

Electronic Supplementary Information

for

**Quantifying the effects of cooperative hydrogen bonds between vicinal diols
on polymer dynamics**

Authors:

Shintaro Nakagawa¹, Jun Xia¹, and Naoko Yoshie^{1*}

*Corresponding author. E-mail: yoshie@iis.u-tokyo.ac.jp.

Affiliations:

1: Institute of Industrial Science, The University of Tokyo, Komaba 4-6-1, Meguro-ku, Tokyo 153-8505 Japan

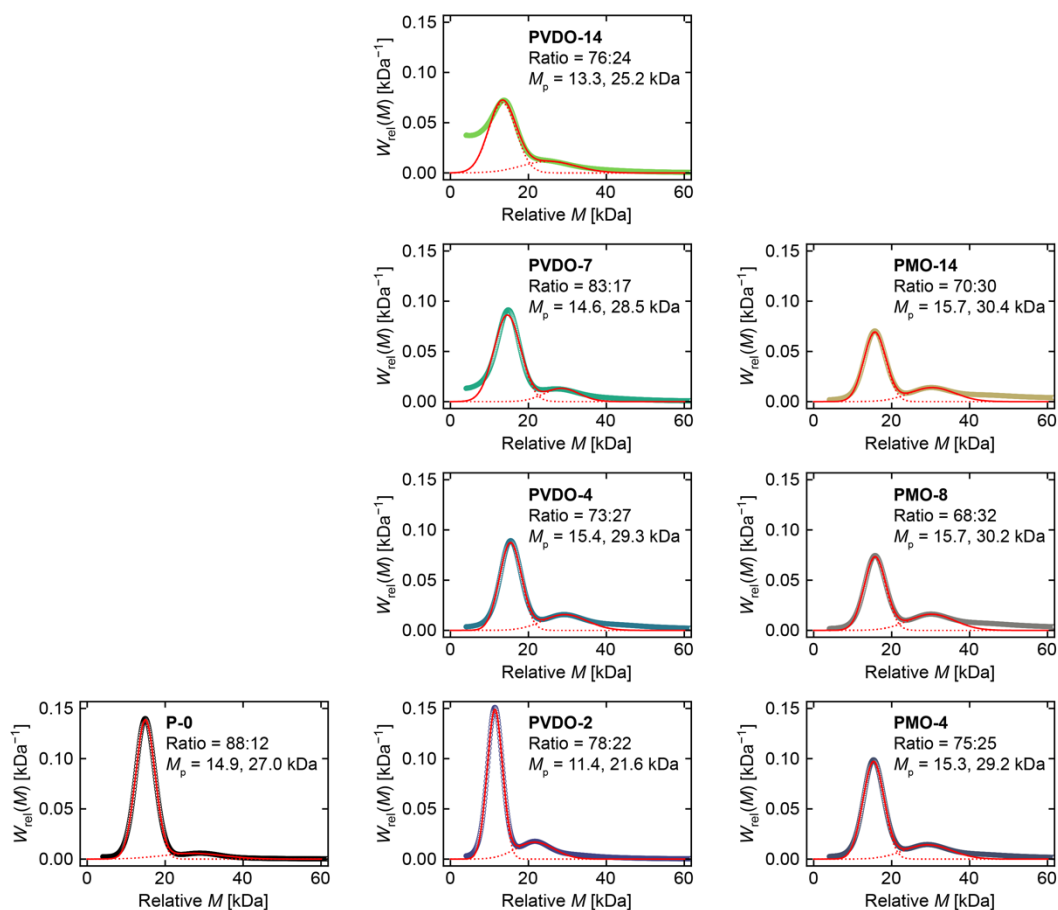


Fig. S1. Weight distribution of relative molecular weight derived from SEC curves in Fig. 2c and d using eqn 5 in the main text. Note that the molecular weight here is relative one based on polystyrene standards and therefore is not equal to the absolute molecular weight. The red curves show the results of peak deconvolution using two Gaussian functions (dotted: individual peaks, solid: sum of two peaks). The weight ratio and the peak relative molecular weight of the two separated peaks are indicated in each panel.

