

Electronic Supplementary Information

Colloidal probe dynamics in gelatin solution during the sol-gel transition

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1. Estimation of the dynamic property of the gelatin solution used in the present study

The molecular weight and molecular dimensions of the gelatin used in the present work can be estimated by intrinsic viscosity measurement results and the literature data. In the present work, the type B gelatin is dissolved in salt-free water at a concentration of 6 wt%. We can only find one light scattering experiment on type B gelatin by Boedtker and Doty (1954) where the molecular weight and the intrinsic viscosity were reported. The intrinsic viscosity is related to the molecular weight by the Flory–Fox relation^{2, 3}

$$[\eta] = \Phi_0 \frac{\langle h^2 \rangle_0^{\frac{3}{2}}}{M} \alpha^3 \quad (1)$$

where $\langle h^2 \rangle_0$ is the unperturbed mean-square end-to-end distance, M is molecular weight, Φ_0 is a factor approaching $2.87 \times 10^{23} \text{ mol}^{-1}$ in the non-free-draining limit.⁴ α is the uniform expansion factor. α is related to the Flory exponent ν by $\alpha = N^{\nu-0.5}$, where $N = L_c / b$ is the number of Kuhn segments per chain, $L_c = M / M_L$ is the contour length of the chain, b is the length of a Kuhn segment, and M_L is the molecular weight per unit length of chain, which was measured to be $28 \pm 8 \text{ g mol}^{-1} \text{ \AA}^{-1}$.⁵ Eq. (1) is then rearranged to be

$$[\eta] = \Phi_0 \frac{b^{3-3\nu}}{M_L^{3\nu}} M^{3\nu-1} \quad (2)$$

Within the same solution condition, the value of ν and the coefficients before $M^{3\nu-1}$ are constants so that a proportional relation holds as $[\eta] \sim M^{3\nu-1}$. To obtain the value of ν we need two sets of data of $[\eta]$ and M . One set can be those from Boedtker and Doty (1954) which are listed in Table 1. The other set has to be measured with our sample. The intrinsic viscosity of our sample was measured to be $0.72 \pm 0.03 \text{ dL/g}$ (data shown in Figure 1A). However, the molecular weight of our sample was not measured due to limited facilities. We then sought to estimate the molecular weight of our sample from other data as following.

Pezron, *et al.* (1991) and Bohidar and Jena (1994) studied Type B gelatin solutions in 0.1 M NaCl at 50 °C. Their reported data are listed in Table 1. To obtain the molecular weight of our sample from eq. (1) or (2), we need to know the value of either the expansion factor α or the Flory exponent ν of the corresponding condition. As noted by Gouinlock, *et al.* (1955), the value of $(\alpha^5 - \alpha^3) / M^{1/2}$ does not vary much among different polymers solutions with the same second virial coefficient A_2 . One can then estimate the expansion factor for the gelatin solution with known A_2 and $M^{1/2}$ from the corresponding values of another polymer. Namely, the expansion factor for gelatin in

0.1 M NaCl at 50 °C was estimated by extrapolation from the data of polyisobutylene solution listed in Table 1. The length of a Kuhn segment b is related to the persistence length l_{p0} at the unperturbed condition by $b = 0.5l_{p0}$. Pezron, *et al.* (1991) measured the persistence length $l_p = 40 \pm 5 \text{ \AA}$ at the swollen state (when the second virial coefficient $A_2 > 0$) as the wave vector q^{-1} where the transition of the scattering intensity from coil ($\sim q^{-2}$) to rod ($\sim q^{-1}$) occurs at the high q regime. This value is expected to relate with its unperturbed counterpart by $l_p = \alpha l_{p0} = 2ab$, giving $b = 16 \text{ \AA}$. Therefore the Flory exponent ν is calculated by $\nu = \log \alpha / \log[M / (M_L b)] + 1/2$. Using the data by Pezron, *et al.* (1991) and Bohidar and Jena (1994) gives nearly identical results of $\nu = 0.53$, justifying the accuracy of the above estimation of molecular dimensions. The molecular weight of our sample is calculated using again the $[\eta] \sim M^{3\nu-1}$ relation and the measured intrinsic viscosity (Figure 1B) to be $M = 5.54 \times 10^5 \text{ g mol}^{-1}$.

With all these data at hand we can calculate the Flory exponent for salt-free water to be $\nu = 0.45$. The end-to-end distance $\langle h^2 \rangle^{1/2} = \alpha \langle h^2 \rangle_0^{1/2} = 536.3 \text{ \AA}$. Using the first-order perturbation, the radius of gyration $\langle S^2 \rangle^{1/2} = 215.3 \text{ \AA}$. The overlap concentration c^* can then be calculated by

$$c^* = \frac{3M}{4\pi N_A \langle S^2 \rangle^{3/2}} \quad (3)$$

to be $20.7 \text{ kg m}^{-3} \sim 2.0 \text{ wt\%}$. Therefore, the gelatin solution used in the present study (6 wt%) is well above the overlap concentration. The correlation length ξ_{blob} at the solution state is estimated by

