Supplementary Materials:

Entropy driven thermo-gelling vitrimer

Xiuyang Xia,†‡§ Peilin Rao,†§ Juan Yang,¶ Massimo Pica Ciamarra,‡ and Ran Ni*†

†School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459
‡Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371
¶Department of Chemistry, National University of Singapore, 117546 Singapore
§These authors contributed equally.

E-mail: r.ni@ntu.edu.sg
S1: Mean-field theory for thermo-crosslinking vitrimers

The free energy of the system per reactive site can be written as

\[
\frac{\beta F}{N_{\text{poly}m}} = \frac{1}{m} \left( \ln \frac{N_{\text{poly}} \Lambda^3}{V} - 1 \right) + \sum_{i=B,C,D} f_i \left( \ln \frac{f_i N_{\text{poly}} m \Lambda^3}{V} - 1 \right)
\]

\[
+ f_{PC} \ln f_{PC} + f_{PD} \ln f_{PD} + \frac{f_{P2C}}{2} \ln \frac{f_{P2C}}{2} + f_P \ln f_P + \left( 1 - \frac{f_{P2C}}{2} \right) \left( \ln \frac{m \Lambda^3}{V_p} - 1 \right)
\]

\[
+ \frac{\beta F_{\text{ex HS}}}{N_{\text{poly}m}} - \frac{f_{P2C}}{2} k_B^{-1} \Delta S - \beta \left( f_{PC} + \frac{f_{P2C}}{2} + f_C \right) \mu_C - \beta \left( f_{PD} + f_D \right) \mu_D - f_B \beta \mu_B
\]

\[
+ \beta \left( f_{PC} + f_{P2C} \right) \left( \Delta G_C + \mu_B \right) + \beta f_{PD} \left( \Delta G_D + \mu_B \right), \quad (S1)
\]

where \( f_{P2C} = 2N_{P2C}/N_{\text{poly}m} \) and \( f_i = N_i/N_{\text{poly}m} \) for \( i=P, PC, PD, B, C \) and \( D \), with \( f_P + f_{PC} + f_{PD} + f_{P2C} = 1 \). The excess free energy \( F_{\text{ex HS}} \) based on the Carnahan–Starling hard-sphere equation of state [36] can be represented as

\[
\beta F_{\text{ex HS}} = \frac{\phi V}{v_0} \frac{4 \phi - 3 \phi^2}{(1 - \phi)^2}, \quad (S2)
\]

with \( \phi = N_{\text{tot}} v_0 / V \) the packing fraction of the system. \( N_{\text{tot}} \) is the total particle number in the system

\[
N_{\text{tot}} = 2N_{PC} + 2N_{PD} + 3N_{P2C} + 2N_P + N_B + N_C + N_D + N_e
\]

\[
= 2m N_{\text{poly}} - N_{P2C} + N_B + N_C + N_D + N_e, \quad (S3)
\]

where \( N_e \) is number of non-reactive backbone beads on the polymers in the system. Here, we use the fact that each dangling P, PC or PD bond contains two particles, while a cross-linking bond (P2C) has three particles. Defining excess chemical potential \( \mu_{\text{ex HS}} \) arising from \( F_{\text{ex HS}} \) for a single particle, we can have

\[
\beta \mu_{\text{ex HS}} = \beta \frac{\partial F_{\text{ex HS}}}{\partial N_{\text{tot}}} = \frac{\phi (3 \phi^2 - 9 \phi + 8)}{(1 - \phi)^3}, \quad (S4)
\]
With the saddle-point approximation

\[ \frac{\partial F}{\partial f_i} = 0, \quad (i = \text{PC, PD, P}_2\text{C, B, C, D}), \]  

(S5)

we can obtain

\[
\begin{align*}
    f_B &= \frac{V}{N_{\text{poly}} m \Lambda^3} e^{\beta \mu_B - \beta \mu_{\text{HS}}} , \\
    f_C &= \frac{V}{N_{\text{poly}} m \Lambda^3} e^{\beta \mu_C - \beta \mu_{\text{HS}}} , \\
    f_D &= \frac{V}{N_{\text{poly}} m \Lambda^3} e^{\beta \mu_D - \beta \mu_{\text{HS}}} ,
\end{align*}
\]

