Non-Isocyanate Polyurethane Microcellular Structures from Bis-Carbonylimidizolide Decarboxylation

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ASU Biodesign Institute
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Outline

Background and Motivation

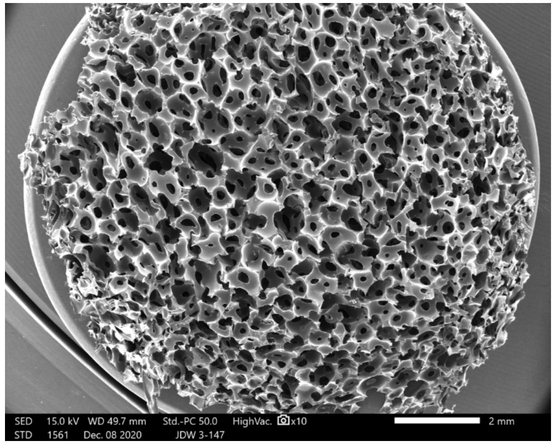
- ❖ Polyurethane uses
- ❖ Traditional polyurethane synthesis
- ❖ Novel pathways towards NIPUs

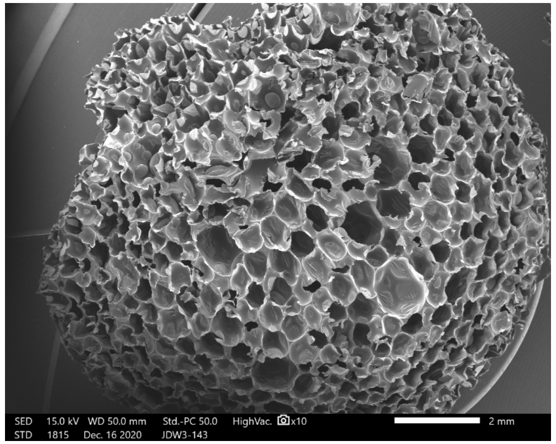
Thermoplastic Polyurethane Capabilities

- ❖ Linear polyurethane synthesis through melt polymerization
- ❖ Thermomechanical characterization

Non-isocyanate Polyurethane Foams

- ❖ Synthetic pathways
- ❖ Avenues for decarboxylation
- ❖ Architecture control through surfactant content
- ❖ Structure property relationships for flexible and rigid foams



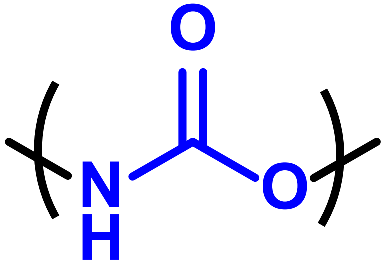


Polyurethanes are ubiquitous in commercial and specialized applications due to high tunability

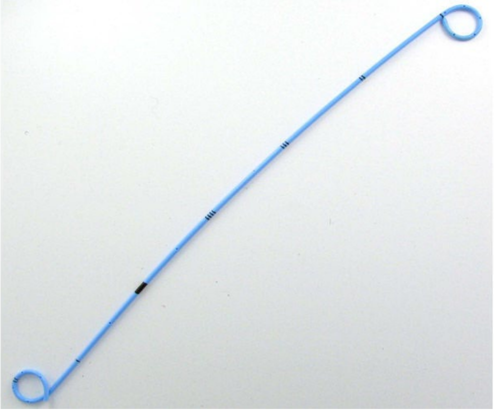
- Polyurethanes contain a urethane (carbamate) linkage in their backbone and have high modularity relative to other classes of polymer

- This allows their use in various applications

Polyurethane



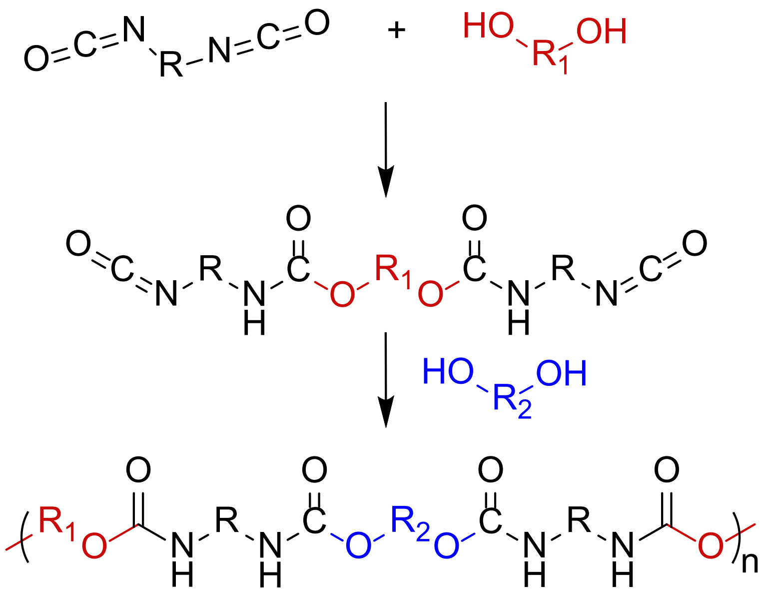
Carbamate



How It’s Made: Thermoplastic polyurethanes (TPUs) and foams

TPUs

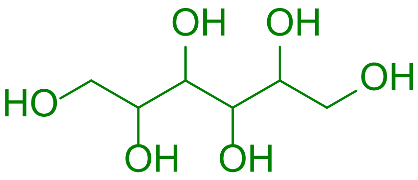
- Typically formed in two-steps:
  1. Diisocyanate reacts with soft-segment to form **iso-terminated prepolymer**
  2. **Chain-extension** by adding small molecule diol to prepolymer



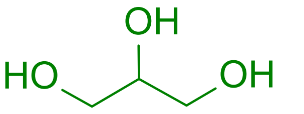
Yilgör, I.; Yilgör, E.; Wilkes, G. L. *Polymer (Guildf).* **2015**, *58*, A1–A36.

PU Foams

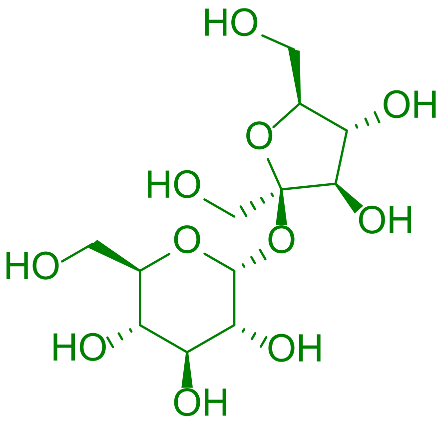
- **Polyols** (high MW for flexible foams) are reacted with diisocyanates
- CO_2 generation achieved through water addition
- Water functions as a **chain extender** to form urea hard segments
- The CO_2 acts as a **blowing agent**



Sorbitol



Glycerol

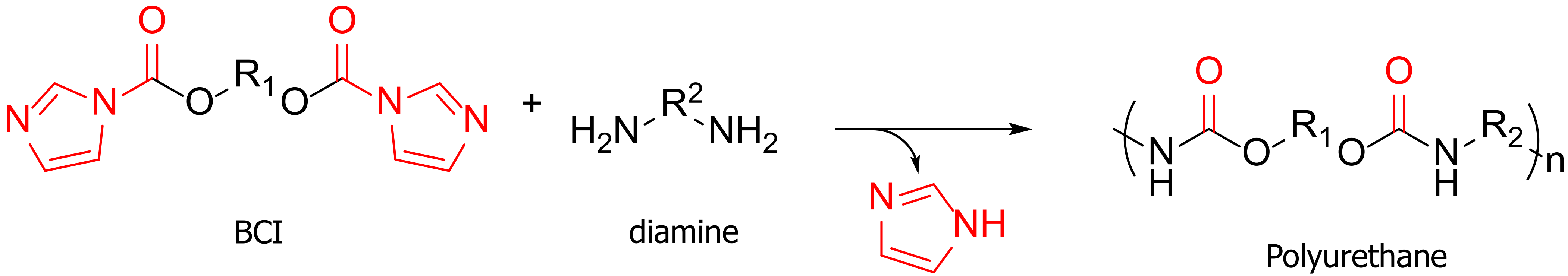


Sucrose

Dutta, A. S. *Plastics Design Library*; William Andrew Publishing, **2018**; pp 17–27.

