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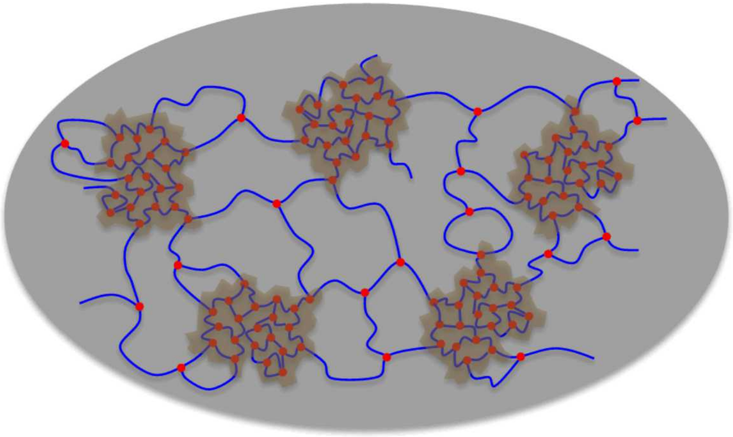

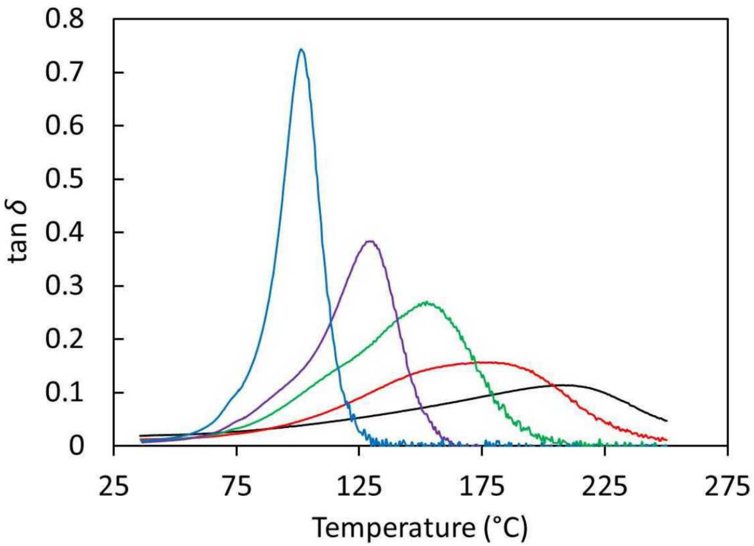

New Insights into the Chain Dynamics and Microstructure of Highly Crosslinked Polymer Networks as a Function of Network Heterogeneity

Brad H. Jones

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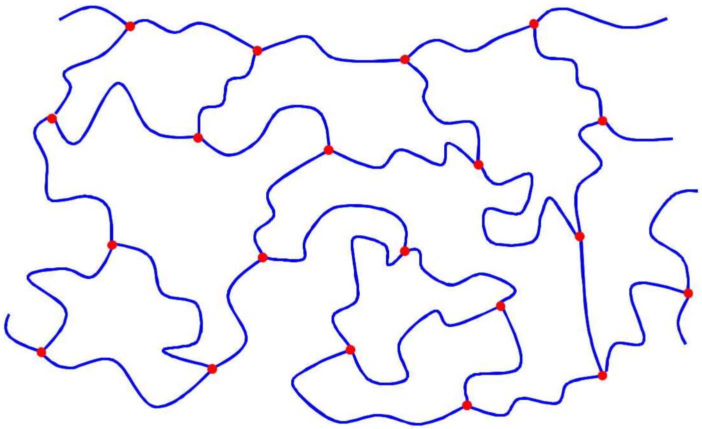
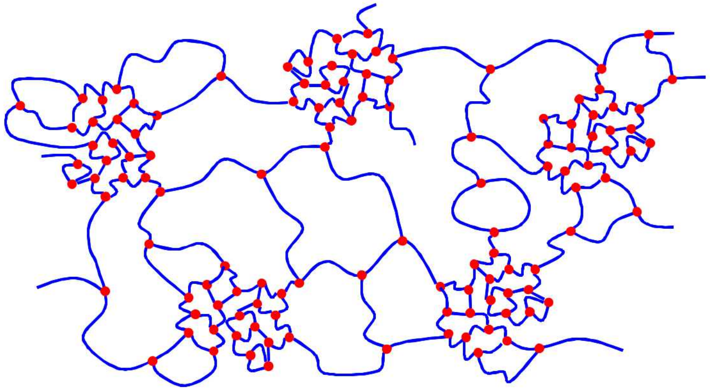
Network Heterogeneity and Cure Behavior