(S6-S8)

and

\[
\begin{align*}
    f_{\text{PC}} &= f_P \Xi_{\text{PC}} = f_P e^{\beta (\mu_C - \mu_B + \epsilon)} , \\
    f_{\text{PD}} &= f_P \Xi_{\text{PD}} = f_P e^{\beta (\mu_D - \mu_B + \gamma \epsilon)} , \\
    f_{\text{P}_2\text{C}} &= f_P^2 \Xi_{\text{P}_2\text{C}} = f_P^2 \frac{2m \Lambda^3}{V_p} e^{\beta (\mu_C - 2\mu_B + 2\epsilon + \mu_{\text{HS}} + k_B \Delta S)} ,
\end{align*}
\]

(S9-S11)

where \( \Xi_{\text{PC}}, \Xi_{\text{PD}} \) and \( \Xi_{\text{P}_2\text{C}} \) can be considered as the effective bond strength for a PC, PD and \( \text{P}_2\text{C} \) bond taking the precursors P as the reference state. Substituting Eq. 4 into Eqs. S9-S11, we can obtain

\[ \Xi_{\text{P}_2\text{C}} f_P^2 + (1 + \Xi_{\text{PC}} + \Xi_{\text{PD}}) f_P - 1 = 0, \]  

(S12)

with a closed-form solution

\[ f_P = \sqrt{(1 + \Xi_{\text{PC}} + \Xi_{\text{PD}})^2 + 4\Xi_{\text{P}_2\text{C}} - (1 + \Xi_{\text{PC}} + \Xi_{\text{PD}})} \frac{2\Xi_{\text{P}_2\text{C}}}{2\Xi_{\text{P}_2\text{C}}}. \]  

(S13)
**S2: Chemical equilibrium and reaction equilibrium**

For reactions in the system

\[
P + C \xleftrightarrow{K_1} PC + B, \quad (S14)
\]
\[
PC + P \xleftrightarrow{K_2} P_2C + B, \quad (S15)
\]
\[
P + D \xleftrightarrow{K_3} PD + B, \quad (S16)
\]

one can have chemical equilibrium with chemical constants \( K_1, K_2 \) and \( K_3 \)

\[
K_1 \rho_P \rho_C = \rho_{PC} \rho_B, \quad (S17)
\]
\[
K_2 \rho_P \rho_{PC} = \rho_{P_2C} \rho_B, \quad (S18)
\]
\[
K_3 \rho_P \rho_D = \rho_{PD} \rho_B, \quad (S19)
\]

and the balances of chemical potentials

\[
\mu_P + \mu_C = \mu_{PC} + \mu_B, \quad (S20)
\]
\[
\mu_P + \mu_{PC} = \mu_{P_2C} + \mu_B, \quad (S21)
\]
\[
\mu_P + \mu_D = \mu_{PD} + \mu_B. \quad (S22)
\]

The chemical potential for species \( i \) can be decomposed into the ideal part and excess parts:

\[
\mu_i = \mu_{i}^{ex} + \mu_{i}^{id}, \quad (S23)
\]
\[
\mu_{i}^{id} = k_B T \ln \rho_i \Lambda^3, \quad (S24)
\]
with $\rho_i = N_i/V$ the density of species $i$ in the system. The excess chemical potential $\mu_i^{\text{ex}}$ for specie $i$ can be approximated as

$$
\mu_i^{\text{ex}} \simeq \ln \left( \frac{V}{N_{\text{poly}} V_p} \right) + 2\mu_{\text{HS}},
$$

(S25)

$$
\mu_{PC}^{\text{ex}} \simeq \ln \left( \frac{V}{N_{\text{poly}} V_p} \right) + 2\mu_{\text{HS}} - \epsilon,
$$

(S26)

$$
\mu_{PD}^{\text{ex}} \simeq \ln \left( \frac{V}{N_{\text{poly}} V_p} \right) + 2\mu_{\text{HS}} - \gamma \epsilon,
$$

