Supporting information

A Role of Electrostatic Repulsion in Gelation of Poly(vinyl alcohol)/Borax Aqueous Solutions

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I. Modified Reversible Gelation model for non-entangled semidilute solution: The complex modulus of this model is expressed as a sum of stress relaxation originating from the Rouse relaxation of the precursor chain G_X^*, the relaxation of the sol chains/gel strands formed in the mean-field and critical percolation regions, G_{MF}^* and G_{CP}^*, respectively, and the dissociation-activated relaxation of the gel network, G_N^*, as classified below for several ranges of the extent of gelation ε.[1, 2]

for $-1 < \varepsilon < -\varepsilon_G$:

$$G^*(\omega) = G_{\text{Rouse}}^*(\omega) + G_{\text{MF}}^*(\omega)$$

$$= i\omega\nu kT\left[\sum_{q=2}^{N_\xi}\frac{\tau_X/q^2}{1+i\omega\tau_X/q^2} + \int_{\tau_X}^{\infty}\frac{(\tau_X/\tau)^1}{i\omega+1/\tau_{\text{char}}+1/\tau}\frac{d\tau}{\tau}\right] \quad \text{(S1)}$$

where $\tau_X = \tau_\xi N_\xi^2$ is the Rouse time of precursor chain, with τ_ξ being the relaxation time of the correlation blob of size ξ, and N_ξ is the number of blobs *per* chain. τ_{char} in eq 1 is the relaxation time of the characteristic sol chain, which scales with ε as $\tau_{\text{char}} = \tau_X|\varepsilon|^{-3}$.

for $-\varepsilon_G \le \varepsilon < -\varepsilon_c$:

$$G^*(\omega) = G^*_{\text{Rouse}}(\omega) + G^*_{\text{MF}}(\omega) + G^*_{\text{CP}}(\omega)$$

$$= i\omega\nu kT\left[\sum_{q=2}^{N_\xi}\frac{\tau_X/q^2}{1+i\omega\tau_X/q^2} + \frac{(N_\xi-1)}{N_\xi}\int_{\tau_X}^{\infty}\frac{(\tau_X/\tau)^1}{i\omega+1/\tau_G+1/\tau}\frac{d\tau}{\tau} + \frac{0.67}{N_\xi}\int_{\tau_G}^{\infty}\frac{(\tau_G/\tau)^{0.67}}{i\omega+1/\tau_{\text{char}}+1/\tau}\frac{d\tau}{\tau}\right] \quad \text{(S2)}$$

$\tau_G = \tau_X N_\xi$ is a characteristic time where a transition from the mean-field type to a critical percolation type occurs. τ_{char} denotes the relaxation time for the characteristic sol chains, which scales with ε as $\tau_{\text{char}} = \tau_G|\varepsilon/\varepsilon_G|^{-4}$, with $\tau_G = \tau_X N_\xi^{-1}$ being the characteristic time of the sol chains at $\varepsilon = -\varepsilon_G$.

for $-\varepsilon_c \le \varepsilon < \varepsilon_c$

$$G^*(\omega) = G^*_{\text{Rouse}}(\omega) + G^*_{\text{MF}}(\omega) + G^*_{\text{CP}}(\omega)$$

$$= i\omega\nu kT\left[\sum_{q=2}^{N_\xi}\frac{\tau_X/q^2}{1+i\omega\tau_X/q^2} + \frac{(N_\xi-1)}{N_\xi}\int_{\tau_X}^{\infty}\frac{(\tau_X/\tau)^1}{i\omega+1/\tau_G+1/\tau}\frac{d\tau}{\tau} + \frac{0.67}{N_\xi}\int_{\tau_G}^{\infty}\frac{(\tau_G/\tau)^{0.67}}{i\omega+1/(\Lambda\tau_c)+1/\tau}\frac{d\tau}{\tau}\right] \quad \text{(S3)}$$

In this range of ε, the system includes very large critical sol chains/gel strands of the relaxation time $\tau_c = \tau_X^{0.25}\tau_s^{0.75}$. τ_c is the Rouse time of a critical sol chain that exhibits the Rouse time identical to the effective breakup time. Λ is a fitting parameter to the order of 1. Rubinstein and Semenove argued[3] that the sol chains/network strands larger than this critical chain (at $-\varepsilon_c \le \varepsilon < \varepsilon_c$) would exhibit effective breakups continuously before the resulting pieces have the critical size, where the pieces further relax through the Rouse-type relaxation to exhibit relaxation time ~ τ_c.

