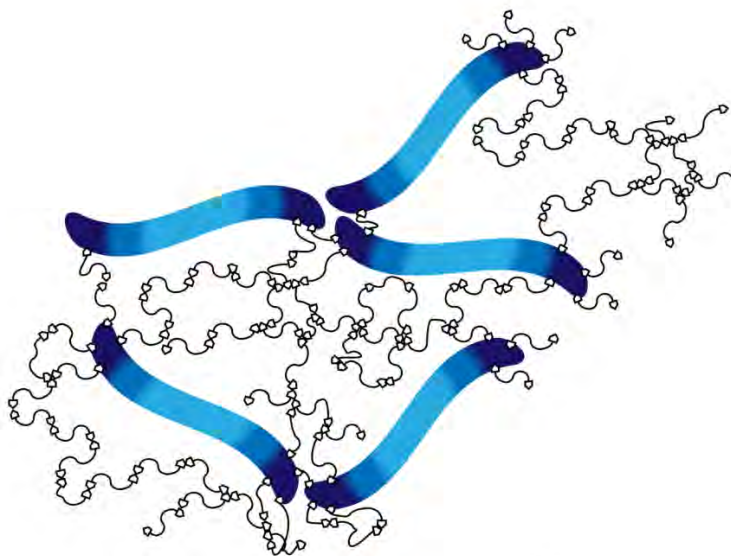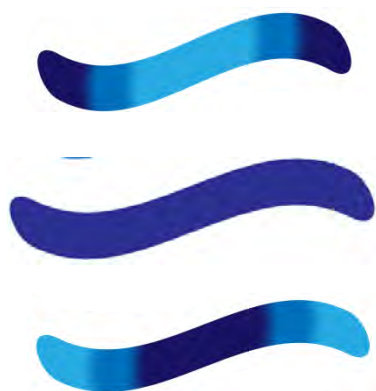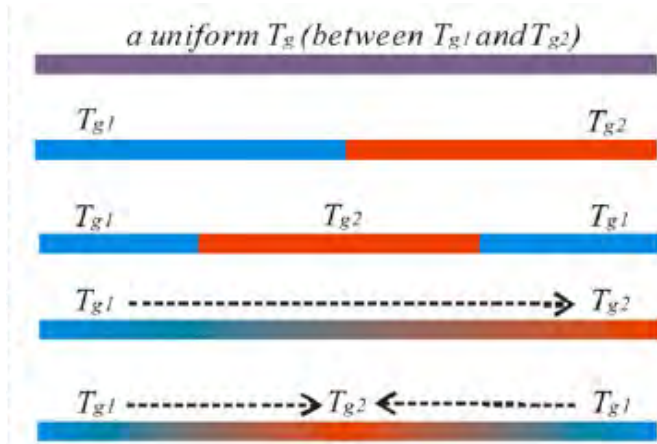# Effects of Photopolymerizable Prepolymer Architecture on Thermomechanical Properties

By Jon Scholte and Allan Guymon

Chemical and Biochemical Engineering
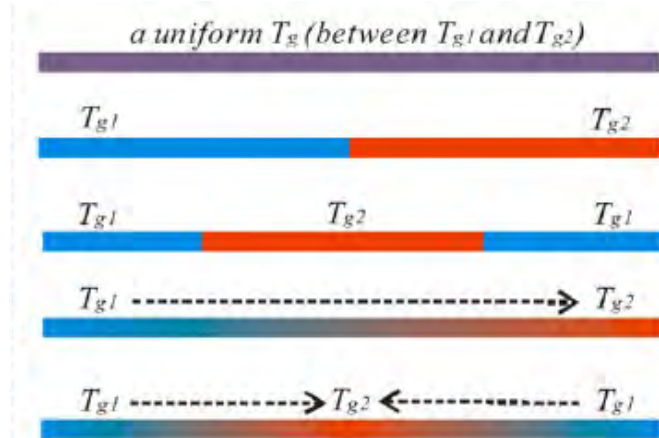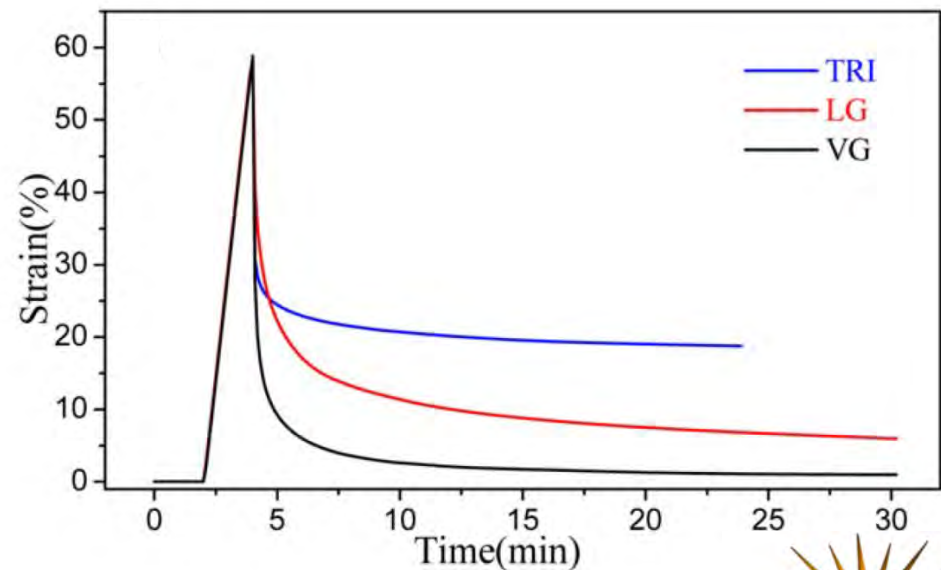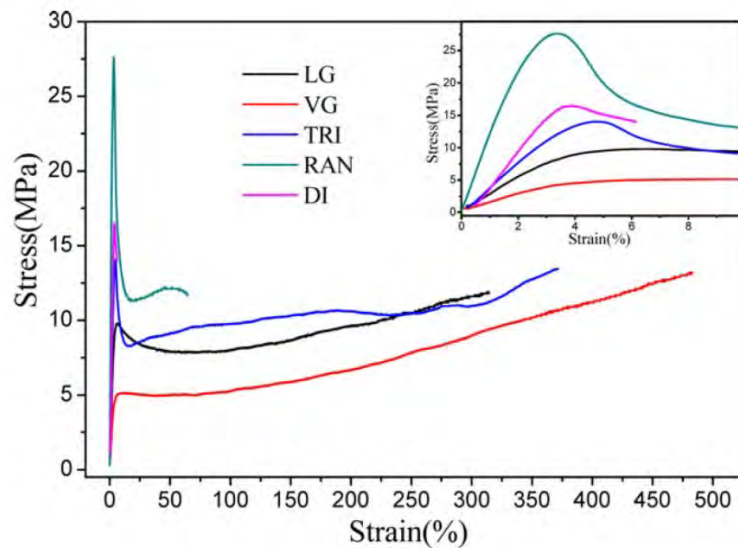
University of Iowa

1

- Linear gradients have been shown to influence the resolution and size of polymer blend morphology.

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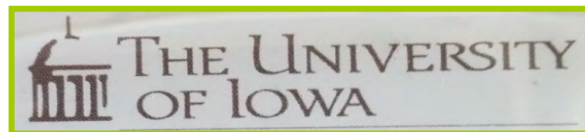Guo et al. J. Poly. Sci. B. **2015**, *53*, 860-868
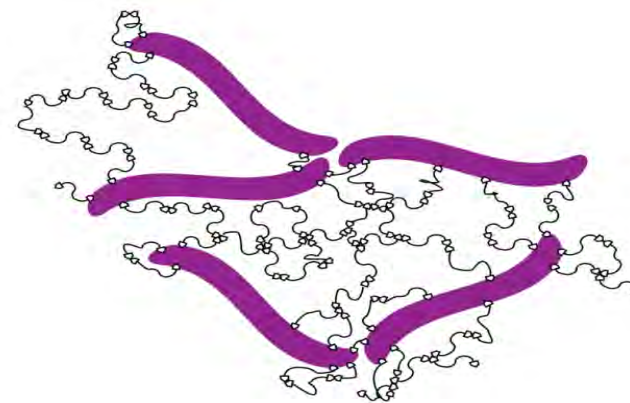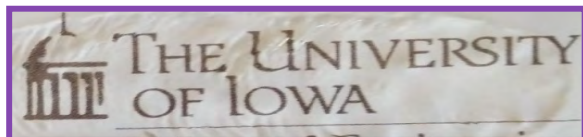
3

