Entropy-Controlled Crosslinking in Linker-Mediated Vitrimers

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Recently developed linker-mediated vitrimers based on metathesis of dioxaborolanes with various commercially available polymers have shown both good processability and outstanding performance, such as mechanical, thermal, and chemical resistance, suggesting new ways of processing crosslinked polymers in industry, of which the design principle remains unknown [1]. Here we formulate a theoretical framework to elucidate the phase behaviour of the linker-mediated vitrimers, in which entropy plays a governing role. We find that with increasing the linker concentration, vitrimers undergo a reentrant gel-sol transition, which explains a recent experiment [2]. More intriguingly, at the low temperature limit, the linker concentration still determines the crosslinking degree of the vitrimers, which originates from the competition between the conformational entropy of polymers and the translational entropy of linkers. Our theoretical predictions agree quantitatively with computer simulations, and offer guidelines in understanding and controlling the properties of this newly developed vitrimer system.

Vitrimers are a new class of polymer materials with exceptional mechanical properties, combining the malleability and recyclability of thermoplastics with the high mechanical performance of thermosets [3–4]. Their unique properties originate from the reversible bond-exchange reaction allowing the covalently bonded polymer networks to change dynamically, which makes vitrimers behave like viscoelastic liquids at high temperatures and as crosslinked thermosets at low temperatures [5–14]. In the past decade, various chemical reactions, such as the transesterification reaction [4–15], transamination reaction [16–17], alkoxamine exchange reaction [18–19], olefin metathesis [20], thiol-disulfide exchange [21], have been used in the production of vitrimers for different applications. However, the reactants or catalysts involved in reactions of the conventional vitrimers are usually not thermally or oxidatively stable, which is particularly detrimental for using the same equipments and conditions of processing thermoplastics [22].

Recently, a new type of linker-mediated vitrimers was developed based on the metathesis reaction of dioxaborolanes, in which the functionalized polymers with pendant dioxaborolane units react with bis-dioxaborolanes (crosslinkers), and the metathesis reaction here both crosslinks the polymers and dynamically changes the polymer network [1]. The linker-mediated vitrimers have superior chemical resistance, dimensional stability, without the need of a catalyst, and can be processed like thermoplastics [23]. In this work, we propose a mean field theory combined with coarse grained computer simulations to study the linker-mediated vitrimer system, and our results show that the entropy of free linkers plays a nontrivial role. We find that with increasing the concentration of free linkers, the vitrimer system undergoes a reentrant gel-sol transition, which was observed in a recent experiment [2]. More interestingly, even at the low temperature limit, the crosslinking degree of vitrimers still depends on the concentration of free linkers, which essentially offers an extra degree of freedom in controlling the mechanical property of the resulting materials.

We consider a system of volume \( V \) consisting of \( N_{\text{poly}} \) polymer chains, in which each polymer comprises of \( n \) hard spheres of diameter \( \sigma \) connected through infinitely deep square-well bonds [24]. As shown in Fig. 1, on each polymer there are \( m \gg 1 \) precursors (reactive sites) \( P \) uniformly distributed, which can react with a crosslinker molecule \( C \) by forming a dangling PC bond and producing a byproduct free molecule \( B \) through metathesis reactions. Moreover, a dangling PC bond can further react with another intact precursor \( P \) to form a crosslinking \( P_2C \) bond and producing an additional free B molecule, and each crosslinker can form at most two bonds with two different precursors creating a crosslinking \( P_2C \) bond. The metathesis reactions are reversible, and \( \Delta G \) is the reaction energy. \( N_C \) and \( N_B \) are the numbers of crosslinker molecule \( C \) and the byproduct molecule \( B \) in the system, which are controlled by the chemical potentials \( \mu_C \) and \( \mu_B \), respectively. We define \( n_{P,C} \) and \( n_{P_2C} \) as the average numbers of PC and \( P_2C \) bonds per polymer, respectively. Similarly, \( n_i \) is the average number of precursors per polymer that remain intact, and \( N_i = N_{\text{poly}} n_i \) is the total number of precursors or bonds of type \( i = P, PC, P_2C \) in the system. The packing fraction of polymers is \( \phi_p = \frac{n}{6} N_{\text{poly}} \alpha^3 \), and \( B \) and \( C \) are both modelled as hard spheres of diameter \( \sigma \).