CDI inspired monomers reveal a new path for non-isocyanate polyurethanes (NIPU)

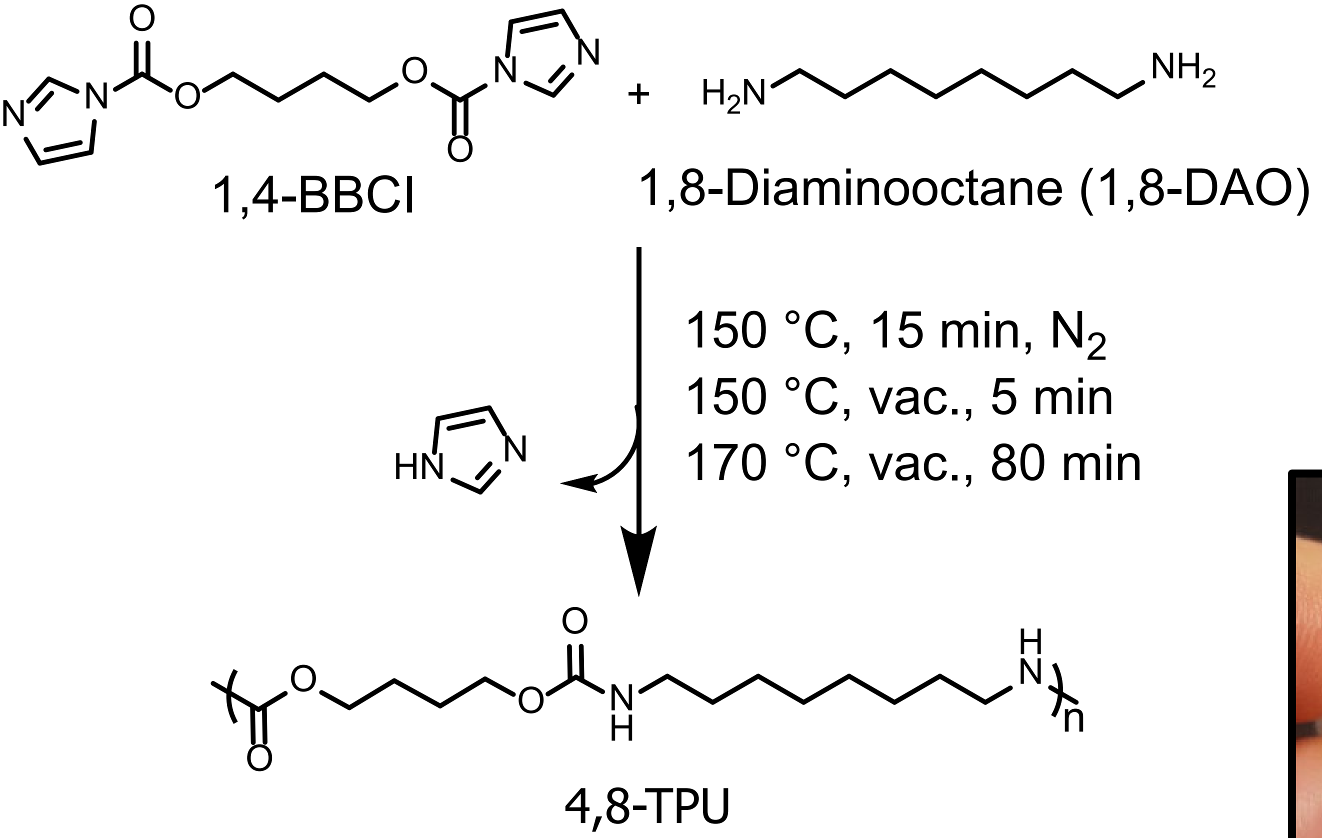
Reacting a diol with carbonyl diimidazole (CDI) affords a bis-carbonylimidazolide (BCI) monomer

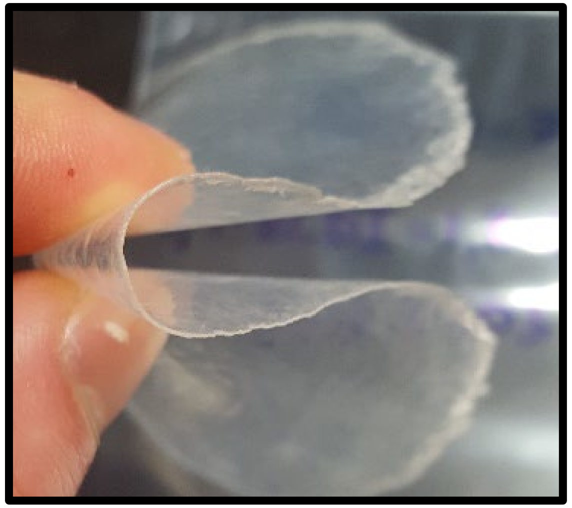


- Using CDI chemistry allows for more flexibility in the applied chemistry
  - Potential for safer synthetic routes
- These monomers are powders, not liquids so exposure chance is reduced

Wolfgang, J. D.; Long, T. E., *Macromolecular Rapid Communications* **2021,** *42* (13), 2100163.

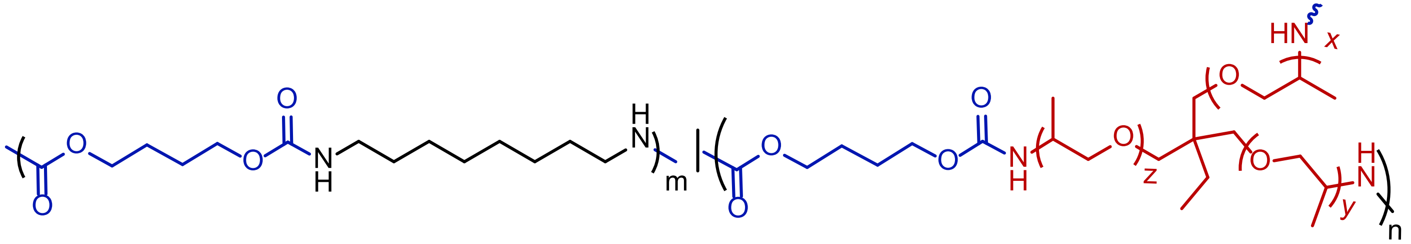
Isocyanate-, solvent-, and catalyst-free TPU synthesis using novel 1,4-BBCI monomer