Architecture Directly Effect Network Formation
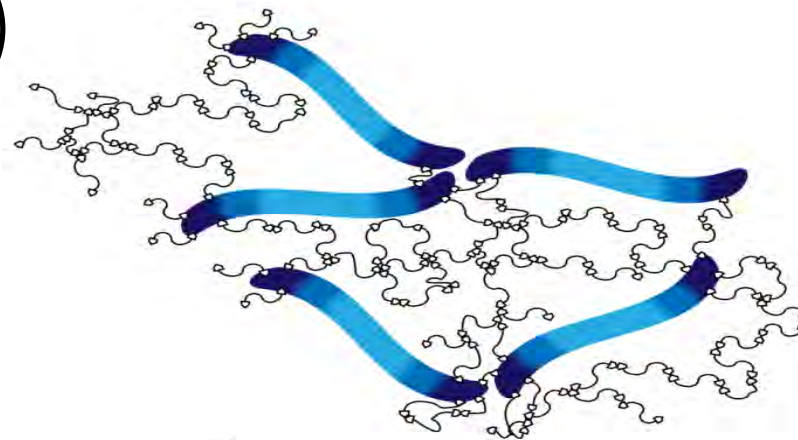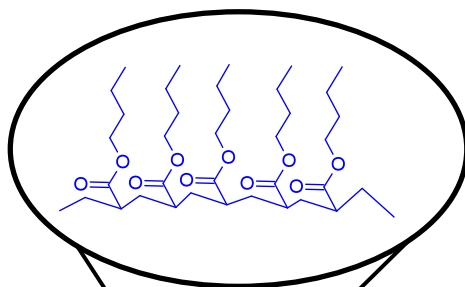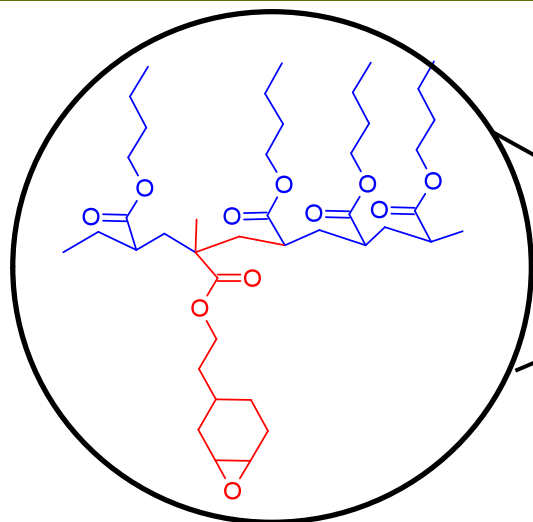
Controlled Radical Polymerization in Polymer Synthesis
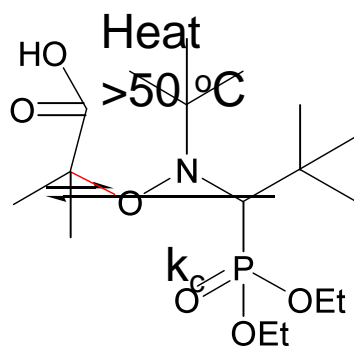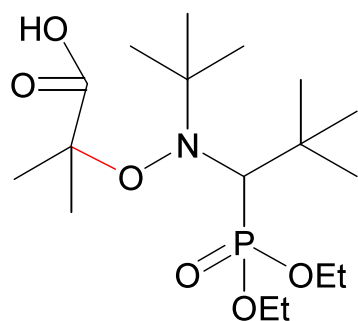
Initiator   Mediating Radical

Heat
>50 ºC

k_c

Alkoxyamines

I   SG-1
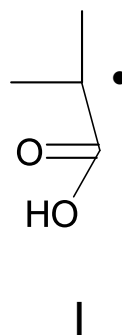
RAFT

Nitroxide Mediated Synthesis
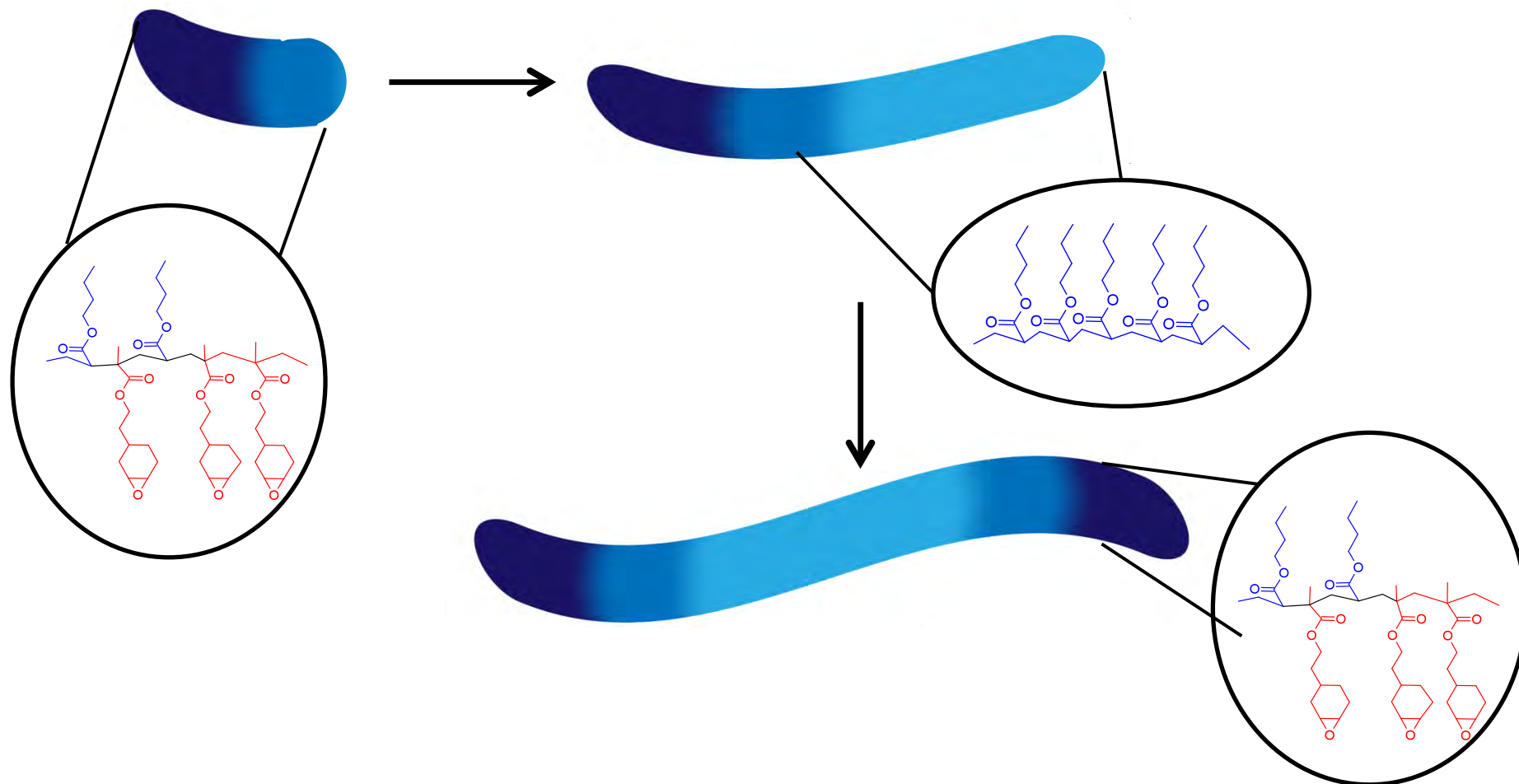
- Nitroxide Mediated Polymerization requires 2 subsequent feeds to synthesize an end functionalized prepolymer
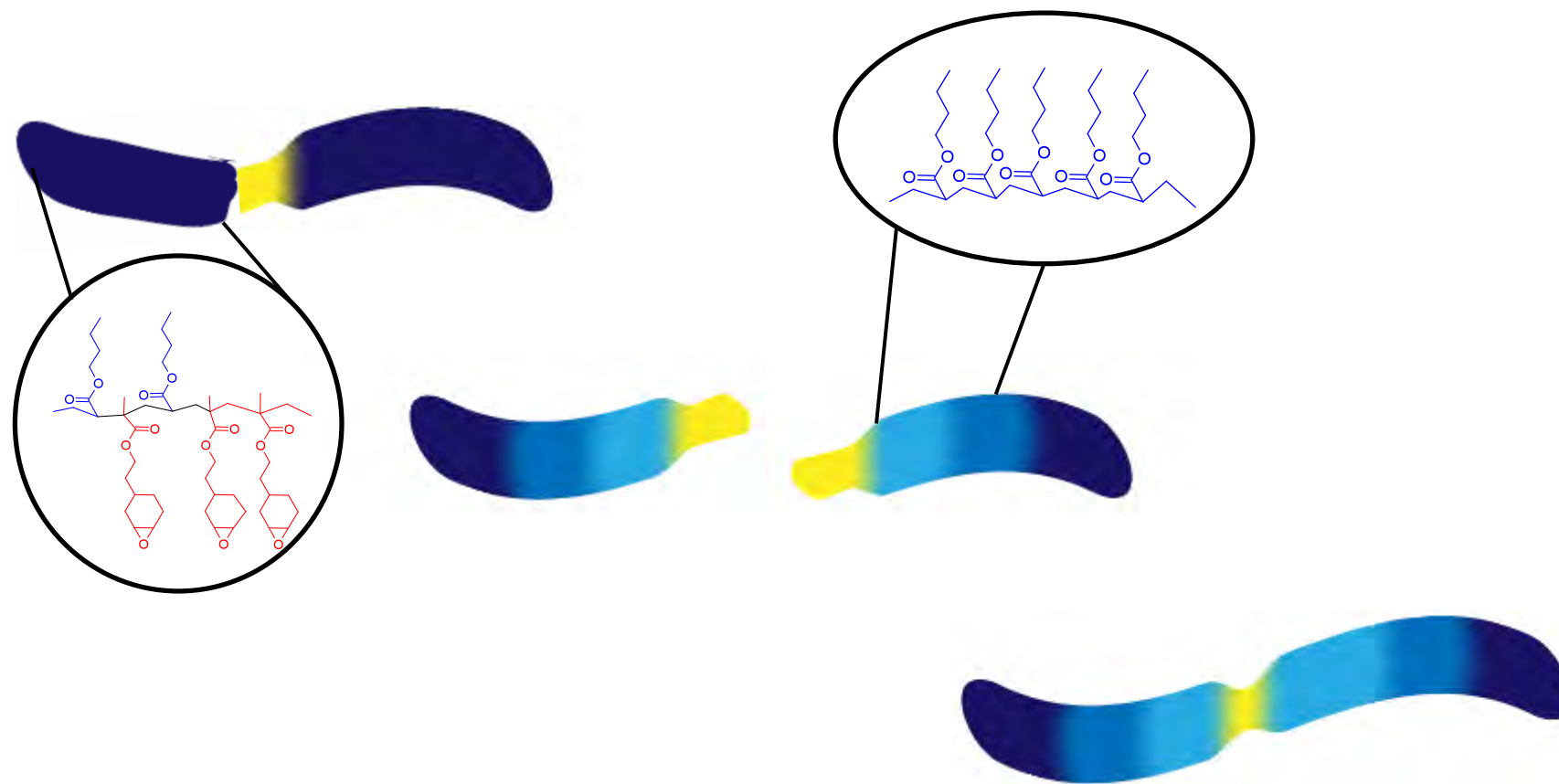
- End functionalized species can be synthesized with a single feed and grows from the inside out
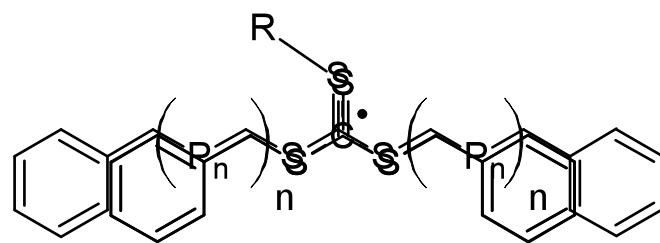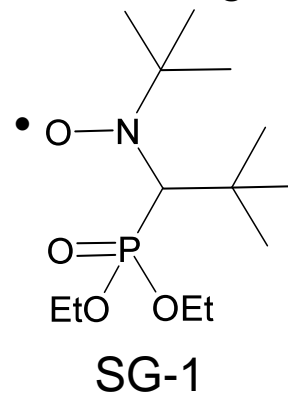
Synthesis of Random Copolymers
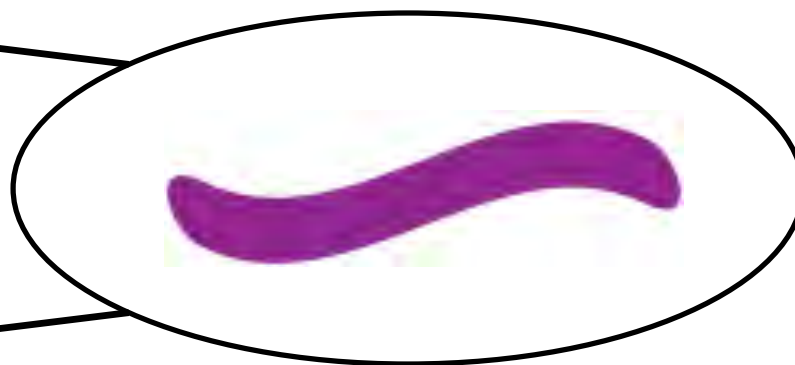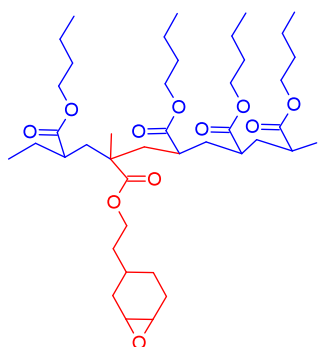
- Both Nitroxide and RAFT methods allow for the synthesis of randomly reactive prepolymers from a simple one pot method