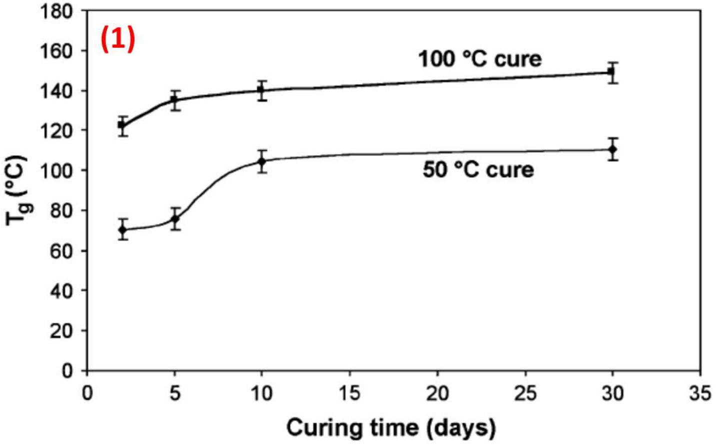
Heterogeneous networks can achieve $T_g \gg T_{cure}$

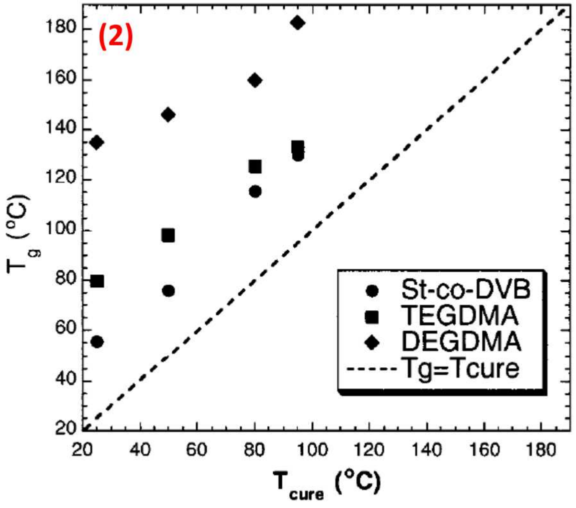
homogeneous network (step-growth)

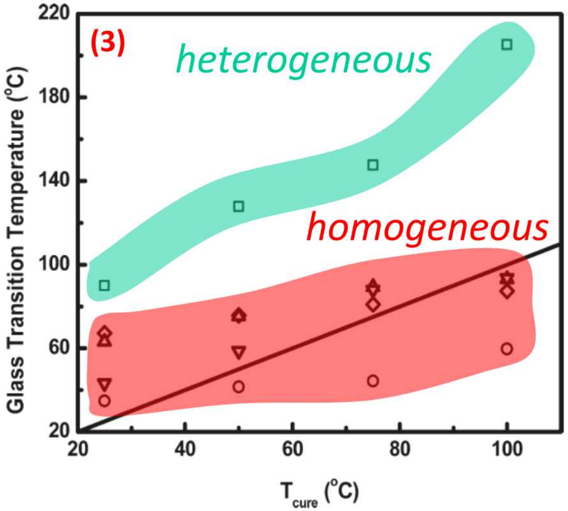


heterogeneous network (chain-growth)







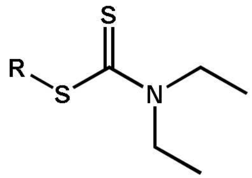


(1) Le Baut, N.; *et al. Polymer* **2007**, *48*, 239-244. **(2)** Lu, H.; Lovell, L. G.; Bowman, C. N. *Macromolecules* **2001**, *34*, 8021-8025. **(3)** Ye, S.; Cramer, N. B.; Bowman, C. N. *Macromolecules* **2011**, *44*, 490-494.

