wt %) was irradiated with a single shot nanosecond pulsed-laser light (λ = 1200 nm, fwhm = 10 ns) to induce the phase separation. A CW laser beam (λ = 532 nm) was co-axially introduced to the sample cell as a probe light. An transient increase in turbidity due to phase separation of the solution was detected as a temporal decay in optical transmittance ($T(t)$) of the probe right. This is the outline of our nanosecond-laser T-jump technique.

Fig. 2 shows $T(t)$ decay curves obtained by the laser T-jump technique. $T(t)$ decays immediately after the start of T-jump. Each decay curve can be well fitted with a single exponential function (eq. (1)).

$$T(t) = A exp\left(-\frac{t}{\tau}\right) + B \qquad (1)$$

Based on these, we can determined the time constant (τ) of the phase separation.

Fig. 3 shows x_{DMA} dependences of both LCST and τ for a sample solution (4.0 wt%). LCST increased from 33 ℃ to 40 ℃ with an increase in x_{DMA}. As expected, the hydrophilicity of the polymer chain should inclease by copolymerization, and hence LCST becomes higher. On the other hand, the time constant, τ decreased from 105 ms to 20 ms with an increase in x_{DMA}, meaning that the phase separation became faster with x_{DMA}.
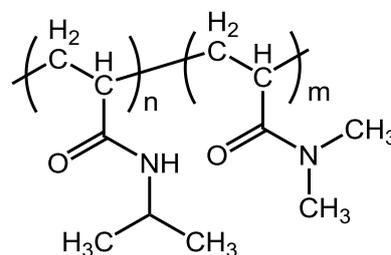
Next, using a technique of dynamic light scattering (DLS), we measured average particle size (d_{ave}) of polymer-rich domains that were formed after the phase separation. d_{ave} of polyNIPAM (homopolymer) and the copolymer was 2 and 6 µm, respectively. This result suggested that intermolecular interactions among chains of copolymer became strong to promote the aggregation of the globules. The strong intermolecular interaction between copolymers would accelerate phase separation process.

We concluded that phase separation behaviors of aqueous PNIPAM solution were considerably accelerated by copolymerization with DMA. It is a new approach to control the phase separation dynamics.
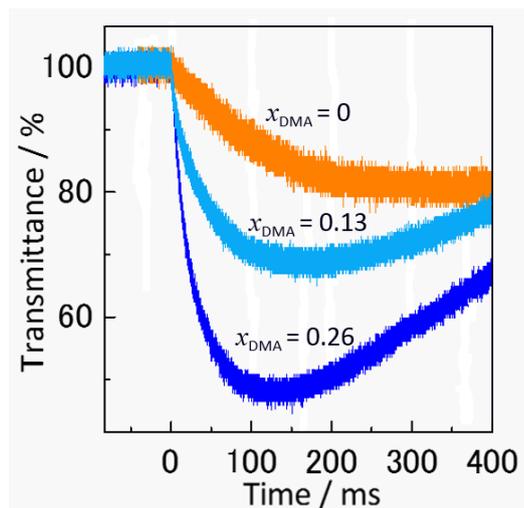

Fig. 2 Transient decay curves of optical transmittance ($T(t)$) obtained by the laser T-jump, in sample solutions (4.0 wt%)
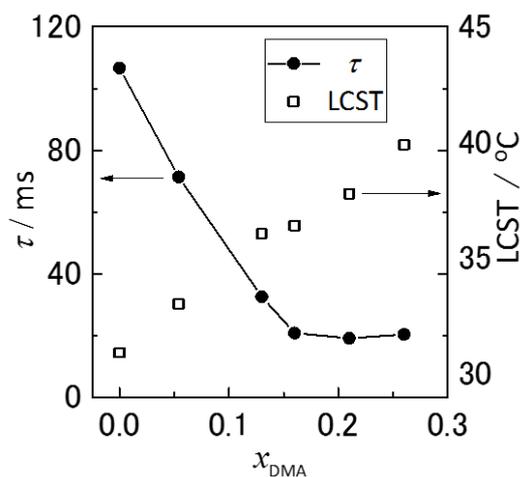

Fig. 3 DMA molar fraction (x_{DMA}) dependences of the phase separation time constant (τ) and LCST in sample solutions (4.0 wt%)

References:

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