Supplementary Information (SI)

Computer Simulations of Entropic Cohesion in Reversibly Crosslinked Polymers

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I. Reversible Bond Exchange Mechanism in a Polymer Matrix:

The number of crosslink bonds in an associative polymer network is constant. They are exchanged between different pairs of monomers during the dynamics. In a dissociative polymer network, a monomer dissociates from its crosslinked partner before finding a new one. Therefore, the total number of crosslinks in a dissociative network fluctuates around a mean value. These two bond exchange mechanisms are schematically shown in Figure S1.

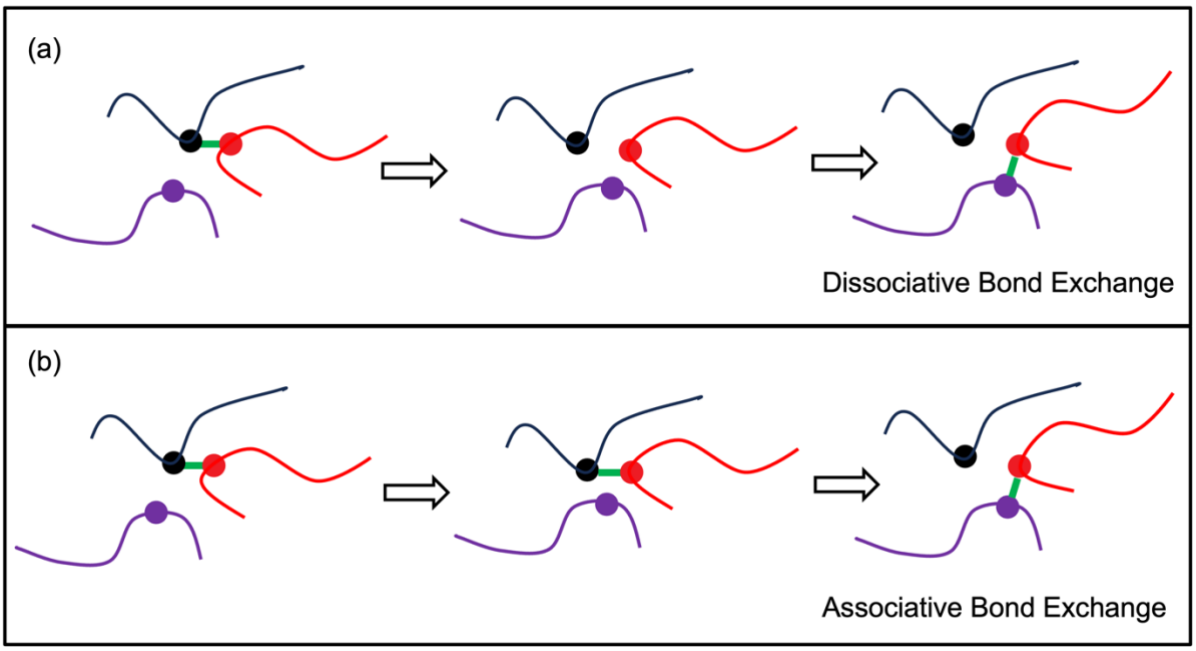

Figure S1: Schematic representations of a dissociative and an associative bond exchange are shown in (a), and (b), respectively. The green bond is exchanged between a pair of polymer chains using the MC simulation.

II. Free Standing Polymer Film Simulations:

Free standing film simulations are done in an orthogonal simulation box with dimensions $25\sigma \times 25\sigma \times 225\sigma$. We have performed the simulations for five different bond lifetimes. The equilibrium properties of all the cases for chain length N=20 are reported in Table S1.

Bond Lifetime ($\boldsymbol{\tau}$)	Bulk Density ($\boldsymbol{\sigma^{-3}}$)	Interfacial width ($\boldsymbol{\sigma}$)	Surface Tension ($\boldsymbol{\epsilon/\sigma^2}$)
1	0.89	1.62	0.97
5	0.90	1.61	0.98
25	0.90	1.62	0.97
250	0.90	1.61	0.97
500	0.90	1.61	0.97

Table S1: Equilibrium properties of the system – bulk density, interfacial width and surface tension are tabulated for different crosslinkers lifetimes. All the properties are in reduced LJ units.

III. Constant Density Bulk Simulations:

We consider 500 polymer chains each of a chain length 20 for the constant density simulations. The polymers are initially placed in a 3D-simulation box with a number density of 0.9. The simulations are conducted for a reduced temperature $T^* = 1$. We perform 10^7 steps of equilibrium followed by a production run of another 10^7 steps. The bond energy and LJ pair energy during the production run are shown in Figure S2, along with the system's entropy.

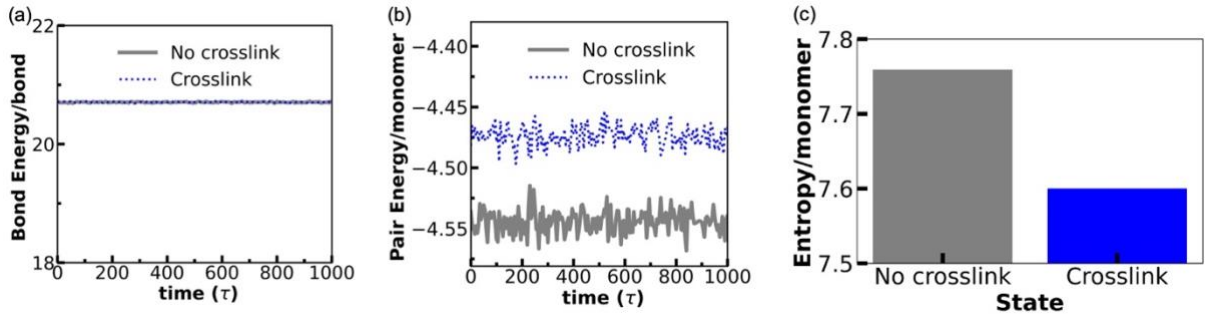

Figure S2: Bond energy and pair energy are shown as a function of time during the production run in (a) and (b), respectively. The entropy per monomer for the crosslinked and no-crosslinked cases are shown in (c).