Supporting Information for

Toward Dynamic Phase Transition Mechanism of a Thermoresponsive Ionic Liquid in the Presence of Different Thermoresponsive Polymers

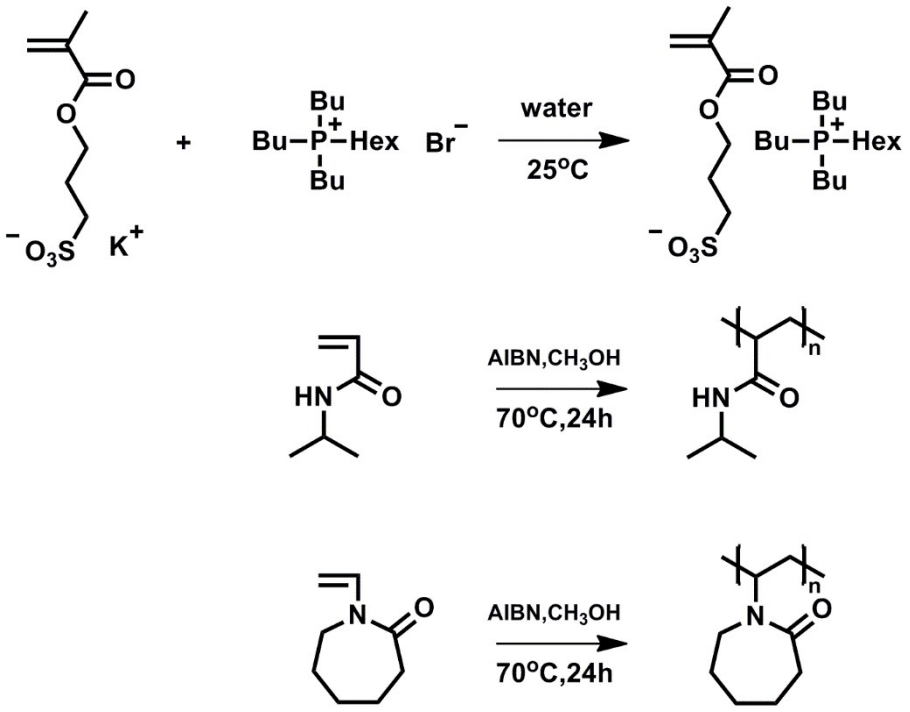
*Ge Wang and Peiyi Wu**

State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Polymers and Polymer Composite Materials, Department of Macromolecular Science and Laboratory for Advanced Materials, Fudan University, Shanghai 200433, China

*corresponding author, email: peiyiwu@fudan.edu.cn

Sample preparation

The chemical structures and reactions are presented in Scheme S1. The LCST-type IL, $[P_{4,4,4,6}][MC3S]$, was prepared *via* ion metathesis reaction of $[P_{4,4,4,6}][Br]$ and [K][MC3S] in distilled water for 24 h according to a previous report.[1] PNIPAM and PVCL were prepared as described previously.[2, 3] A typical procedure for the preparation of polymers was as followed. The polymers were synthesized by free radical polymerization in methanol using AIBN as the initiator. The Schlenk flask was placed in a 70 °C hot bath with stirring for 24 h after three freeze–vacuumization–thaw cycles. After purified *via* dialysis (MWCO 14000) against distilled water exhaustively, the final products were obtained by freeze-drying. The number-average molecular weight (M_n) and polydispersity index (PDI = M_w / M_n) of the polymers were measured by GPC with THF as eluent and monodisperse polystyrene as standard as shown in Figure S1. For PNIPAM, M_n = 12000 g/mol with PDI = 1.43; for PVCL, M_n = 13000 g/mol with PDI = 1.69. PNIPAM or PVCL was added into the 20% (w/v) $[P_{4,4,4,6}][MC3S]$ solution. Additionally, the concentration of polymer was calculated with respect to the IL content. The samples of $[P_{4,4,4,6}][MC3S]$-PNIPAM and $[P_{4,4,4,6}][MC3S]$-PVCL solutions were placed at 4 °C for at least 3 days to ensure complete dissolution before various measurements.



Scheme S1. Chemical structures and synthesis of the ionic liquid and polymers.