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Photopolymerizations Center

Prepolymer Acrylation
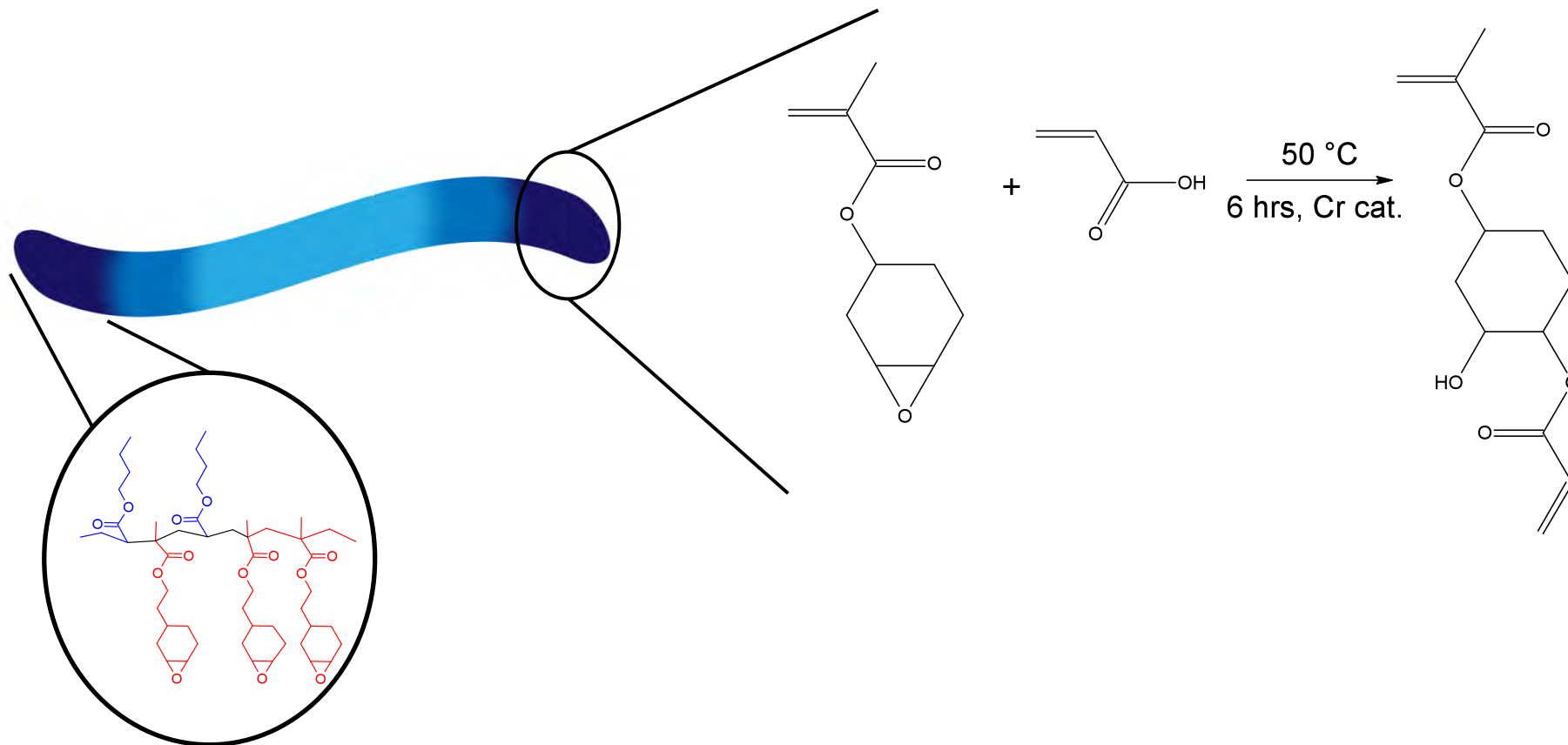
Polymer	M_n	PDI	Functionality
N-End	11,000	1.4	8
N-Random	15,000	1.4	8
R-End	12,000	1.2	8

50 °C
6 hrs, Cr cat.