High T_g Tunable Thiol-Ene Networks

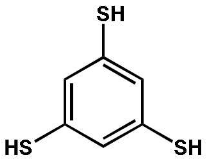
High T_g and tunable heterogeneity can be achieved with rigid thiol-ene monomers

radical photoinitiator

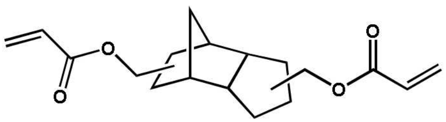


+

benzenetrithiol
(BTT)



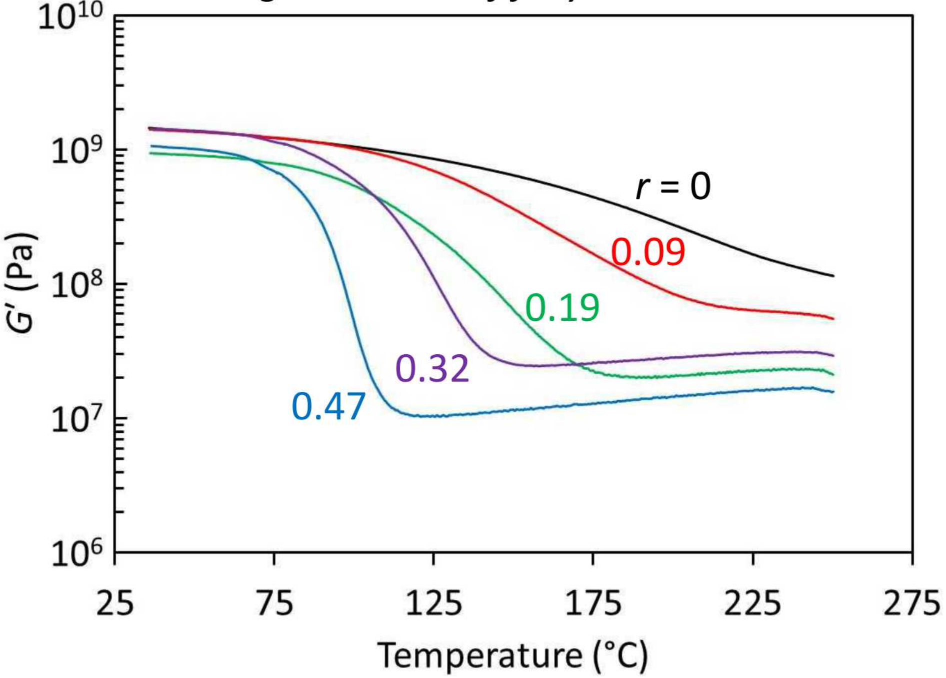
tricyclodecane diacrylate
(TCDDA)