In the dilute limit (Fig. 1.), polymer chains are iso-
The distribution of reactive sites in the vitrimer system is heterogeneous and the reactive sites can be seen as ideal gases confined in individual polymer blobs of volume $V_p = R_g^3$ with $R_g$ the radius of gyration of the polymer. Treating the polymer backbones implicitly as the crowding background, the free energy of the system can be written as

$$
\beta F = \sum_{i=\text{poly}, B, C} N_i \left[ \ln \left( \frac{N_i A^3}{V} \right) - 1 \right] + \sum_{i=P, PC, P_2C} N_i \left[ \ln \left( \frac{n_i A^3}{V} \right) - 1 \right] + \beta F_{\text{HS}}^{\text{ex}} - N_P C_k B^{-1} \Delta S - \beta (N_{PC} + N_{P_2C} + N_C) \mu_C + \beta (N_{PC} + 2N_{P_2C}) (\Delta G + \mu_B) - \beta N_B \mu_B,
$$

where the first summation is on the ideal gas terms of polymer chains, free crosslinkers and byproduct molecules, and the second summation is on the ideal gas terms of different reactive sites in polymer blobs. Here $\beta = 1/k_B T$ with $k_B$ and $T$ the Boltzmann constant and the temperature of the system, respectively, and $\Lambda$ is the de Broglie wavelength. This ideal gas approximation of reactive sites offers a simple estimation of the conformational entropy change during the formation of crosslinking $\text{P}_2\text{C}$ bonds, for which we introduce $\Delta S$ as the entropy correction per crosslinking bond. $F_{\text{HS}}^{\text{ex}}$ is the excess free energy based on Carnahan-Starling hard-sphere equation of state [25] arising from the excluded volume interaction, which accounts for the crowding effect in the system. The last three terms arise from the metathesis reactions and the exchange of molecules with reservoir. As the system approaching the dense regime (Fig. 1d), polymer blobs begin to overlap and the distribution of reactive site become homogeneous. Thus, $V_p$ can be replaced by the available volume per polymer, i.e., $V_p = V/N_{\text{poly}}$.

We define the crosslinking degree of system as $f_{P_2C} = 2N_{P_2C}/(N_{\text{poly}} m)$, i.e., the fraction of reactive sites that are crosslinked, and $f_i = N_i/(N_{\text{poly}} m)$, $(i = \text{PC}, B, C)$. Using the saddle-point approximation, $\partial F/\partial f_i = 0$, $(i = \text{PC}, \text{P}_2\text{C}, B, C)$, one can obtain the equilibrium $f_{PC}$ and $f_{P_2C}$ as

$$
f_{P_2C} = \frac{-(1 + a) + \sqrt{(1 + a)^2 + 4c}}{4c},
$$

$$
f_{PC} = \frac{-(1 + a) + \sqrt{(1 + a)^2 + 4c}}{2c},
$$

where $\mu_{\text{HS}}^{\text{ex}}$ is the excess chemical potential originating from $F_{\text{HS}}^{\text{ex}}$. As $\mu_{\text{HS}}^{\text{ex}}$ is a function of the packing fraction of the system, which also depends on $f_i$, for simplicity, to calculate $f_{PC}$ and $f_{P_2C}$, one can use the average packing fraction measured in simulations without resorting to self-consistent iterations. Here we note that the effect of $\mu_B$ is the same as $\Delta G$.