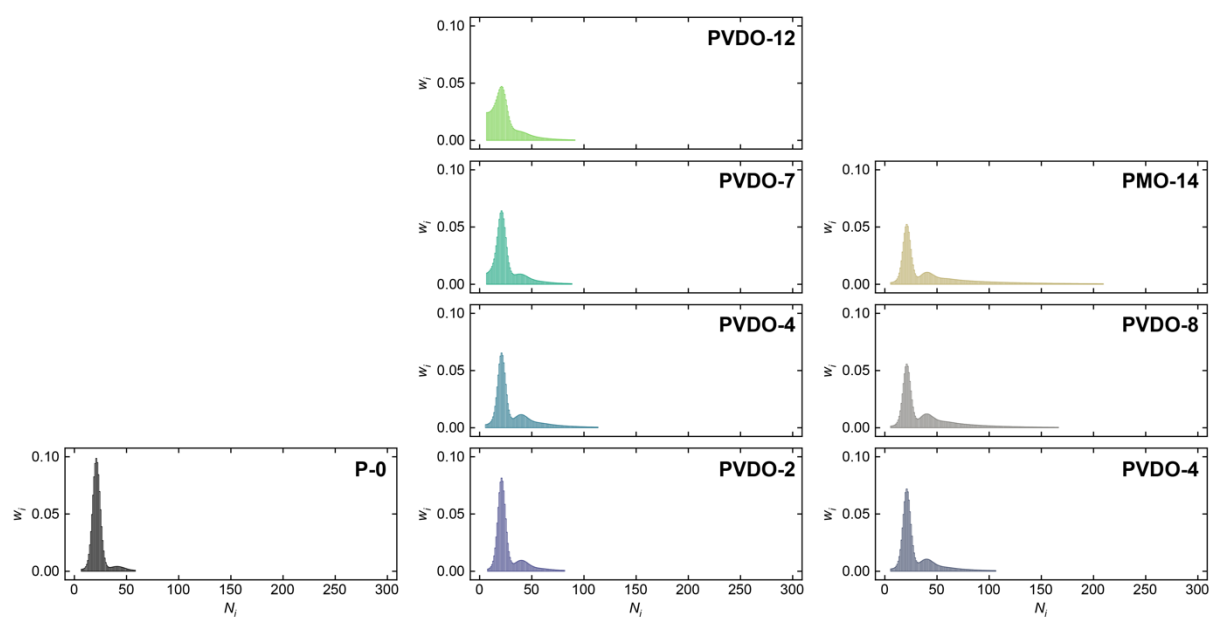


Fig. S2. Weight fraction w_i of the chains consisting of N_i Rouse segments derived from the SEC traces in Fig. 2c and d. Refer to the main text for details.

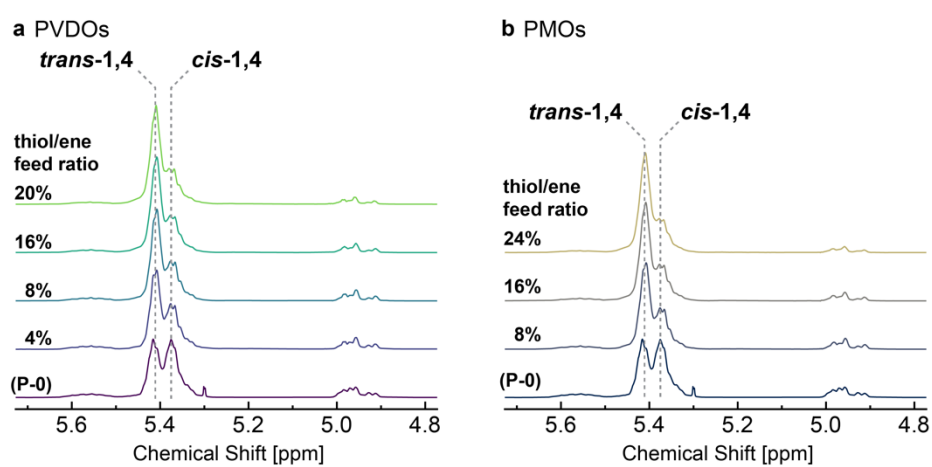


Fig. S3. Enlarged ^1H NMR spectra of PVDOs (a) and PMOs (b).

