

Supplementary Materials

**A molecular dynamics study of bond exchange
reactions in covalent adaptable networks**

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S1. Glassy transition temperature of the simulation system

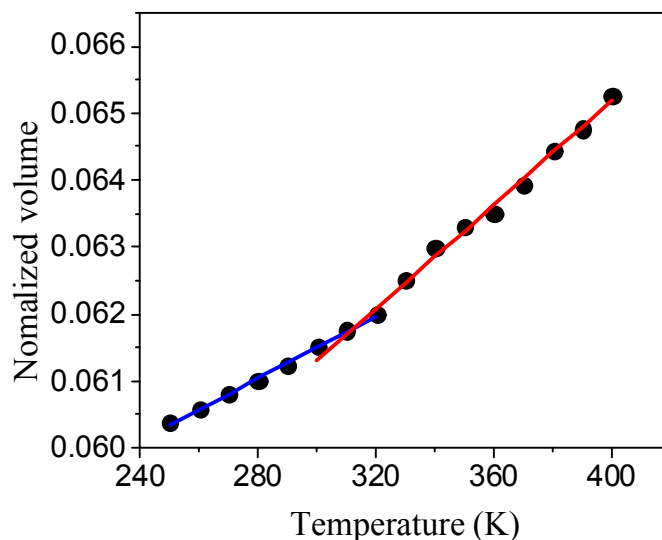


Figure S1 Normalized volume as function of temperatures.

The effect of temperature plays an important role in polymers. The bond exchange reaction within CANs can be affected by temperatures, where the glass transition temperature is one of the most important parameters for CANs. In order to obtain the glass transition temperature, the system was first equilibrated by using NVT and NPT ensembles sequentially for 500ps at 600K and atmosphere pressure respectively. NPT ensemble is then used to generate a volume-temperature plot at atmosphere pressure. The volume at each temperature is obtained by cooling the system with a cooling rate of 10K/200ps. Figure S1 shows the results about the dependence of the volume of the system on temperatures, where two linear regions are apparent with volumetric thermal expansion coefficients of $\sim 2.29 \times 10^{-6} \text{K}^{-1}$ below T_g and $3.86 \times 10^{-6} \text{K}^{-1}$ above T_g . The glass transition temperature T_g of the network can be determined by the intersection of the two straight lines as shown in Figure S2, giving 312 K, which is very close to experimentally measured glass transition temperature of $\sim 303 \text{K}$ on an epoxy with similar structure[1]. The deviation between experimental and prediction results could be due to different in thermal rates and crosslinking density between the simulation and experiment.

S2. Number of BERs in each iteration

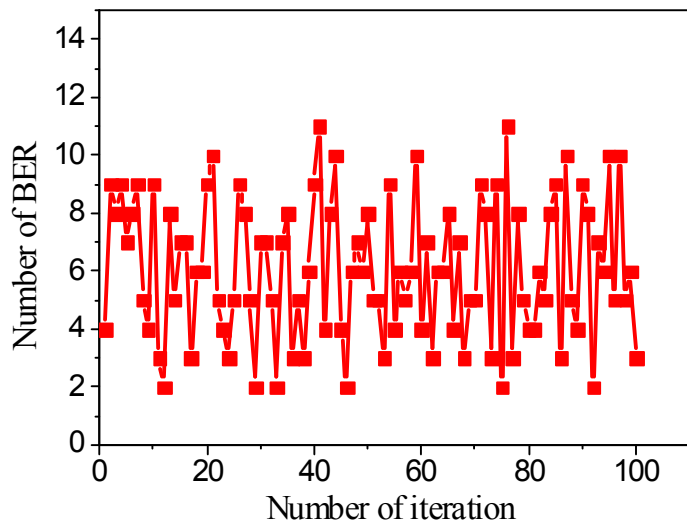
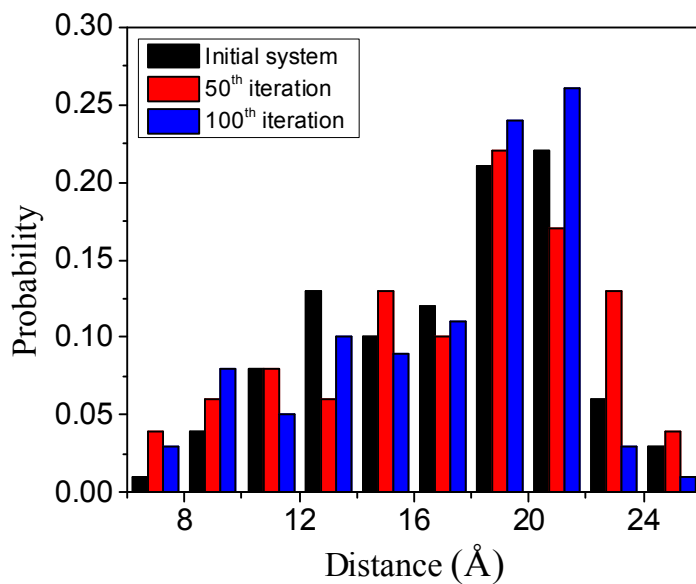


