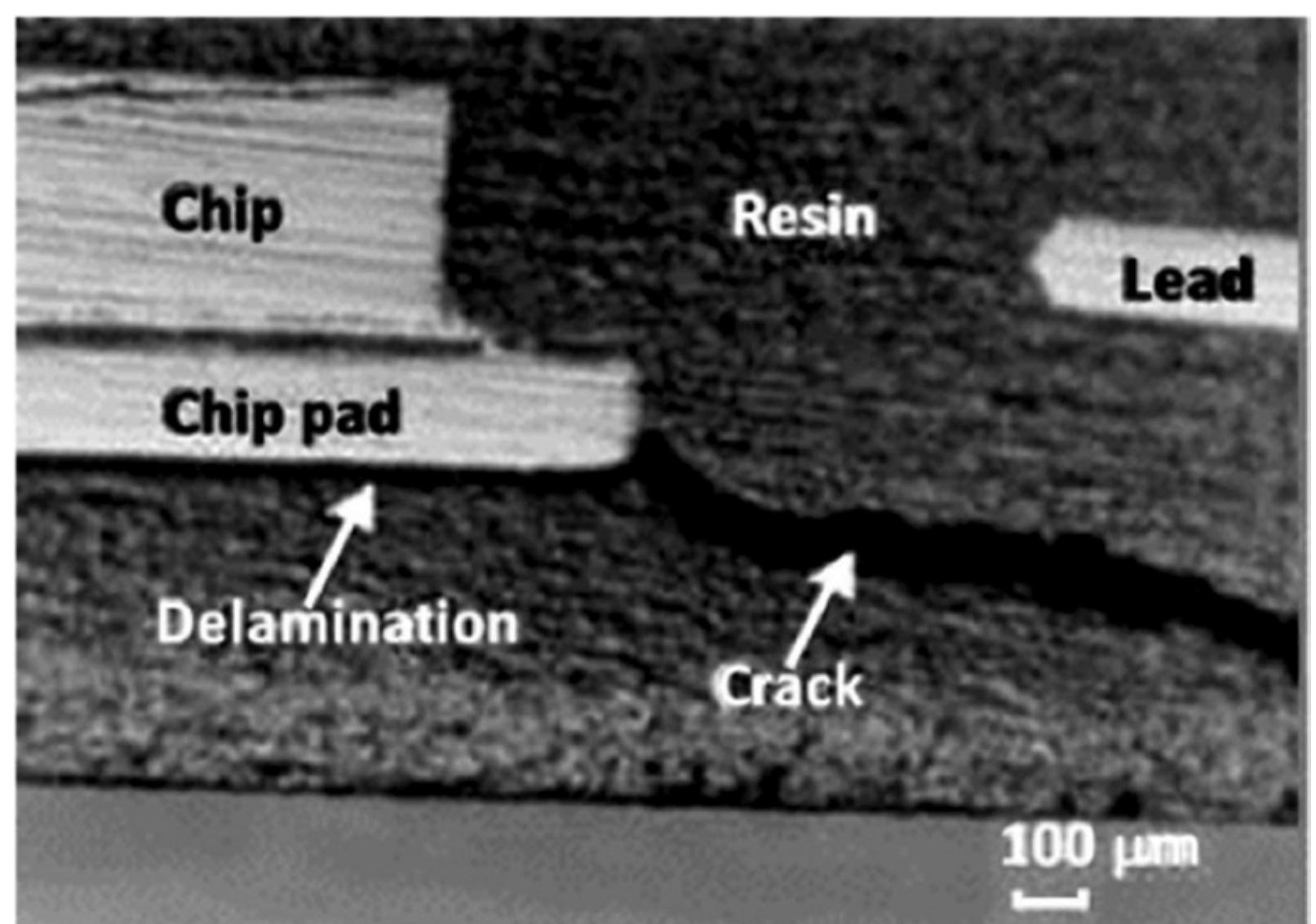




Resolving Thermal Expansion Mismatch in Epoxy

Authors: Meghan Kiker (UT, PhD Candidate in Chemistry), Jeffrey Foster (SNL, Dept. 1853), Chad Staiger (SNL, Dept. 8924), Jason Dugger (SNL, Dept. 7585), Erica Redline (Sandia, Dept. 1853), Zachariah Page (UT, Dept of Chemistry)

Motivation



Material	Typical CTE Range (ppm/K)
Substrates	3-20
Unfilled epoxy	50-80
Filled epoxy (~45 vol%)	30-50