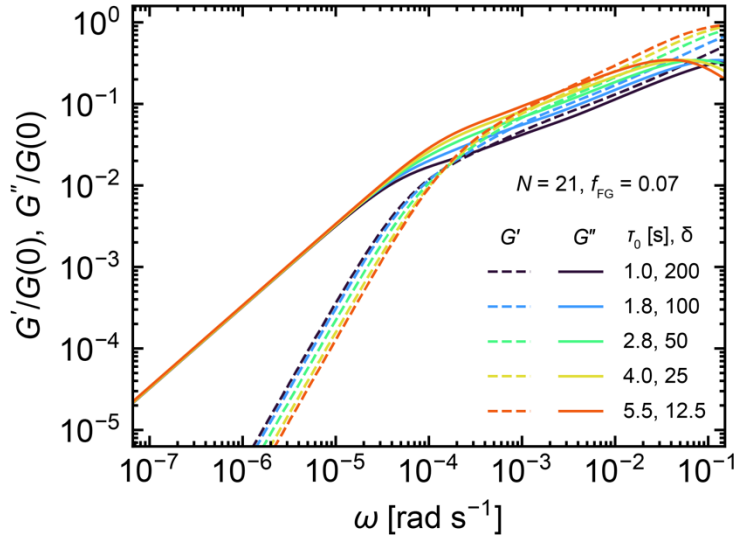


Fig. S4. Theoretical dynamic moduli calculated by using the sticky Rouse model highlighting the impact of the choice of τ_0 and δ on the terminal flow behavior. All calculations were carried out using $N = 21$ (corresponding to the molecular weight of 5 kDa for PB) and $f_{FG} = 0.07$ without the molecular weight distribution. The average was taken over 10,000 randomly-generated chain sequences for each parameter set (see Theory section in the main text). The parameters τ_0 and δ were chosen as follows. First, reference curves were obtained by setting $\tau_0 = 1.0$ s and $\delta = 200$. Then, calculations were performed for four different values of $\delta = 100, 50, 25$, and 12.5 . τ_0 was adjusted so that the terminal decay of G'' ($\omega < 10^{-5}$ rad s $^{-1}$) overlapped with the reference curves.

Table S1. Parameters used for the Rouse model and the sticky Rouse model plots in Fig. 5a-c.

Code	f_{FG} [%]	δ (sticky Rouse with fixed $\tau_0 = 0.012$ μ s) ^a
P-0	0	-
PVDO-2	1.7	4.0×10^2
PVDO-4	3.8	8.5×10^2
PVDO-7	7.4	1.9×10^3
PVDO-12	12.4	6.0×10^3
PMO-4	3.6	- ^b
PMO-8	8.4	- ^b
PMO-14	14.4	- ^b

a: Parameter δ used for the sticky Rouse model fitting in Fig. 5a and b, with τ_0 being fixed to 0.012 μ s, which was not successful for PVDOs. b: These values are reported in Table 2.

Detailed analysis of the molecular weight distribution and possibility of entanglement.

Fig. S1 shows the weight distribution function $W_{rel}(M)$ of the relative molecular weight calculated based on the SEC curves in Fig. 2c and d using eqn 5. The main peak at around ~ 15 kDa is accompanied by an additional smaller peak at the higher molecular weight side. We fitted observed

$W_{\text{rel}}(M)$ by the sum of two Gaussian functions. The results of the fitting are also shown in Fig. S1, together with the peak relative molecular weight M_p and the area ratio of the two peaks. The M_p of the additional peak is roughly two times that of the main peak, suggesting that the additional peak is due to intermolecular coupling of two original chains. The absolute M_n of these chains would be approximately twice that of the original PB (~ 5 kDa), i.e., ~ 10 kDa.

Next, we verify whether the coupled chains are entangled or not. As has been explained in the main text, onset molecular weight of entanglement (M_c) is 2-3 times the entanglement molecular weight (M_e)¹. The lowest reported value of entanglement molecular weight (M_e) of PBs with low 1,2-unit ratios is ~ 1.9 kDa². Using this value and $M_c \sim 3M_e$, $M_c \sim 5.7$ kDa. While the M_n of the original PB (~ 5 kDa) is safely below M_c , that of the coupled chains (~ 10 kDa) exceeds M_c . However, the coupled chains are diluted with the shorter unentangled chains, which would increase the effective M_c . It is known that M_c in polymer solutions scales as $M_c(\phi) \sim 1/\phi$ where ϕ is the polymer volume fraction^{3,4}. It leads to $M_c(\phi) = M_c(1)/\phi$ where $M_c(1)$ is the entanglement molecular weight in the solvent-free polymer melt. Assuming that M_c would behave similarly, $M_c(\phi) = M_c(1)/\phi$. The critical value of ϕ at which the molecular weight of 10 kDa reaches $M_c(\phi)$ is estimated to be $(5.7 \text{ kDa}/10 \text{ kDa}) \sim 57\%$. That is, the coupled chains with $M_n \sim 10$ kDa are entangled above the volume fraction of 57% (which is almost equal to the weight fraction). The ratios of the coupled chains shown in Fig. S1 are at most 32%, which is well below the threshold. Thus it can be concluded that our modified PBs were unentangled.

References.

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