Both Architectures Allow High Conversions

0.5 %wt DMPA
10 mW/cm² 6 min
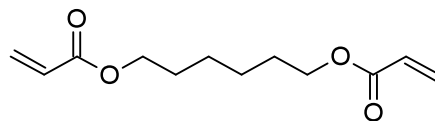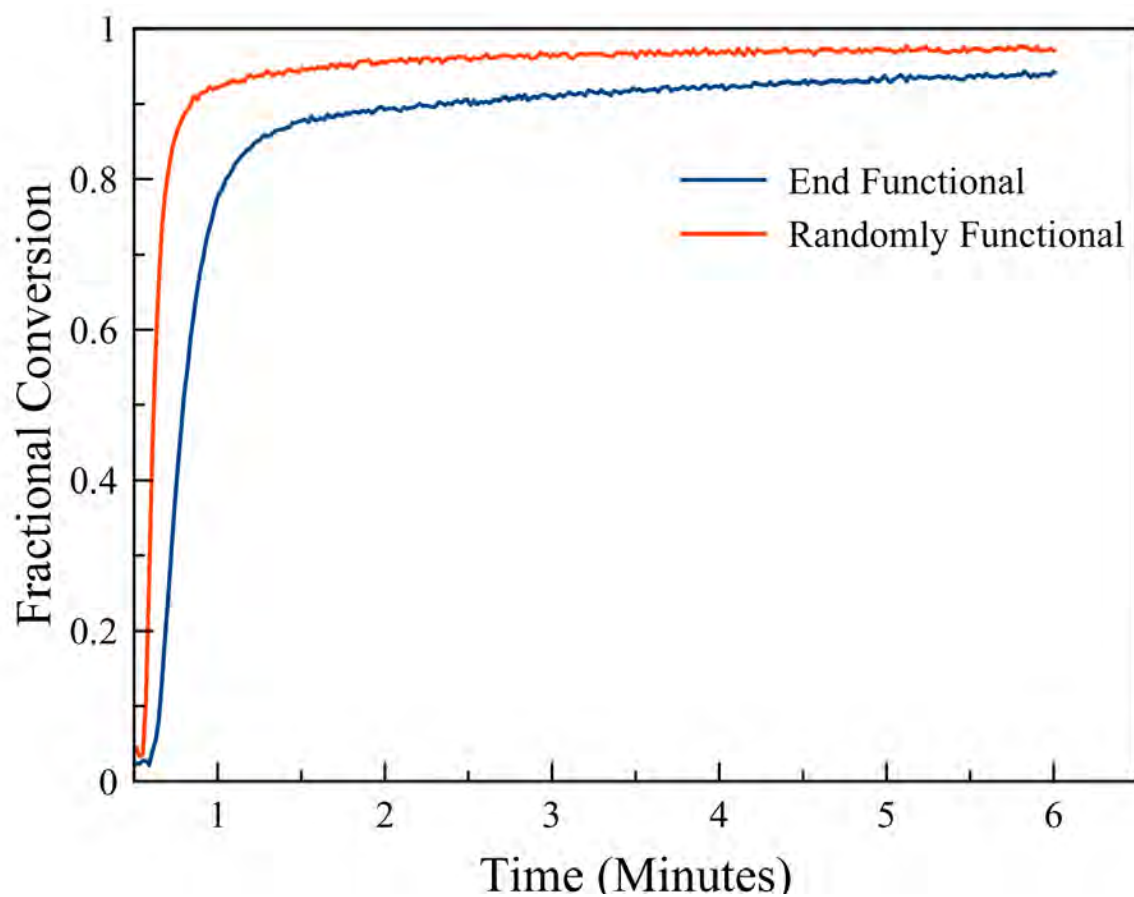
0.5 %wt DMPA
10 mW/cm² 6 min
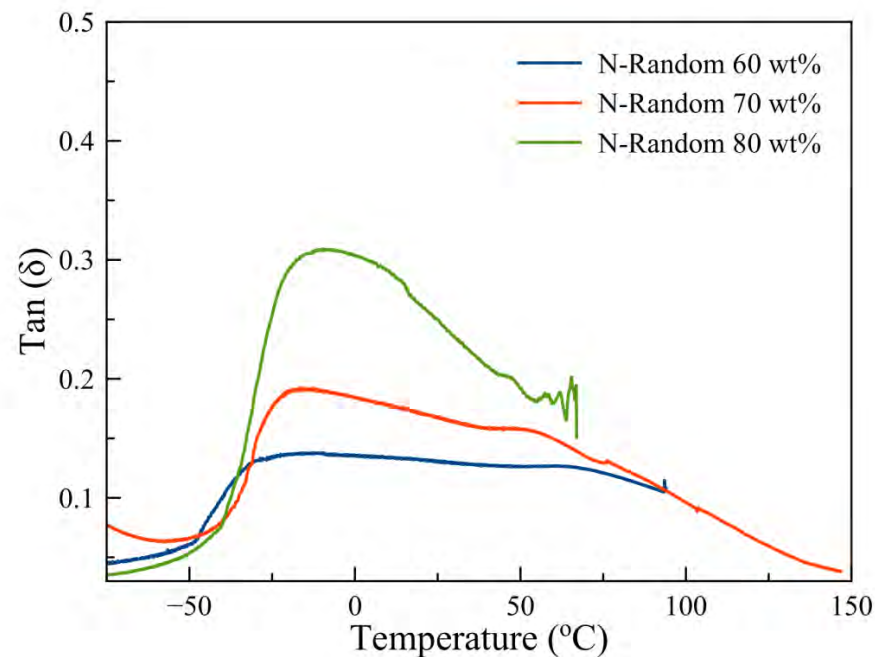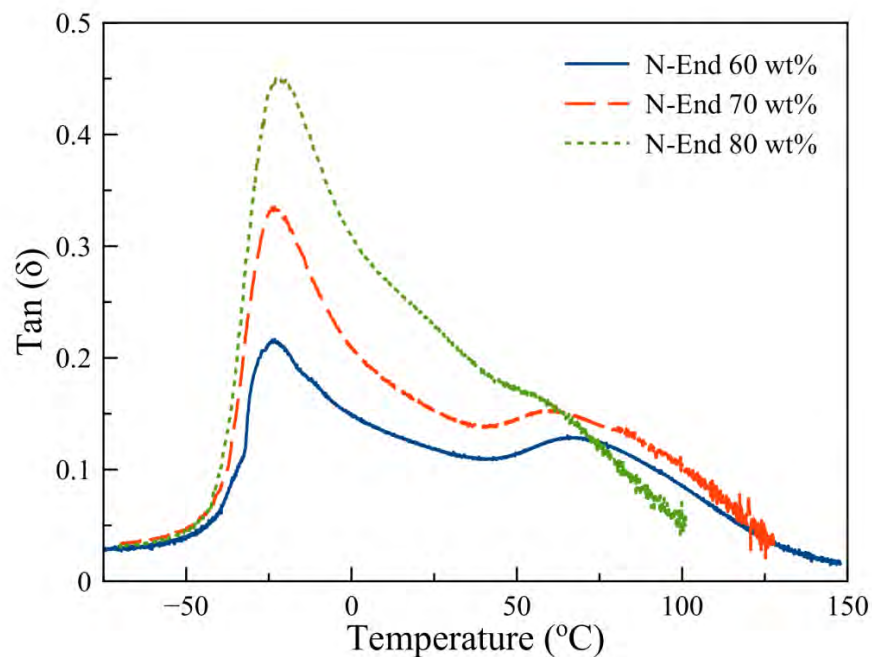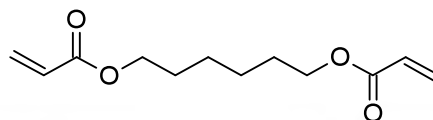
End functional formulations show large glass transition for butyl acrylate backbone and second for hdda domain

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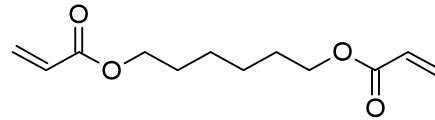Photopolymerizations Center

Multiple Domains Enhance Toughness

0.5 %wt DMPA
10 mW/cm² 6 min
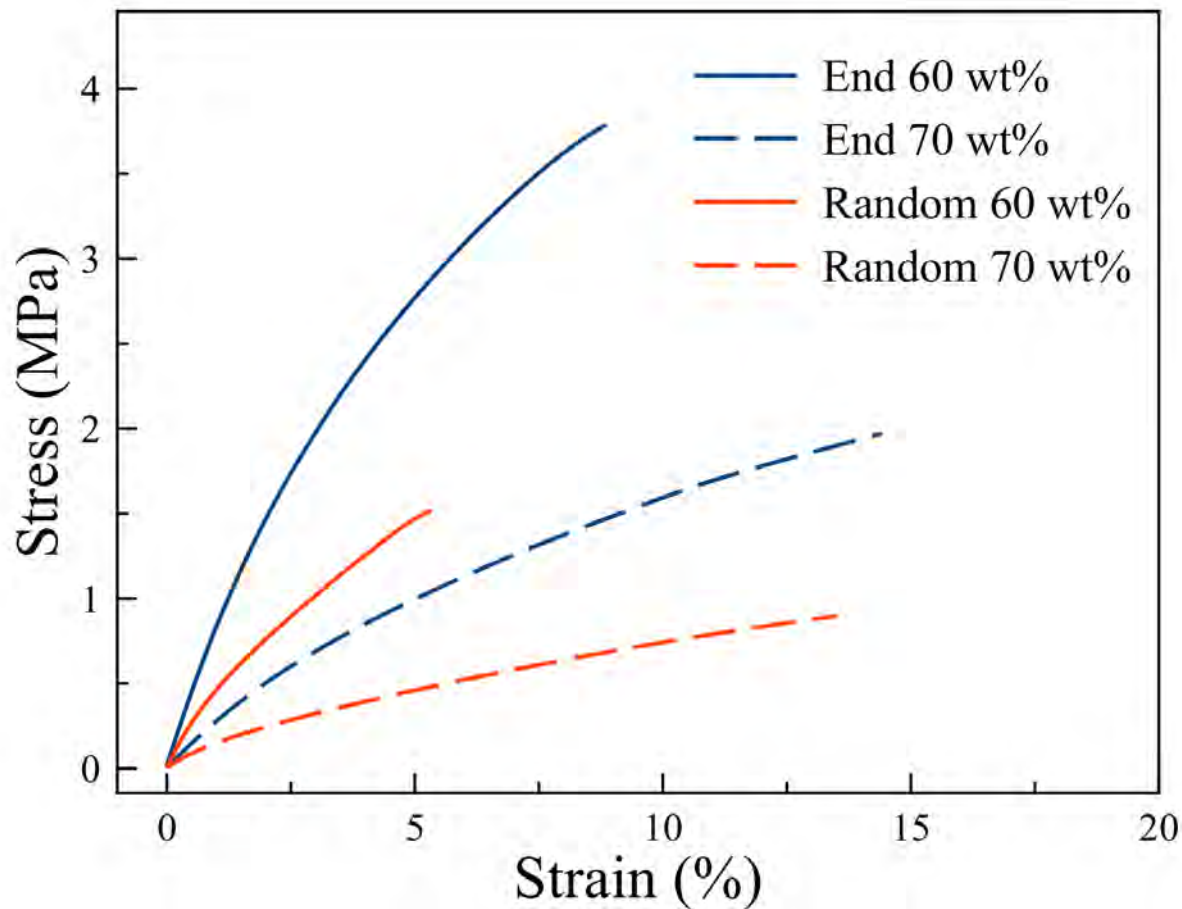
Continuous hard domain **improves modulus** of **end functionalized** formulations
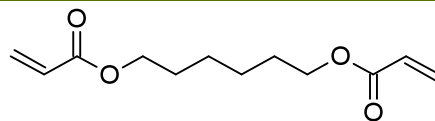
0.5 %wt DMPA
10 mW/cm² 6 min
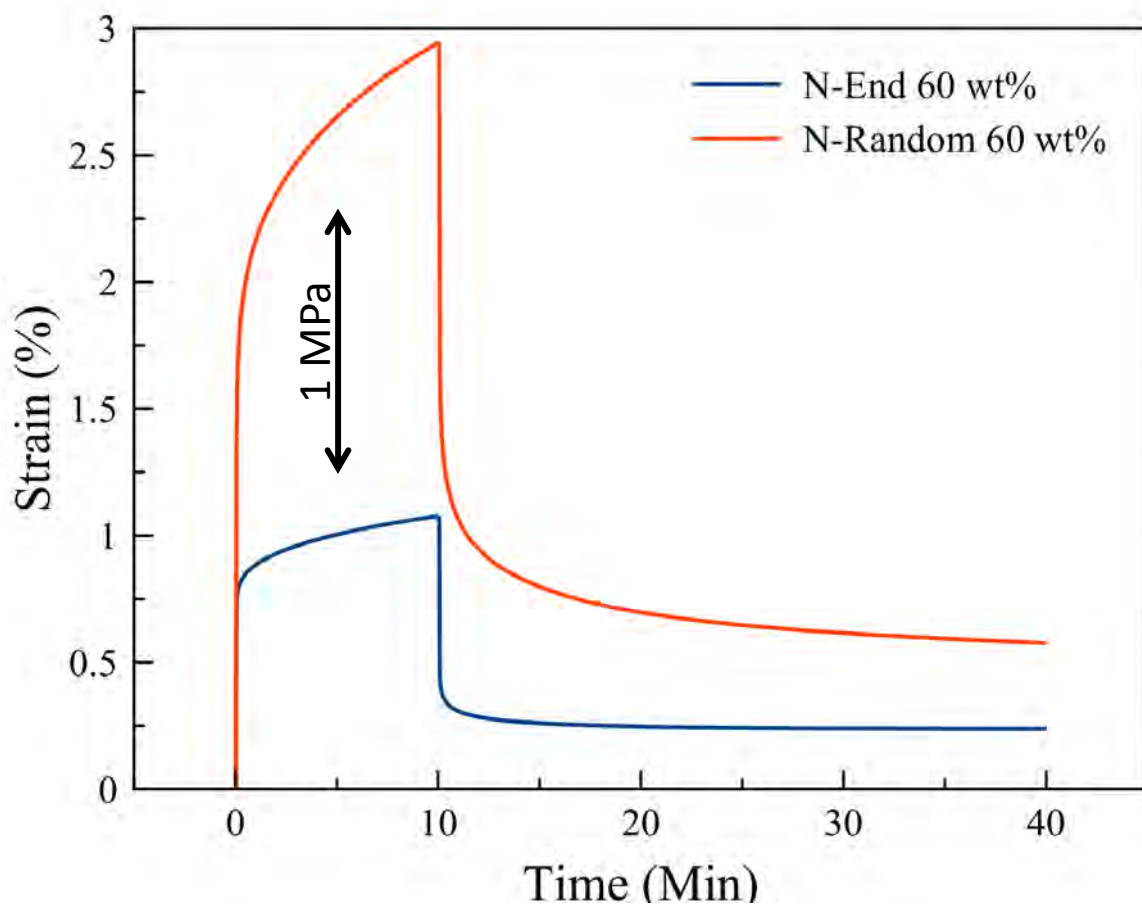
Continuous hard domains in **end functional materials** increases resistance to sudden stress

