Kinetic Study for Thermally-Induced Phase Separation of Stereo-Controlled Poly(*N*,*N*-diethylacrylamide) by Means of Transient Photometry Technique

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Poly(*N*-isopropylacrylamide) (PNIPAM), which is a representative thermoresponsive polymer, undergoes phase separation in water upon heating above a critical temperature (T_c) (Figure 1a). Since the first observation of thermoresponse for PNIPAM, such unique behavior has attracted broad interests from basic researches to applications such as sensors, actuators, and drug delivery systems. For such applications, it is important to control the temporal response of the phase separation process. We have systematically investigated kinetics and dynamics of phase separation for PNIPAM in terms of polymer concentration, molecular weight, and stereoregularity using a laser temperature-jump (T-jump) technique combined with transient photometry [1-3].

In the present study, we focused on poly(*N*,*N*-diethylacrylamide) (PDEA), whose aqueous solution shows analogous phase separation behavior to PNIPAM. In spite of the analogous chemical structure and similar T_c to PNIPAM (Figure 1b), several static properties of PNIPAM and PDEA are different to each other. For instance, the critical temperature for PDEA becomes higher with increasing the meso-diad ratio, although that for PNIPAM becomes lower. This suggests that the stereoregularity is a key factor to control the phase separation behavior. The aim of this study is to control the phase separation rate for PDEA in terms of the stereoregularity.
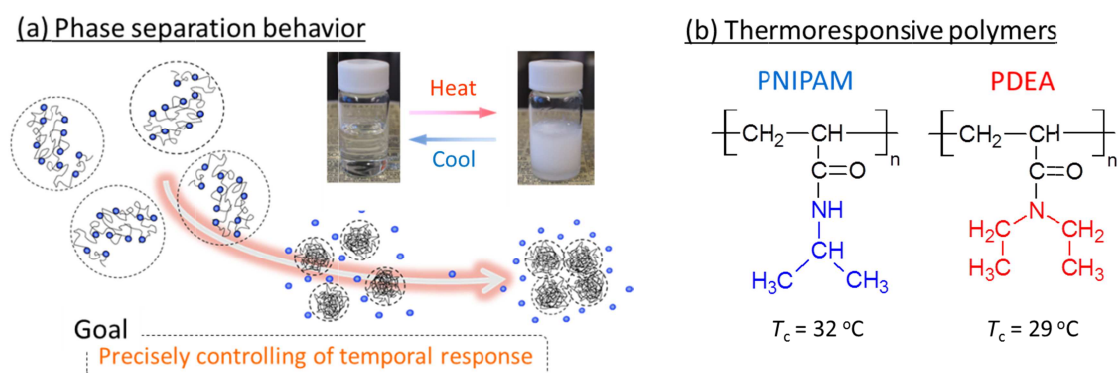

Figure 1 Phase separation behavior of thermoresponsive polymers: a) Phase separation mechanism and goal of our study, b) Chemical structures of poly(*N*-isopropylacrylamide) (PNIPAM) and poly(*N*,*N*-diethylacrylamide) (PDEA).

PDEAs with different stereoregularity were synthesized using RAFT polymerization in the presence of a Lewis acid catalyst. Each sample solution (0.50 wt%) was irradiated with a single nanosecond-laser-pulse (λ = 1200 nm) to induce phase separation (a laser T-jump technique). An increase in turbidity of the sample solution was monitored as a transient decay of optical transmittance of a probe light (λ = 532 nm). More details have been already described our published paper [4].

Figure 2a show a representative transient decay curve obtained by the laser T-jump technique. All decay curves can be well fitted with a double exponential function. It presented two types of time constants with different time scale (τ_{fast} and τ_{slow}). In Figure 2b, τ_{fast} and τ_{slow} were plotted against the meso-diad ratio of samples. τ_{fast} was insensitive to the meso-diad ratio (about 10 ms). By contrast, τ_{slow} was decreased with increasing the meso-diad ratio from 250ms to 100 ms. Here, Figure 3 is an illustration of this acceleration behavior of the phase separation.
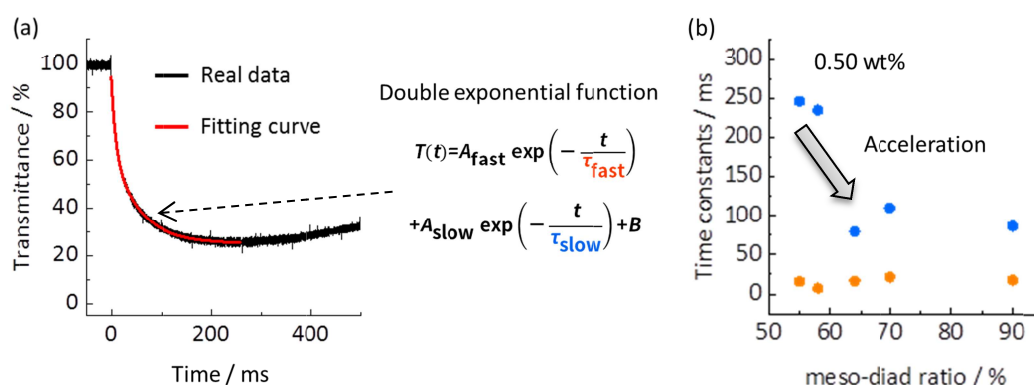

Figure 2 Phase separation dynamics for PDEA: a) A representative transient decay curve obtained by the laser T-jump technique, and fitting function, b) Stereoregularity effect on the time constants of the phase separation.
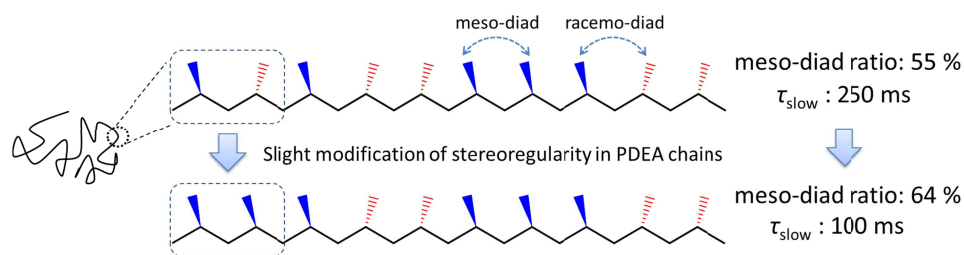

Figure 3 Acceleration behavior of slow phase separation for PDEA by slight modification of the stereoregularity.

In this study, we succeeded in controlling the phase separation rate for PDEA by the stereoregularity. This stereoregularity effect can be explained by a diffusion-aggregation model.

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