Supporting information

Strain Hardening and Strain Softening of Reversibly Cross-linked Supramolecular Polymer Networks

Donghua Xu[†,*] *and Stephen L. Craig*[‡,*]

† State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

‡ Department of Chemistry and Center for Biologically Inspired Materials and Material Systems, Duke University, Durham, NC, 27708-0346, USA.

[*] Corresponding authors. Email: dhxu@ciac.jl.cn, stephen.craig@duke.edu

Lissajous-Bowditch curves of ~0.11 g/mL PVP with 5% 1a during strain softening.

In Figure S1, Lissajous-Bowditch curves of ~0.11 g/mL PVP with 5% **1a** in strain softening regime at different scanning frequency (0.3 rad/s and 3 rad/s) are shown. Lissajous-Bowditch curves appear as ellipses in Figure S1, indicating single-harmonic sinusoidal stress response in the strain-softened regime and ruling out substantial non-Gaussian stretching of polymer chains, for which the Lissajous-Bowditch curves would not be elliptical.[S1]

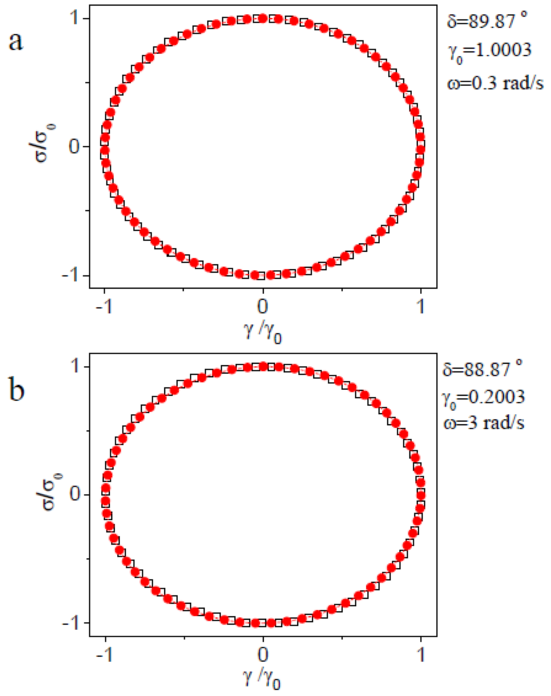

Figure S1. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of ~ 0.11 g/mL PVP with 5% **1a** at strain softening regime under different scanning frequency. (a) 0.3 rad/s; (b) 3 rad/s. The phase angle and the strain during strain softening are also shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments.

Lissajous-Bowditch curves of ~0.11 g/mL PVP with 5% 1b at strain softening regime under 0.3 rad/s.

In Figure S2, Lissajous-Bowditch curves of ~0.11 g/mL PVP with 5% **1b** in strain softening regime under 0.3 rad/s is shown. The Lissajous-Bowditch curves are elliptical in the strain softening regime, indicating single-harmonic sinusoidal stress response in the strain-softened regime and ruling out substantial non-Gaussian stretching of polymer chains.[S1]

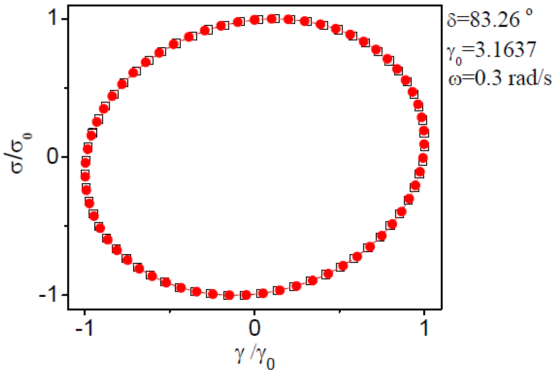

Figure S2. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of ~ 0.11 g/mL PVP with 5% **1b** at strain softening regime under 0.3 rad/s. The phase angle and the strain during strain softening are also shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments.

Relaxation time (τ) of ~0.11 g/mL PVP with 5% 1a or 5% 1b.

The relaxation time (τ) of the samples with **1b** can be obtained from the crossover points between G' and G'' during linear oscillatory frequency sweep.[S2, S3] Because the accessible range of frequencies is limited, it is impossible to get the relaxation time (τ) of the samples with cross-linkers **1a** directly. However, as the dynamic mechanical properties of the **1a** PVP and **1b** PVP networks can be superposed onto a single master curve by the scaled frequency (ω/k_d), the relaxation time (τ) of the samples with **1a** is obtained by this scaling law.[S2, S3] Hereafter, we refer to the frequency at the crossover point of G' and G'' as the crossover frequency. In our previous work, the characteristic relaxation time (τ_f) of the samples were calculated by [S2-S7]

$\tau_f = 1/f$ (1)

where f is the crossover frequency of G' and G'' during frequency sweep with unit as Hz (cycle/s). In this work, to be consistent with the angular frequency (ω, unit is rad/s), the relaxation time (τ) of the samples were calculated by

$\tau = 1/\omega_c$ (2)

where ω_c is the crossover frequency of G' and G'' during frequency sweep with unit as rad/s. As 2π rad/s = 1 Hz, there is $\tau_f = 2\pi\ \tau$.