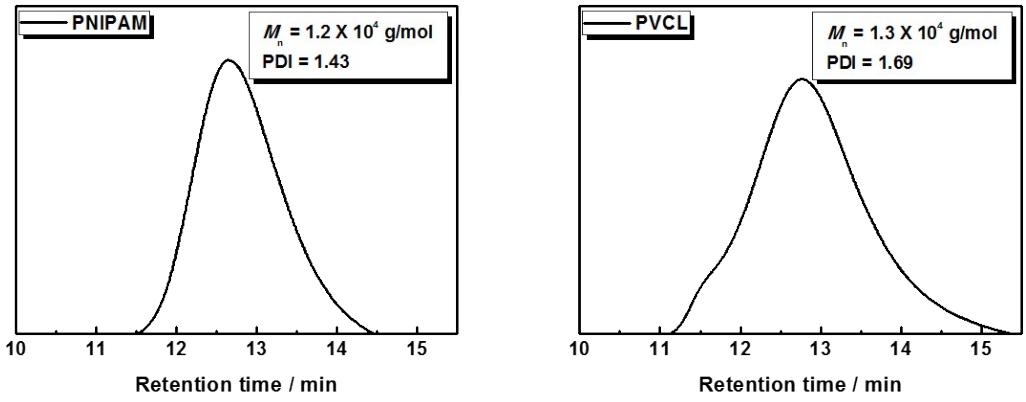


Figure S1. The number-average molecular weight (M_n) and polydispersity index (PDI = M_w / M_n) of the synthetic PNIPAM (left) and PVCL (right).

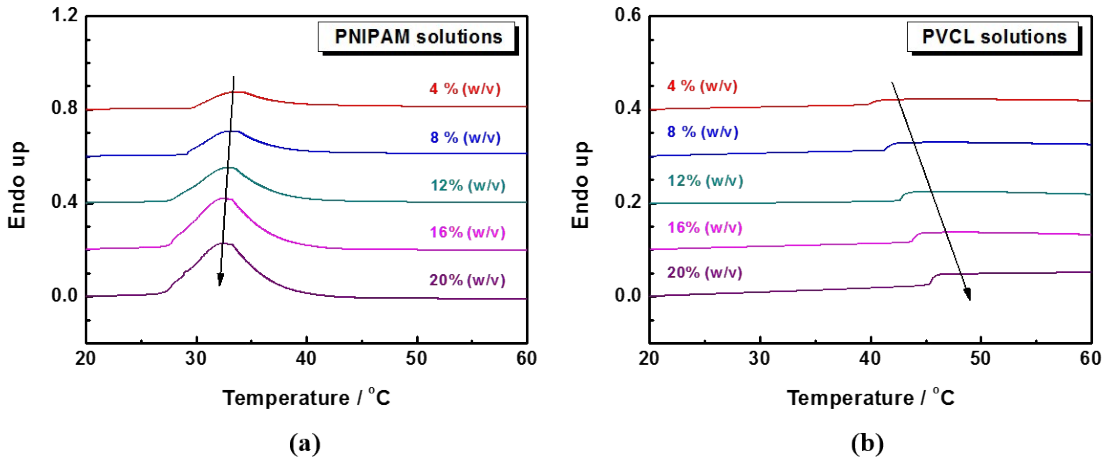


Figure S2. DSC heating curves of (a) PNIPAM and (b) PVCL solutions with concentrations of 4, 8, 12, 16, 20% (w/v) at a scanning rate of 10 °C/min.

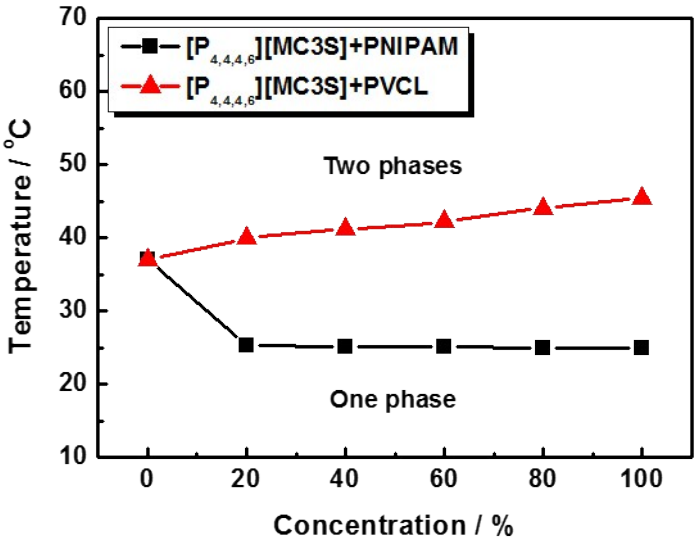


Figure S3. Phase diagrams for $[P_{4,4,4,6}][MC3S]$ solutions (20% (w/v)) after mixing with different amounts of PNIPAM (black) or PVCL (red).

