

Supporting Information

On the Thermodynamic Phase Behavior of Poly(*N*-Vinylcaprolactam) Solution with the Presence of Different Ionic Liquids

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Results of Dynamic Light Scattering (DLS) and Zeta-potential measurements were presented in Fig. S1 and S2.

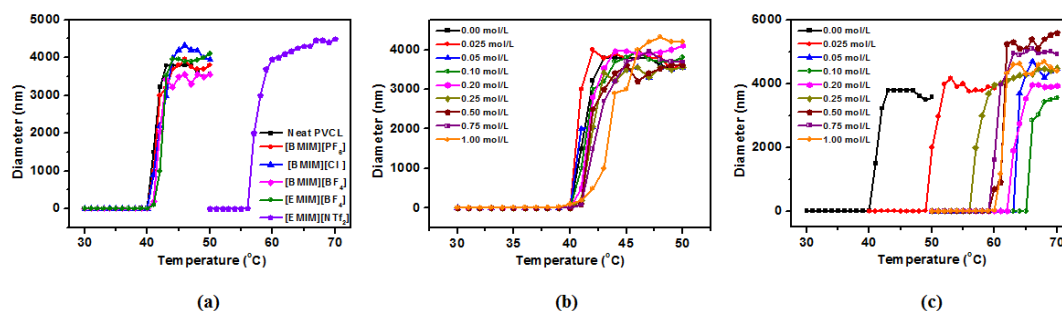


Fig. S1 Z-average diameter of (a) 10 wt% PVCL solution with addition of different ILs, 10 wt% PVCL solution with different concentrations of (b) [BMIM][BF₄] and (c) [EMIM][NTf₂].

Fig. S1 (a) presents the variation of Z-average diameter of PVCL solutions with different ILs added. The diameter experiences a sudden increase when temperature was heated above the LCST. It can be found that addition of the four ILs, [BMIM][BF₄], [EMIM][BF₄], [BMIM][Cl] and [BMIM][PF₆] has only little influence on the LCST of PVCL solution, which is similar with results of turbidity measurements. To investigate the influence of [EMIM][NTf₂] on the diameter of PVCL solution, measurements of samples with different [EMIM][NTf₂] concentration were also performed. The LCST first undergoes an increase and then decreases as the concentration of [EMIM][NTf₂] increases from 0 to 0.25 mol/L as illustrated in Fig. S1 (c). And then it reaches to stability at about 60 °C in spite of the continuing increase of [EMIM][NTf₂] concentration.

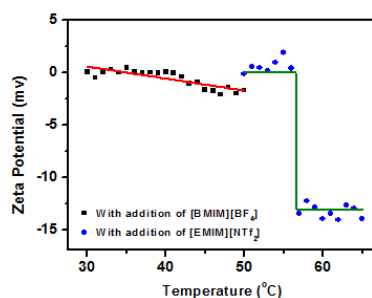


Fig. S2 Zeta-potential of 10 wt% PVCL solution with 0.25 mol/L [BMIM][BF₄] and [EMIM][NTf₂].

In Fig. S2, Zeta-potential of the PVCL solution with 0.25 mol/L [BMIM][BF₄] added almost behaves in a linear curve upon heating. That is to say, for most molecules of hydrophilic ILs, their position undergoes no great change upon heating. However, what appears is another scenario after adding hydrophobic ILs into the solution. When the temperature is heated above LCST, the polymer chains aggregate together gradually under the driving of hydrophobic interactions, [EMIM][NTf₂] molecules are wrapped in polymer chains of the aggregates. The anions may tend to distribute at the shell of the aggregates and the cations are close to polymer chains. As a result, these aggregates exhibit negative potential after phase transition which explains the sudden decrease of the Zeta potential appearing in Fig. S2.