In Figure S3a, the relaxation time (τ) of ~0.11 g/mL PVP with 5% **1b** can be obtained from the crossover points between G' and G'' during linear oscillatory frequency sweep. As ω_c is 17.4 rad/s, τ of ~0.11 g/mL PVP with 5% **1b** is 5.7×10^{-2} s. In Figure S3a, because the accessible range of frequencies is limited, it is impossible to get the relaxation time (τ) of the samples with cross-linkers **1a** directly. However, as the dynamic mechanical properties of the **1a** PVP and **1b** PVP networks can be superposed onto a single master curve by the scaled angular frequency (ω/k_d) by dissociation rate of cross-linkers (Figure S3b), the relaxation time (τ) of the samples with **1a** is obtained by this scaling law. And accordingly, τ of ~0.11 g/mL PVP with 5% **1a** is $(5.7\times10^{-2})\times17/1450$ s, which is about 6.7×10^{-4} s. In our previous work, the characteristic relaxation time (τ_f) of ~0.11 g/mL PVP with 5% **1a** or 5% **1b** were $\tau_f = 4.2 \times 10^{-3}$ s and 0.36 s , respectively.[S2-S7] It is apparent that there is $\tau_f = 2\pi\,\tau$.

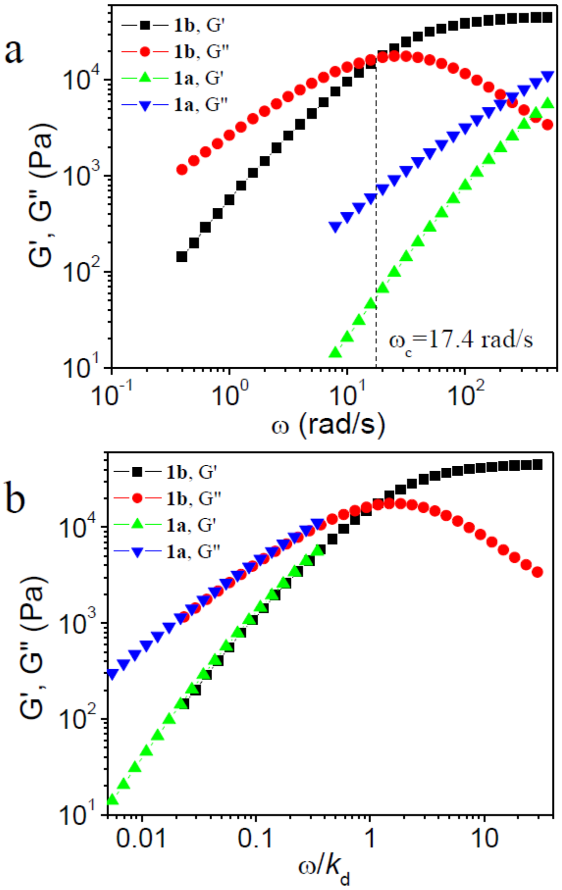

Figure S3. (a) Storage (G') and loss (G'') moduli versus angular frequency (ω) for ~0.11 g/mL PVP with 5% **1a** or 5% **1b**; (b) Storage (G') and loss (G'') moduli versus scaled angular frequency (ω/k_d) for ~0.11 g/mL PVP with 5% **1a** or 5% **1b**. $T = 25$ °C. For **1a**, $k_d = 1450\ \mathrm{s}^{-1}$, and for **1b**, $k_d = 17\ \mathrm{s}^{-1}$.

Lissajous-Bowditch curves of 0.261 g/mL PVP with 5% 1a at strain softening regime under different scanning frequency

In Figure S4 and Figure S5, Lissajous-Bowditch curves of 0.261 g/mL PVP with 5% **1a** at different scanning frequency 0.3 rad/s and 5 rad/s are shown. Lissajous-Bowditch curves of 0.261 g/mL PVP with 5% **1a** in the strain softening regime appear as ellipses at scanning frequencies of from 0.3 rad/s to 5 rad/s, again ruling out a substantial amount of non-Gaussian stretching of polymer chains.[S1]

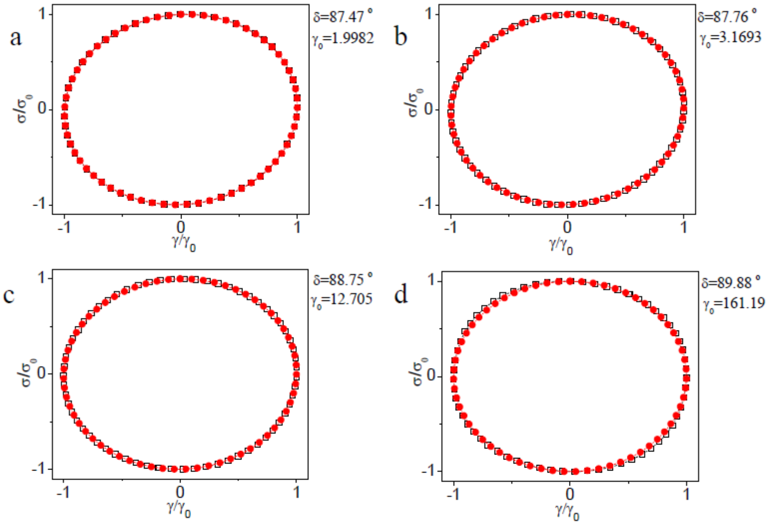

Figure S4. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of 0.261 g/mL PVP with 5% **1a** at strain softening regime under 0.3 rad/s. The phase angle and the strain during strain softening are also shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments.

