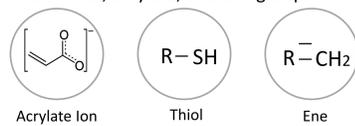


Fabrication and Mechanical Characterization of Thiol-ene Polymers and Thiol-acrylate Liquid Crystal Elastomers

Viren Patel, Dan Merkel, Amanda Cordes, Dr. Carl Frick
Mechanical Engineering, University of Wyoming

Introduction

- Thiol-based click chemistries represent a class of reactions defined by simplicity and high predictability
- This study uses thiol-acrylate and thiol-ene reactions to fabricate liquid-crystalline elastomers (LCEs) and glassy thiol-ene polymer networks.
- LCEs were fabricated by a two-stage thiol-acrylate Michael addition and photo-polymerization reaction.
- Thiol-ene polymer networks were fabricated by photo-initiated radical reaction.
- Mechanical properties can be tailored by manipulating molar concentrations of thiol, acrylate, and ene groups.



Objectives

- Develop a fabrication technique to rapidly synthesize LCEs and thiol-ene networks.
- Design a variety of LCEs with excess acrylate to accommodate a secondary photochemical programming reaction.
- Design thiol-ene networks with different molar ratios of thiol and ene groups.
- Characterize mechanical properties by dynamic mechanical analysis (DMA).

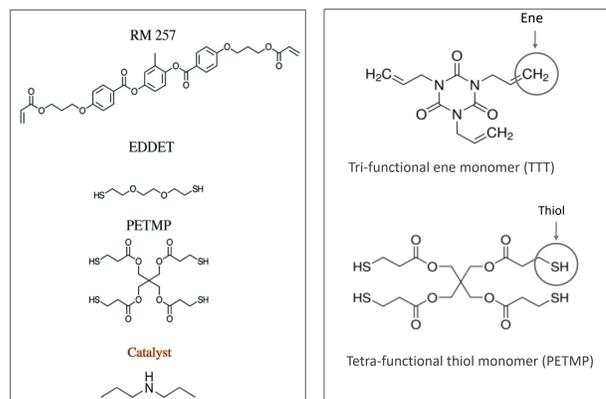
Materials

The monomers used in the fabrication process of LCE's were:

RM 257	4-(3-Acryloyloxypropoxy)-benzoic acid 2-methyl-1
EDDET	2'-(ethylenedioxy)-diethanethiol
PETMP	Pentaerythritol Tetra(3-mercaptopropionate)
DPA	Dipropyl amine (catalyst)
HHMP	2-hydroxyethoxy-2-methylpropiophenone (photo-initiator)

The monomers used in the fabrication process of Thiol-ene polymer were:

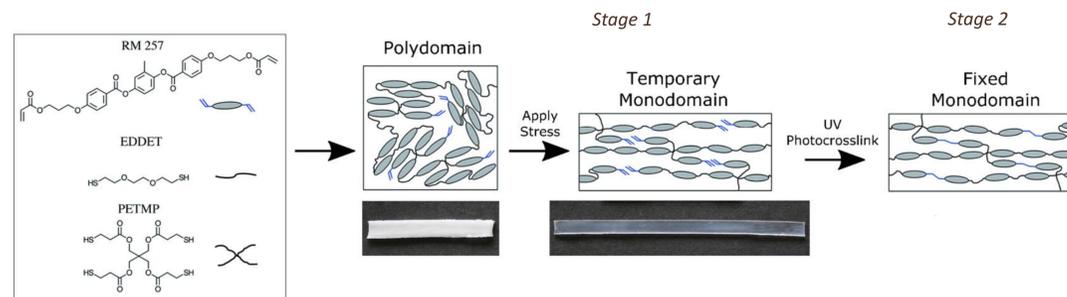
TTT	Triallyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione
PETMP	Pentaerythritol Tetra(3-mercaptopropionate)
HHMP	2-hydroxyethoxy-2-methylpropiophenone (photo-initiator)



Methods

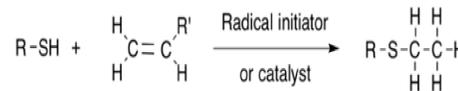
Liquid Crystalline Elastomers

LCEs were fabricated by thiol-acrylate Michael addition of di-function thiol monomer (EDDET) and tetra-functional thiol monomer (PETMP) with a di-functional acrylate mesogen (RM 257) followed by photochemical reaction of excess acrylate groups. Liquid monomers were mixed with photo-initiator (HHMP) and catalyst (DPA), then poured into a glass/Teflon mold to polymerize over 12 hours forming a polydomain LCE. A secondary photochemical reaction under UV light was possible when a molar excess of acrylate groups was designed into the stoichiometry. A shape-switching monodomain LCE was made by elongating polydomain LCEs and crosslinking excess acrylate groups under UV light. The molar concentration of acrylate was increased up to 45 mol% excess to change properties of monodomain LCEs by increasing crosslink density.



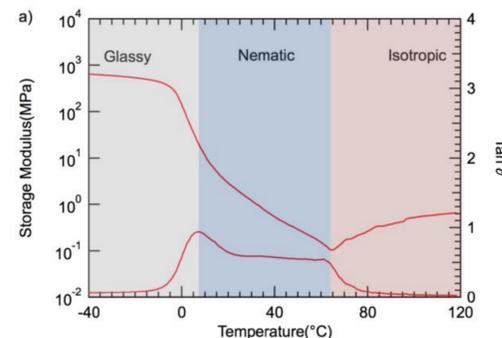
Thiol-ene Polymers

Thiol-ene polymer networks were formed by photochemical reaction of a tetrathiol monomer (PETMP) with a tri-ene monomer (TTT) using a photo-initiator (HHMP). Liquid monomers and photo-initiator were mixed and poured into glass/Teflon molds with 1-2 mm thickness. The mixture was photopolymerized under UV light for several minutes forming polymers with high crosslink density. The molar concentration of thiols was increased up to 80 mol% excess to change mechanical properties by reducing crosslink density.