Macromolecules, 2018, 51, 8477-8485

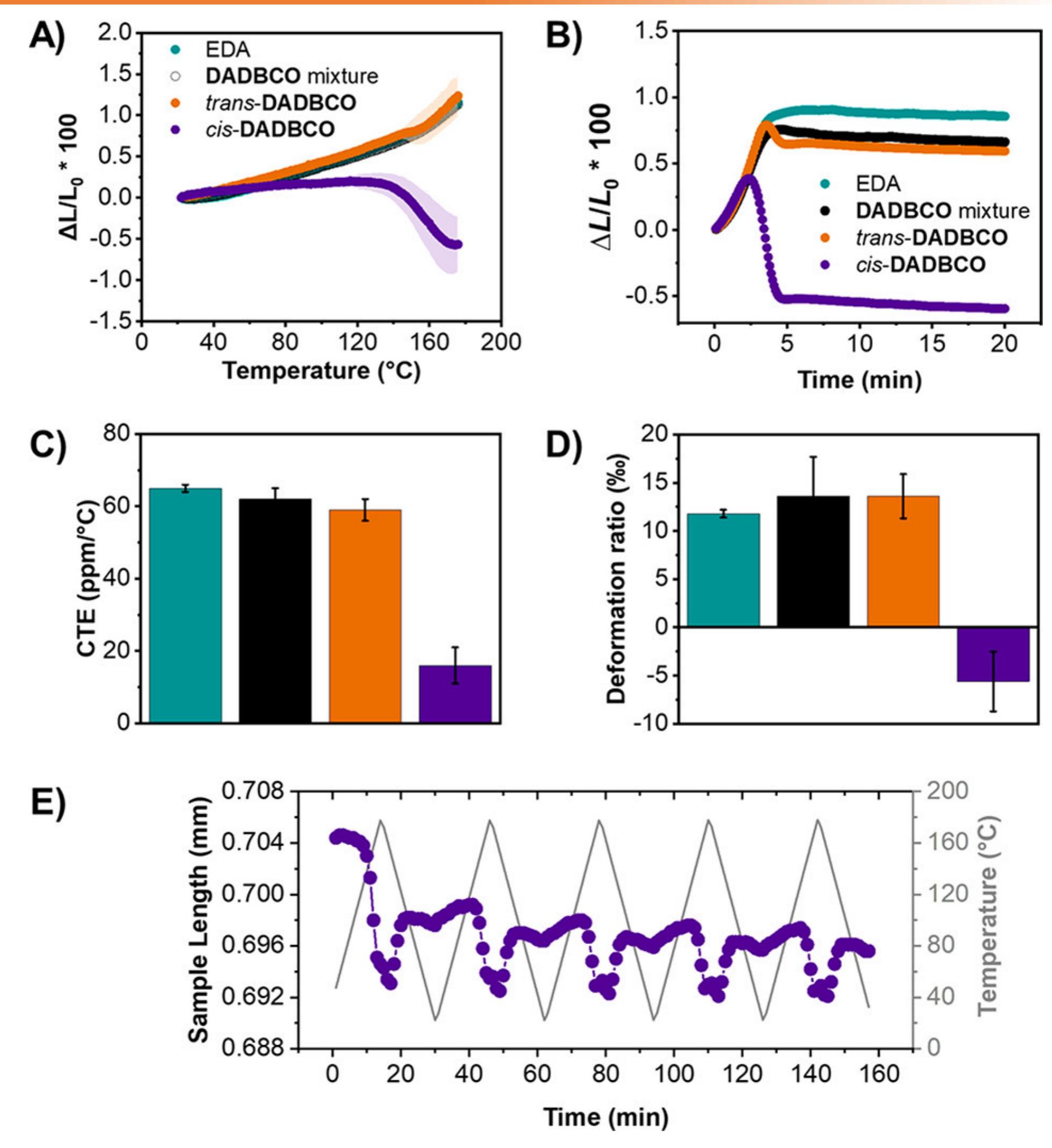
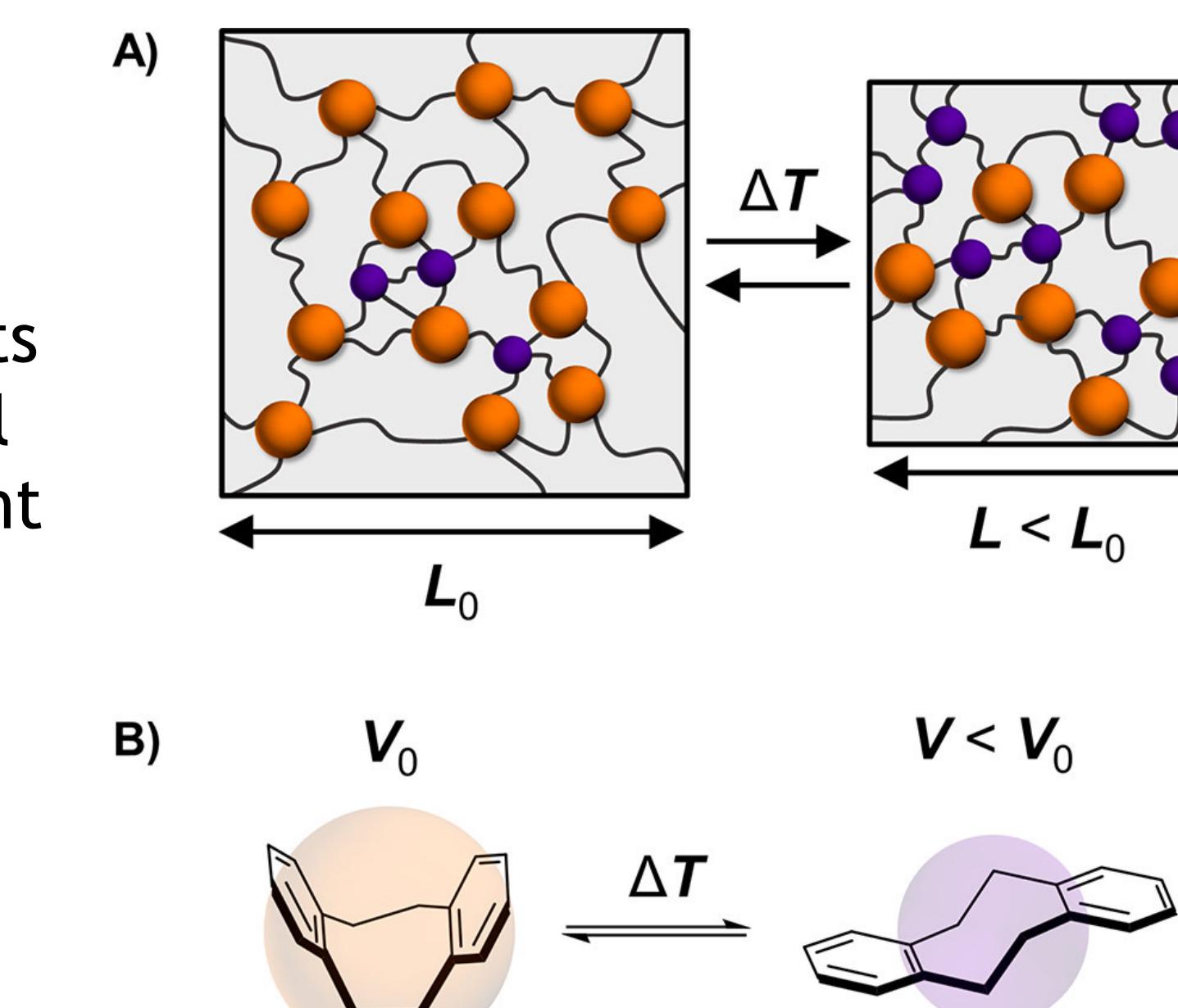
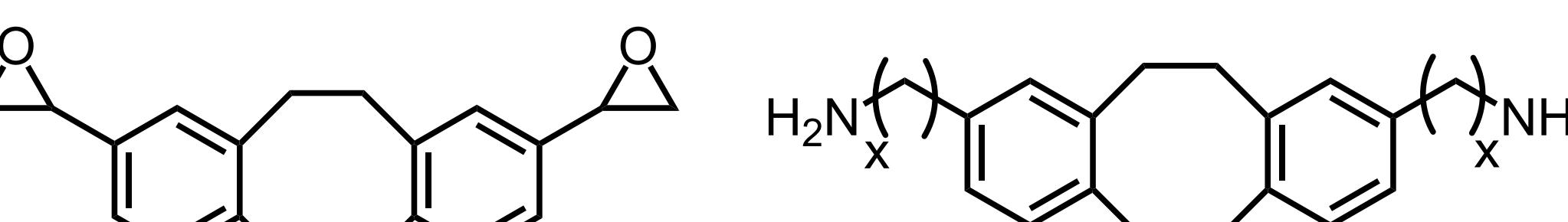
- CTE mismatch between encapsulants and underlying components often leads to cracking, delamination, or other issues.
- Attempts to mitigate this by using fillers such as mica or alumina create further issues like brittleness or stiffness.