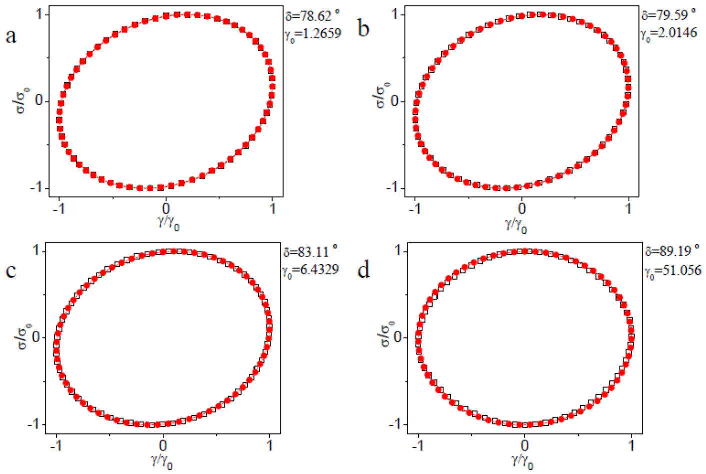

Figure S5. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of 0.261 g/mL PVP with 5% **1a** at strain softening regime under 5 rad/s. The phase angle and the strain during strain softening are also shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments.

Relationship between strain hardening and the relaxation time of the network.

For the mechanism of the strain hardening, the increasing number of elastically active chain, it can be understood by the increasing relaxation time (τ) of the network. Accordingly to single Maxwell model [S2,S3]

$$G' = (\nu k_B T)(\omega\tau)^2/[1+(\omega\tau)^2] \qquad (3)$$

$$G'' = (\nu k_B T)(\omega\tau)/[1+(\omega\tau)^2] \qquad (4)$$

where v is apparent number density of elastically active chains, k_B is Boltzmann's constant, and T is the temperature. From equation 3 and 4, it is easy to get below equation

$$G'_{\max}/G'_{\mathrm{Lin}} = (\nu_{\max}/\nu_{\mathrm{Lin}})(\tau_{\max}/\tau_{\mathrm{Lin}})^2\left\{\left[1+(\omega\tau_{\mathrm{Lin}})^2\right]/\left[1+(\omega\tau_{\max})^2\right]\right\} \qquad (5)$$

$$G''_{\max}/G''_{\mathrm{Lin}} = (\nu_{\max}/\nu_{\mathrm{Lin}})(\tau_{\max}/\tau_{\mathrm{Lin}})\left\{\left[1+(\omega\tau_{\mathrm{Lin}})^2\right]/\left[1+(\omega\tau_{\max})^2\right]\right\} \qquad (6)$$

where $G'_{\max}$ and $G''_{\max}$ are the storage moduli and loss moduli at the maximum strain of strain hardening, respectively. G'_{Lin} and G''_{Lin} are the storage moduli and loss moduli at the strain in the linear regime, respectively. $v_{\max}$ and v_{Lin} is apparent number density of elastically active chains at the maximum strain of strain hardening and at the strain in the linear regime, respectively. $\tau_{\max}$ and τ_L are the relaxation time of the network at the maximum strain of strain hardening and at the strain in the linear regime, respectively. From equation 5 and 6, we get

$$G'_{\max}/G'_{\mathrm{Lin}} = (G''_{\max}/G''_{\mathrm{Lin}})(\tau_{\max}/\tau_{\mathrm{Lin}}) \qquad (7)$$

As the relaxation time of the network (τ) increase with the larger number of elastically active chains,[S3] and accordingly, $G'_{\max}$ / G'_{Lin} is larger than $G''_{\max}$/ G''_{Lin}.

Oscillatory frequency sweep from 10 to 30 rad/s at three different applied strains for ~0.11 g/mL PVP with 2~5% of 1b.

To explore how the relaxation time of samples change with strain during strain sweep, we perform the oscillatory frequency sweep from 10 rad/s to ~30 rad/s at three different strain from linear to non-linear regime, respectively. In Figure S6, 0.11 g/mL PVP with 5% **1b** is used as an example to illustrate how the experiment was performed. In Figure S6a, the strain sweep for 0.11 g/mL PVP with 5% **1b** at different scanning frequency (10 rad/s and 30 rad/s) are shown, respectively. Three dashed lines are shown in Figure S6a to indicate the principle to choose the strain for next oscillatory frequency sweep. Two strains (0.005 and 0.1) are in the linear regime and the third strain (0.48) is in the nonlinear regime for both scanning frequency (10 rad/s and 30 rad/s). In Figure S6b, oscillatory frequency sweep for 0.11 g/mL PVP with 5% **1b** at the three strains are shown. In Figure S6b, the cross-over frequency (ω_c) of G' and G'' during oscillatory frequency sweep at two strains (0.005 and 0.1) are almost the same, while the cross-over frequency (ω_c) of G' and G'' during oscillatory frequency sweep at the strain 0.48 move to lower frequency. And accordingly, the relaxation time (τ) of 0.11 g/mL PVP with 5% **1b** at different strains were calculated from the cross-over frequency (ω_c) of G' and G'' during oscillatory frequency sweep by $\tau=1/\omega_c$, which is shown in Figure 15 in main text.