for $\varepsilon_c \le \varepsilon < \varepsilon_G$

$$G^*(\omega) = G^*_{\text{Rouse}}(\omega) + G^*_{\text{MF}}(\omega) + G^*_{\text{CP}}(\omega) + G^*_{\text{N}}(\omega)$$

$$= i\omega\nu kT\left[\sum_{q=2}^{N_\xi}\frac{\tau_X/q^2}{1+i\omega\tau_X/q^2} + \frac{(N_\xi-1)}{N_\xi}\int_{\tau_X}^{\infty}\frac{(\tau_X/\tau)^1}{i\omega+1/\tau_G+1/\tau}\frac{d\tau}{\tau} + \frac{1}{0.67N_\xi}\int_{\tau_G}^{\infty}\frac{(\tau_G/\tau)^{0.67}}{i\omega+1/\tau_{\text{strand}}+1/\tau}\frac{d\tau}{\tau} + \frac{(\varepsilon/\varepsilon_G)^{2.7}}{N_\xi}\frac{\tau_{\text{life}}}{1+i\omega\tau_{\text{life}}}\right] \quad \text{(S4)}$$

$\tau_{\text{strand}} = \tau_G|\varepsilon/\varepsilon_G|^{-4}$ is an average Rouse time of a network strand, and $\tau_{\text{life}} = \tau_s N_\xi^{-1/3}(\varepsilon/\varepsilon_G)^{1.33}$ is the lifetime of the strand controlled by ionic dissociation time τ_s.

for $\varepsilon_G \le \varepsilon < 1$

$$G^*(\omega) = G^*_{\text{Rouse}}(\omega) + G^*_{\text{MF}}(\omega) + G^*_{\text{N}}(\omega)$$

$$= i\omega\nu kT\left[\sum_{q=2}^{N_\xi}\frac{\tau_{\text{X}}/q^2}{1+i\omega\tau_{\text{X}}/q^2} + \frac{(N_\xi - 1)}{N_\xi}\int_{\tau_{\text{X}}}^{\infty}\frac{(\tau_{\text{X}}/\tau)}{i\omega + 1/\tau_{\text{strand}} + 1/\tau}\frac{\mathrm{d}\tau}{\tau} + \varepsilon^3\frac{\tau_{\text{life}}}{1+i\omega\tau_{\text{life}}}\right] \quad \text{(S5)}$$

where $\tau_{\text{strand}} = \tau_{\text{X}}\varepsilon^{-3}$ and $\tau_{\text{life}} = \tau_{\text{s}}\varepsilon$.

Equations S1-S5 give the modulus for the ionomers at $-1 \le \varepsilon \le 1$, i.e., those still containing sol chains. At $\varepsilon > 1$, all the precursor chains in the system are incorporated in the gel, and the modulus becomes sticky Rouse type: [1, 2, 4]

<u>for $1 \le \varepsilon$</u>

$$G^*(\omega) = G^*_{\text{Rouse}}(\omega) + G^*_{\text{SR}}(\omega)$$

$$= i\omega\nu kT\left[\sum_{q=\varepsilon+1}^{N_\xi}\frac{\tau_{\text{X}}/q^2}{1+i\omega\tau_{\text{X}}/q^2} + \sum_{q=1}^{\varepsilon}\frac{\tau_{\text{s}}\varepsilon^2/q^2}{1+i\omega\tau_{\text{s}}\varepsilon^2/q^2}\right] \quad \text{(S6)}$$

Here, G_{Rouse}^* and G_{SR}^* are the *intrinsic* Rouse and sticky Rouse parts of the moduli, respectively. When the sticky Rouse relaxation manifests (at $\varepsilon \ge 1$), the intrinsic Rouse relaxation of the chain is limited for a portion of chain between stickers and thus to the mode indices $q > \varepsilon$. The terminal relaxation of the chain becomes sticky-Rouse type at larger length scales, as represented by the second summation for $q \le \varepsilon$.[1, 2, 4]

II. Shear rate dependences of viscosity: As an example, Figure 1 plots the viscosity η against shear rate $\dot{\gamma}$ for the PVA135 and PVA92 aqueous solutions of different weight fraction w as indicated. At low concentration ($w \le 6$wt% for PVA135 and $w \le 10$wt% for PVA92), the solutions behave as Newtonian fluid for shear rate $\dot{\gamma} < 10^3\text{s}^{-1}$, for which the zero-shear viscosity η_0 can be determined as an average value of all data points (lines attached). In contrast, for high concentration ($w \ge 8$wt% for PVA135 and $w \ge 12$wt% for PVA92), shear thinning is observed at high shear rate, for which the data are fit to the Carreau model (see curves),[5]

$$\eta(\dot{\gamma}) = \frac{\eta_0}{\left[1 + (\dot{\gamma}\tau)^2\right]^m} \quad \text{(S7)}$$

where η_0 is the zero-shear viscosity, τ is a characteristic relaxation time for shear thinning to occur, and m characterizes power law behavior at high shear.