$$\xi_{\text{blob}} = \langle S^2 \rangle^{1/2} \left(\frac{c}{c^*} \right)^{-\nu/(3\nu-1)} \quad (4)$$

to be 59.3 \AA , with the corresponding relaxation time $\tau_{\text{blob}} = 6\pi\eta_s \xi_{\text{blob}}^3 / (k_B T) = 5.95 \times 10^{-7} \text{ s}$ at 40.2 °C (using $\eta_s = 6.736 \times 10^{-4} \text{ Pa s}$ for water at the same temperature). The viscosity of the solution can be estimated by

$$\eta = \eta_s \left(\frac{c}{c^*} \right)^{1/(3\nu-1)} \quad (5)$$

by Rouse dynamics to be $1.568 \times 10^{-2} \text{ Pa s}^{-1}$, assuming no entanglements.⁸ This is reasonably close to the value of $3.134 \times 10^{-2} \text{ Pa s}^{-1}$ calculated from the MSD of the earliest observed gel time $t_w = 12 \text{ min}$ by the Stokes–Einstein relation, again justifying the accuracy of the above estimations of molecular dimensions. The mesh size at the gel state is estimated by the plateau modulus G_p measured by macroscopic rheology using the relation by Nijenhuis (1991)

$$G_p = \frac{2cRT}{M} \left(\frac{M}{M_c} \frac{f-2}{f} - 1 \right) (1 - w_s) \quad (6)$$

$$\frac{M}{M_c} = - \frac{\ln w_s}{1 - w_s} \frac{1 - w_s^{0.5f}}{1 - w_s^{0.5f-1}} \quad (7)$$

c is the concentration of the uncrosslinked polymer. M_c is the molecular weight of crosslinking. f is the functionality of the crosslinking. For gelatin the crosslinking was consist of triple helix formation, so we take $f = 6$. w_s is the sol fraction. From eqs. (6) and (7) the molecular weight between crosslinking $M_c = 2.3 \times 10^5 \text{ g mol}^{-1}$ and the sol fraction $w_s = 0.14$ can be obtained from the measurement of G_p (Figure 1C). The low value of w_s guaranteed that the measured G_p is close to equilibrium modulus. The mesh size at the gel state ζ_{mesh} is assumed to be the end-to-end distance of a strand between crosslinking, which is $\zeta_{\text{mesh}} = \langle h^2 \rangle^{1/2} = b^{1-\nu} (M_c / M_L)^\nu = 266.6 \text{ \AA}$, with the corresponding relaxation time $\tau_{\text{mesh}} = 6\pi\eta_s \zeta_{\text{mesh}}^3 / (k_B T) = 7.83 \times 10^{-6} \text{ s}$ (with the water viscosity $\eta_s = 9.003 \times 10^{-4} \text{ Pa s}$ at $24.5 \text{ }^\circ\text{C}$).

Table 1 Literature data of polymer solution experiments

	M (10^5 g mol^{-1})	A_2 ($10^{-4} \text{ mol cm}^3 \text{ g}^{-2}$)	l_p (\AA)	$[\eta]$ (dL g^{-1})	$(\alpha^5 - \alpha^3)/M^{1/2}$ ($10^{-3} \text{ mol}^{1/2} \text{ g}^{-1/2}$)
Type B gelatin, 0.1 M NaCl, $50 \text{ }^\circ\text{C}$ ⁵	1.9 ± 0.1	3 ± 1	40 ± 5		
Type B gelatin, 0.1 M NaCl, $50 \text{ }^\circ\text{C}$ ⁶	2.81 ₇	2.60 ₅		0.37 ₂	
Type B gelatin, salt-free, $40.2 \text{ }^\circ\text{C}$ ¹	92000			0.381	
Polyisobutylene, cyclohexane, $30 \text{ }^\circ\text{C}$		$5.7^{10,12}$			$4.9^{10,13}$
Polyisobutylene, benzene, $40 \text{ }^\circ\text{C}$		$1.6^{11,12}$			$0.50^{10,13}$