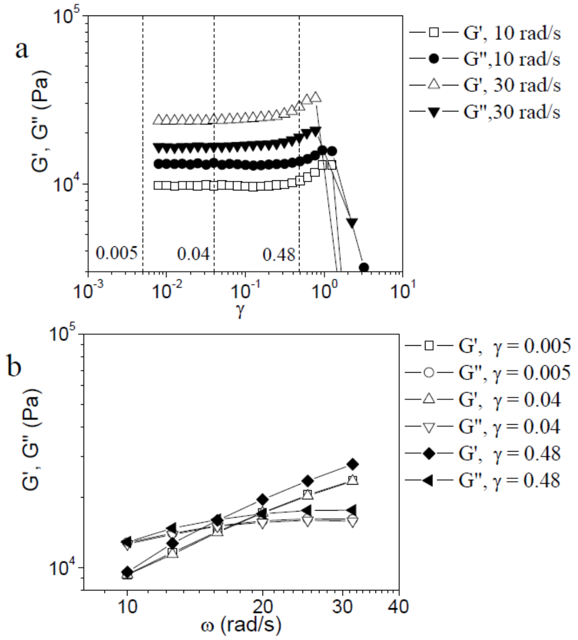

Figure S6. (a) Storage modulus (*G′*) and loss modulus (*G″*) versus strain for ~0.11 g/mL PVP with 5% **1b** during strain sweep experiments at different scanning frequency; (b) Storage (*G′*) and loss (*G″*) moduli versus frequency for ~0.11 g/mL PVP/DMSO solution with 5% **1b**. Three different strains from linear to non-linear regime are used, respectively.

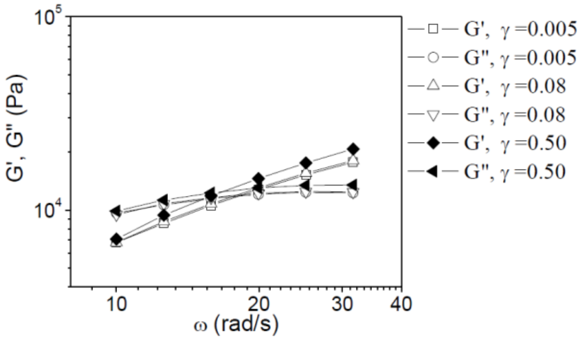

Figure S7. Storage (*G′*) and loss (*G″*) moduli versus frequency for ~0.11 g/mL PVP/DMSO solution with 4% **1b**. Three different strains from linear to non-linear regime are used, respectively.

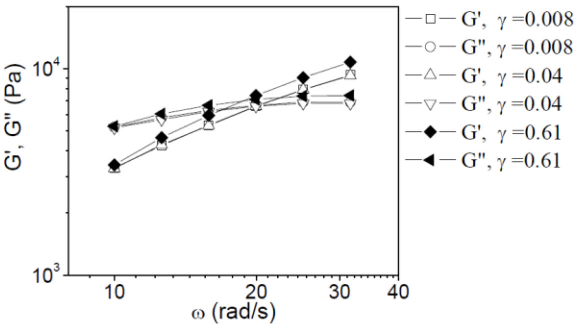

Figure S8. Storage (G') and loss (G'') moduli versus frequency for ~0.11 g/mL PVP/DMSO solution with 3% **1b**. Three different strains from linear to non-linear regime are used, respectively.

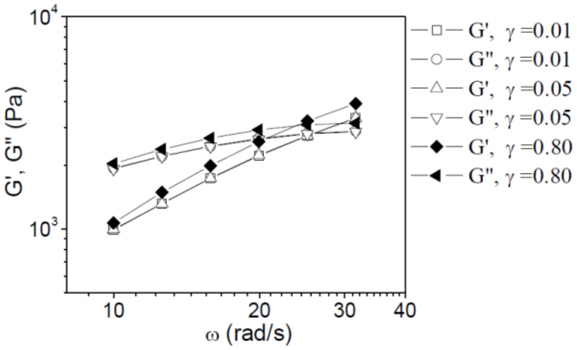

Figure S9. Storage (G') and loss (G'') moduli versus frequency for ~0.11 g/mL PVP/DMSO solution with 2% **1b**. Three different strains from linear to non-linear regime are used, respectively.

In Figure S7-S9, oscillatory frequency sweep for 0.11 g/mL PVP with 2-4% **1b** at three different strains from linear to non-linear regime are shown. The relaxation time (τ) of samples at different strains was calculated from the cross-over frequency (ω_c) of G' and G'' during oscillatory frequency sweep by $\tau=1/\omega_c$, which are shown in Figure 15 in main text.

Lissajous-Bowditch curves from the critical strain (γ_{crit}) to maximum strain (γ_{max}) during strain hardening of ~ 0.11 g/mL PVP with 2-4% 1b at 1 rad/s.

In Figure S10-S12, Lissajous-Bowditch curves from the critical strain (γ_{crit}) to maximum strain (γ_{max}) during strain hardening of ~ 0.11 g/mL PVP with 2-4% **1b** are shown (scanning frequency is 1 rad/s). Only at the end of strain hardening, Lissajous-Bowditch curves deviate from ellipticity, while the Lissajous-Bowditch curves at smaller strains appear as ellipses.

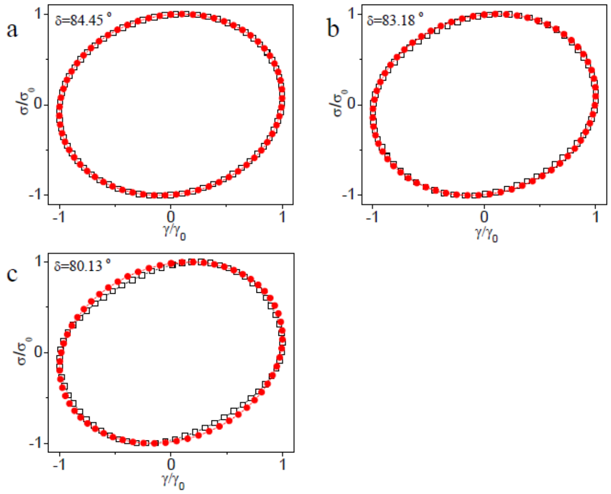

Figure S10. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of ~ 0.11 g/mL PVP with 2% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments. Scanning frequency is 1 rad/s.

