

Electronic Supplementary Information for

Effects of Component Molecular Weight on the Viscoelastic Properties of Thermoreversible Supramolecular Ion Gels via Hydrogen Bonding

Yu Lei and Timothy P. Lodge*

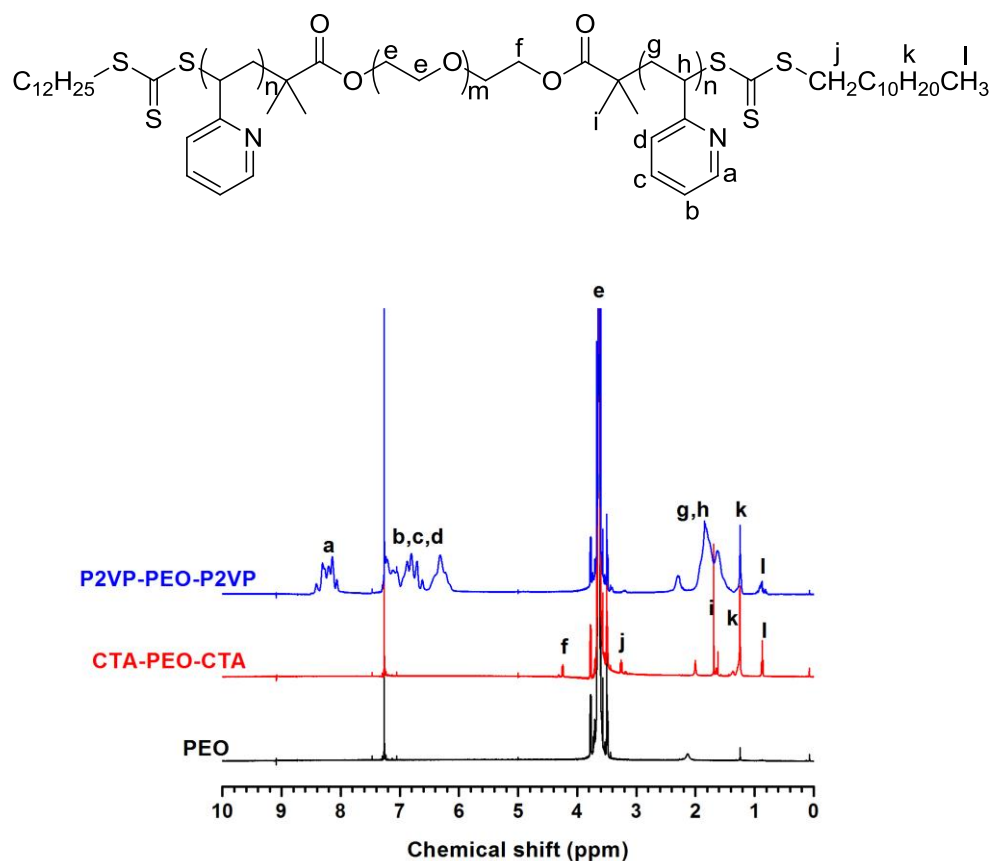


Figure S1. ¹H NMR spectra of the PEO precursor, the CTA-PEO-CTA difunctional macroinitiator, and a P2VP-PEO-P2VP triblock copolymer.

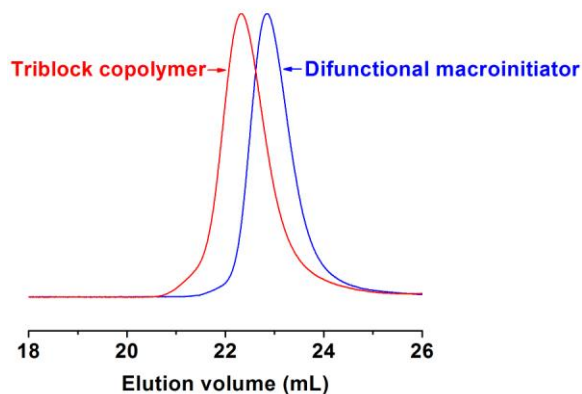


Figure S2. SEC traces of the CTA-PEO-CTA difunctional macroinitiator and a P2VP-PEO-P2VP triblock copolymer.