As shown in Fig. 1, the formation a crosslinking $\text{P}_2\text{C}$ bond requires two metathesis reactions, with $K_1$ and $K_2$ the corresponding reaction constants, which satisfy

$$
K_1 \rho_P \rho_{PC} = \rho_{PC} \rho_B,
$$

$$
K_2 \rho_P \rho_{PC} = \rho_{P_2C} \rho_B,
$$

where $\rho_i = N_i/V$ is the density of specie $i$ in the system. In Ref. [1, 2], the metathesis reactions in the first and second steps are of the same type, and one might think that the two reaction constants $K_2$ and $K_1$ should be equal. However, a recent experiment indicates that $K_2/K_1$ calculated from Eqs. 6 and 7 can be significantly larger than 1 [2]. To understand this, we first use the fact that in chemical equilibrium, the chemical potentials for all species satisfy

$$
\mu_P + \mu_C + \mu_{\text{PC}} + \mu_B = 0,
$$

$$
\mu_P + \mu_C - \mu_{\text{PC}} + \mu_B = 0,
$$

where $\mu_i$ $(i = \text{P}, \text{PC}, \text{P}_2\text{C})$ can be obtained by taking a direct derivative of Eq. 1 with respect to $N_i$. Combining Eqs. 6 and 7 with Eqs. 8 and 9 we have

$$
\frac{K_2}{K_1} = \frac{V}{N_{\text{poly}} V_p} e^{k_B^{-1} \Delta S} = \begin{cases} \frac{n_{\text{poly}}}{\phi_p R_g^3} e^{k_B^{-1} \Delta S} & (R_g \ll V/N_{\text{poly}}) \\ e^{k_B^{-1} \Delta S} & (R_g \gg V/N_{\text{poly}}) \end{cases}
$$

FIG. 1: Vitrimers model. (a): Illustration of the two step metathesis reactions in the vitrimer system. (b): $K_2/K_1$ as a function of $\phi_p$ for different $m$ and $\mu_C$ at $n = 100$ and $\beta \mu_B = -3$. (c,d): Illustration of the heterogeneous dilute (c) and homogeneous dense (d) systems of the vitrimers.
where $v_0 = \frac{\pi}{6} \sigma^3$ is the volume of a single bead on the polymer chain. This predicts a powerlaw scaling $K_2/K_1 \sim \phi_p^{-1}$ in the homogeneous dilute regime, which saturates to $e^{K_0} \Delta S$ in the homogeneous dense regime. In Fig. 1, we plot $K_2/K_1$ measured in simulations as a function of $\phi_p$ for different $m$ and $\mu_C$ with $n=100$, which confirms our theoretical predictions of Eq. 10 for different regimes. Therefore, the observation of $K_2/K_1 > 1$ in experiments could result from the inhomogeneous distribution of reactive sites in the system [20, 21, 22, 23]. Moreover, at the heterogeneous dilute regime, $R_g$ decreases with increasing $m$ due to more crosslinking within each polymer blob, which also raises $K_2/K_1$ as shown in Fig. 1.

With the introduction of $K_2/K_1$, Eq. 5 can be rewritten as

$$c = \left( \frac{K_2}{K_1} \right) \frac{2 N_{\text{poly}} m \Delta S^3}{V} e^{\beta(\mu_B - \mu_C)}$$

which does not explicitly depend on $V_p$ or $\Delta S$. As $K_2/K_1$ is measurable both in experiments and simulations, one can predict $f_{P2C}$, $f_{PC}$ based on Eqs. 2 and 3 and the measured $K_2/K_1$ without invoking exact values of $V_p$ and $\Delta S$. In Fig. 2a-f, we plot $f_{P2C}$ and $f_{PC}$ as functions of $\mu_C$ obtained from the systems for systems of various $m$ and $\phi_p$ with $n=100$ and $\beta \mu_B = -3$, which well agree with the theoretical prediction (Eqs. 2 and 3) in a wide range of $\phi_p$ and $m$. This suggests that our theoretical framework is robust and capable of quantitatively predicting the phase behaviour of the vitrimers in both heterogeneous dilute and homogeneous dense regimes.