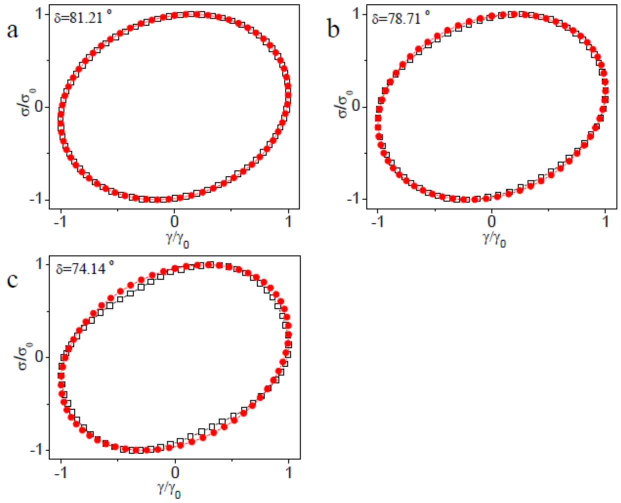

Figure S11. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of ~ 0.11 g/mL PVP with 3% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments. Scanning frequency is 1 rad/s.

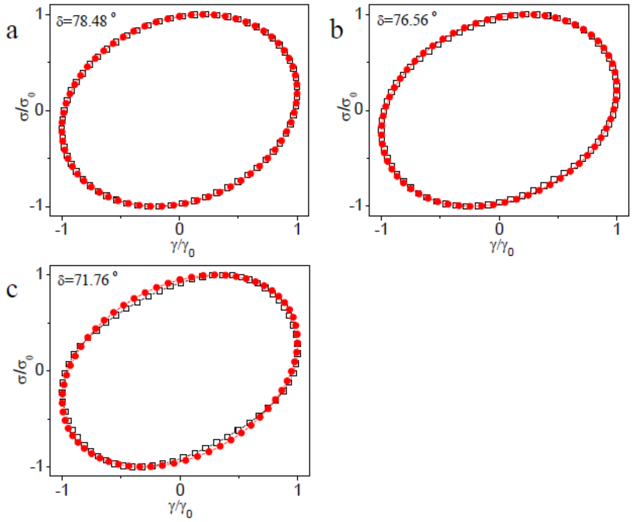

Figure S12. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of ~ 0.11 g/mL PVP with 4% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments. Scanning frequency is 1 rad/s.

Lissajous-Bowditch curves from the critical strain (γ_{crit}) to maximum strain (γ_{max}) during strain hardening of ~ 0.11 g/mL PVP with 5% 1b at 30 rad/s.

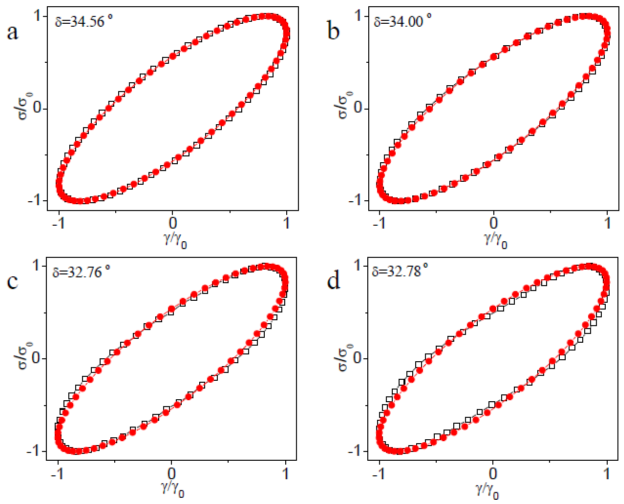

Figure S13. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of ~ 0.11 g/mL PVP with 5% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments. Scanning frequency is 30 rad/s.

In Figure S13, Lissajous curves from the critical strain (γ_{crit}) to maximum strain (γ_{max}) during strain hardening of ~ 0.11 g/mL PVP with 5% **1b** is shown (scanning frequency is 30 rad/s). At the start of strain hardening (Figure S13a and Figure S13b), the Lissajous-Bowditch curves of raw data are elliptical. With the further increasing of strain (Figure S13c and Figure S13d), the Lissajous-Bowditch curves are not elliptical. The phase angle in Figure S13d is a little larger than that in Figure S13c, this means that the network is partial break under larger deformation.

Relaxation time (τ) of ~0.11 g/mL PVP with 1% 1b.

In Figure S14, the relaxation time (τ) of ~0.11 g/mL PVP with 1% **1b** in the linear regime can be obtained from the crossover points between *G′* and *G″* during linear oscillatory frequency sweep. As ω_c is 87.1 rad/s, τ of ~0.11 g/mL PVP with 1% **1b** is 1.1×10^{-2} s.

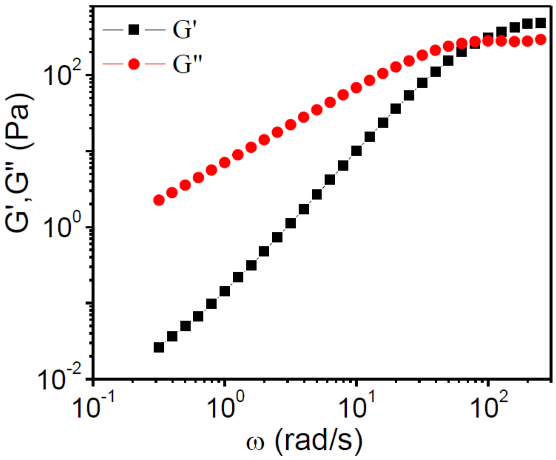

Figure S14. (a) Storage (*G′*) and loss (*G″*) moduli versus angular frequency (ω) for ~0.11 g/mL PVP with 1% **1b**.