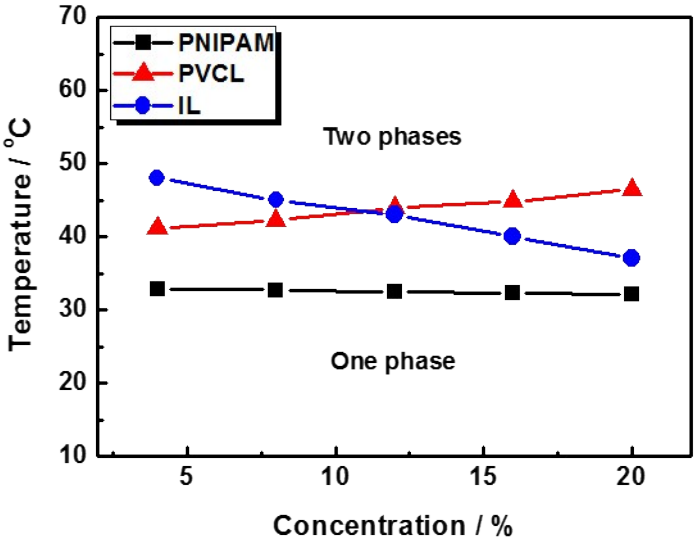


Figure S4. Phase diagrams for PNIPAM (black), PVCL (red) and $[P_{4,4,4,6}][MC3S]$ (blue) after mixing with different amounts of water.

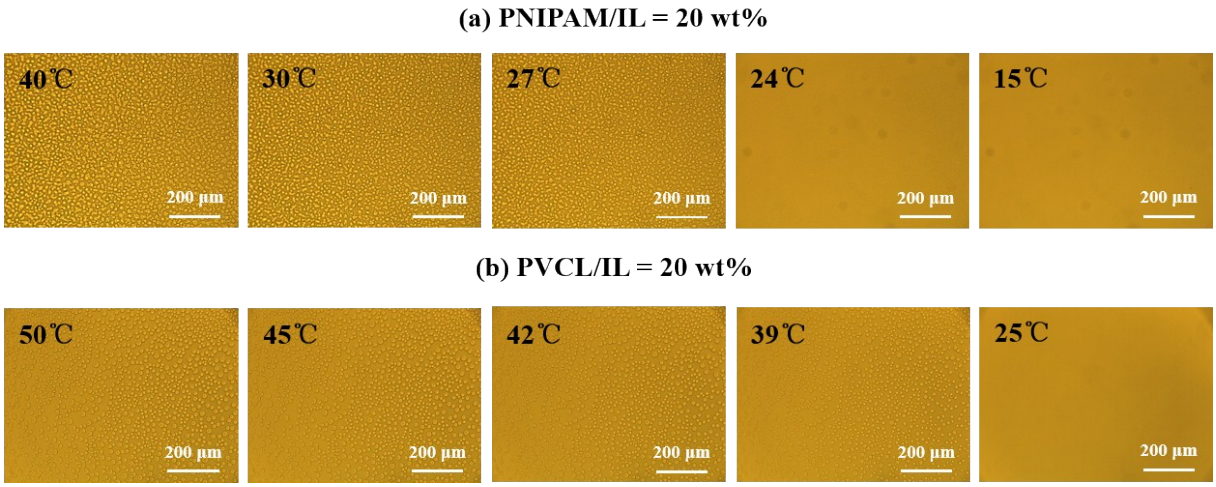


Figure S5. Optical micrographs of (a) 20% (w/v) $[P_{4,4,4,6}][MC3S]$ solution with 4% (w/v) PNIPAM and (b) 20% (w/v) $[P_{4,4,4,6}][MC3S]$ solution with 4% (w/v) PVCL (polymers/IL = 20 wt%, cooling rate = 0.5 °C/min) in the cooling process from 40 °C to 15 °C for (a) and 50 °C to 25 °C for (b).

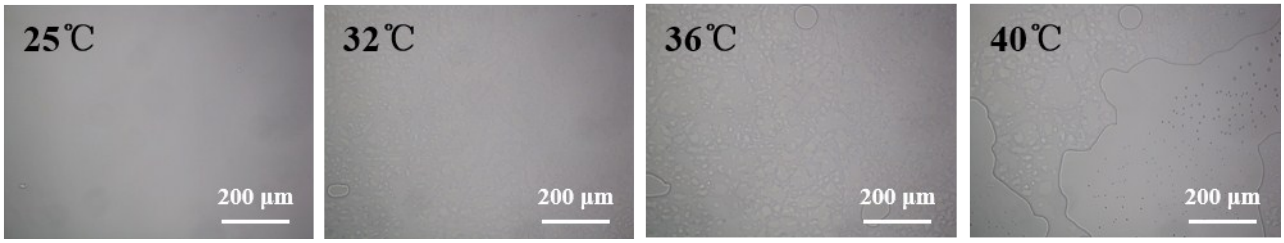


Figure S6. Optical micrographs of pure $[P_{4,4,4,6}][MC3S]$ solution (20% (w/v)) (heating rate = 0.5 ^{o}C/min) in the heating process from 25 to 40 ^{o}C.