Image from: NDT & E Int., 34, 49–56 (2001)

Approach

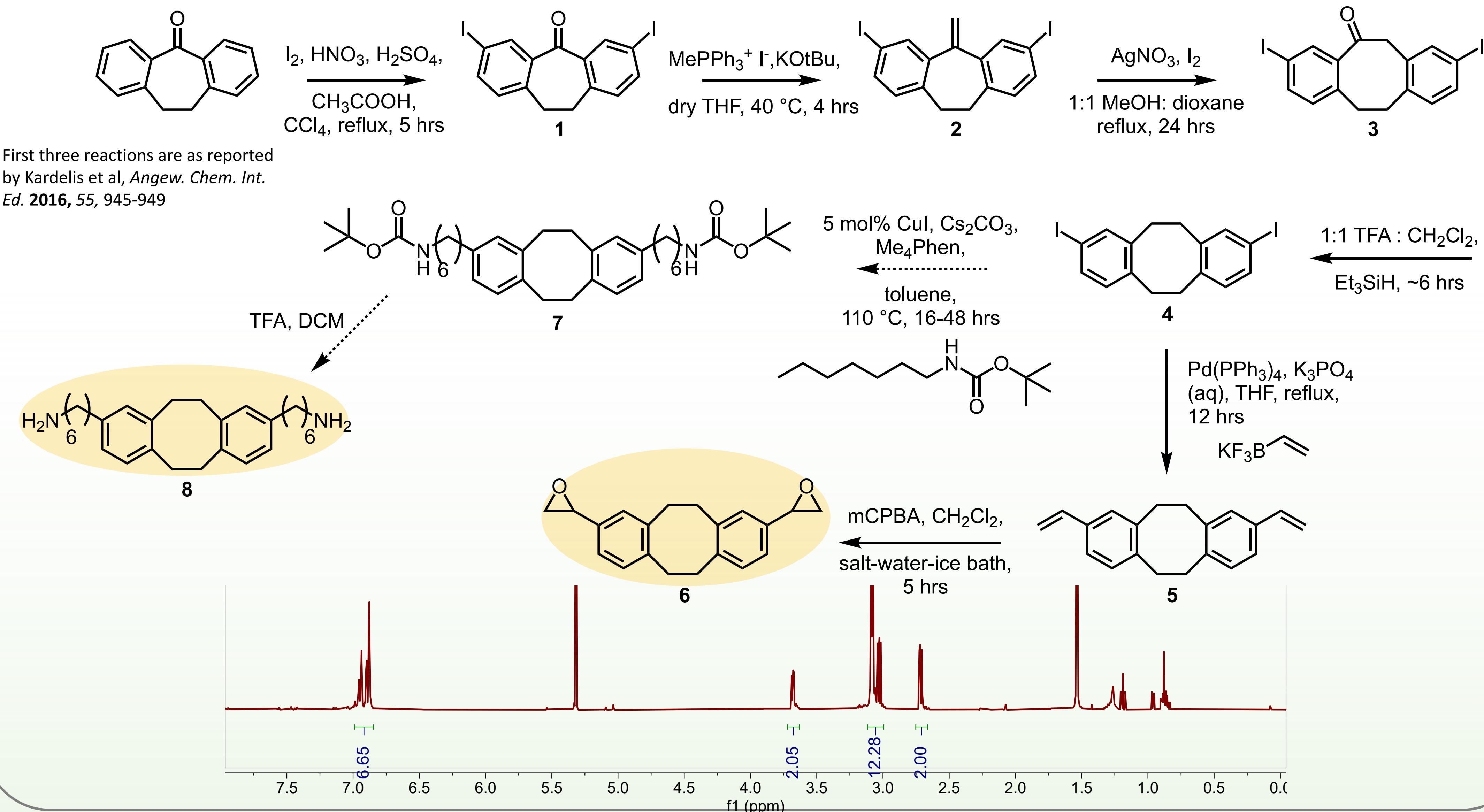
- Synthesize materials that exhibit a tunable CTE by incorporating a molecule with high negative CTE behavior into the backbone chemistry.
- The targeted molecule cyclic framework exhibits this NTE property. We plan to synthesize several novel derivatives to incorporate into encapsulant material.
- Previous methods give a mixture of the cis- and trans- substituted molecule. Our approach uses more steps but guarantees the cis- product.