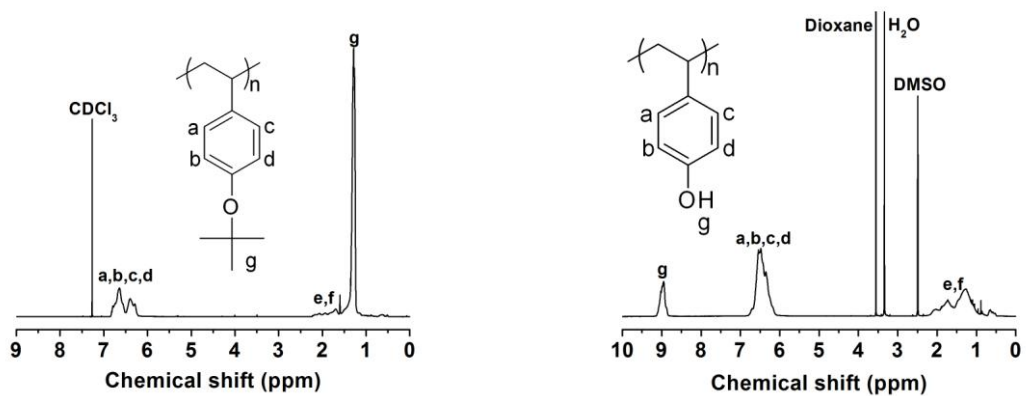


Figure S3. ¹H NMR spectra of a PtBOS precursor and a PVPh homopolymer.

tTS shift factors

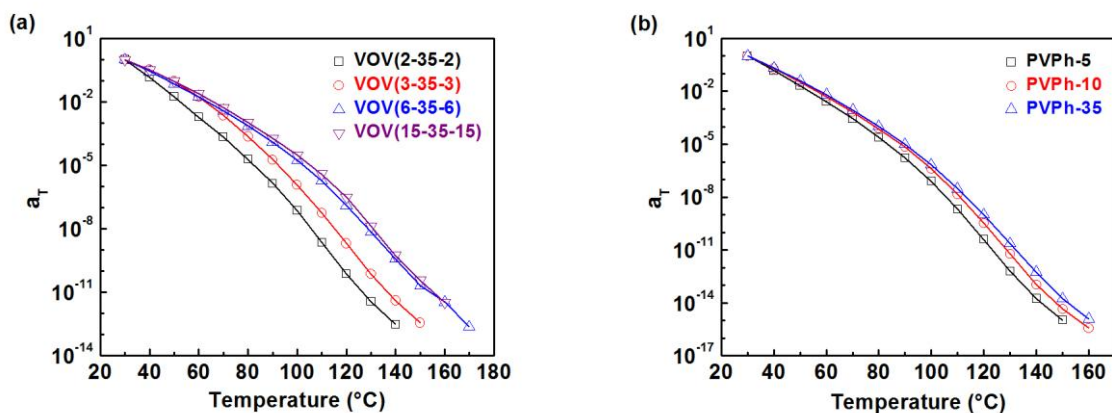
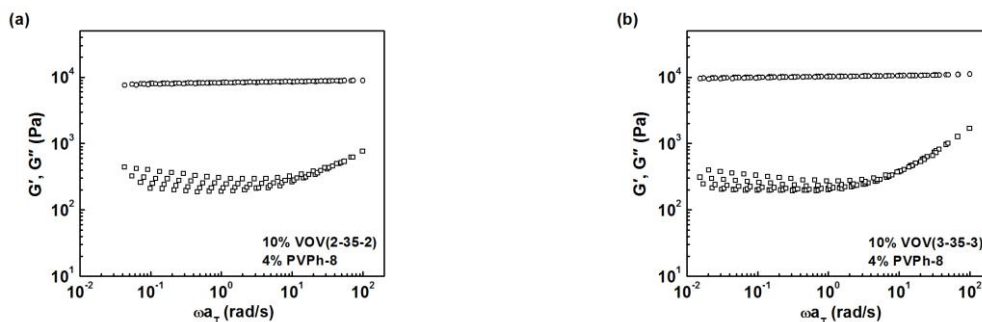


Figure S4. Temperature dependence of tTS shift factors used in generating the master curves of (a) Figure 3 and (b) Figure 4.

