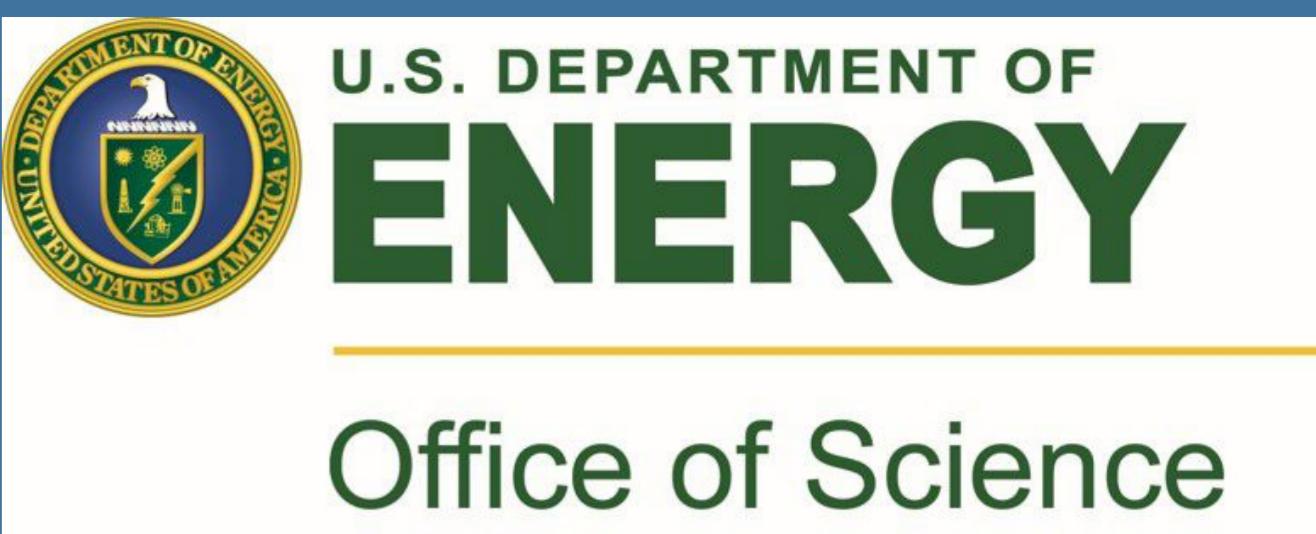




In-silico Glass Transition Behavior of Crosslinked Epoxy/Amine Resins with Prospective Self-Healability

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Introduction

- The utility of self-healing polymers is evident, with the ability of a material to dynamically heal a wound with minimal or no human intervention having significant benefit for that material's longevity and environmental impact.
- Despite this, strategies for transformation of useful and market-ready commodity polymers into self-healable polymers are of limited availability.
- Commodity polymers modified into highly branched networks with supramolecular (hydrogen bonding) interactions at the termini of the networks are proposed to lead to strong, glassy materials with possess sufficient mobility to undergo self-healing.
- This study focuses on large scale coarse-grained molecular dynamics simulations of such polymers, with an initial focus on the influence of the polymer architecture and supramolecular interactions on the glass transition behavior.

Model and Methods

- We model three-component blends (one stiff epoxy ($N = 10$), one flexible epoxy ($N = 20$), and a linker amine ($N = 2$)) as Lennard-Jones beads on springs, with an additional bead species modeling hydrogen bonding sites.
- The following interactions define the model. For Lennard-Jones interactions:

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] - 4\epsilon \left[\left(\frac{\sigma}{r_c} \right)^{12} - \left(\frac{\sigma}{r_c} \right)^6 \right] \quad (r \leq r_c) \quad (1)$$

$$= 0 \quad (r > r_c) \quad (2)$$

- Where ϵ and σ are the energy and length scales of the LJ model, respectively, and all units are parameterized in terms of these quantities. r_c is the cutoff of the interactions and is set at $2 \times 2^{1/6}\sigma$ to include attractive interactions.
- For bonded (FENE) interactions:

$$U_{bond}(r) = 0.5R_0^2k \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right] \quad (r \leq R_0) \quad (3)$$

$$= \infty \quad (r > R_0) \quad (4)$$

- Where $R_0 = 1.5\sigma$ and $k = 30\frac{\epsilon}{\sigma^2}$.
- For angle interactions:

$$U_{angle}(\theta) = k_l [1 - \cos(\theta)] \quad (5)$$

- Where θ is the angle formed between three consecutive beads. We set $k_l = 5.0$ for beads representing the stiff epoxy, as well as for beads constituting newly formed crosslinks.
- Lastly, an additional species represents hydrogen-bonding sites. These beads have $\sigma_{aa} = 0.35\sigma$ and their interactions with other hydrogen-bonding sites are cutoff at $r_c = 2.5\sigma_{aa}$, and are cutoff at $r_c = 2^{1/6}\sigma_{aa}$ otherwise (to be purely repulsive).
- The equations of motion are integrated with the velocity-verlet algorithm using LAMMPS. The timestep of integration is $\delta t = 0.006 \sigma \sqrt{m/\epsilon} = 0.006\tau$.