Figure S2 Number of BER occurred in each iteration.

Fig. S2 shows the variations of the number of BERs in each iteration. It is clear that although the number varies in each iteration, a stable of average ~ 6 BERs can also be observed.



(a)

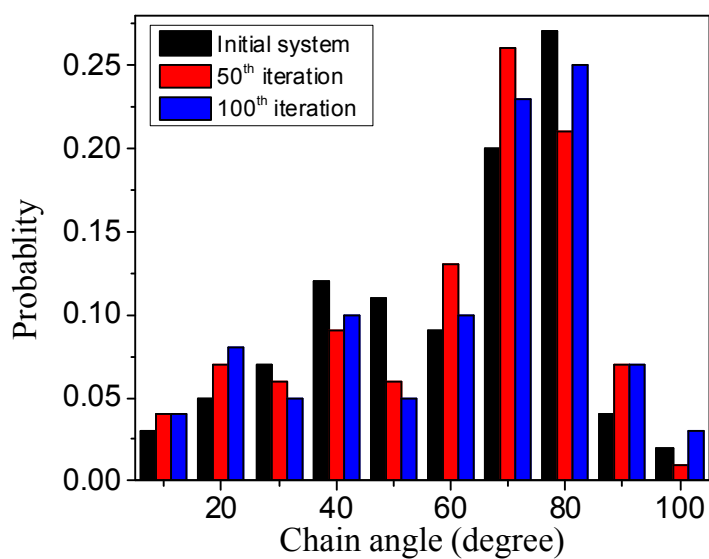


Figure S3 (a): Distribution of distance between two neighboring crosslink sites; (b) Distribution of chain angle.

Fig. S3a shows the distribution of the distance between two crosslink sites, or chain end-to-end distance. The average chain end-to-end distance is calculated to be 15.6Å. Fig. S3b shows the distribution of chain angle at 50th iteration of BER, the distribution didn't change too much during BER process, and the average chain angle is 58.8°.

S3. Network without BERs

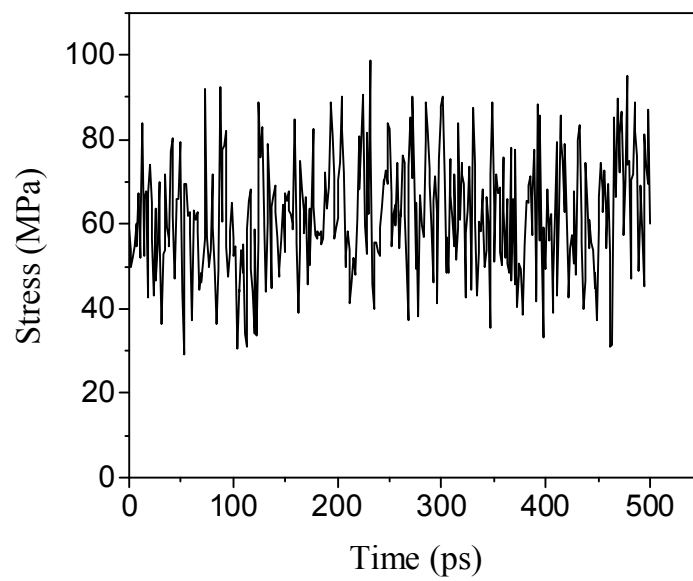


Figure S4. Stress of the system without BER

Fig. S4 shows the stress as a function of time after we turn off the BER. It can be seen a constant stress can be maintained, indicating a stable network.