RAFT Synthesized Prepolymers Allow Rearrangement
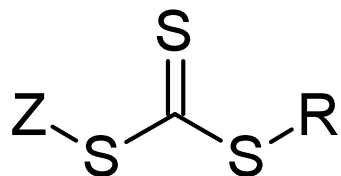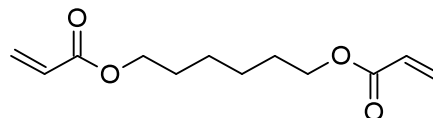
- Rearrangement around Trithiocarbonate bond will allow for both relaxation and a greater distribution of soft segments through out the network
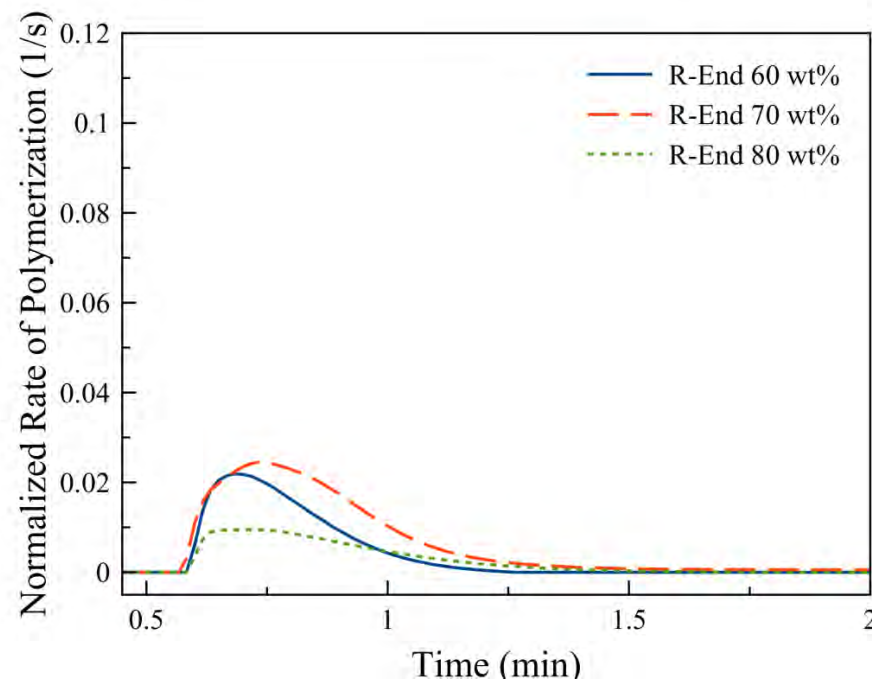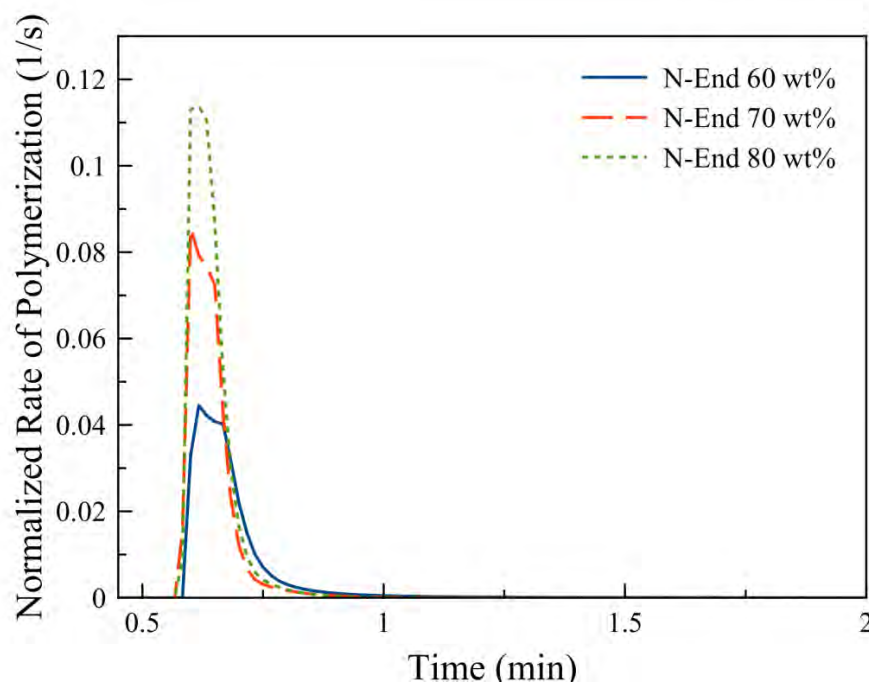