Change of relaxation time of network during strain hardening for samples with 1% 1b in the semidilute entangled regime.

To explore how the relaxation time of the samples change with the increasing of strain, we perform the oscillatory frequency sweep from 10 rad/s to ~30 rad/s at three different strain from linear to nonlinear regime for samples with 1% **1b** and PVP concentration from 0.164g/mL to 0.272 g/mL. In Figure S15, change of relaxation time versus applied strain for samples with 1% **1b** and PVP concentration from 0.164g/mL to 0.272 g/mL is shown. The increasing of relaxation time of network during strain hardening is found.

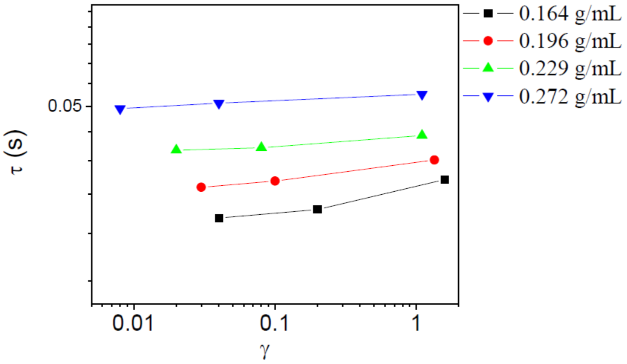

Figure S15. Plot of relaxation time (τ) of samples with 1% **1b** in different concentration of PVP/DMSO solution versus applied strain during oscillatory frequency sweep.

Lissajous-Bowditch curves from the critical strain (γ_{crit}) to maximum strain (γ_{max}) during strain hardening of samples with 1% 1b in the semidilute entangled regime.

In Figure S16-S19, Lissajous-Bowditch curves from the critical strain (γ_{crit}) to maximum strain (γ_{max}) during strain hardening of samples with 1% **1b** with PVP concentration from 0.164 g/mL to 0.272 g/mL is shown (Scanning frequency is 1 rad/s). Only at the end of strain hardening, Lissajous-Bowditch curves deviate from ellipticity, while the Lissajous-Bowditch curves at smaller strains appear as ellipses.

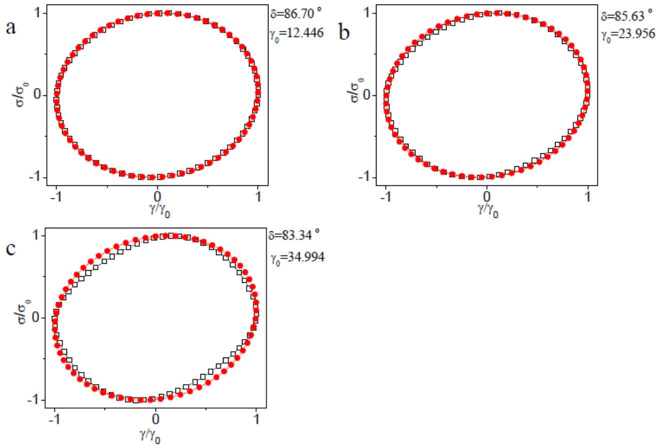

Figure S16. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of 0.164 g/mL PVP with 1% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments. Scanning frequency is 1 rad/s.

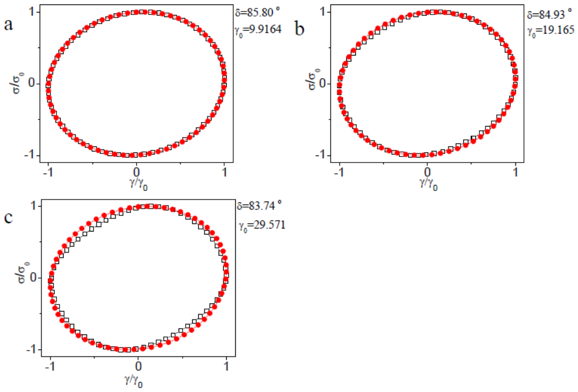

Figure S17. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of 0.196 g/mL PVP with 1% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments. Scanning frequency is 1 rad/s.

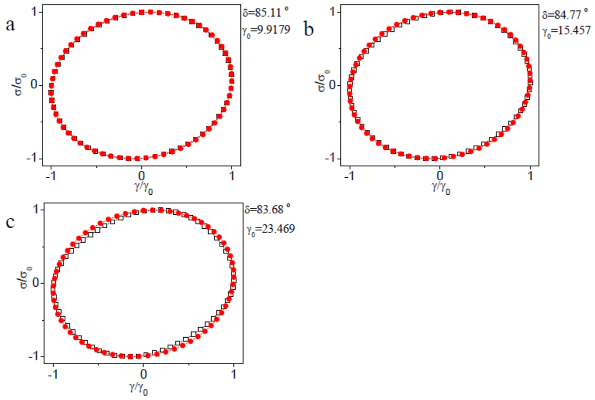

Figure S18. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of 0.229 g/mL PVP with 1% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments. Scanning frequency is 1 rad/s.