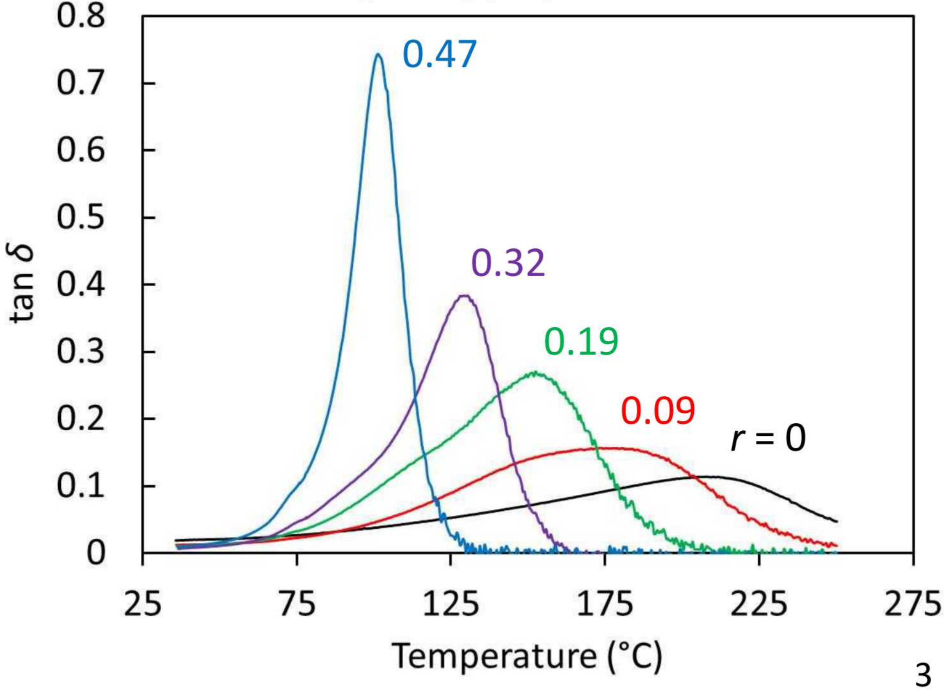
$$r = \frac{[SH]_0}{[C{=}C]_0}$$

***r* ↑ more step-growth**
***r* ↓ more chain-growth**

Storage modulus of fully cured networks



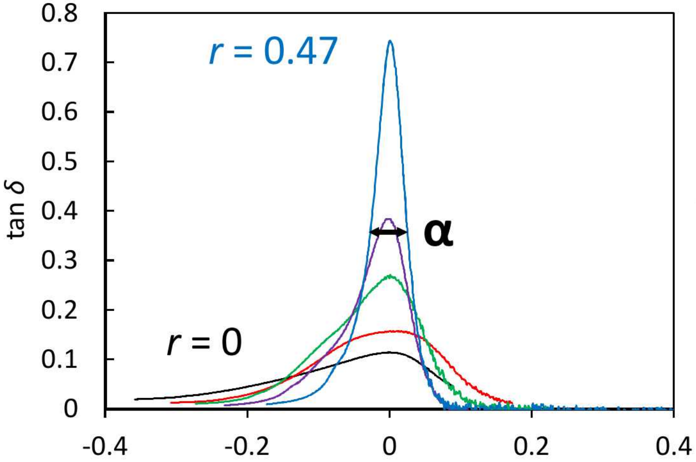
Loss tangent of fully cured networks



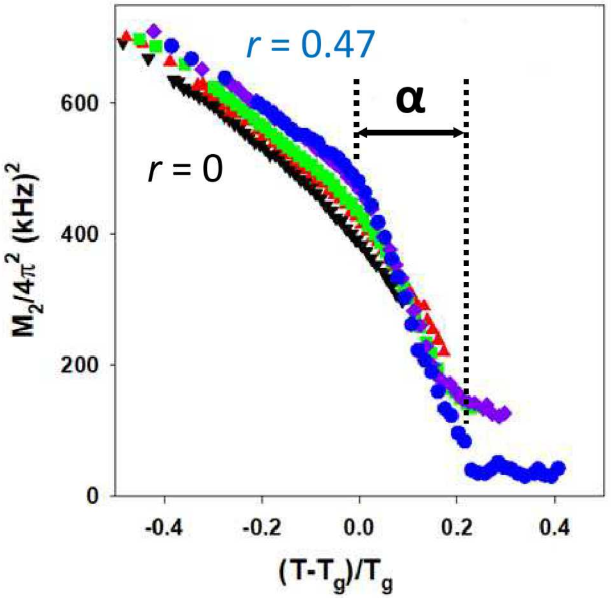
Predicting T_g Relative to T_{cure}

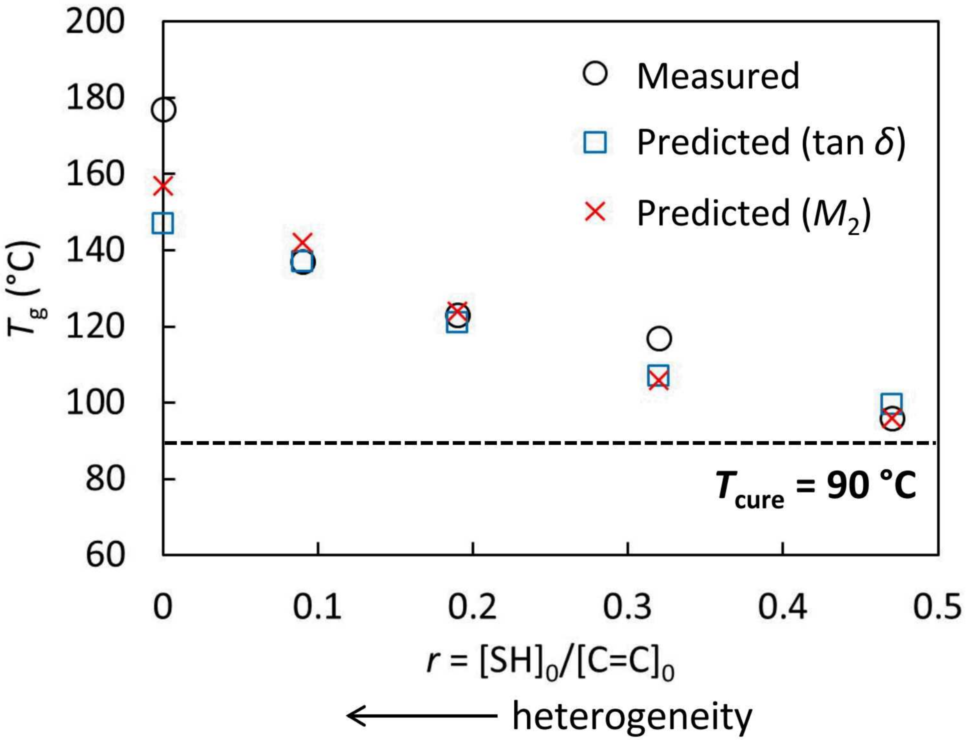
T_g can be estimated using measurements that probe chain dynamics