- If rearrangements are occurring, they would compete with propagation and thus alter reaction kinetics
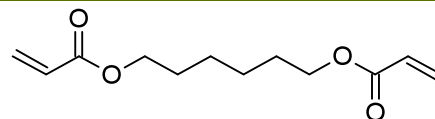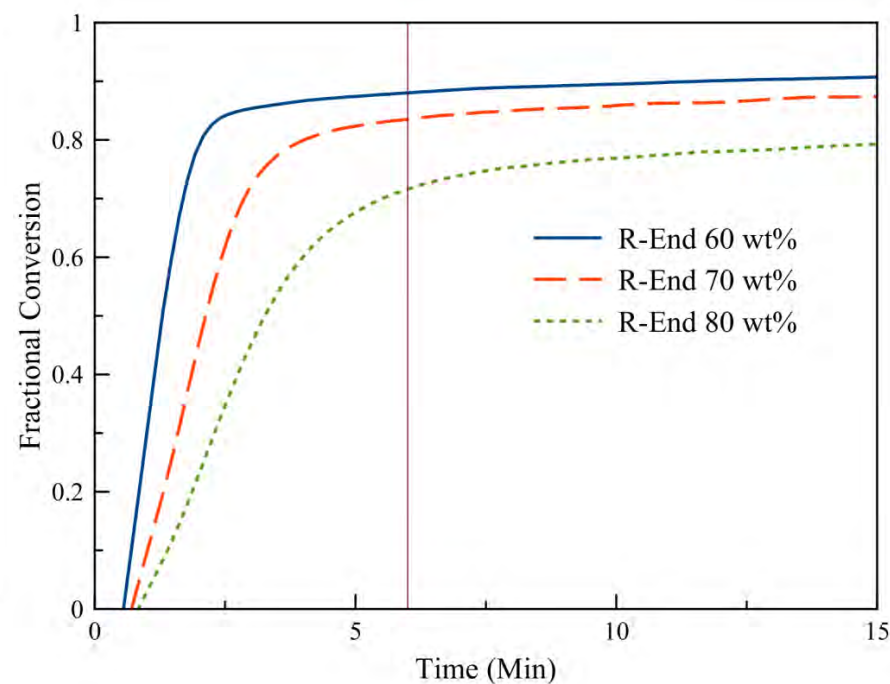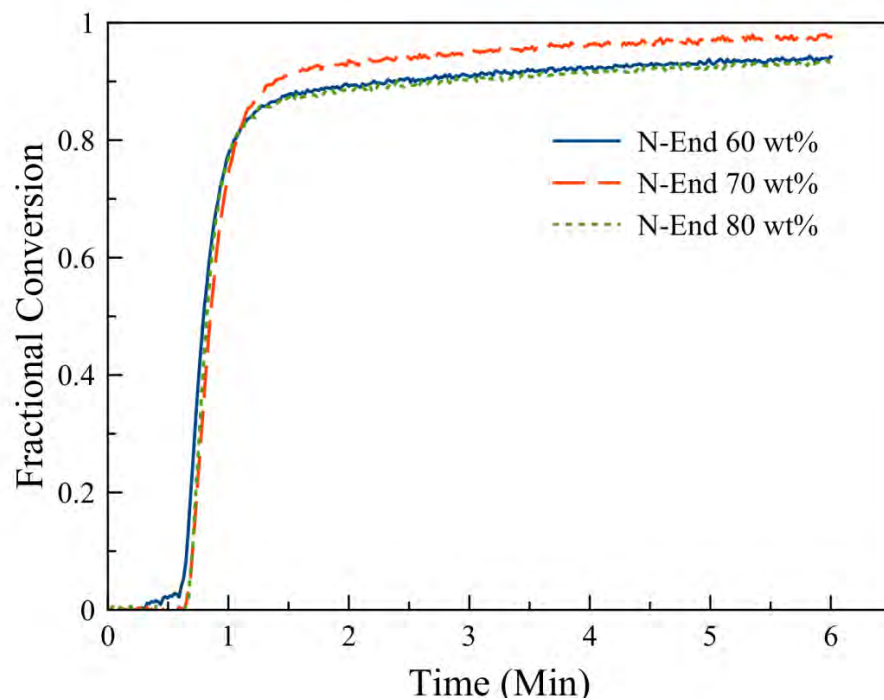
14

0.5 %wt DMPA
10 mW/cm² 15 min

RAFT rearrangement retards the polymerization at high prepolymer concentations

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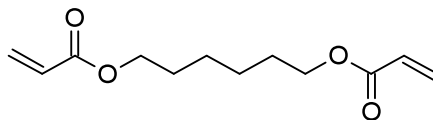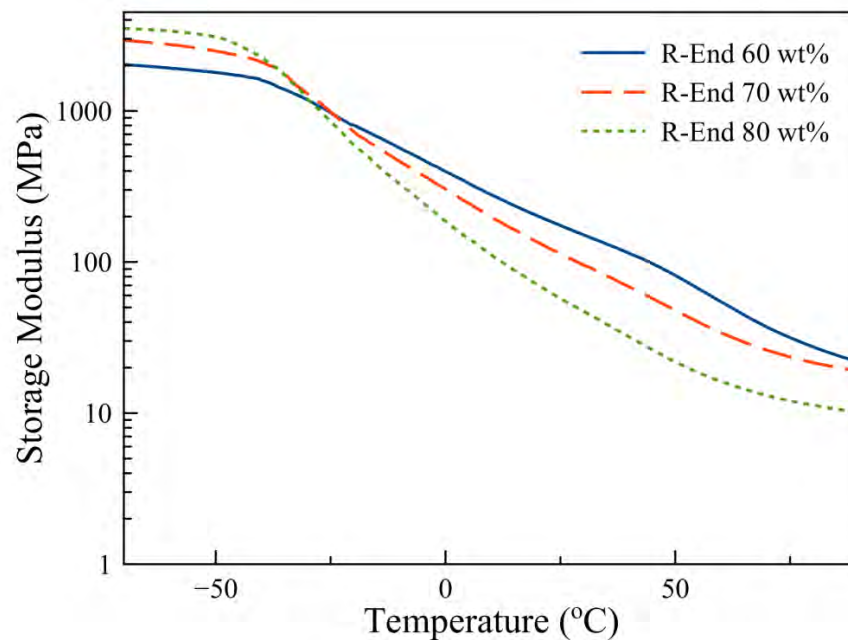# Conversion Lowers with Increased Transfer

0.5 %wt DMPA
10 mW/cm² 15 min

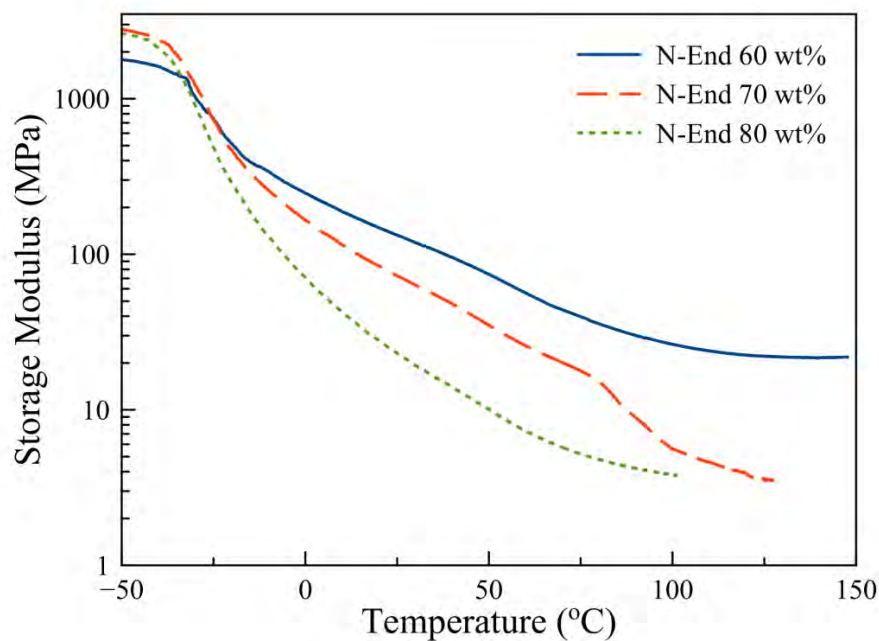Network rearrangement prevents complete cure in RAFT formulations

Nitroxide Formulations Display Multiple Regimes
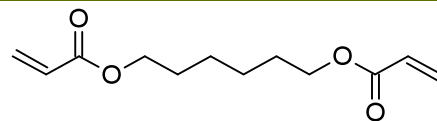
0.5 %wt DMPA
10 mW/cm^2 15 min

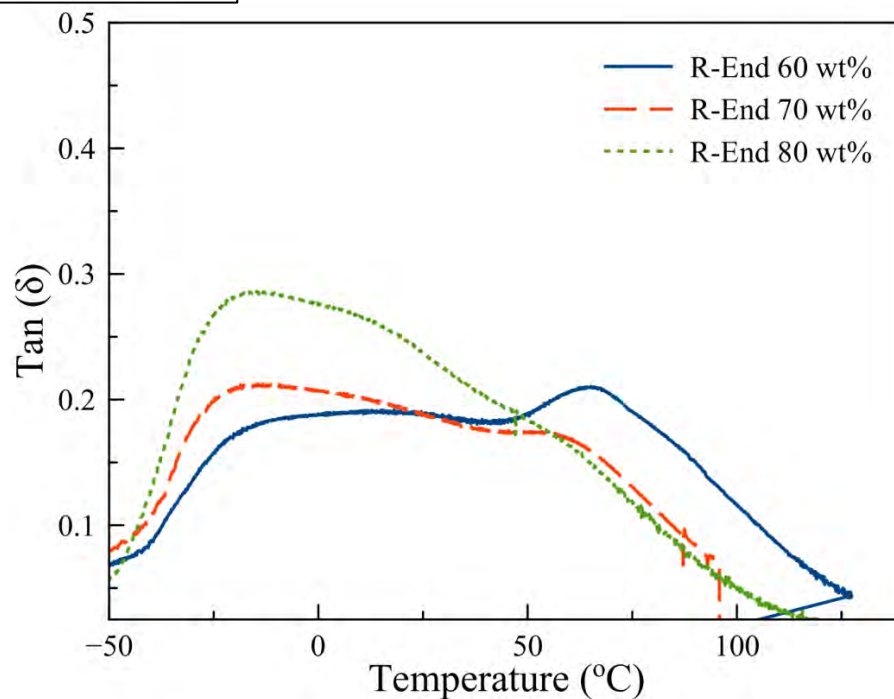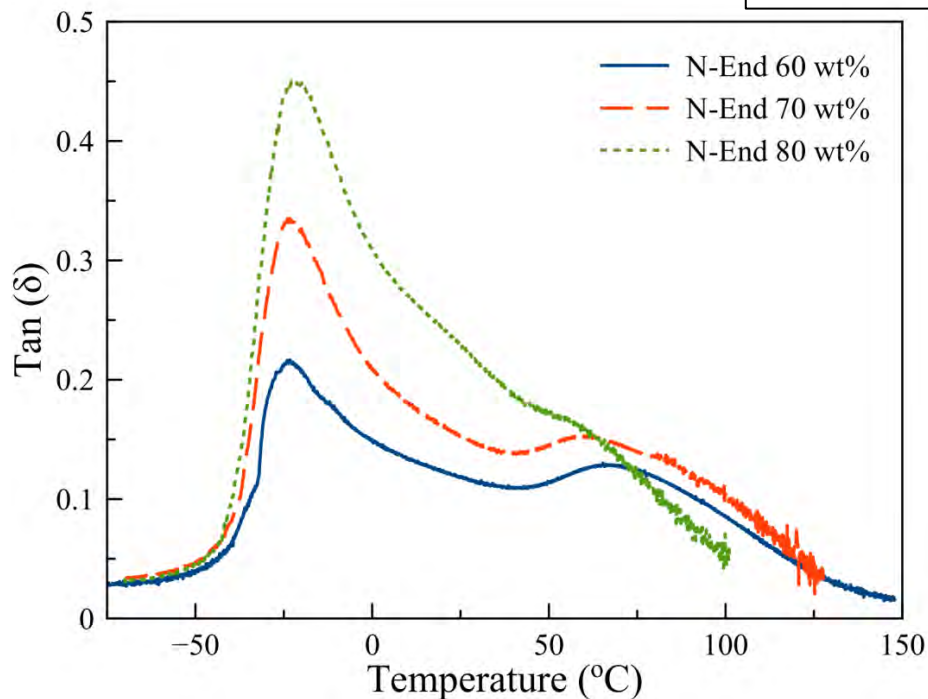Rearrangement around RAFT group diminishes phase separation and leads to gradual decreases in storage moduli

