Supporting Information for

Multiple Dynamic Processes Contribute to the Complex
Steady Shear Behavior of Cross-Linked Supramolecular
Networks of Semidilute Entangled Polymer Solutions

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Equilibrium constants and dissociation rate constants for pincer Pd complexes

Equilibrium constants and dissociation rate constants for pincer Pd complexes (1a, 1b) with pyridine in DMSO at 25 °C have been characterized previously.\(^ {51}\) The equilibrium association constants (\(K_{eq}\)) and pyridine dissociation rate constants (\(k_d\)) for 1a•pyridine are 29 M\(^{-1}\) and 1450 s\(^{-1}\) respectively. \(K_{eq}\) and \(k_d\) for 1b•pyridine are 33 M\(^{-1}\) and 17 s\(^{-1}\) respectively. \(K_{eq}\) and \(k_d\) for 1c•pyridine in DMSO at 25 °C cannot be obtained by NMR method, but previous work has shown that binding constants of the Pt(II) complexes that are analogous to 1a and 1c are indistinguishable.\(^ {52}\) We therefore infer that \(K_{eq}\) of 1c•pyridine is \(\sim\) 30 M\(^{-1}\).

The \(k_d\) for 1c•pyridine is obtained from rheological data. As previously reported, the dynamic mechanical properties of the 1a•PVP and 1b•PVP networks are superposed onto a single master curve
by the scaled frequency (oscillatory frequency divided by cross-linker dissociation rate; \(\omega/k_d\)).\textsuperscript{S1} The same superposition is used here to determine the dissociation rate of cross-linkers 1c while the samples with cross-linker 1b and 1c have similar network structure but different relaxation time. As \(k_d\) of cross-linker 1b is 17 s\(^{-1}\), \(k_d\) of cross-linker 1c is inferred to be 1355 s\(^{-1}\) from the data in Figure S1.

Figure S1. Storage (\(G'\)) and loss (\(G''\)) modulus versus scaled frequency for ~0.1 g/mL (A) and ~ 0.26 g/mL (B) PVP/DMSO solution with 2% of 1b or 1c. Unfilled symbols represent cross-linker 1b, filled symbols represent cross-linker 1c.

**Steady shear behavior of 1c•PVP**

The \(k_d\) of cross-linker 1c is very close to \(k_d\) of cross-linker 1a, and similar steady shear behavior is observed (Figure S2). In ~ 0.26 g/mL PVP/DMSO solution, samples with 2% cross-linkers 1c also show shear thinning, while networks formed from ~ 0.1 g/mL PVP/DMSO solution show shear thickening. These experiments reaffirm that the differences in nonlinear steady shear behavior are due to the differences in cross-link dissociation rate.
Figure S2. Steady shear viscosity versus scaled shear rate for ~0.1 g/mL (A) and ~ 0.26 g/mL (B) PVP/DMSO solution with 2% of 1b or 1c. Squares represent cross-linker 1b, triangles represent cross-linker 1c.

**Estimates of polymer entanglements**

The average number of entanglements per polymer chain $N/Ne(\phi)$ in the semidilute entangled regime can be calculated as follows:

For a polymer solution in a theta-solvent,$^3$1

$$\phi_\text{e} = \left[ \frac{Ne(1)}{N} \right]^{3/4} \quad (1)$$

where $\phi_\text{e}$ is the entanglement concentration, $Ne(1)$ is the number of Kuhn monomers in the entangled strands in the melt, and $N$ is the number of Kuhn monomers per polymer chain. In this paper, the critical concentration of entanglement is about 0.16 (volume concentration),$^4$ and so $N/Ne(1)$ is calculated to be $\sim 11.4$. 

The relationship between the number of Kuhn monomers in the entangled strands in the semidilute entangled regime \( (N_e(\phi)) \) and the concentration of polymer in solution is given by\textsuperscript{S3}

\[
N_e(\phi) = N_e(1)\phi^{4/3}
\]  

(2)

where \( \phi \) is the volume concentration of polymer solution.

Combining equations 1-2, we get

\[
\frac{N}{N_e(\phi)} = \frac{N}{N_e(1)}\phi^{4/3}
\]  

(3)

So the values of \( N/N_e(\phi) \) for solutions of PVP in DMSO are calculated to be \( \sim 1.00, \sim 1.27, \sim 1.55 \) and \( \sim 1.93 \) for concentrations of 0.160 g/mL, 0.191 g/mL, 0.222 g/mL and 0.262 g/mL, respectively.

REFERENCES


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