Targeted molecules:



ACS Macro Lett. 2021, 10, 7, 940-944

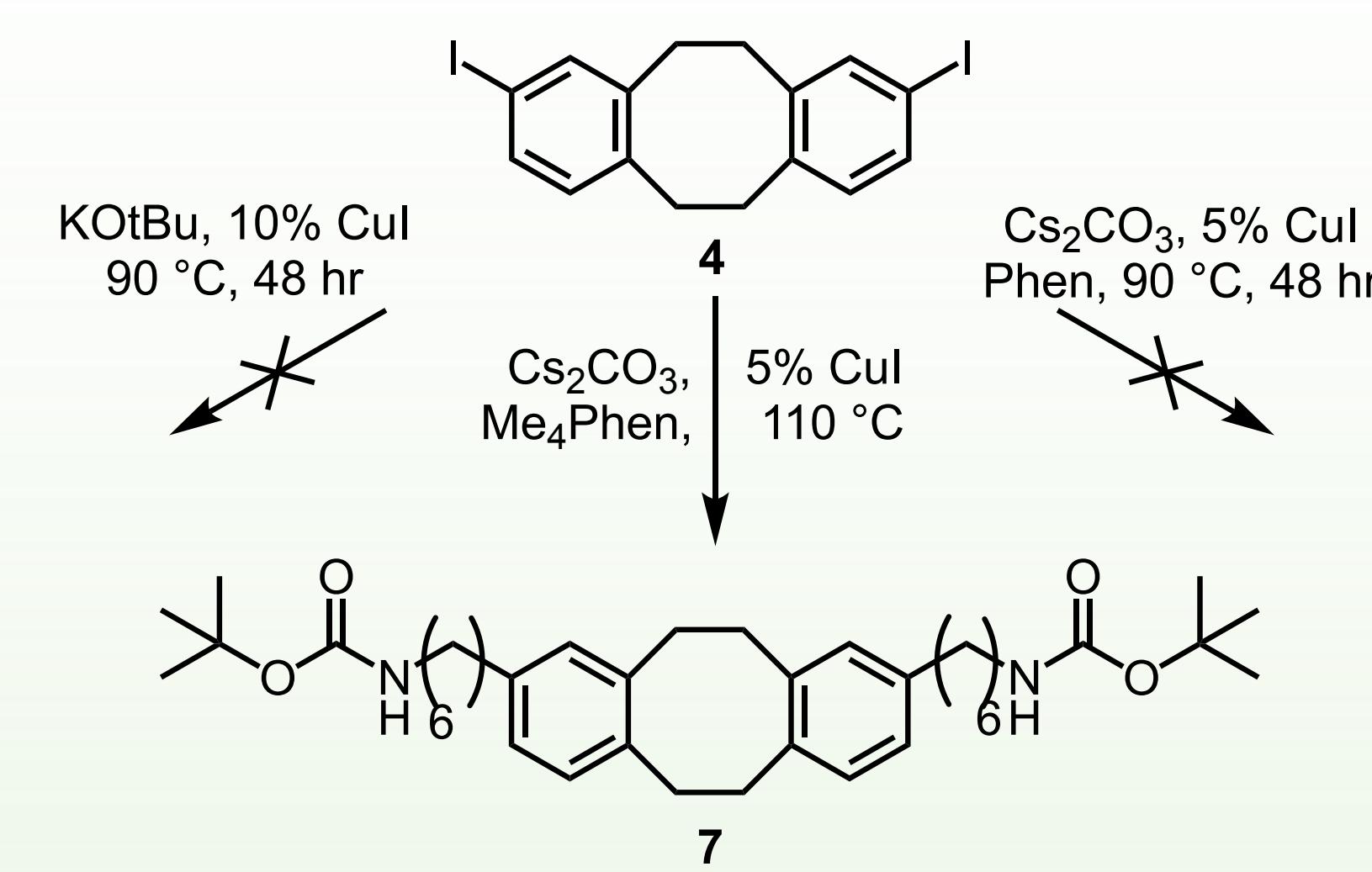
Current Status / Results



First three reactions are as reported by Kardelis et al, Angew. Chem. Int. Ed. 2016, 55, 945-949

Challenges

- While this route gives the cis only product, the overall yield is quite low and requires large amounts of starting material.
- Purification of diepoxy product can be difficult and lead to degradation of product.
- Ullmann couplings are selective towards N-arylation and require more optimized conditions to proceed to O-arylate in good conversion and yield.



Next Steps / Future Work

- Characterize the reaction kinetics of 6 with EDA by Fourier Transform-Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC).
- Further optimize Ullmann coupling conditions to get BOC-protected 7 in good yield.
- After deprotection of 7, polymerize with a commercial epoxy and gather kinetic and thermal characterization data and quantify NTE behavior.
- Work on synthesizing derivatives with -NCO and -OH functionalities to expand the scope of possible polymerizations.