Nitroxide Prepolymers Increased Butyl Acrylate Domains

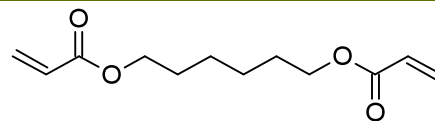0.5 %wt DMPA
10 mW/cm^2 15 min

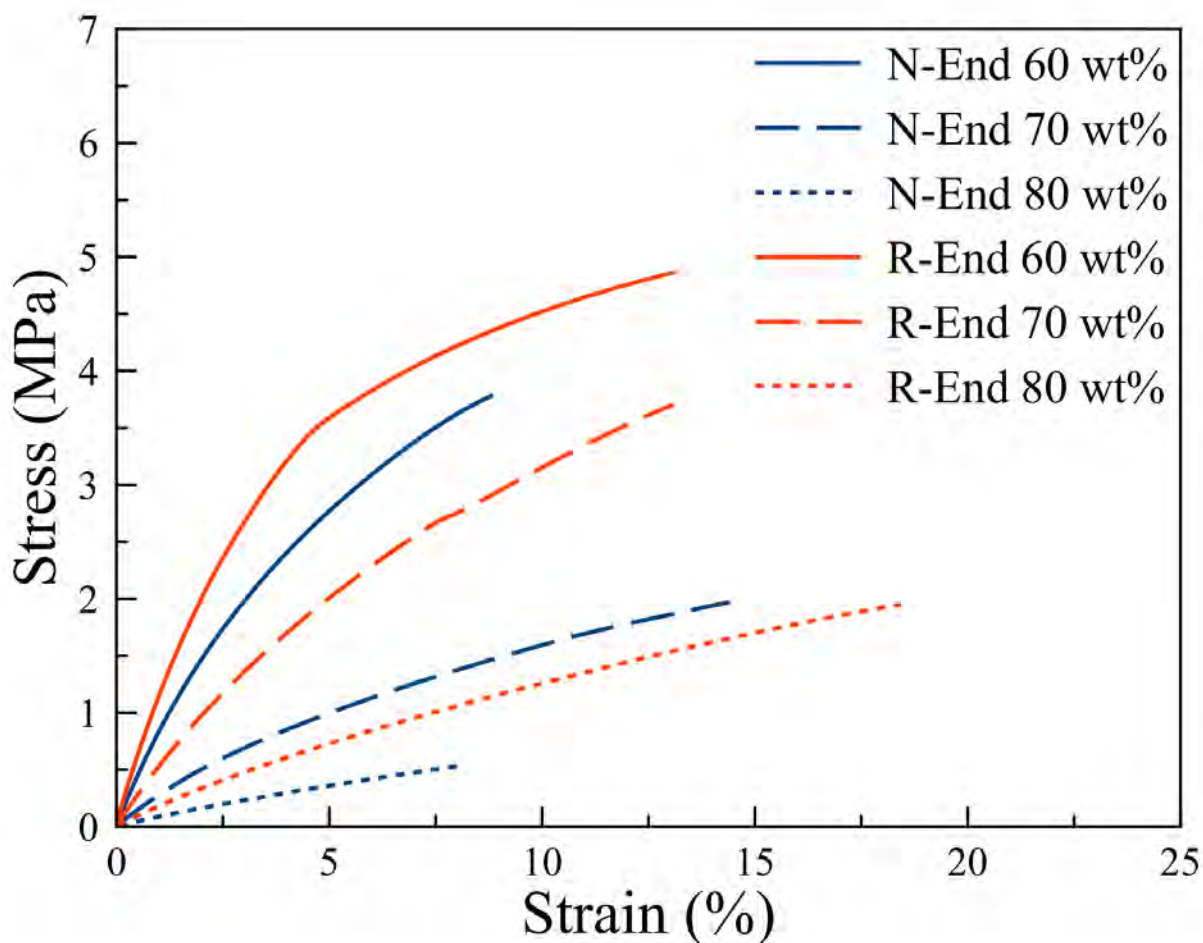
RAFT rearrangement diminishes primary butyl acrylate glass transition

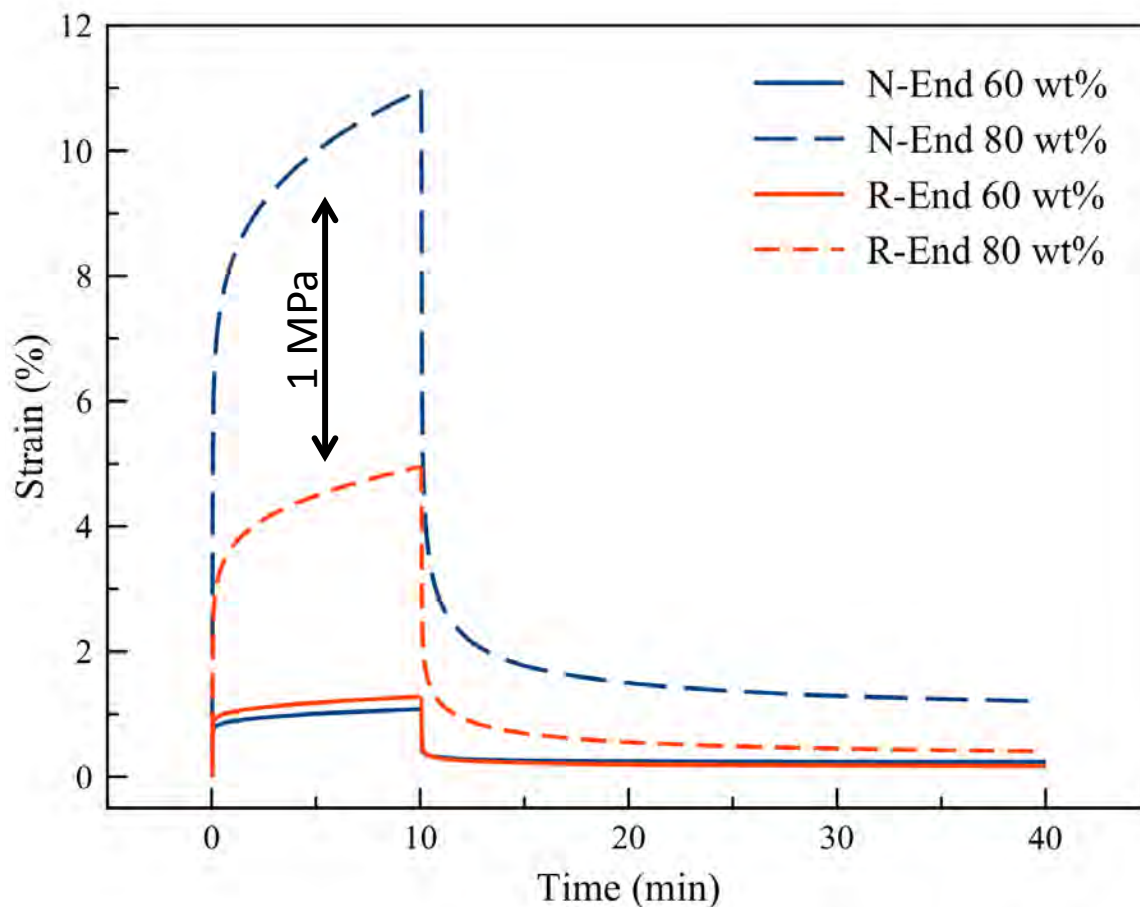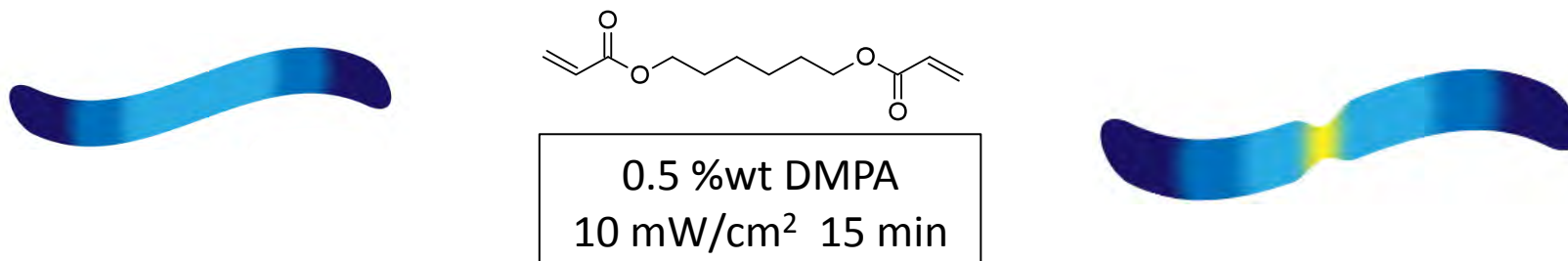# RAFT Process Relieves Internal Shrinkage Stress