Formation of Crosslinked Network Polymers

The system is initialized, crosslinked, and equilibrated by the following procedure:

- $m = 12000$ total chains are generated and relaxed for 30000τ at $T = 1.0$ and $P = 0.0$. The blend composition is determined by:
 - $r = (\text{stiff} + \text{flexible})/(2.0 \times \text{linker})$ is the ratio of all epoxy chains to twice the number of amine chains in the system, a stand-in for the number of epoxy groups (from difunctional epoxy chains) to the number of amine groups (from tetrafunctional amine chains).
 - $E = (\text{flexible})/(\text{stiff} + \text{flexible})$ is the ratio of flexible chains to the total number of epoxy chains in the system.
- The system is cooled to $T = 0.5$ to promote bead-bead contacts in preparation for crosslinking. To crosslink, a new bond forms between a linker-type bead and an epoxy-type bead with 1% probability when those beads come within 1.3σ . Each epoxy bead may form one new bond; each linker bead may form two. The crosslinking is run until 95% of possible bonds have formed, or for 15000τ , whichever comes first.
- Any linker chains which have formed no new bonds are removed from the system; any remaining linker beads which themselves have formed no new bonds (terminal beads of the network) have a hydrogen-bonding site attached to them. The system is relaxed for a further 30000τ .