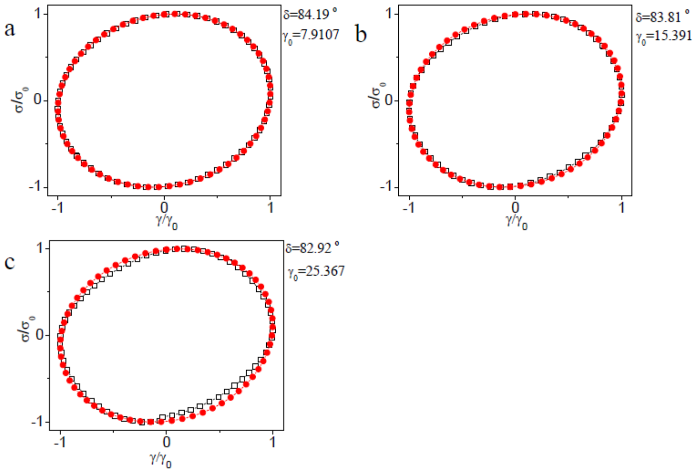

Figure S19. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of 0.272 g/mL PVP with 1% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments. Scanning frequency is 1 rad/s.

Change of relaxation time of network during strain hardening for 0.259 g/mL PVP with 5% 1b from 10rad/s to 30 rad/s.

To explore how the relaxation time of the samples change with the increasing of strain, we perform the oscillatory frequency sweep from 10 rad/s to ~30 rad/s at three different strain from linear to nonlinear regime for 0.259 g/mL PVP with 5% **1b**. In Figure S20, the relaxation time of 0.259 g/mL PVP with 5% **1b** increase a little during strain hardening.

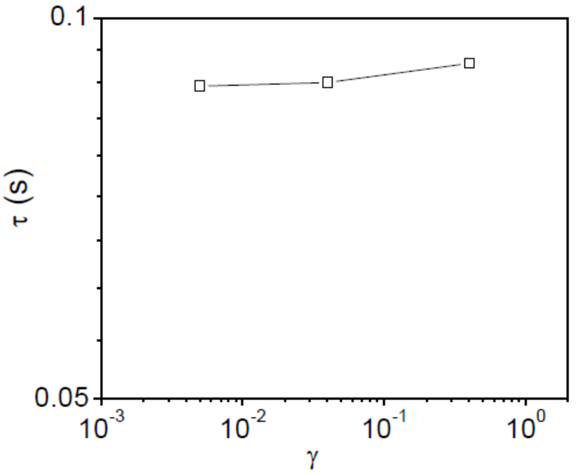

Figure S20. Plot of relaxation time (τ) of 0.259 g/mL PVP with 5% **1b** versus applied strain during oscillatory frequency sweep.

Lissajous-Bowditch curves from the critical strain (γ_{crit}) to maximum strain (γ_{max}) during strain hardening of 0.259 g/mL PVP with 5% 1b from 10rad/s to 30 rad/s.

In Figure S21-S23, Lissajous-Bowditch curves from the critical strain (γ_{crit}) to maximum strain (γ_{max}) during strain hardening of 0.259 g/mL PVP with 5% **1b** is shown (Scanning frequency range from 10rad/s to 30 rad/s.). Only at the end of strain hardening, Lissajous-Bowditch curves deviate from ellipticity, while the Lissajous-Bowditch curves at smaller strains appear as ellipses.

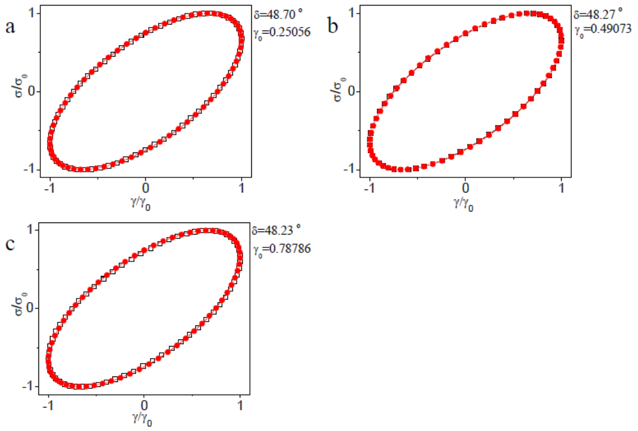

Figure S21. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of 0.259 g/mL PVP with 5% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. Scanning frequency is 10 rad/s. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments.

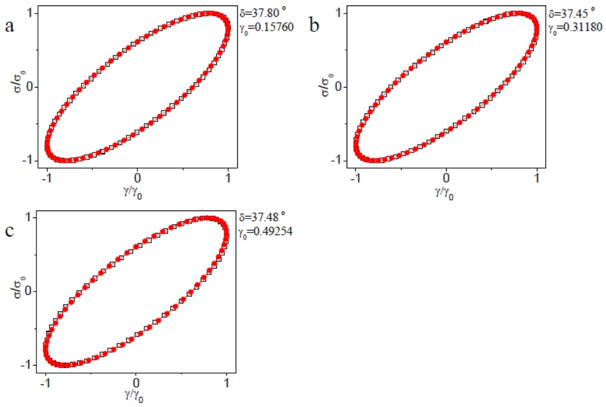

Figure S22. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of 0.259 g/mL PVP with 5% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. Scanning frequency is 20 rad/s. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments.

