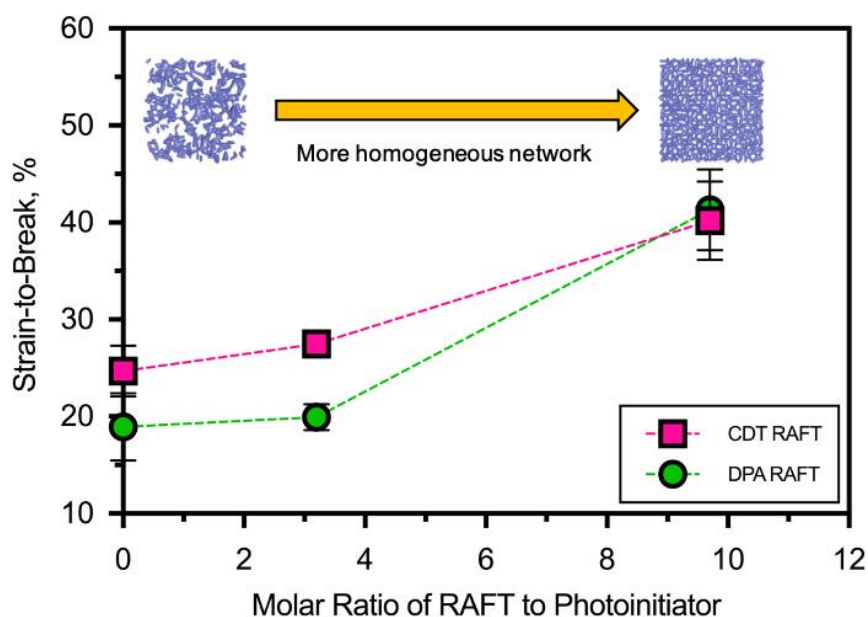


## Directed network structure through controlled radical photopolymerization

Huayang Fang<sup>1</sup> and Allan Guymon<sup>1</sup>

1. The University of Iowa, Iowa City, Iowa, United States

Reversible addition-fragmentation chain transfer (RAFT) has shown great utility in controlled radical polymerization to synthesize monodisperse linear polymers and block copolymers. However, little is known about effects of RAFT on cross-linked materials. In this work, we investigate the effect of RAFT agents on photopolymerization behavior and ultimate polymer properties in urethane acrylate systems. Our results have shown that RAFT agent addition has a significant impact on polymerization behavior and ultimate polymer properties in model systems. When incorporating RAFT agents, the final monomer conversion of RAFT modified polymerization is approximately 80% which is very similar to systems that do not contain RAFT. However, the polymerization rate is slightly decreased with increased RAFT concentrations. This decrease in polymerization rate results from the creation of RAFT-adduct radicals during chain propagation that delay gelation and retard the termination process. Moreover, dynamic mechanical analysis shows that the RAFT-modified films exhibit narrower half width of  $\tan(\delta)$  profiles, indicating more homogeneous networks are generated. The effect of RAFT agents on photopolymerization kinetics and thermomechanical properties by varying R group are also investigated. Cyanomethyl dodecyl trithiocarbonate (CDT) and 2-(dodecylthiocarbonothioylthio) propionic acid (DPA) are different RAFT agents which share the same Z- group but have different R- groups. Much faster photopolymerization rates are observed from DPA-modified polymerization as the DPA R group results in more rapid RAFT-adduct radical dissociation that allows more chain propagation. Additionally, incorporating DPA and CDT RAFT into model systems enhance elongation at break by approximately 119% and 63%, respectively. These results demonstrate the impact of the RAFT agents to alter polymerization, especially for CDT-modified polymerization which leads to lower reaction rates and higher molecular weight between crosslinks.



Films strain of CDT and DPA RAFT at different concentrations.