Dynamic Mechanical Analysis

DMA was used to investigate the physical and mechanical properties of LCEs and thiol-ene polymers. Samples were analyzed in tensile clamps under oscillatory conditions over a wide range of temperatures. During oscillation, the instrument measured storage modulus and tangent delta between -50C and 150 C which revealed transition temperatures. Under these conditions, LCEs exhibited glassy, liquid-crystalline nematic, and isotropic behavior defined by glass and isotropic transition temperatures. Thiol-ene polymers exhibited glassy and rubbery behavior defined by a glass transition temperature.



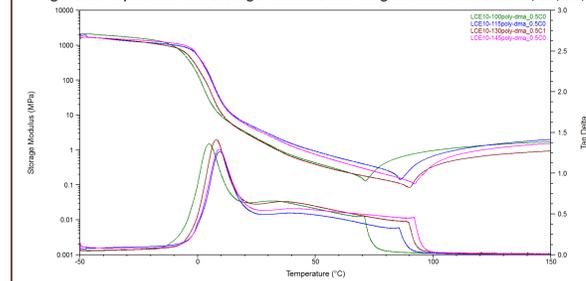
References

- Yakacki, C. M., Saed, M., Nair, D. P., Gong, T., Reed, S. M., & Bowman, C. N. (2015). Tailorable and programmable liquid-crystalline elastomers using a two-stage thiol-acrylate reaction. *RSC Advances*, 5(25), 18997-19001.
- Podgórski, M., Becka, E., Chatani, S., Claudino, M., & Bowman, C. N. (2015). Ester-free thiol-X resins: new materials with enhanced mechanical behavior and solvent resistance. *Polymer chemistry*, 6(12), 2234-2240.

Results

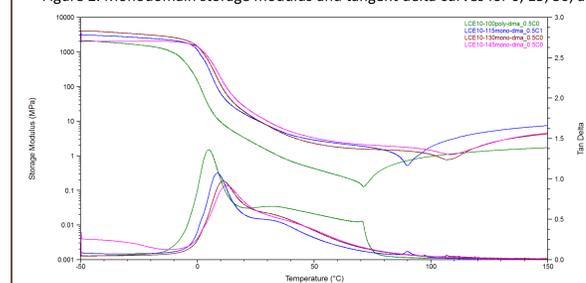
Liquid Crystalline Elastomers

Figure 1. Polydomain LCE storage modulus and tangent delta curves for 0, 15, 30, and 45 mol% excess acrylate.



- Polydomain LCEs were white at room temperature and took the shape of the mold.
- Samples could be stretched to become clear.
- Heating beyond the isotropic transition temperature cause the LCE to become clear and return to the original shape.
- DMA showed low modulus, glass transition around 5C, and isotropic transition temperature increasing with acrylate content up to 95C.

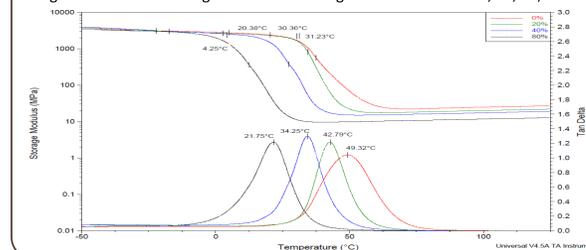
Figure 2. Monodomain storage modulus and tangent delta curves for 0, 15, 30, and 45 mol% excess acrylate.



- Monodomain LCEs were formed by crosslinking polydomain samples in the clear elongated shape.
- Heating and cooling between the nematic and isotropic states caused the LCE actuate between the original and elongated shape.
- DMA showed higher modulus, glass transition around 10C, and isotropic transition temperature increasing with acrylate content up to 110C.

Thiol-ene Polymers

Figure 3. Thiol-ene storage modulus and tangent delta curves for 0, 20, 40, and 80 mol% excess thiol.



- Thiol-ene polymer networks were rigid and glassy at room temperature.
- At room temperature, polymers softened with increasing thiol content.
- Glass transition temperature decreased from 40C to 22 C with increasing thiol content.

Conclusion

- Polydomain and monodomain LCEs were successfully fabricated by thiol-acrylate click chemistry with up to 45 mol% excess acrylate.
- Polydomain LCEs showed reduced storage modulus and transition temperatures with increased acrylate as a result of reduced crosslink density.
- Monodomain LCEs showed higher storage modulus and transition temperatures with increased acrylate due to increased crosslink density after photochemical reaction.
- Thiol-ene polymer networks were successfully fabricated by thiol-ene click chemistry with up to 80 mol% excess thiol.
- Network room-temperature rigidity and glass transition temperature decreased with increasing thiol content.

Acknowledgement

This material is based upon work supported by Wyoming INBRE with additional support from the National Science Foundation, Wyoming NASAEPSCoR, Advanced Materials Lab, NIH and Science, Math and Research Transformation (SMART). Special thanks to Dan Merkel, Amanda Cordes and all members of the Advanced Materials Lab