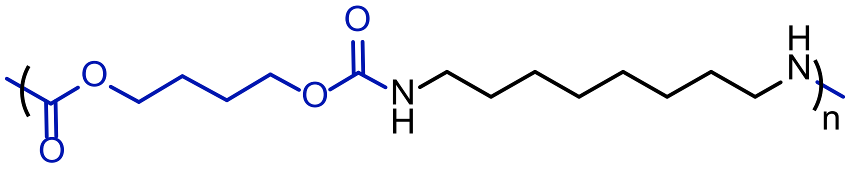


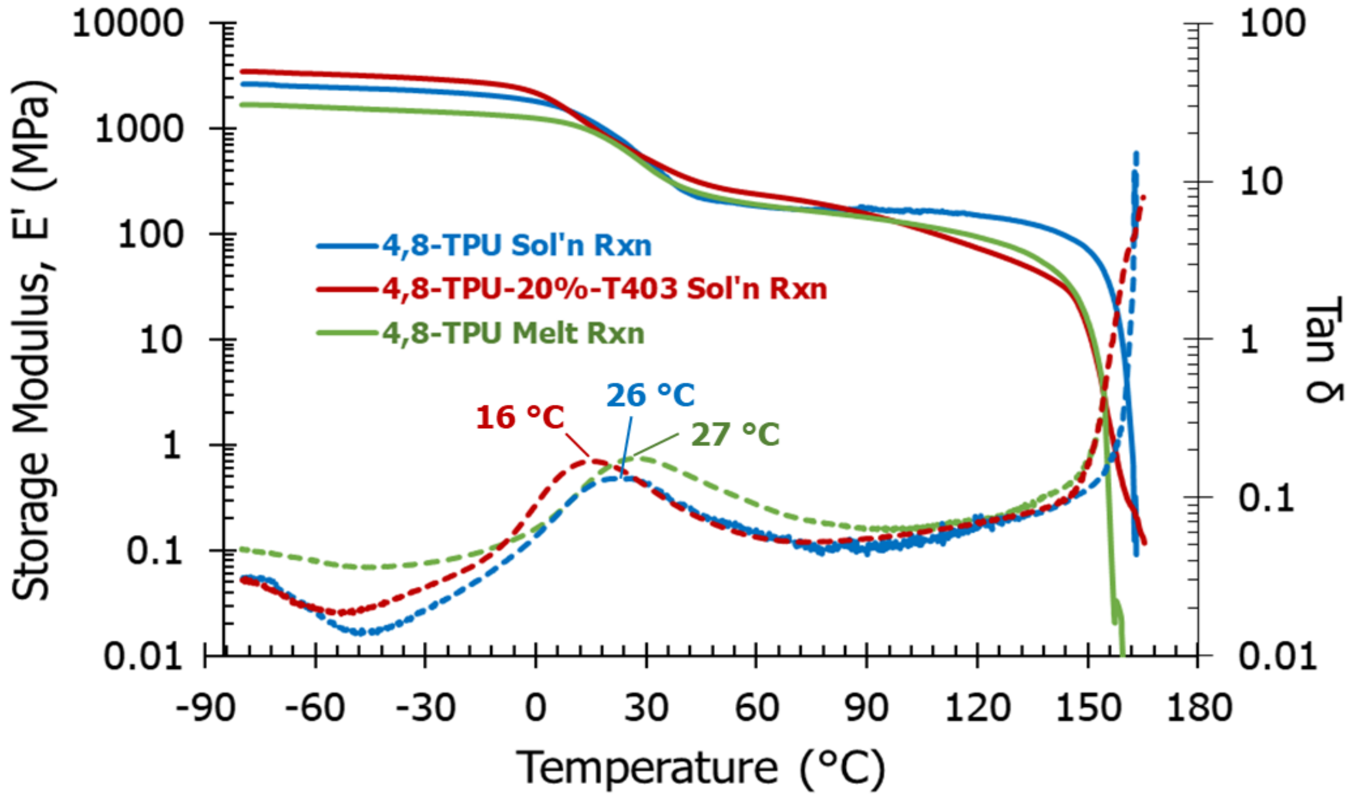
Wolfgang, J. D.; White, B. T.; Long, T. E., *Macromolecular Rapid Communications* **2021,** *42* (13), 2100163.

Branching results in a decrease in T_g; solution- and melt-polymerization techniques yield comparable results



OR





T_{flow} = 164 °C
T_{flow} = 163 °C
T_{flow} = 157 °C

DMA Q800: Temp ramp, 3 °C/min to 200 °C, 1 Hz, T_g from tan δ peak

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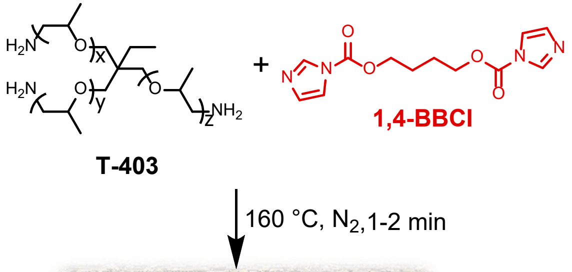
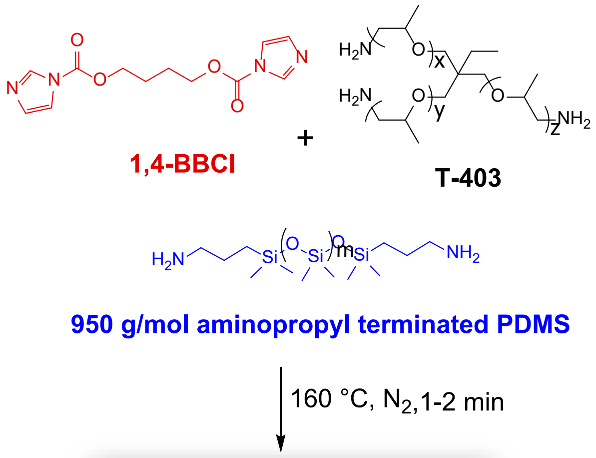
Versatility of BCI design allows for tailoring foam thermomechanical properties and pore geometry

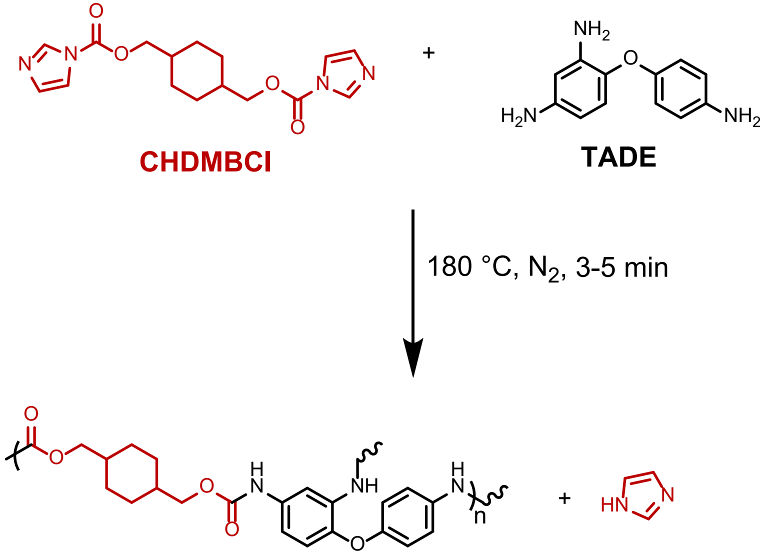
Aliphatic flexible foams



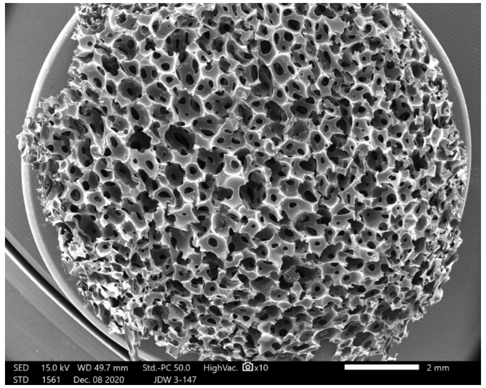
PDMS-doped foams with uniform cell shape