0.5 %wt DMPA
10 mW/cm^2 15 min

- RAFT relieves stress and creates smaller soft domain

RAFT Process Allows for Less Permanent Deformation
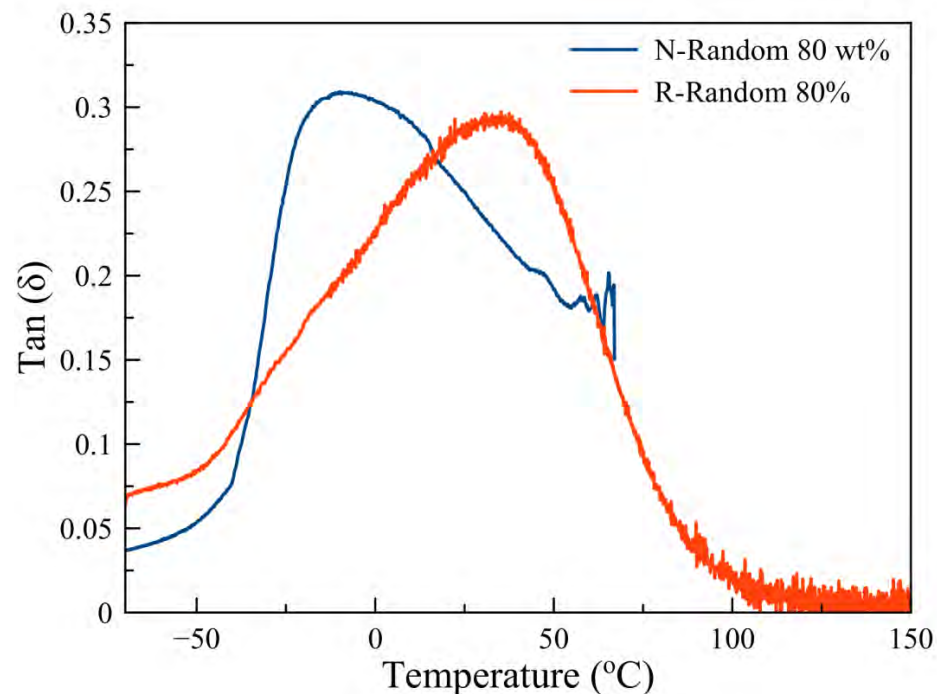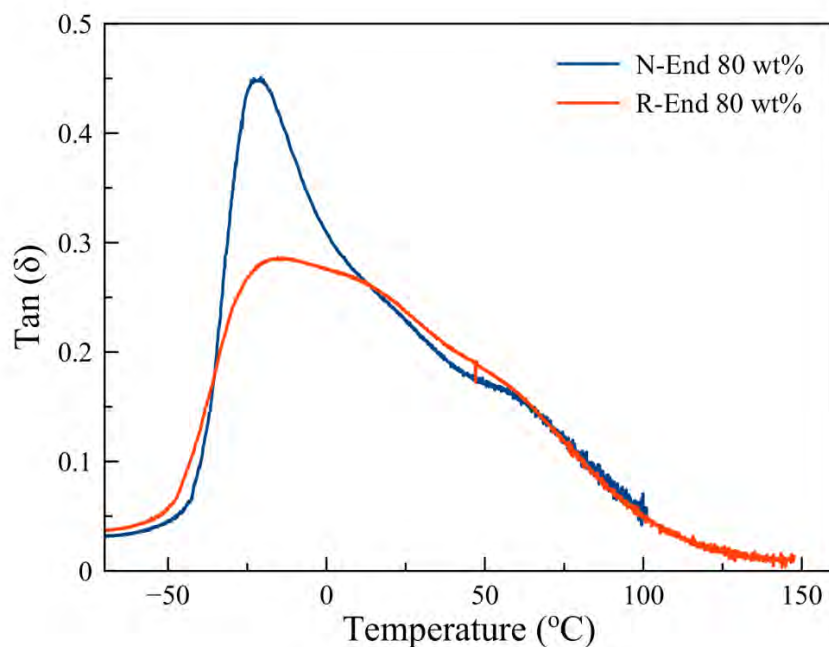

0.5 %wt DMPA
10 mW/cm² 15 min

Greater continuity of **hard domains** further **increases resistance** to sudden stress

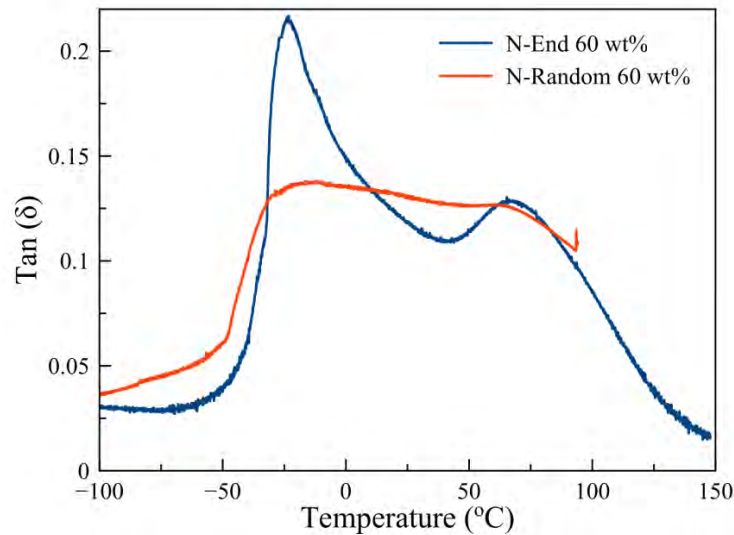# Rearrangments Allow for Highly Crosslinked Materials
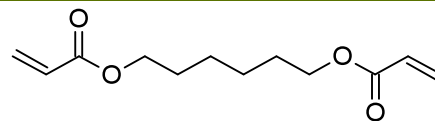
0.5 %wt DMPA
10 mW/cm² 6 min

Transfer in random systems produces extremely robust films allowing for further tuning of the systems.

Conclusions

- Nitroxide and RAFT processes can be used to make functional Prepolymers.

- Architecture of prepolymer molecules directly effects morphology

- RAFT processes allows smaller soft domains and network relaxation producing tougher more robust films

The University of Iowa

Acknowledgements

- Guymon Group
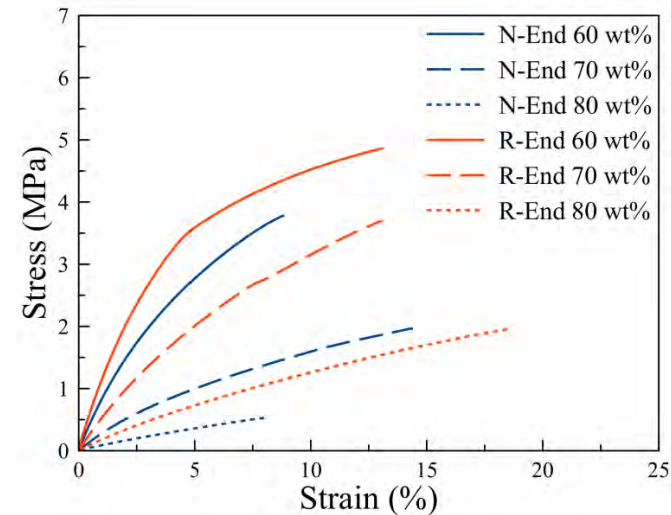- The Unversity of Iowa
- IUCRC

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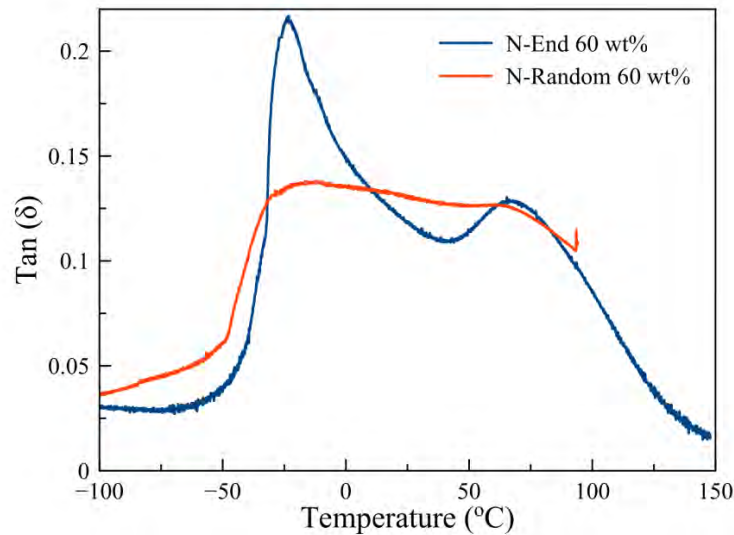

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