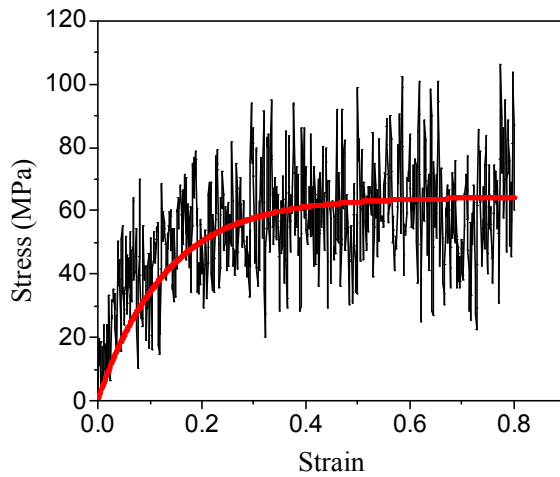
S4. Relaxation time due to chain diffusion

Comment [MU]: Response to comment 2.

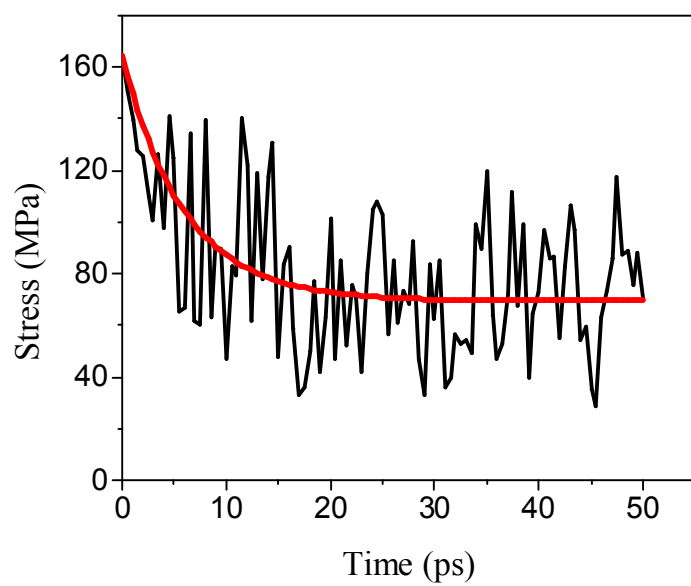
For the relaxation due to chain diffusion, we measure it in two ways. The first approach is to use standard linear solid model to fit the uniaxial tensile simulation (without BERs) directly. Here, we use E_0 to denote Young's modulus of equilibrium branch, E_1 as the Young's modulus of nonequilibrium branch, and τ_{diff} as the relaxation time due to chain diffusion. These three parameters can be fitted by the stress-strain curve, which is shown in Fig. S5a, where $E_1 = 1.0 \text{ MPa}$, $E_0 = 0.45 \text{ MPa}$, and $\tau_{diff} = 2 \text{ ps}$. In the second approach, the relaxation time is measured by the stress relaxation simulation (without BERs). Here, we load the sample to 15% at the strain rate of $1 \times 10^{10} \text{ s}^{-1}$, hold the deformation and measure the stress during relaxation. Fig. S5b shows the decay of the stress. We then use

$$\sigma = \sigma_1 + (\sigma_0 - \sigma_1) \exp\left(-\frac{t}{\tau_{diff}}\right)$$

to obtain τ_{diff} . In the above equation, σ_0 is the initial stress, σ_1 is the stress at the plateau. By fitting the curve, we obtain $\tau_{diff} = 6 \text{ ps}$.



(a)



(b)

Figure S5. (a) Stress-strain curves of MD simulation and standard linear solid model fit; (b) Stress relaxation and model fit.