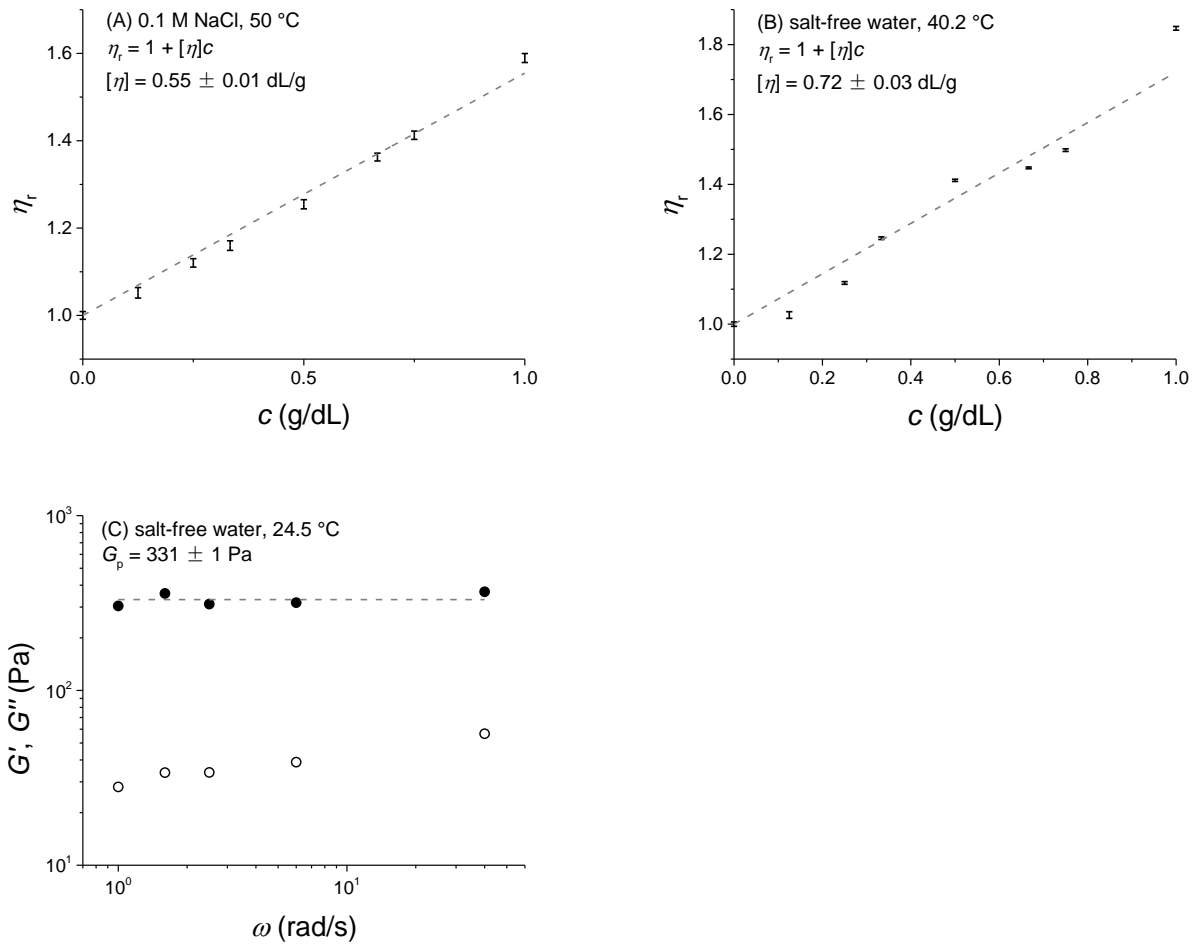


Figure 1 (A) Relative viscosity of gelatin in 0.1 M NaCl at 50 °C. (B) Relative viscosity of gelatin in salt-free water at 40.2 °C. The dash lines in (A) and (B) corresponds to the fit of the relation $\eta_r = 1 + [\eta]c$ for the intrinsic viscosities which are indicated in the figures. (C) Storage and loss moduli of gelatin in salt-free water, 24.5 °C. The dash line corresponds to a fit for the plateau modulus which are indicated in the figure.

2. Shifting method of the time–cure superposition master curves

The master curves were constructed by two-dimensional minimization according to the essence of previously reported algorithm.¹⁴ After the curves are shifted, a local residue \mathbf{r}_i can be defined as the vector between a pair of adjacent points between the reference and the shifted curves (see Figure 2 for an illustration). An error χ^2 characterizing how well a shifted curve overlaps with the reference curve can then be defined for each shift factor as

$$\chi^2 \equiv \frac{\sum_{i=1}^n |\mathbf{r}_i|}{n} \quad (8)$$

where n is the total pairs of adjacent points within the overlapping region of the two curves.

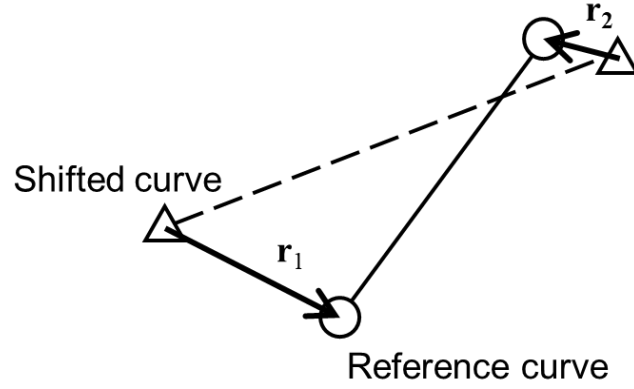


Figure 2 Illustration of the definition of local residues

In the present study, the shift factors were obtained from the construction of the master curves of the dynamic moduli converted from the MSD by the GSER. The local residues were calculated using the values under the units of modulus (Pa) and angular frequency (rad/s), respectively. The errors corresponding to each shift factors were listed in Table 2.

Table 2 Errors of shifting corresponding to the shift factors

Pre-gel		Post-gel	
t_w (min)	χ^2	t_w (min)	χ^2
12	(reference)	30	(reference)
16	0.09985	32	0.04560
20	0.06465	34	0.12004
22	0.09308	60	0.02579
24	0.08501		
25	0.08663		
26	0.03896		
28	0.08766		
29	0.09894		

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