

Supporting Information

Understanding the application of covalent adaptable networks in self-repair materials based on molecular simulation

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By performing continuous cooling under NPT ensemble, and plotting the specific volume ν (the volume occupied by per unit mass, $\nu = V/M$, M represents the mass) against temperature T , we can calculate the T_g of all systems. According to free volume theory, there is an abrupt volume variation around the glass transition temperature T_g , as shown in Figure S1.

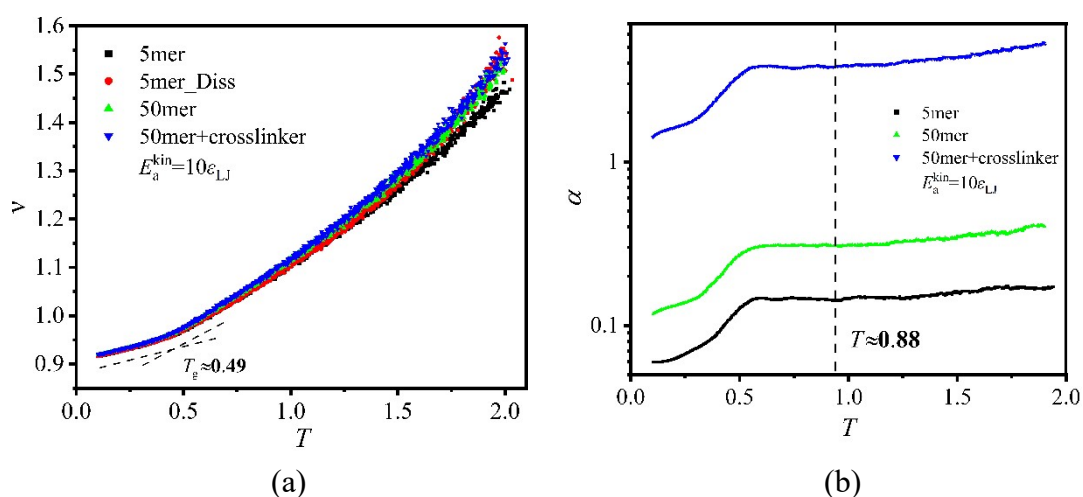


Fig.S1 (a) Specific volume ν and (b) thermal expansivity α as a function of temperature of different systems. Black squares represent Asso-CANs of telechelic short chains with 5-mer and crosslinkers, red dots represent Diss-CANs of 5-mer and crosslinkers, green triangles represent pendant crosslinked Asso-CANs of 50-mer, and blue triangles represent pendant crosslinked Asso-CANs of 50-mer and crosslinkers. The activation energies in all systems are $E_a^{kin} = 10\epsilon_{LJ}$. T_g is inferred by the extrapolated crossover of two fitted lines. T_v is inferred by the local minimum of thermal expansivity.

By taking the partial derivation of v , we can calculate the thermal expansivity α :

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \#(S - 1)$$

where P is the pressure. By applying finite differences and smoothing the curves, the plot of thermal expansivity α versus temperature is shown in Figure S2. Perego et al.¹ proposed that, for Asso-CANs, as the chemical reaction initiates, the thermal expansivity α will increase along with the temperature. Therefore, the temperature above T_g , which corresponds to the local minimum of α , can be considered as T_v . It should be noted that the T_v calculated by this way differs from the experimental definition. The method used here infers the temperature at which a chemical reaction begins from the perspective of molecular motion.

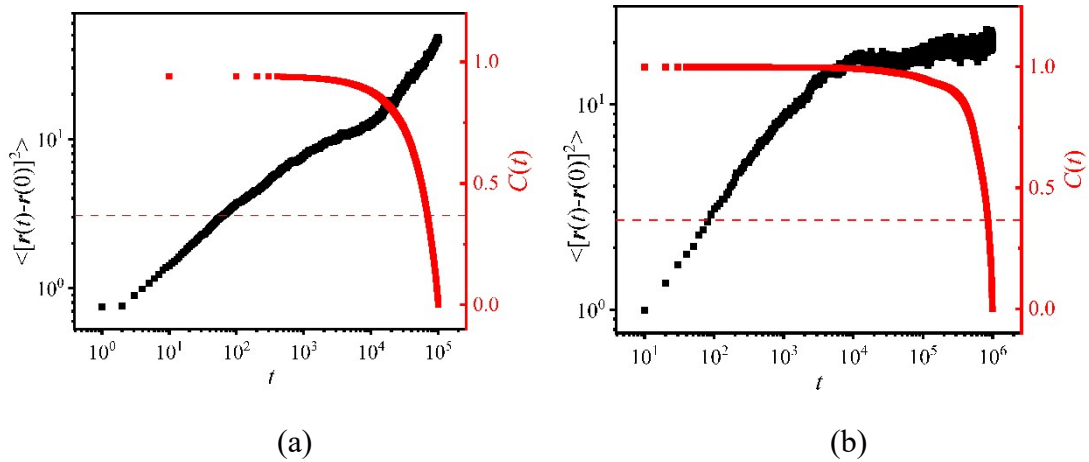


Fig. S2 Mean-squared distance, $\langle [r(t) - r(0)]^2 \rangle$ (MSD) and corresponding autocorrelation function $C(t)$ as a function of time for self-adhesion of (a) 5-mer and (b) 50-mer. Red dashed lines in (a) and (b) refer to the attenuation of $C(t)$ to $1/e$.

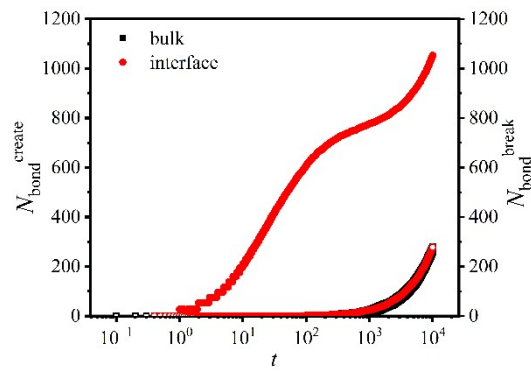


Fig. S3 The number of formed bonds and broken bonds as a function of time. The red solid dots represent the number of formed bonds at the interface, the red hollow dots represent the number of broken bonds at the interface, the black solid and hollow squares represent the number of formed bonds and broken bonds in bulk, respectively.

REFERENCES

1. A. Perego and F. Khabaz, *Macromolecules*, 2020, **53**, 8406-8416.