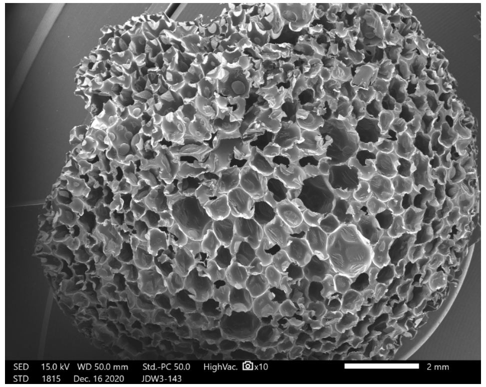


Cyclic aliphatic and aromatic rigid foam



Predicting pore geometry





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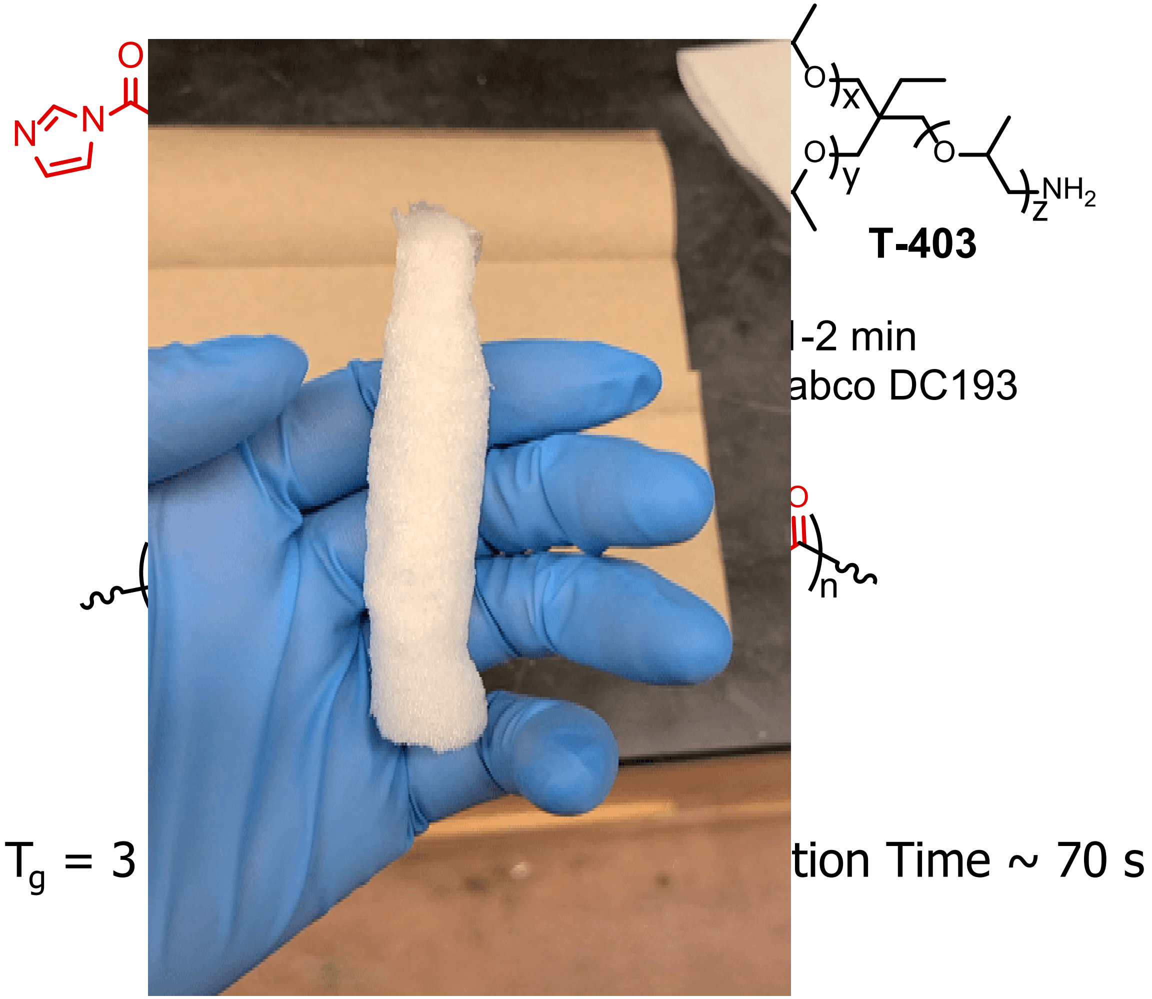
Butanediol based BCI monomer reacts with a triamine to form a flexible foam

0-15 s

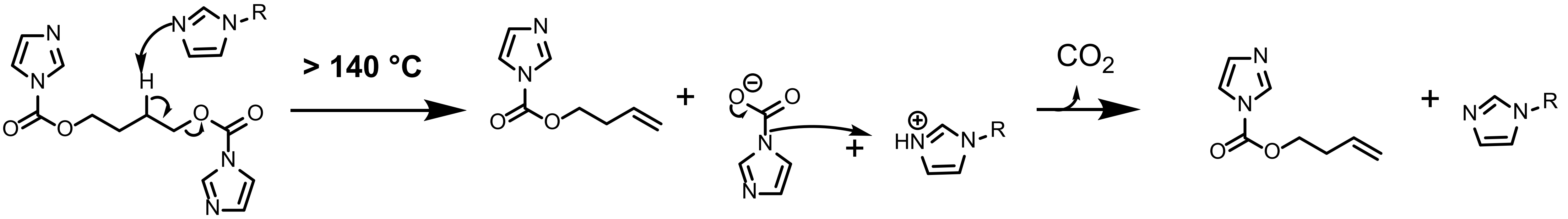
30-45 s



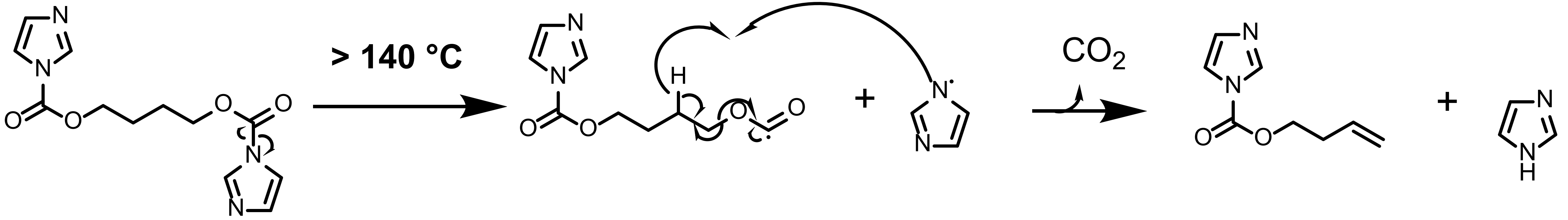
Wolfgang, J. D.; White, B. T.; Long, T. E., *Macromolecular Rapid Communications* **2021,** *42* (13), 2100163.

Potential mechanisms for decarboxylation explored in the BCI system

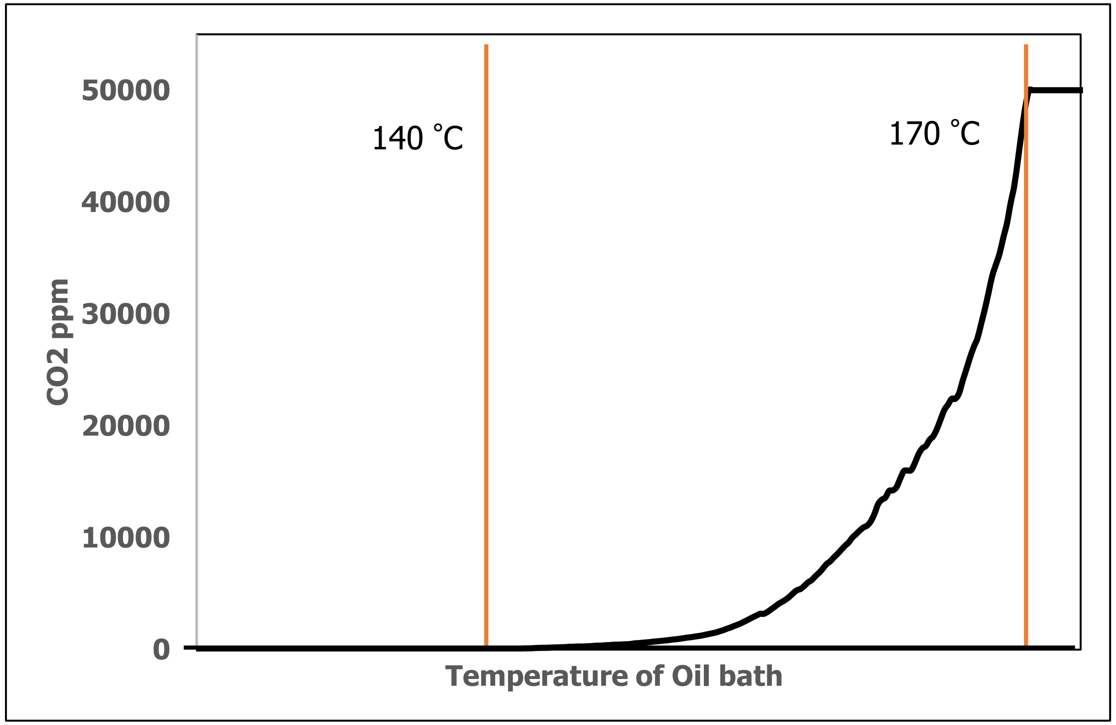
Intermolecular β-elimination leading to terminal vinyl