Moreover, Eq. 5 has the limiting behaviour:

$$f_{P2C}(\mu_C \to -\infty) \approx \frac{a_2}{a^2} \to 0,$$

$$f_{PC}(\mu_C \to +\infty) \approx c \to 0.$$

One can also prove that $f_{P2C}$ reaches the maximum at $\mu_C = \mu_B + \Delta G$ (see Supplementary Materials), and this implies that the crosslinking degree first increases and then decreases with increasing the concentration of crosslinkers, which quantitatively agrees with simulations as shown in Fig. 2a-f. This non-monotonic dependence of $f_{P2C}$ on the concentration of crosslinkers was also observed in a recent experiment [2]. The counter-intuitive decrease of $f_{P2C}$ with increasing $\mu_C$ at high crosslinker concentration is a purely entropic effect. At high $\mu_C$ limit, the reactive sites are fully bonded with crosslinkers forming either PC or P2C bonds. Changing one P2C bond to two dangling PC bonds hardly changes the energy of the system but increases the conformational entropy of polymer chains. Therefore, forming dangling PC bonds is more entropically favoured than forming crosslinking P2C bonds, which drives the crosslinking degree towards zero at high $\mu_C$. This non-monotonic dependence of $f_{P2C}$ on $\mu_C$ provides an additional axis in controlling the mechanical properties of vitrimers. As the percolation of the connected polymer cluster is an important indicator of the sol-gel transition of the sys-

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**FIG. 2: Reentrant gel-sol transition.** (a-i): $f_{PC}$, $f_{P2C}$, $x_p$ as a function of $\mu_C$ for different $m$ and $\phi_p$. The solid lines in (a-f) are the theoretical predictions of Eqs. 2 and 3 (j-l): Simulation snapshots for systems with $m=10$ and $\phi_p=0.1$ at $\beta \mu_B = -8.0$ (j), $-5.0$ (k) and $-2.0$ (l). Different colors represent different type of bonds based on Fig. 1a, i.e., PC, P2C, P and polymer backbone bonds in blue, red, green and grey, respectively, and free B and C molecules are not drawn. In all simulations, $\beta \mu_B = -3.0$, $\beta \Delta G = -2.0$, and $n=100$. 

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FIG. 3: Entropy-driven crosslinking at low temperature limit. (a-b): $f_{PC}$ and $x_p$ as a function of reaction energy $\Delta G$ for different $\mu_C$ at $m=5$, where the solid lines in (a) are the theoretical predictions of Eq. 2. (c-d): Saturated $f_{PC}^\infty$ and $x_p^\infty$ as a function of $\mu_C$ for different $m$ at $\beta \Delta G= -8.0$, where the solid lines in (c) are the theoretical predictions of Eq. 14. In all simulations, $\beta B_B = -3.0$, $n=100$, and $\phi_p = 0.1$.

Another interesting theoretical prediction is that in the limit of $\beta \Delta G \rightarrow -\infty$, one has $f_{PC} + f_{PC} \geq 1$ and