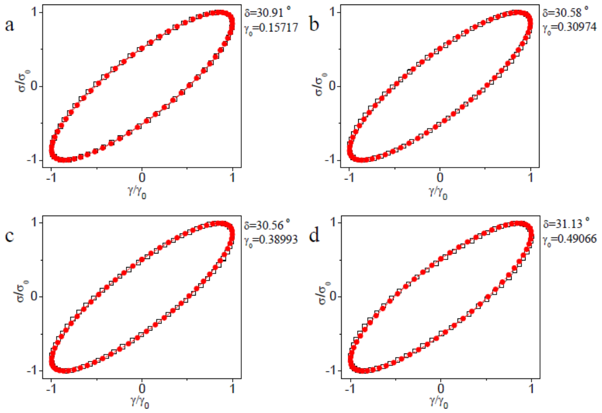

Figure S23. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of ~ 0.259 g/mL PVP with 5% **1b** during strain sweep from the critical strain (γ_{crit}) to maximum strain (γ_{max}) of strain hardening. Scanning frequency is 30 rad/s. The phase angle at different strain is shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments.

Lissajous-Bowditch curves of 0.259 g/mL PVP with 5% 1b at strain softening regime under different scanning frequency

In Figure S24 and Figure S25, Lissajous-Bowditch curves of 0.259 g/mL PVP with 5% **1b** at different scanning frequency 0.3 rad/s and 1 rad/s in the nonlinear regime are shown. The Lissajous-Bowditch curves appear as ellipses at small strain and there is little deformation before the break of the network.

From Figure S20, the apparent relaxation times (τ) of 0.259 g/mL PVP with 5% **1b** in the linear regime is about 8.8×10^{-2} s. At the strain before the break of the network (Figure S24d and Figure S25d), Weissenberg number ($W_i = \gamma_0\omega\tau$) are about 0.3.[S8]

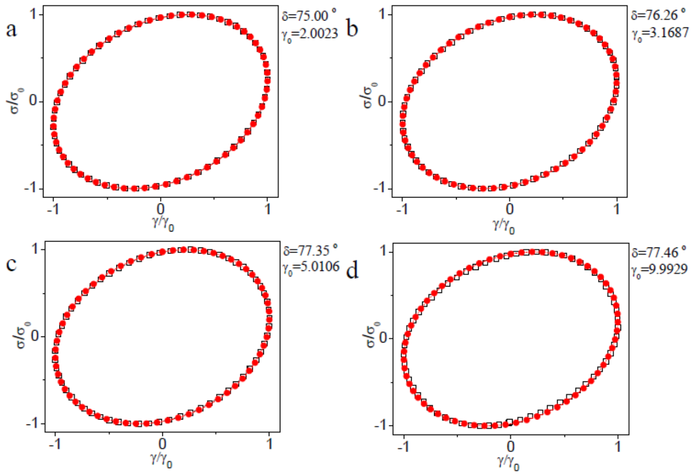

Figure S24. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of 0.259 g/mL PVP with 5% **1b** at strain softening regime under 0.3 rad/s. The phase angle and the strain in the nonlinear regime are shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments.

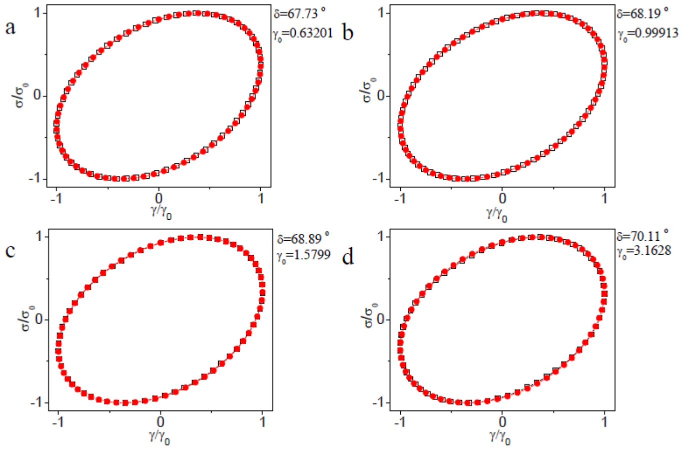

Figure S25. Normalized stress versus strain (Lissajous-Bowditch curves) for the raw data of 0.259 g/mL PVP with 5% **1b** at strain softening regime under 1 rad/s. The phase angle and the strain in the nonlinear regime are shown. Unfilled square symbol represent the raw data. Filled cycle symbol represent the fitted data by the Lissajous-Bowditch curves while time dependent strain and stress are both single-harmonic sinusoid. The phase angle for the fitted data is from the raw phase angle of experiments.

References and Notes

(S1) Ewoldt, R. H.; Hosoi, A. E.; McKinley, G. H. *J. Rheol*. **2008**, *52*, 1427-1458.

(S2) Yount, W. C.; Loveless, D. M.; Craig, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 14488-14496.

(S3) Xu, D.; Hawk, J.; Loveless, D. M.; Jeon, S. L.; Craig, S. L. *Macromolecules* **2010**, *43*, 3556-3565.

(S4) Loveless, D. M.; Jeon, S. L.; Craig, S. L. *Macromolecules* **2005**, *38*, 10171-10177.

(S5) Xu, D.; Craig, S. L. *J. Phys. Chem. Lett*. **2010**, *1*, 1683-1686.

(S6) Xu, D.; Liu, C. Y. ; Craig, S. L. *Macromolecules* **2011**, *44*, 2343-2353.

(S7) Xu, D.; Craig, S. L. *Macromolecules* **2011**, *44*, 5465-5472.

(S8) Larson, R. G. *The Structure and Rheology of Complex Fluids* Oxford University Press, **1999**.