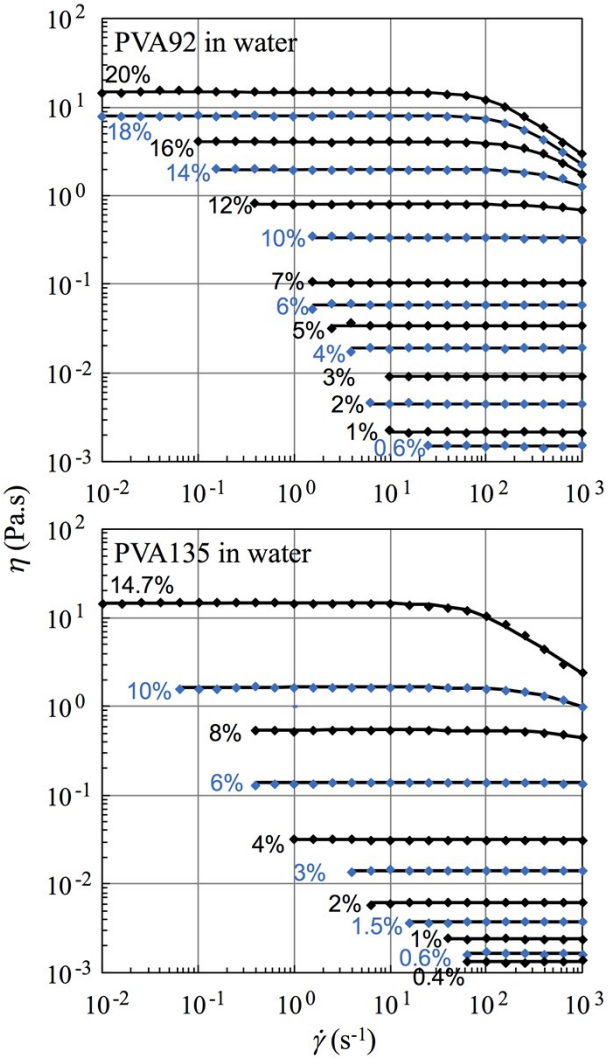

Figure S1: plots of shear viscosity η as a function of shear rate $\dot{\gamma}$ for the PVA92 and PVA135 aqueous representative solutions with concentrations of PVA as indicated.

III. Analysis of LVE reported by Narita and Indei: Since the concentration of PVA is similar to present study, we used $M_\xi \sim C_{\mathrm{PVA}}^{-1/(3\nu-1)}$ and $\tau_0 \sim M_\xi \xi^2 \sim M_\xi^{1+2\nu}$ to estimate M_ξ = 14.1kDa and τ_0 = 0.13μs for the 5.5wt% PVA89 (M_w = 89kDa) solution on a basis of M_ξ = 16.0kDa and τ_0 = 0.16μs of the 5wt% PVA92 solution. τ_s is assumed to be the same as that of the PVA92 sample. By taking ε as the only fitting parameter, we can fit LVE as shown in Figure S2. During the fitting, we tried to fit both G'' and G' for the samples of [borax] ≥ 1.7mM. Nevertheless, for samples having [borax] ≤ 1.2mM, the similar agreement cannot be achieved for G'' and G', where we try to fit G'' that is less vulnerable to the inertia effect than G'.

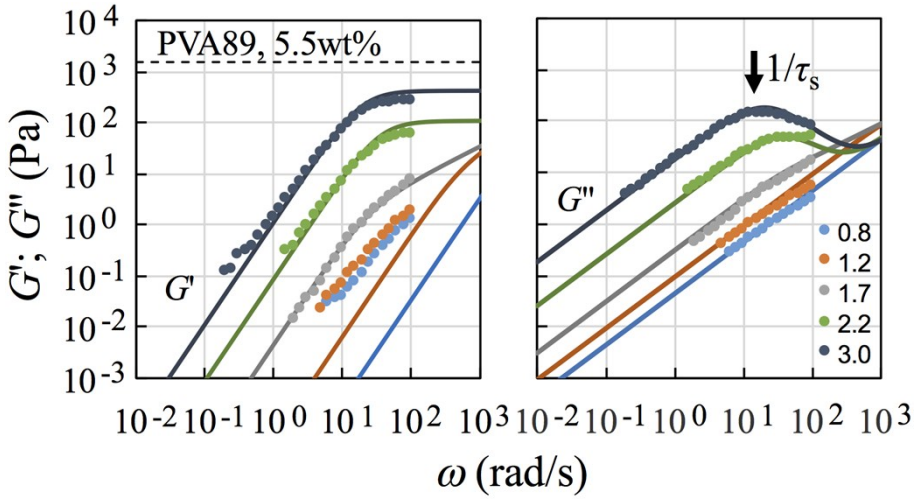

Figure S2: Storage and loss moduli, G' and G'' as function of angular frequency ω reported by Narita and Indei. The symbols are experimental results and the curves are fitting curve of the reversible gelation model, with degree of gelation ε as an adjustable parameter. For the two samples having 0.8mM and 1.2mM borax, the fitting can only be achieved simultaneously for G' and G'', the fitting is focused on G'' that is less vulnerable to instrument inertia.

References

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5. J. D. Ferry, *Viscoelastic Properties of Polymers, 3rd ed.*, Wiley, New York, 1980.