Interpretation of the Systematic Deviations from tTS master curves in Figures 3 and 4

To elucidate the origin of the systematic deviations from tTS master curves (G'' upturns at the high-frequency end of low-temperature data) in Figures 3 and 4, these G'' upturns were also superposed to generate master curves. The resulting shift factors were found to have very similar temperature dependence with the viscosity of the solvent, suggesting that a possible origin of these G'' upturns is the relaxation of the network strands.



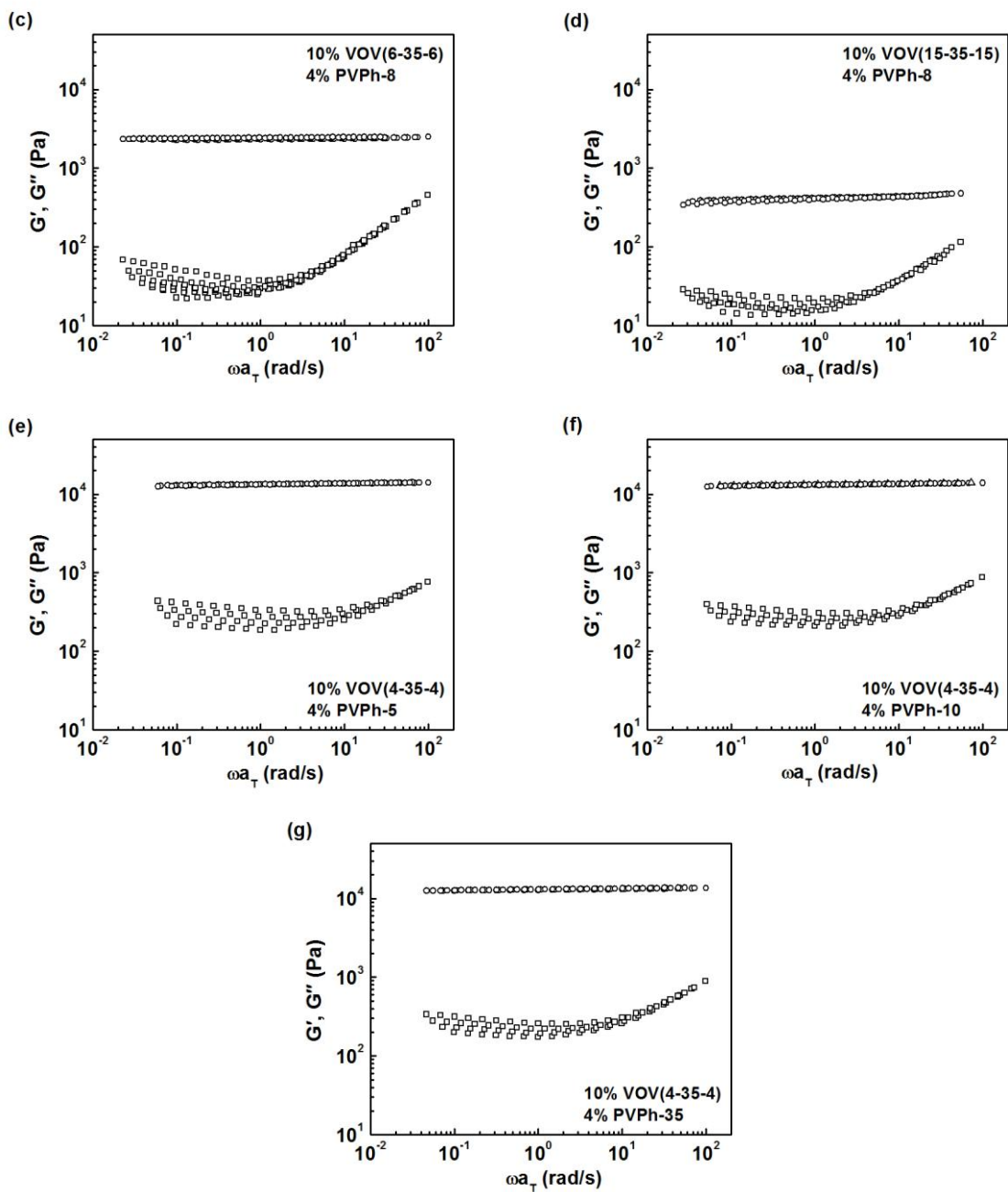
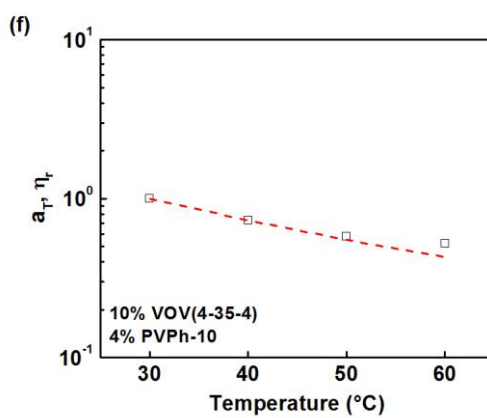
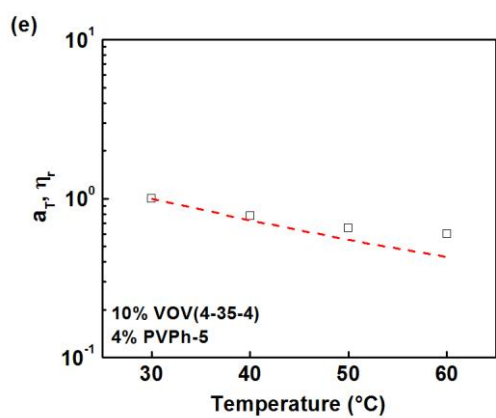
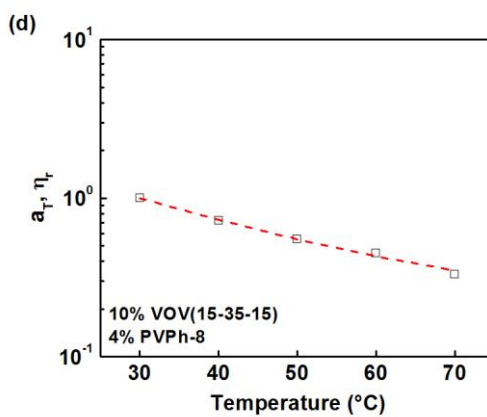
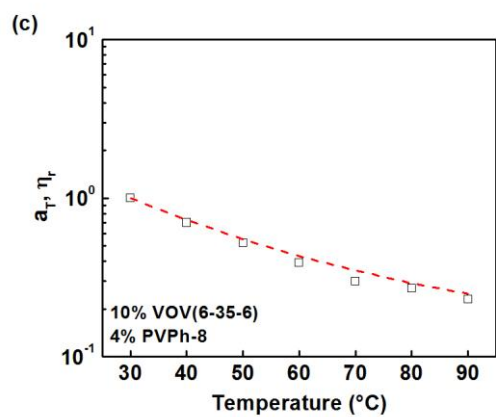
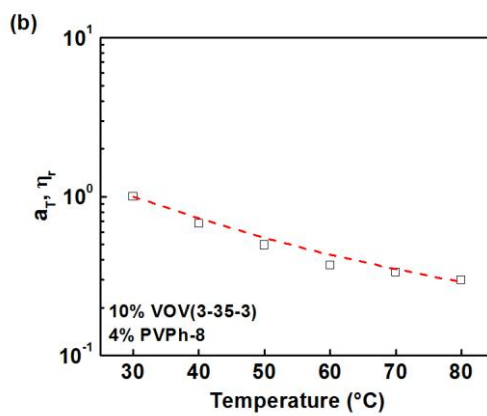
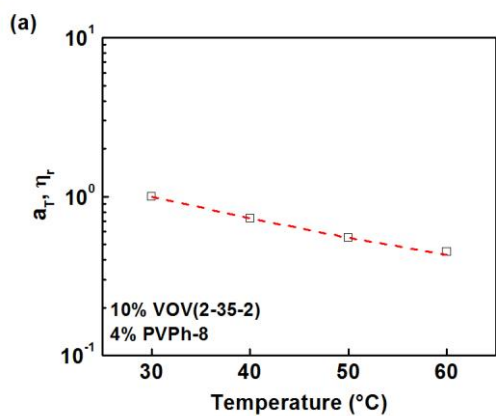