Dynamic mechanical analysis



Solid-state ^{1}H NMR spectroscopy





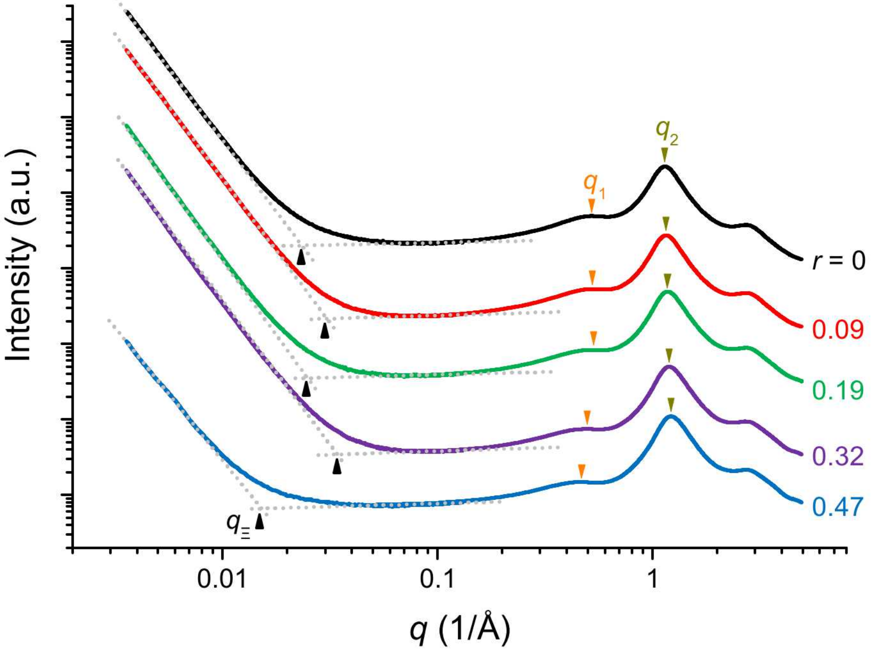
*Predictions use $T_g = T_{cure} + \alpha_{half\text{-}width}$

*Ye, S.; Cramer, N. B.; Bowman, C. N. *Macromolecules* **2011**, *44*, 490-494.

Compositional vs. Dynamic Heterogeneity

The microstructures of thiol-ene networks are defined by periodic fractal microgels

**X-ray scattering patterns of fully cured networks*



- Power law scattering at low q indicates presence of fractal structures (microgels)
- Microgels persist at all network compositions
- Microgel spacing (from q_Ξ) ranges from 18-41 nm

↑ (dynamic) heterogeneity

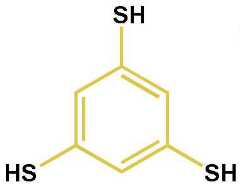
Both the dynamically heterogeneous and dynamically homogeneous extremes exhibit compositional heterogeneity!