(S27)

$$
\mu_{P2C}^{\text{ex}} \simeq \ln \left( \frac{V}{N_{\text{poly}} V_p} \right) + 3\mu_{\text{HS}} - 2\epsilon - k_B^{-1} \Delta S,
$$

(S28)

$$
\mu_{B}^{\text{ex}} \simeq \mu_{\text{HS}},
$$

(S29)

$$
\mu_{C}^{\text{ex}} \simeq \mu_{\text{HS}},
$$

(S30)

$$
\mu_{D}^{\text{ex}} \simeq \mu_{\text{HS}}.
$$

(S31)

Combining the chemical equilibrium and the balances of chemical potentials, we can obtain

$$
K_1 = e^{\beta \epsilon},
$$

(S32)

$$
K_2 = \frac{V}{N_{\text{poly}} V_p} e^{\beta \epsilon + k_B^{-1} \Delta S},
$$

(S33)

$$
K_3 = e^{\beta \gamma \epsilon},
$$

(S34)

$$
K_2 \frac{K_1}{K_2} = \frac{V}{N_{\text{poly}} V_p} e^{k_B^{-1} \Delta S},
$$

(S35)

which indicates the unknown values $V_p$ and $\Delta S$ can be obtain by computer simulation or experiments. The excess chemical potential $\mu_{\text{HS}}^{\text{ex}}$, or equilibrated packing fraction $\phi_{\text{eq}}$, can be obtained by solving the following equation for $\phi_{\text{eq}}$ based on Eq. S4

$$
\phi_{\text{eq}} = \phi_P \frac{m + n}{n} + \frac{N_{\text{poly}} m v_0}{V} \left[ - f_{P2C}(\phi_{\text{eq}}) + f_B(\phi_{\text{eq}}) + f_C(\phi_{\text{eq}}) + f_D(\phi_{\text{eq}}) \right].
$$

(S36)
S3: Mean-field theory at the high temperature limit

At the high temperature limit, i.e. $\beta \epsilon \to 0$, the saddle point solutions of $f_{PC}$, $f_{PD}$, and $f_{P2C}$ at the limit can be represented by

$$f^\infty_{PC} = f^\infty_P \Xi^\infty_{PC} = f^\infty_P e^{\beta(\mu_C - \mu_B)}, \tag{S37}$$

$$f^\infty_{PD} = f^\infty_P \Xi^\infty_{PD} = f^\infty_P e^{\beta(\mu_D - \mu_B)}, \tag{S38}$$

$$f^\infty_{P2C} = f^\infty_P^2 \Xi^\infty_{P2C} = f^\infty_P^2 e^{\beta(\mu_C - 2\mu_B + \mu_{HS}) + k_B^{-1} \Delta S_{eff}}, \tag{S39}$$

where $f^\infty_P$ is the unbound sites fraction and $\Xi^\infty_{PC}$, $\Xi^\infty_{PD}$ and $\Xi^\infty_{P2C}$ are effective bond strengths at the limit. Similarly, we can obtain a self-consistent equation

$$\Xi^\infty_{P2C} f^\infty_P^2 + (1 + \Xi^\infty_{PC} + \Xi^\infty_{PD}) f^\infty_P - 1 = 0, \tag{S40}$$

with a closed-form solution

$$f^\infty_P = \frac{\sqrt{(1 + \Xi^\infty_{PC} + \Xi^\infty_{PD})^2 + 4\Xi^\infty_{P2C}} - (1 + \Xi^\infty_{PC} + \Xi^\infty_{PD})}{2\Xi^\infty_{P2C}}, \tag{S41}$$

which does not depend on $\gamma$. 
S4: Mean-field theory at the low temperature limit ($\gamma = 1$)