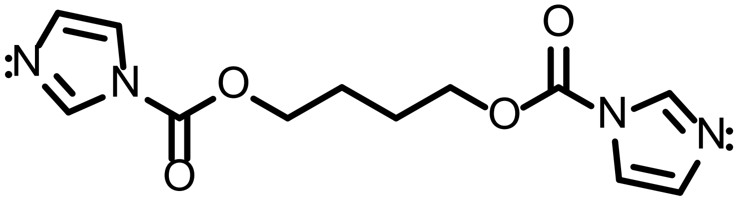


Homolysis and disproportionation leading to terminal vinyl



BBCI monomer releases CO_2 at high temperatures



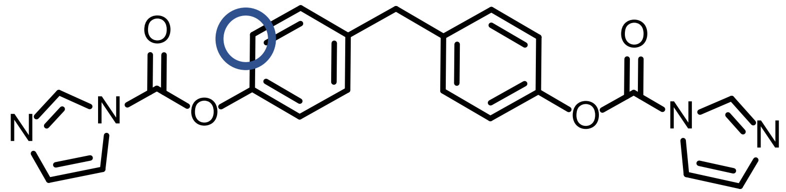


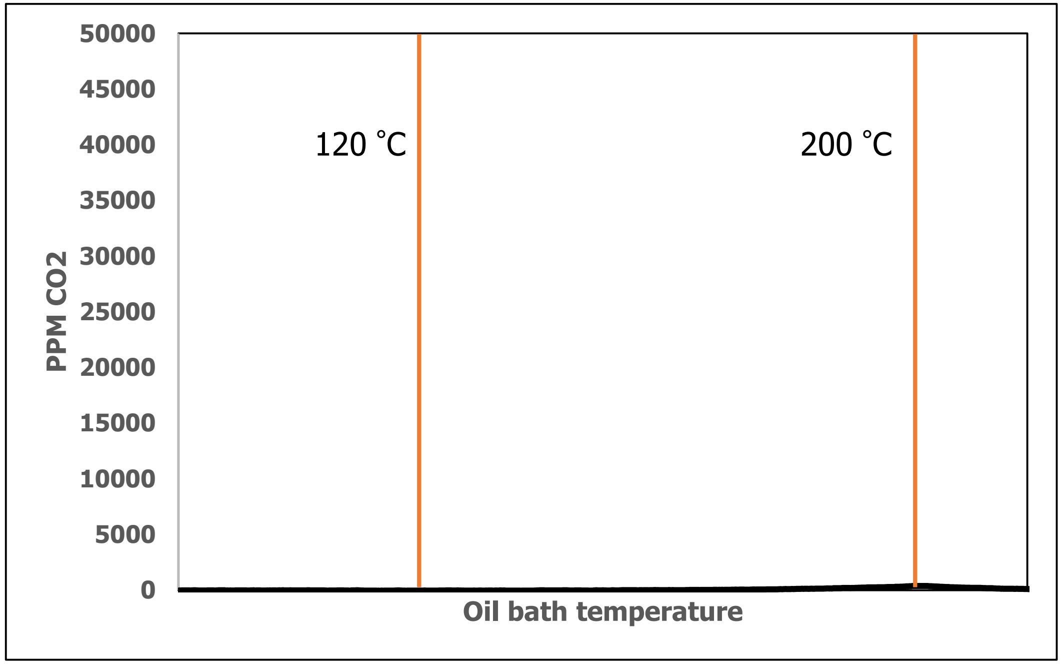
- 2 g, 7.35 mmol
- CO_2 generation begins at 140 °C

GasLab 5% CO_2 detector CM-0124

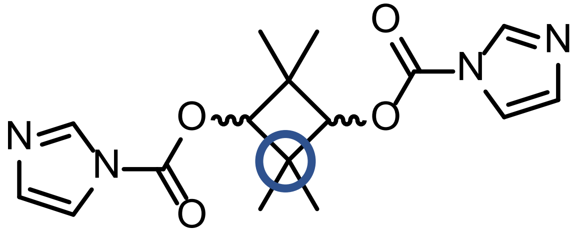
Elimination of abstractable hydrogens inhibits CO_2 generation

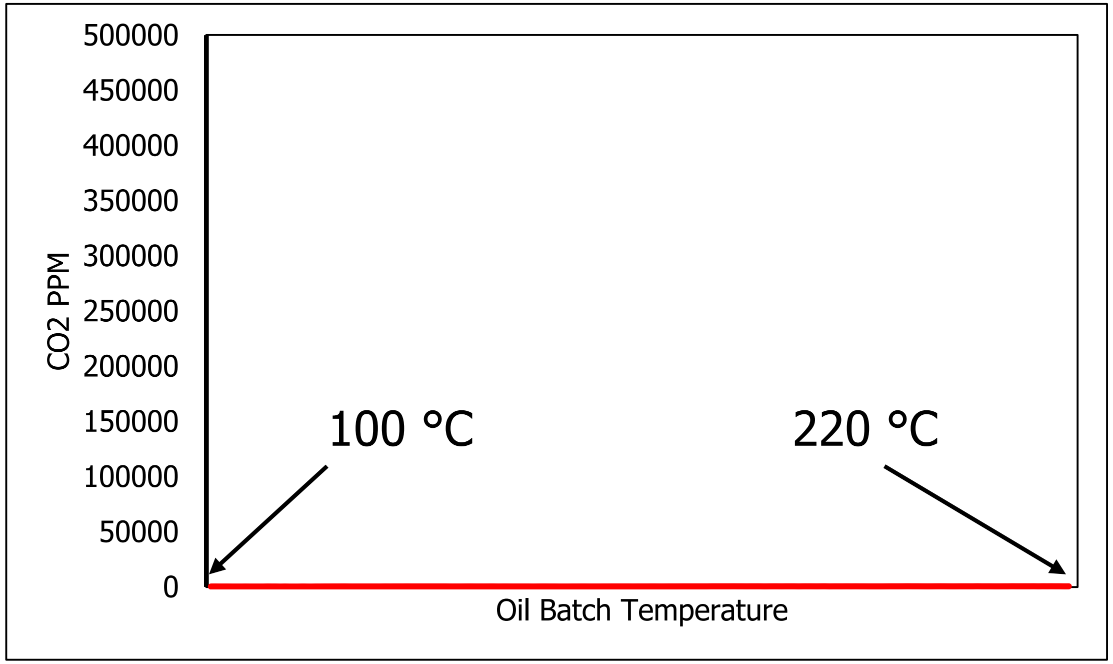
Aromatic BCI monomers do not produce CO_2





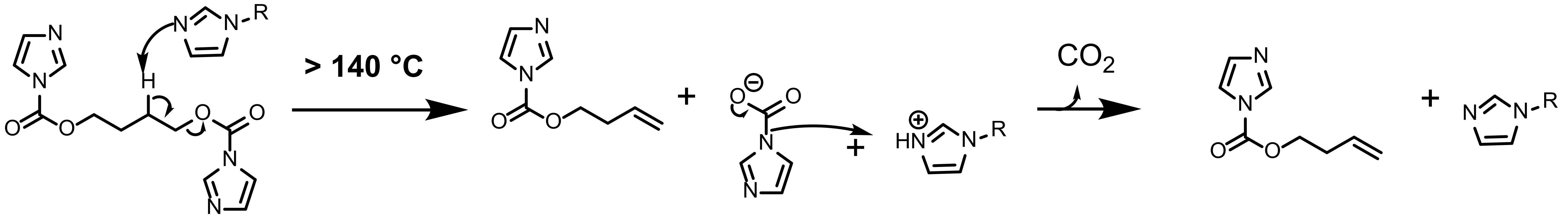
Aliphatic BCI monomer without β-hydrogen