*Scattering characterization courtesy of Prof. Sangwoo Lee, RPI

Compositional vs. Dynamic Heterogeneity

Compositional heterogeneity likely persists due to differences in reactivity

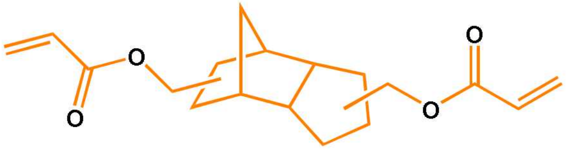
benzenetrithiol
(BTT)



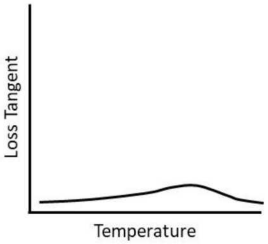
slow copolymerization

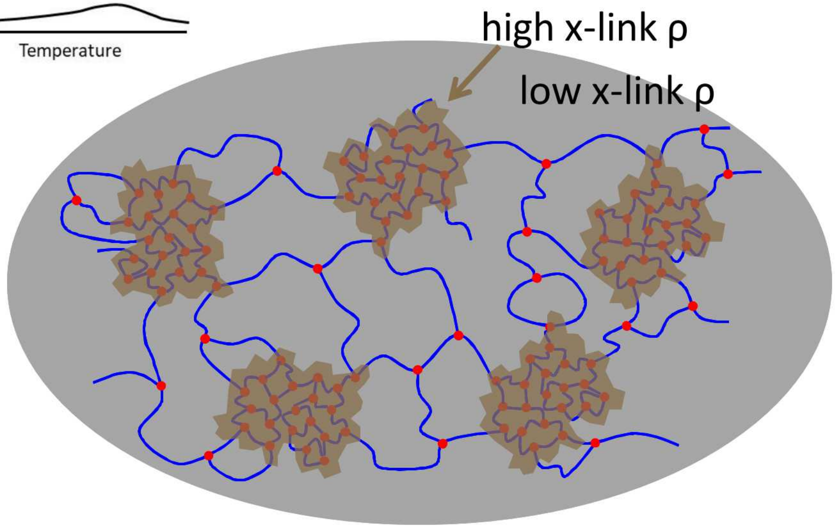
$$r = \frac{[SH]_0}{[C=C]_0}$$

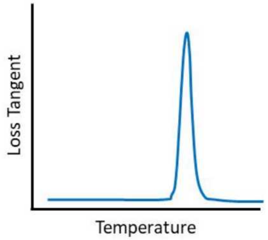
tricyclodecane diacrylate
(TCDDA)