When $\gamma = 1$ and at the low temperature limit, i.e. $\beta \epsilon \to +\infty$, the unbound sites fraction $f^0_P \to 0$. We can then write down the free energy of the system at the limit

$$\beta F^0 = \sum_{i = \text{poly,B,C,D}} N_i \left[ \ln \left( \frac{N_i \Lambda^3}{V} \right) - 1 \right] + \sum_{i = \text{PC,PD,P}_2C} N_i \left[ \ln \left( \frac{n_i \Lambda^3}{V_p} \right) - 1 \right]$$

$$+ \beta F^\text{ex}_{\text{HS}} - N_{P_2C} k_B^{-1} \Delta S - \beta (N_{PC} + N_{P_2C} + N_C) \mu_C - \beta (N_{PD} + N_D) \mu_D - \beta N_B \mu_B$$

$$+ \sum_{i = \text{PC,PD,P}_2C} \beta N_i (-\epsilon + \mu_B), \quad (S42)$$

where $\sum_{i = \text{PC,PD,P}_2C} - \beta N_i \epsilon$ contributes an infinite constant due to the total number of the sites fixed. The saddle point solution under the constraint $f^0_{PC} + f^0_{PD} + f^0_{P_2C} = 1$ is given by minimizing the Lagrange function

$$\mathcal{L} = \frac{\beta F^0}{N_{poly} m} - \lambda \left( f^0_{PC} + f^0_{PD} + f^0_{P_2C} - 1 \right) \quad (S43)$$

via

$$\frac{\partial \mathcal{L}}{\partial \{f_i, \lambda\}} = 0, \quad (i = \text{PC,PD,P}_2C, B, C, D), \quad (S44)$$

one can arrive at the solution

$$f^0_B = f_B, \quad (S45)$$

$$f^0_C = f_C, \quad (S46)$$

$$f^0_D = f_D, \quad (S47)$$

and

$$f^0_{PC} = e^{\lambda \Xi^\infty_{PC}}, \quad (S48)$$

$$f^0_{PD} = e^{\lambda \Xi^\infty_{PD}}, \quad (S49)$$

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\[ f_{P_2C}^0 = e^{2\lambda_\infty P_{2C}}, \]  

(S50)

and the self-consistent equation

\[ \Xi_{\infty P_2C} e^{2\lambda} + (\Xi_{\infty P_2C} + \Xi_{\infty P_D}) e^{\lambda} - 1 = 0, \]  

(S51)

with the solution

\[ e^\lambda = \sqrt{\frac{(\Xi_{\infty P_2C} + \Xi_{\infty P_D})^2 + 4\Xi_{\infty P_2C} - (\Xi_{\infty P_2C} + \Xi_{\infty P_D})^2}{2\Xi_{\infty P_2C}}}. \]  

(S52)
Figure S1: **Tuning thermo-crosslinking by various parameters.** Thermo-crosslinking for different (a) $\phi_p$, (b) $\beta \mu_B$, (c) $\beta \mu_C$ and (d) $\beta \mu_D$. The symbols are values obtained from simulations and solid lines are the theoretical prediction of Eq. 6. $\times$ symbols indicates the location of maximum value of $f_{p;C}$ obtained by simulations. (a,c): grey lines are the theoretical predictions of transition temperature $k_B T^*/\epsilon$ from Eq. 15. Fixed parameters: $N_{poly} = 100$, $\chi_{att} = 0$, $\gamma = 1.2$, $\phi_p = 0.25$ for (b, c and d), $\beta \mu_B = -2$ for a, c and d, $\beta \mu_C = -4$ for a, b and d and $\beta \mu_D = -5$ for a, b and c.
Figure S2: Structure factor $S(k)$ for systems with different temperature $k_B T / \epsilon$ for various $\chi_{\text{att}}$, in which the temperatures below $T_c$ are colored by grey. Critical temperatures $T_c$ are obtained by Fig. 2b in the main text. In all simulations, $N_{\text{poly}} = 100$, $\phi_p = 0.20$, $\gamma = 2.0$, $\beta \mu_B = -2$, $\beta \mu_C = -4$ and $\beta \mu_D = -5$. 
Figure S3: (a) Additional double bond-swap reactions were performed in the EDMD-MC simulation. (b) Highlighted reactions which effect the dynamics of vitrimer besides the reactions shown in Fig. 1a.