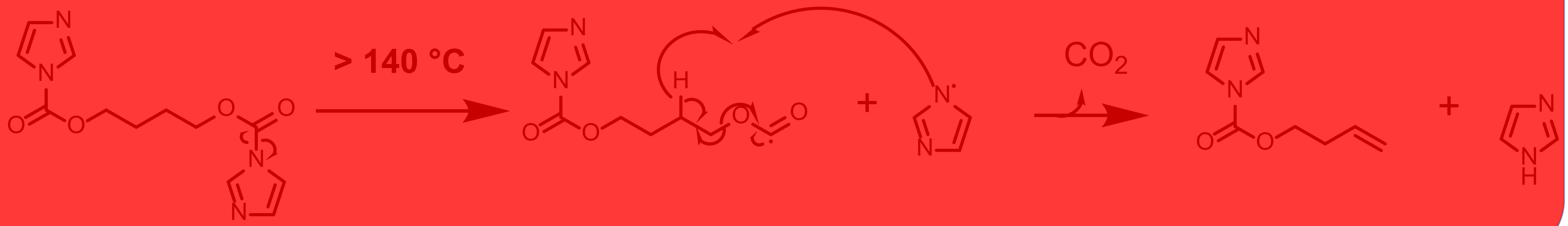


B-hydrogen elimination confirmed as mechanism for decarboxylation

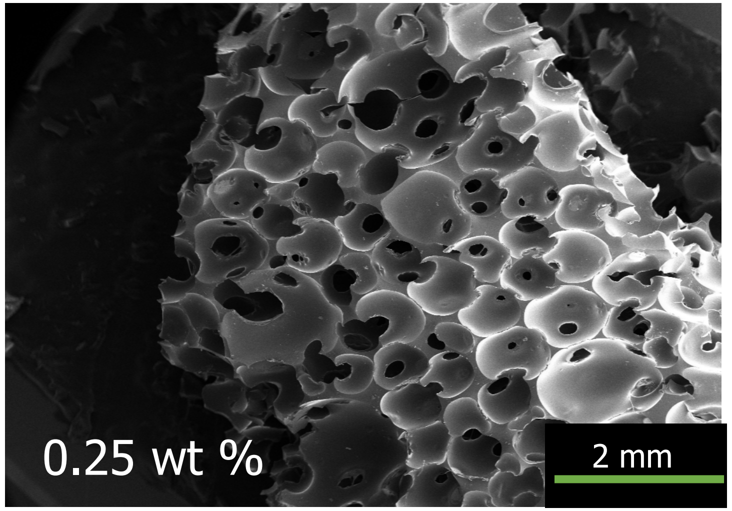
Intermolecular β-elimination leading to terminal vinyl

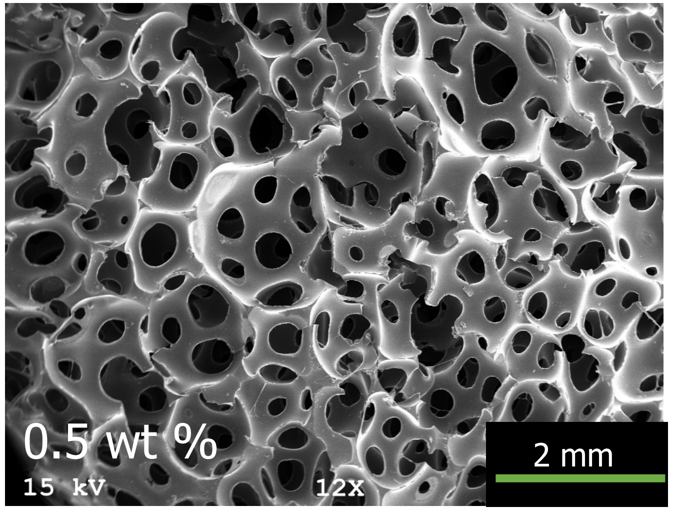


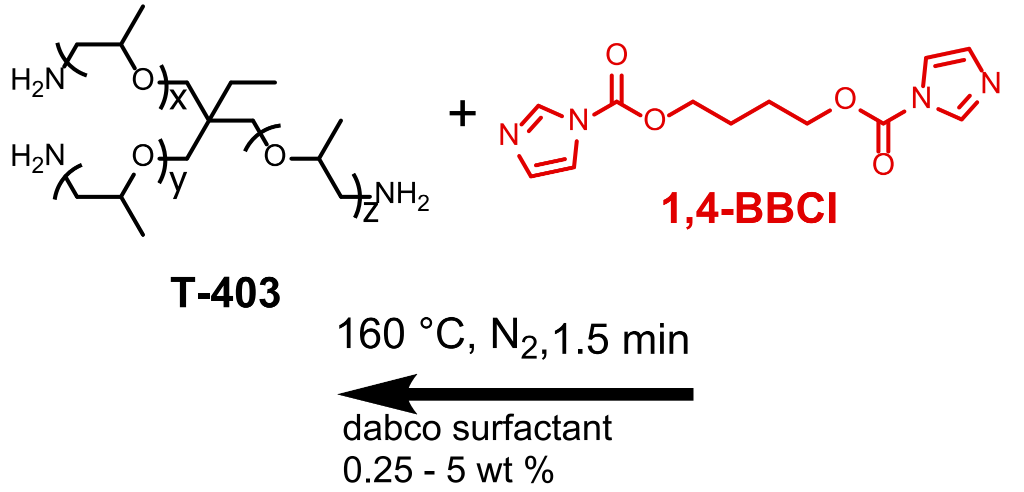
Homolysis and disproportionation leading to terminal vinyl

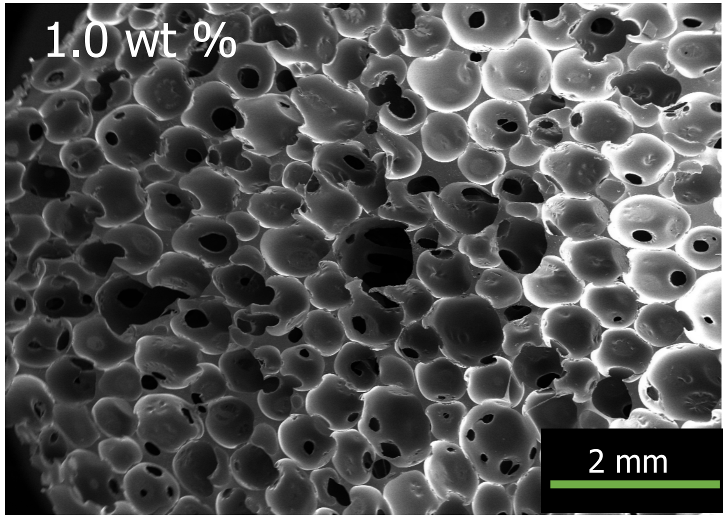


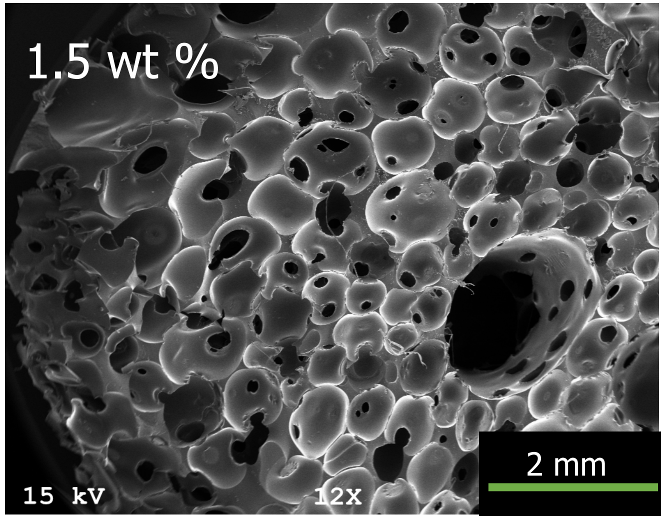
Surfactant concentration controls cell architecture