Figure S5. tTS master curves obtained by superposing the G'' upturns at the high-frequency end of low-temperature data, with a uniform reference temperature of 30 °C.



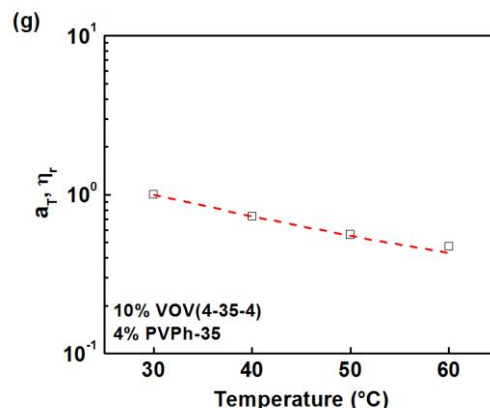


Figure S6. Temperature dependence of tTS shift factors (□) used in generating the master curves of Figure S2. The viscosities of [EMI][TFSA] relative to its value at the tTS reference temperature (30 °C) are also included (red dashed lines) for comparison.

Estimation of the ratio of the phenol–pyridine bonds to the phenol–phenol bonds

In this system, the phenolic hydroxyl groups are present in three different states: free, self-associated, and hydrogen-bonded with P2VP, and their infrared absorption peaks are located at 3492, 3446, and 3334 cm^{-1} (reference 7), respectively. Coleman and coworkers (Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* **1985**, 26, 228–234.) have employed the frequency difference ($\Delta\nu$) between the hydrogen-bonded hydroxyl absorption and the free hydroxyl absorption to roughly estimate the average hydrogen bonding strength. From this perspective, the phenol–pyridine bond ($\Delta\nu = 158 \text{ cm}^{-1}$) is significantly stronger and more favorable than the phenol–phenol bond ($\Delta\nu = 46 \text{ cm}^{-1}$). For a quantitative analysis, we can estimate the ratio of $A_{\text{ph-py}}/A_{\text{ph-ph}}$ assuming the Boltzmann distribution is followed:

$$\frac{A_{\text{ph-py}}}{A_{\text{ph-ph}}} = \exp\left(\frac{hc\Delta(\Delta\nu)}{k_{\text{B}}T}\right) \quad (\text{S1})$$

where $A_{\text{ph-py}}$ is the amount of the phenol–pyridine bond, $A_{\text{ph-ph}}$ is the amount of the phenol–phenol bond, h is the Planck constant, c is the speed of light in vacuum, $\Delta(\Delta\nu)$ is the frequency difference between the phenol–pyridine bond and the phenol–phenol bond, k_{B} is the Boltzmann constant, and T is the absolute temperature. Estimating $A_{\text{ph-py}}/A_{\text{ph-ph}}$ by eq S1 yields $A_{\text{ph-py}}/A_{\text{ph-ph}} \approx 1.7/1$, which corresponds to a 2.2:1 ratio of phenol/pyridine units. This value is in reasonable agreement with the experimentally determined stoichiometric balance between phenol and pyridine units.