$$f_{PC} \simeq 1 - \frac{1+4e-2\mu_p}{1+4e-2\mu_p} < 1,$$

which implies that at the low temperature limit ($\beta \Delta G \rightarrow -\infty$) or the dilute limit of byproduct molecules ($\beta B_B \rightarrow -\infty$), the system is not fully crosslinked. Since $c$ depends on $\mu_C$, $m$ and $V_p$ (Eq. 5), this suggests that even at the low temperature limit, the crosslinking degree of the system can still be tuned by the concentration of free linkers or the precursor density on polymer chains. As shown in Fig. 3a,b, we plot $f_{PC}$ and $x_p$ as functions of $\beta \Delta G$ measured in simulations of systems with various $\mu_C$ at $m=5$, $n=100$ and $\beta B_B = -3$, which agree quantitatively with the theoretical prediction. One can see that both $f_{PC}$ and $x_p$ increase and reach a plateau at low $\beta \Delta G$. We plot the crosslinking degree at the low temperature limit $f_{PC}^\infty$ as a function of $\beta \mu C$ in Fig. 3c, and $f_{PC}^\infty$ decreases with increasing $\beta \mu C$ or decreasing $m$, which quantitatively agrees with Eq. 14. The physical explanation is that at $\beta \Delta G \rightarrow -\infty$, all reactive sites form either dangling $PC$ bonds or crosslinking $P_2C$ bonds. Breaking a crosslinking $P_2C$ bond into two dangling $PC$ bonds does not change the energy of the system but increases the conformational entropy of the polymers by $\Delta S_{conf}$, which simultaneously absorbs one free crosslinker from the solution, and the translational entropy of the free crosslinker drops by $\Delta S_{trans} \simeq k_B \ln \rho_{PC} \sim -\mu_C/T$. With increasing $\mu_C$, $\Delta S_{trans}$ decreases, which breaks more $P_2C$ into dangling $PC$ bonds. Similarly, at the fixed polymer length $n$ and $\phi_p$, increasing $m$ decreases $\Delta S_{conf}$, which drives the formation of more crosslinking $P_2C$ bonds. Similar entropic effects in linker-mediated self-assembly were recently also observed in linker-mediated DNA-coated colloids [29]. In Fig. 3i, we plot the resulting saturated value of percolation parameter $x_p^\infty$ at $\beta \Delta G \rightarrow -\infty$ as a function of $\mu_C$ for various $m$. One can see that $x_p^\infty$ also increases with decreasing $\mu_C$, but changes more sharply than $f_{PC}^\infty$. This suggests a practical way to control the mechanical property of the vitrimer at low temperature limit by tuning the crosslinker concentration.

In conclusion, we have proposed a theoretical framework to describe the newly developed linker-mediated vitrimer system, in which entropy plays a determining role. First, we find that the density heterogeneity of reactive sites can result in the mismatch of reaction constants of the same metathesis reaction in the first and second crosslinking steps, which offers a possible mechanism to explain the recent experiment [2]. This mechanism of heterogeneity-enhanced reactions rates also has implications in biochemical reactions in molecular crowding conditions, which has been utilized by cells in form of membraneless compartment to enhance RNA transcription and protein translations [30]. A similar effect of self-concentration was also reported in polymer glasses [31].

Second, we find that increasing the crosslinker concentration can induce a reentrant gel-sol transition of the vitrimer. This offers a new way to control over the reshaping or recycling of vitrimers without heating up and cooling down the system. Lastly, in the low temperature limit, we find that the crosslinking degree of the system can still be effectively tuned by the concentration of crosslinkers, which suggests that in experiments, one should be careful with the crosslinker concentration, and lowering the temperature does not always produce highly crosslinked polymer gels. Therefore, our theory not only reveals intriguing physics in this linker-mediated vitrimer system, but also provides important guidelines in controlling the mechanical properties of the novel functional materials.

**METHOD**

We employ hard-sphere potential to model the excluded volume interaction between all particles, including
polymer beads, precursors, B and C molecules,

\[ V(r, r') = \begin{cases} 0 & |r - r'| > \sigma \\ \infty & \text{else} \end{cases} \tag{15} \]

with the diameter \( \sigma \) of hard spheres. A infinitely deep square-well tethered bond potential below is used to mimic the connectivity among covalently bonded polymer beads and crosslinkers,

\[ V_{\text{bonds}}(r, r') = \begin{cases} 0 & |r - r'| < r_{\text{cut}} \\ \infty & \text{else} \end{cases} \tag{16} \]

where \( r_{\text{cut}} \) is the cutoff distance of the tethered bond, and we use \( r_{\text{cut}} = 1.5\sigma \) throughout all simulations. Periodic boundary conditions are applied in all three directions, and grand canonical (\( \mu_{\text{BEC}} N_{\text{poly}} V T \)) Monte Carlo simulations are performed with an event-chain algorithm \[32, 33\] for the translational moves of particles in the system. We devise a bond swap algorithm (see Supplementary Materials) to simulate reversible bond swap metathesis reactions in the vitrimer system.

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