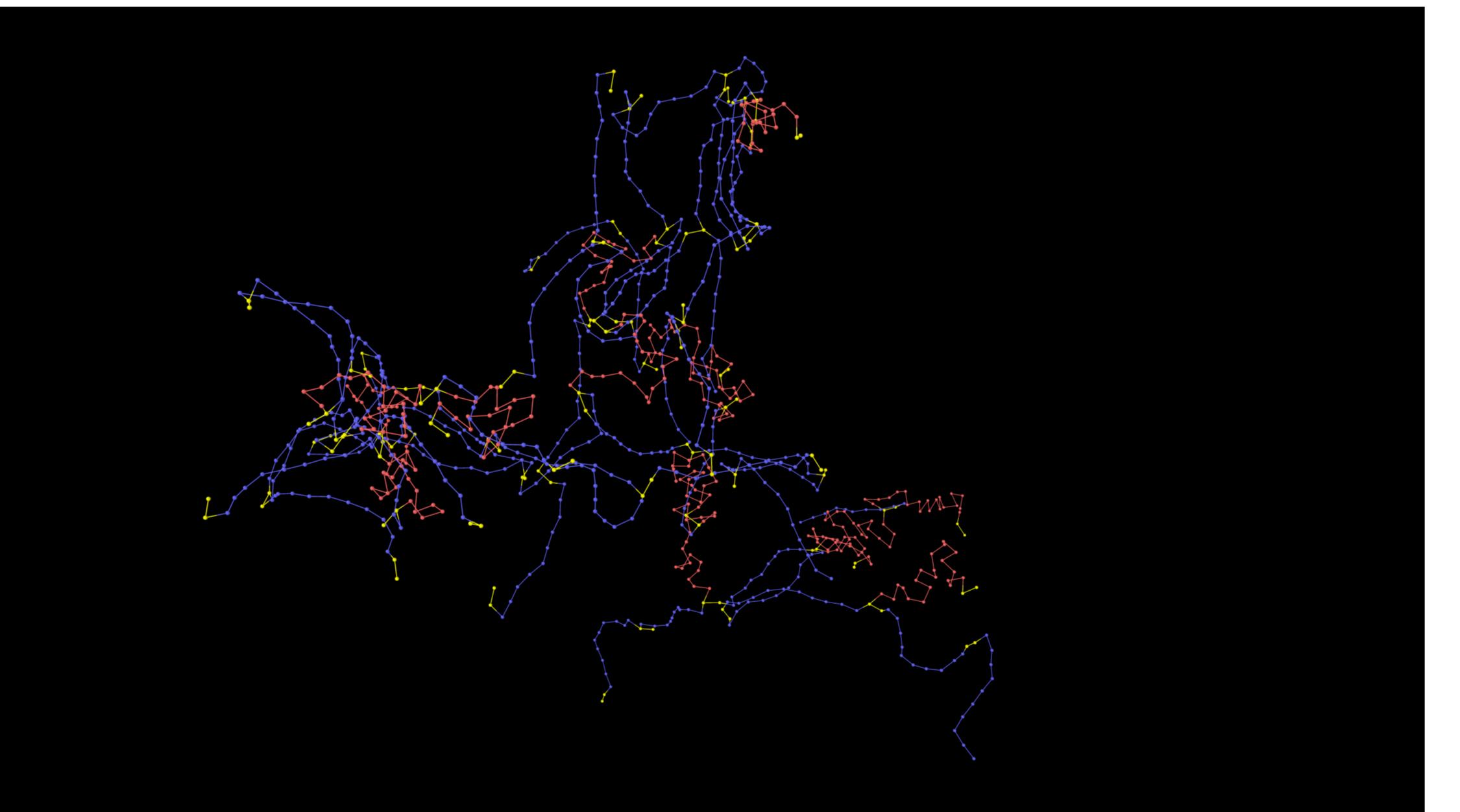


Figure 1. A representative crosslinked molecule formed at $E = 0.2$ and $r = 0.33$. Red beads are flexible, blue beads are stiff, and yellow beads are linkers.

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Glass Transition Behavior - Mixed Component Networks Show a T_g Maximum

To probe the glass transition temperature T_g , the newly formed polymers are first brought up to $T = 1.0$, then subjected to three cooling/heating cycles - first to $T = 0.2$, then back up to $T = 1.0$, then back down to $T = 0.2$, each at a rate of τ , at $P = 0.0$. A piecewise bilinear regression is fit to the resulting $\ln V$ vs T data. The breakpoint between the two lines is taken as T_g .

When $E = 0.0$, T_g increases with r , as expected. However, when $E = 0.2$, a maximum in T_g for intermediate r is observed. The same trend is also observed in experiment.