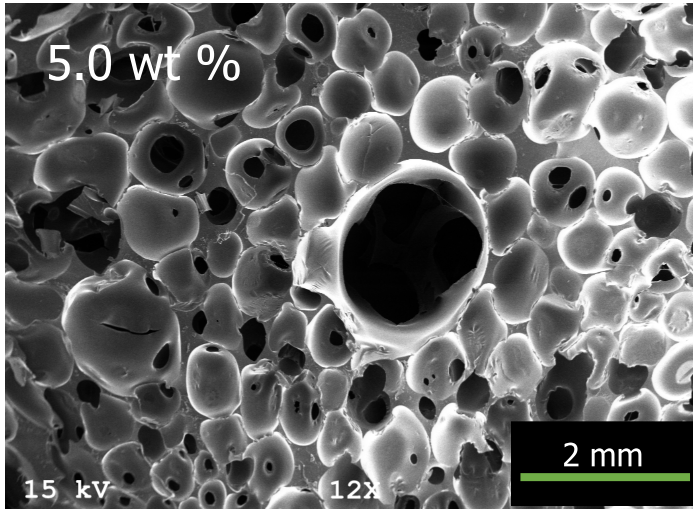






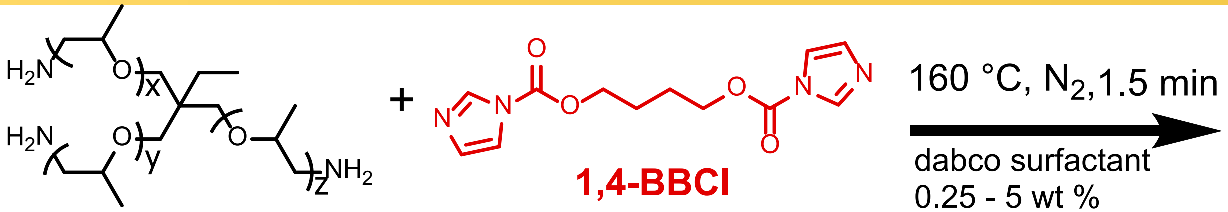




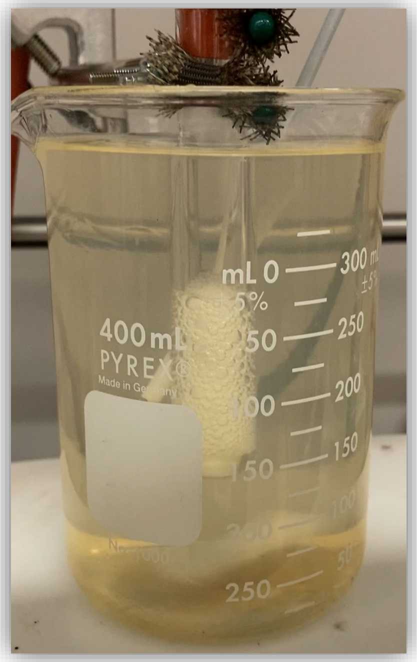


JEOL 6300 SEM, 15 KV accelerating voltage Sputtercoated 10 Å Au

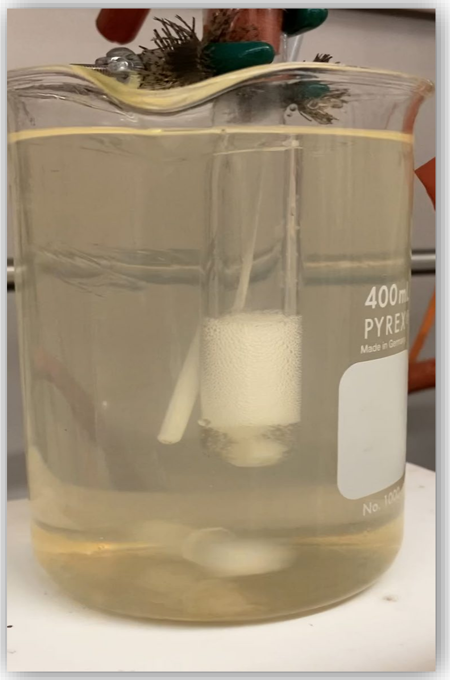
Surfactant loading affects pore stability



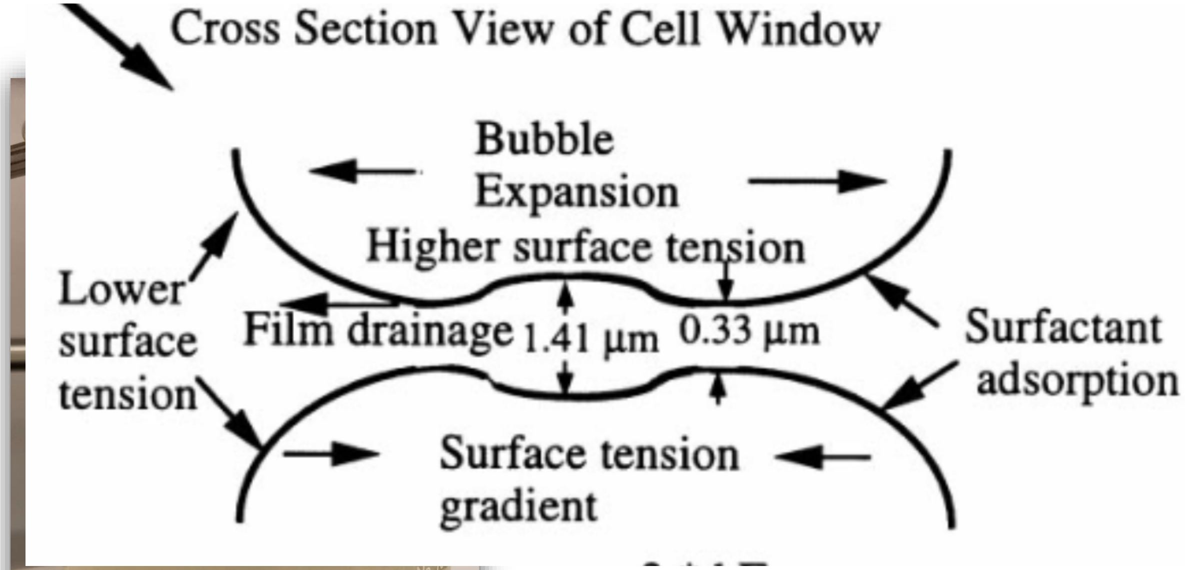
T-403



No surfactant



1.0 wt %



5.0 wt %

- 1 wt % surfactant loading produces most stable pore formation

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BCI foams display minimal water uptake at multiple architectures