We chose Raman under an optical microscope to obtain the information of the liquid phases after phase transition.[4, 5] We used the integrated intensity ratio of the ν(C-H) band of solute to the ν(O-H) of water ($A_{C\text{-}H}$ / $A_{O\text{-}H}$) to represent the distribution of solute, as shown in Figure S7 and Table S1. Obviously, after phase transition, the solute concentration of IL-rich domains is higher than that of the solution below LCST. While water-rich matrix lower than it. Moreover, *ca.* 82% of solute remains in the aqueous solution in [$P_{4,4,4,6}$][MC3S]-PNIPAM, while that percentage is about 60% in [$P_{4,4,4,6}$][MC3S]-PVCL. As for IL-rich domains, *ca.* 85% of water remains in [$P_{4,4,4,6}$][MC3S]-PNIPAM system and *ca.* 47% of water remains in [$P_{4,4,4,6}$][MC3S]-PVCL one. Additionally, this data is in good agreement with the temperature-variable ^{1}H NMR result that a weaker dehydration process happens to IL after the addition of PNIPAM.

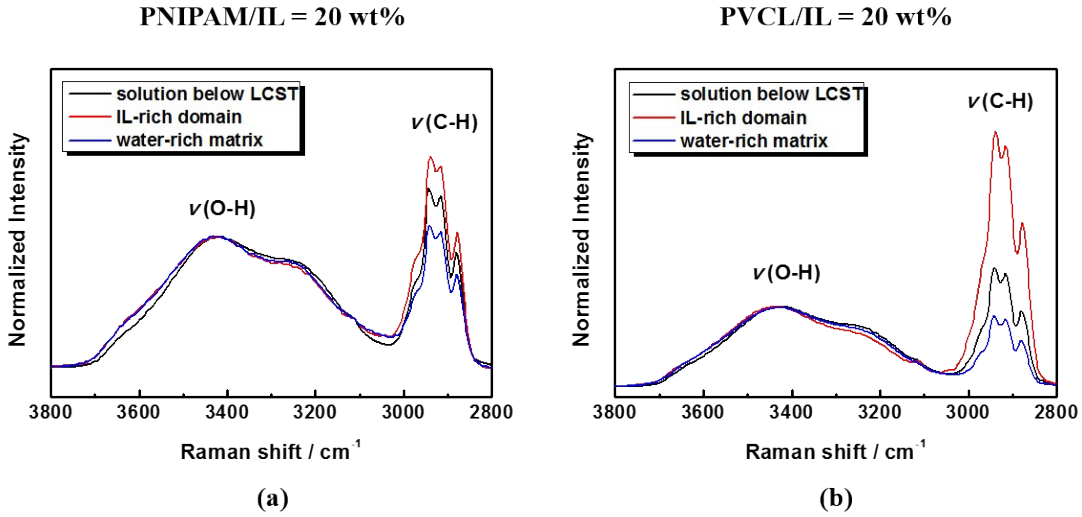


Figure S7. Raman spectra measured in the IL-rich domains (red) and water-rich matrix (blue) phases for (a) [P4,4,4,6][MC3S]-PNIPAM and (b) [P4,4,4,6][MC3S]-PVCL solution ([P4,4,4,6][MC3S]/H2O = 20% (w/v), polymers/[P4,4,4,6][MC3S] = 20 wt%) above LCST. When the temperature is below LCST, reference Raman spectra (black) are also shown.

Table S1. Integrated intensity ratio of the ν(C-H) band of solute to the ν(O-H) of water ($A_{C\text{-}H}$ / $A_{O\text{-}H}$) in [$P_{4,4,4,6}$][MC3S]-PNIPAM and [$P_{4,4,4,6}$][MC3S]-PVCL solutions.

Solute	$A_{C\text{-}H}$ / $A_{O\text{-}H}$		
	Below LCST	Above LCST	
		IL-rich domain	water-rich matrix
[$P_{4,4,4,6}$][MC3S]-PNIPAM	0.339	0.4	0.278
[$P_{4,4,4,6}$][MC3S]-PVCL	0.374	0.803	0.226

1. Y. Kohno, Y. Deguchi and H. Ohno, *Chemical Communications*, 2012, 48, 11883-11885.
2. B. Sun, Y. Lin, P. Wu and H. W. Siesler, *Macromolecules*, 2008, 41, 1512-1520.
3. S. Sun and P. Wu, *The Journal of Physical Chemistry B*, 2011, 115, 11609-11618.
4. Y. Maeda, H. Yamamoto and I. Ikeda, *Macromolecules*, 2003, 36, 5055-5057.
5. T. Shoji, R. Nohara, N. Kitamura and Y. Tsuboi, *Analytica chimica acta*, 2015, 854, 118-121.