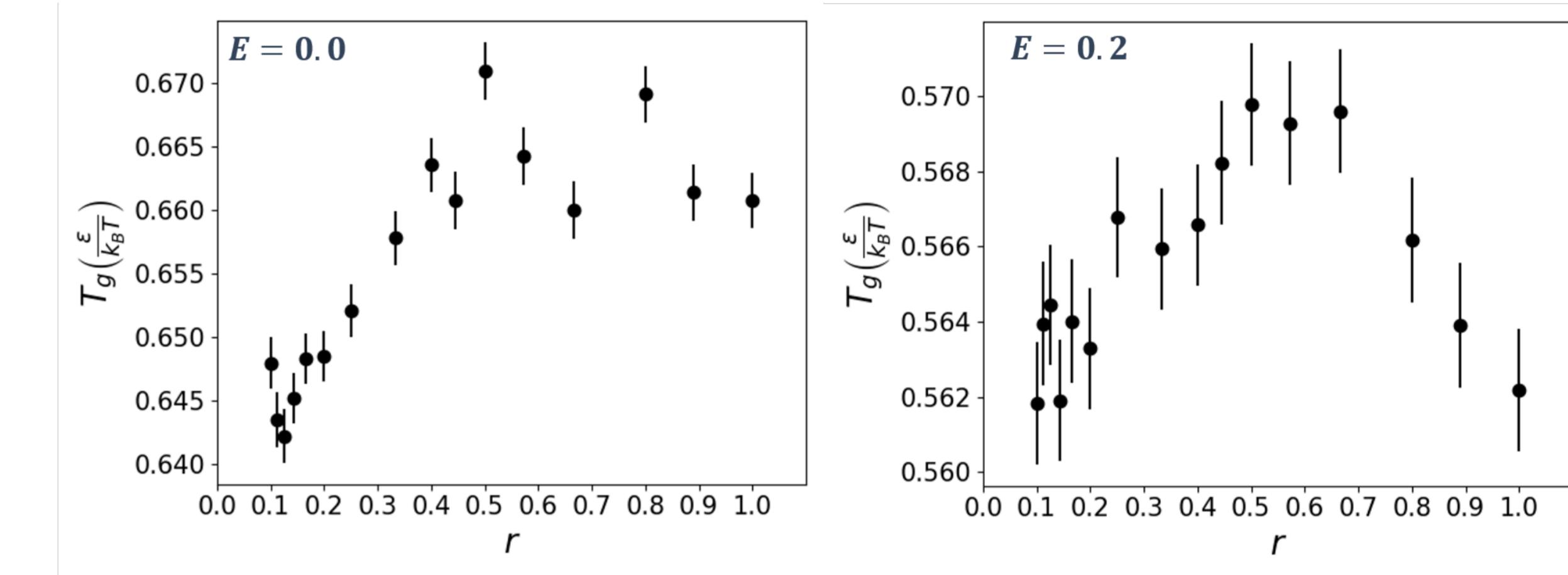


Figure 2. T_g as a function of r for $E = 0.0$ and $E = 0.2$

Network Architecture and Hydrogen Bonding Compete to Determine T_g

We hypothesize that two trends compete against each other to determine T_g of the network. First, T_g increases with increasing crosslink density. Secondly, T_g increases with more hydrogen bonds in the system. As r increases, crosslink density increases but the number of hydrogen bonds decreases.

When $E = 0.0$, the units connecting the crosslinks are relatively short and stiff molecules. When $E = 0.2$, however, the average distance between crosslinks must increase for the same fundamental network structure (as the flexible molecule is longer than the stiff molecule). The same network structure results in a lower T_g , depressing T_g at high r . Furthermore, more amine termini connected to flexible molecules may promote hydrogen bonding at lower r .

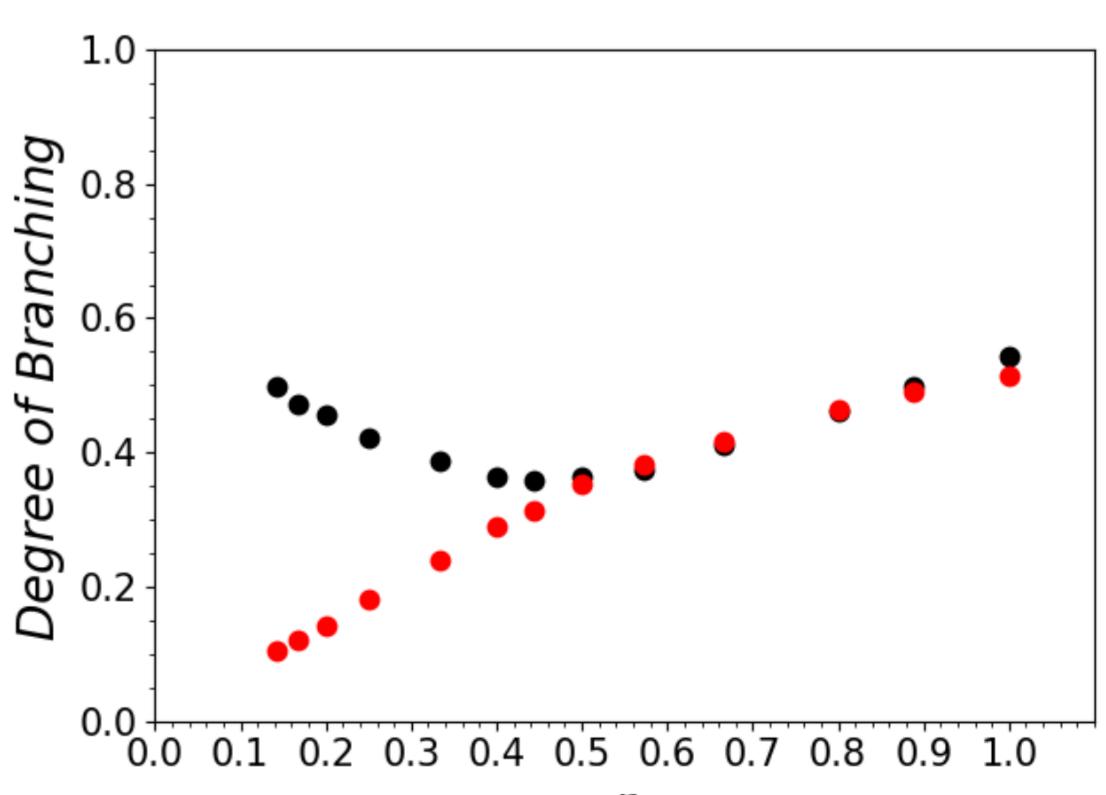


Figure 3. Degree of branching, emphasizing dendritic links (crosslinks), and the total number of amine-termini. Each junction in the network polymers is characterized as terminal (T), linear (L), or dendritic (D) to perform this calculation.