

Effects of the Stereoregularity on the Phase Separation of Poly(*N*-isopropylacrylamide) in Water and Organic Solvents.

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Stimuli-responsive polymers, which undergo relatively large and abrupt physical or chemical changes in response to a small external stimulus, have received increasing attention during recent years in both academic and industrial contexts.¹ Temperature is the most widely used stimulus in these polymer systems, and poly(*N*-substituted acrylamide) is representative of the group of temperature-responsive polymers. The phase diagram for these polymers in water is very important to provide fundamental insights into the temperature-responsiveness. Several researchers have recently suggested that the diad tacticity (*m*:*r*) affects the temperature-responsiveness of PNiPA in aqueous media^{2,3}. To clarify the tacticity effect on the phase behavior of PNiPA in water, we have to complete the phase diagram.

Table 1 compiles the characterization results of the stereocontrolled PNiPAs used in the present study. By carrying out RAFT polymerization, well-defined polymers with a narrow polydispersity were prepared. Fig. 1 shows the phase boundary curves for the aqueous solutions of PNiPAs *m*-46r, *m*-60r, and *m*-64r, which are obtained by plotting T_c against the polymer concentration. The phase boundary curve for the PNiPA aqueous solution shifts to lower temperature and changes its shape from a monotonic decreasing form to concentration-independent one with increasing *m*.

Fig.2 shows the turbidity curves for *m*-8f in diglyme at the concentrations of 3 and 4 wt %. In the heating process, the transmittance of the diglyme solution turns transparent with elevating temperature. When the temperature goes down, the transmittance of both solutions decreases gradually. The results indicate that the diglyme solution of PNiPA *m*-8 exhibits the UCST type phase separation behavior.

References

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Table 1. Characterization of PNiPAs

	<i>m</i> : <i>r</i>	M_n / g mol ⁻¹	M_w / M_n
<i>m</i> -46r ^a	46:54	32,000	1.12
<i>m</i> -60r ^a	60:40	30,000	1.30
<i>m</i> -64r ^a	64:36	34,000	1.29
<i>m</i> -84f ^b	84:16	23,000	2.24

^a prepared by RAFT polymerization. ^b prepared by free radical polymerization.

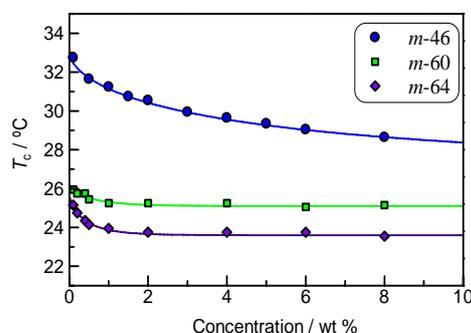


Fig 1. Phase diagram for the aqueous solutions of stereocontrolled PNiPAs.

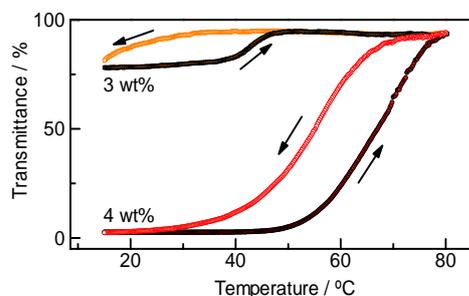


Fig 2. Temperature dependence of transmittance of 650 nm light for the diglyme solution of PNiPA *m*-84f.