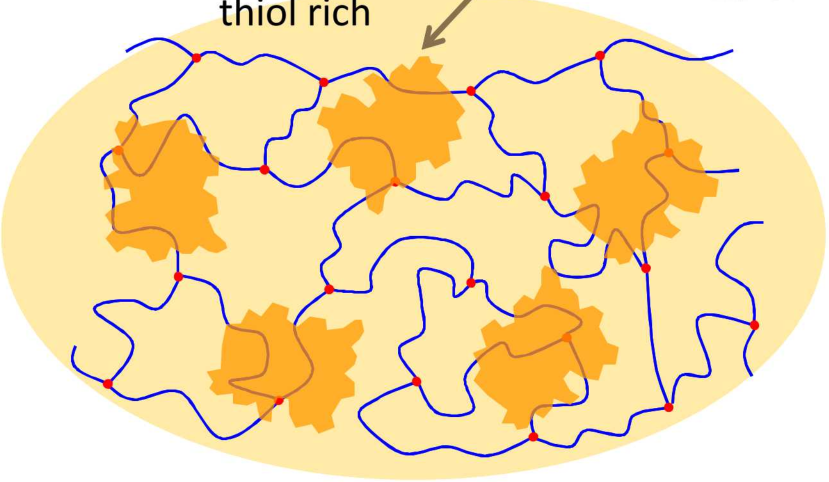


fast homopolymerization



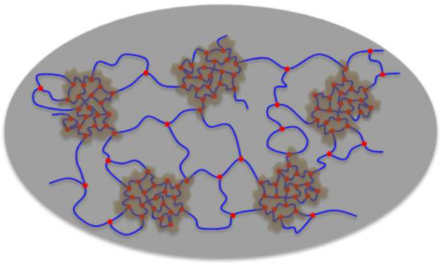


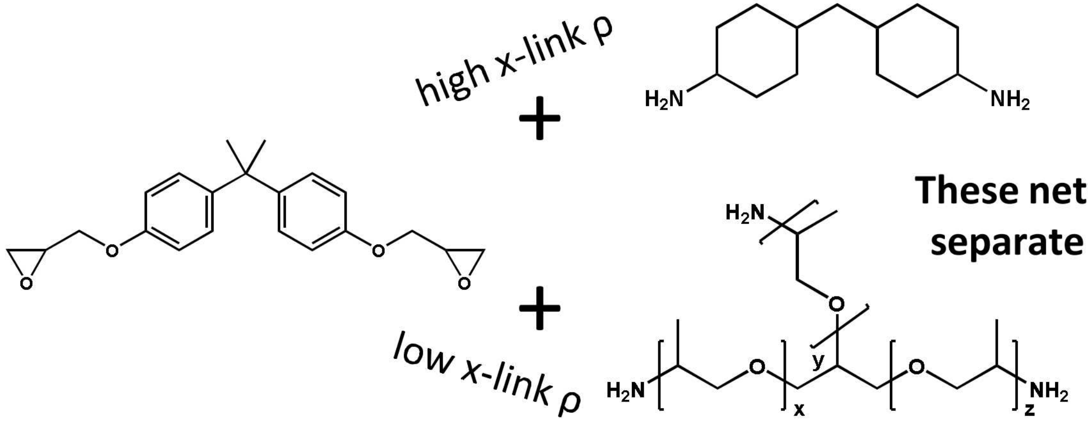




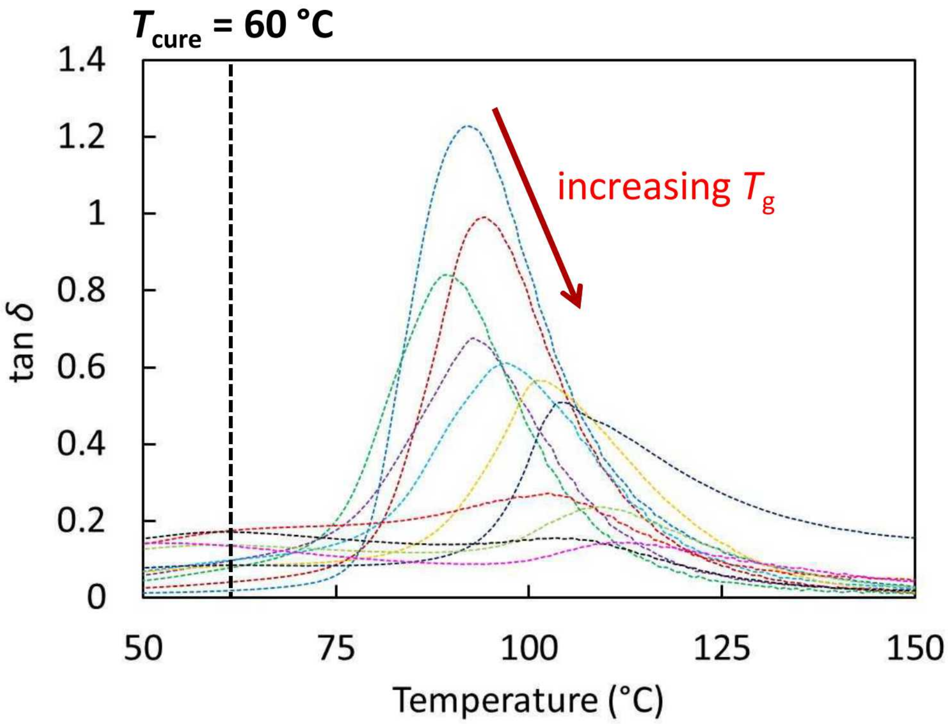
Towards T_g>>T_{cure} in Homogeneous Networks

Polymerization-induced phase separation can be exploited to drive T_g higher





These networks phase separate during cure



Summary

1. **Dynamically heterogeneous networks can achieve T_g>>T_{cure}**
2. **The value of T_g at a given T_{cure} can be readily predicted**
3. **Dynamically homogeneous networks can still be compositionally heterogeneous**
4. **Controlled phase separation offers the possibility to achieve T_g>>T_{cure} in otherwise homogeneous networks**

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