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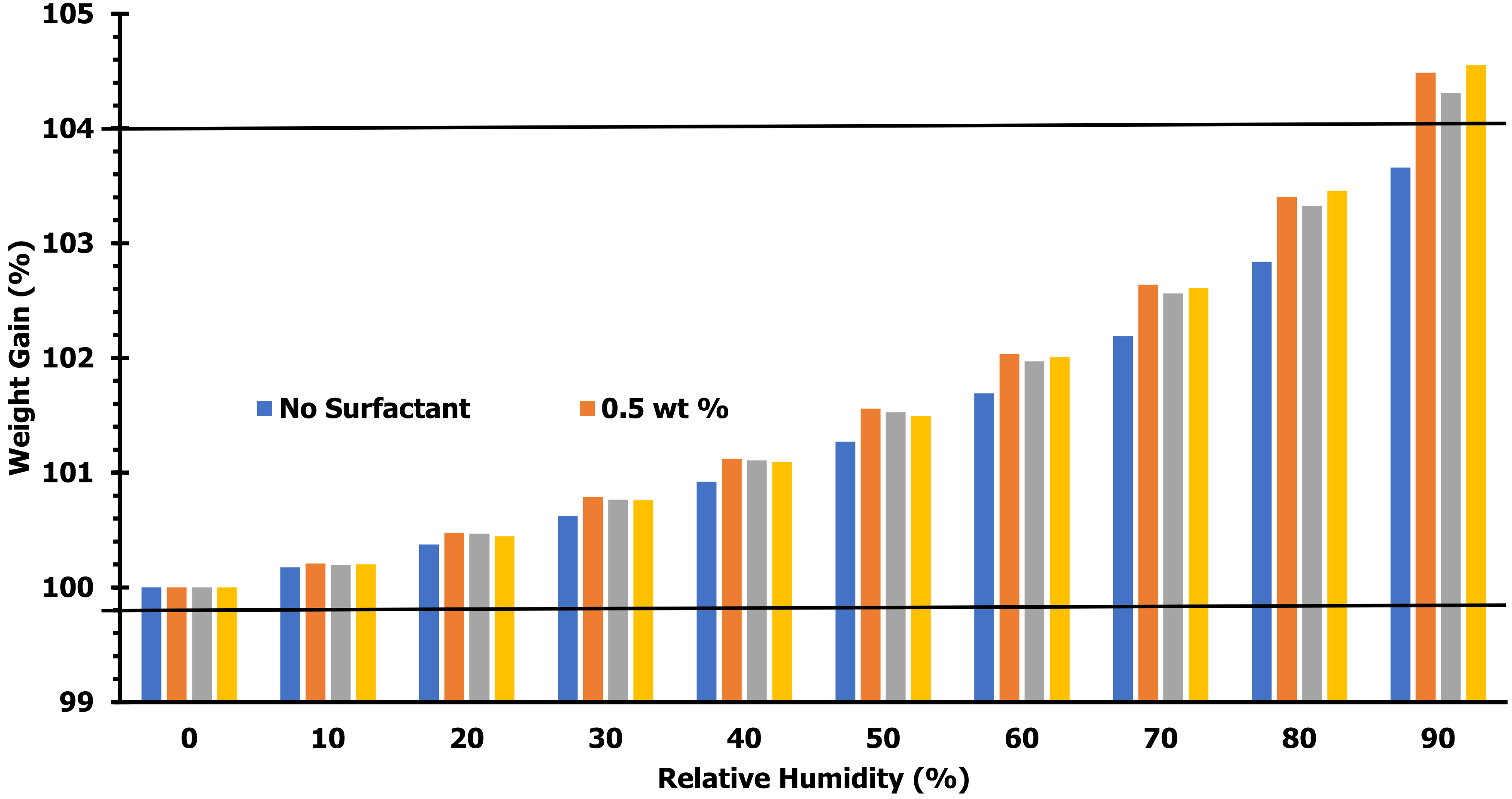
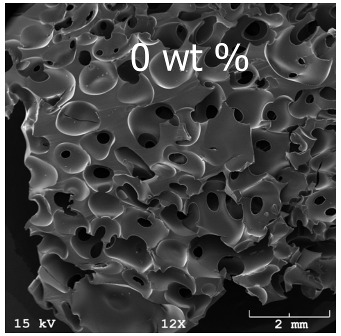
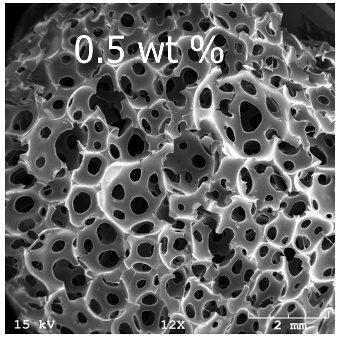
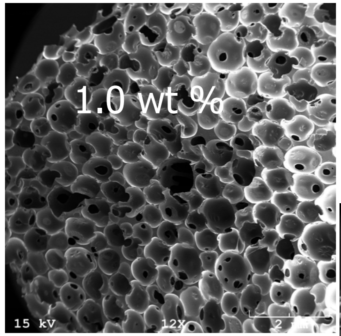
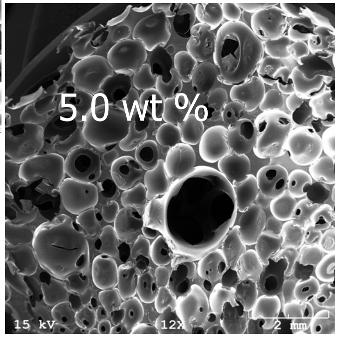
- All foam compositions display minimal water uptake (4 wt. % at 90 % relative humidity)





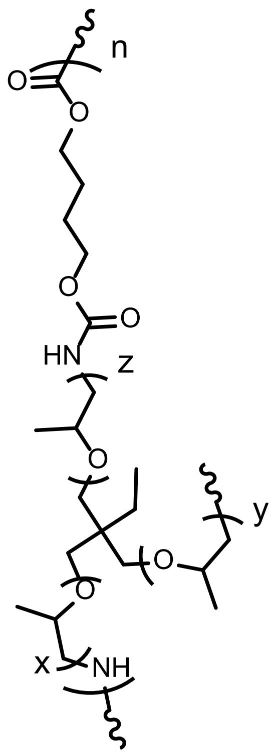


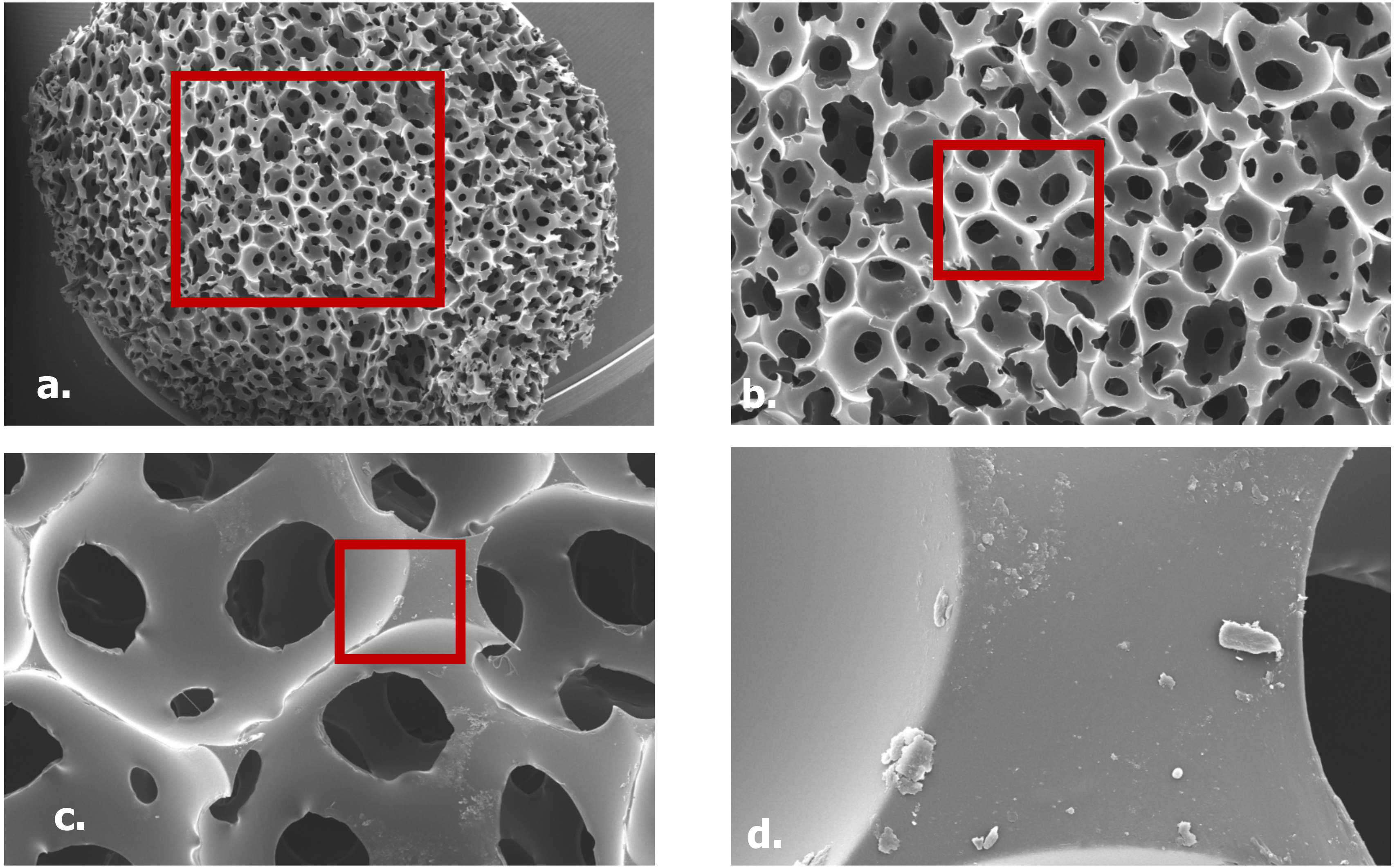




Surfactant produces a higher fraction of open-cells in butanediol-based foams

BBCI-T403 + 0.8 wt % Dabco DC193

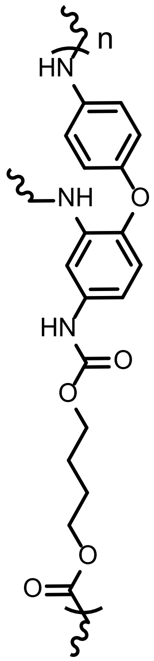


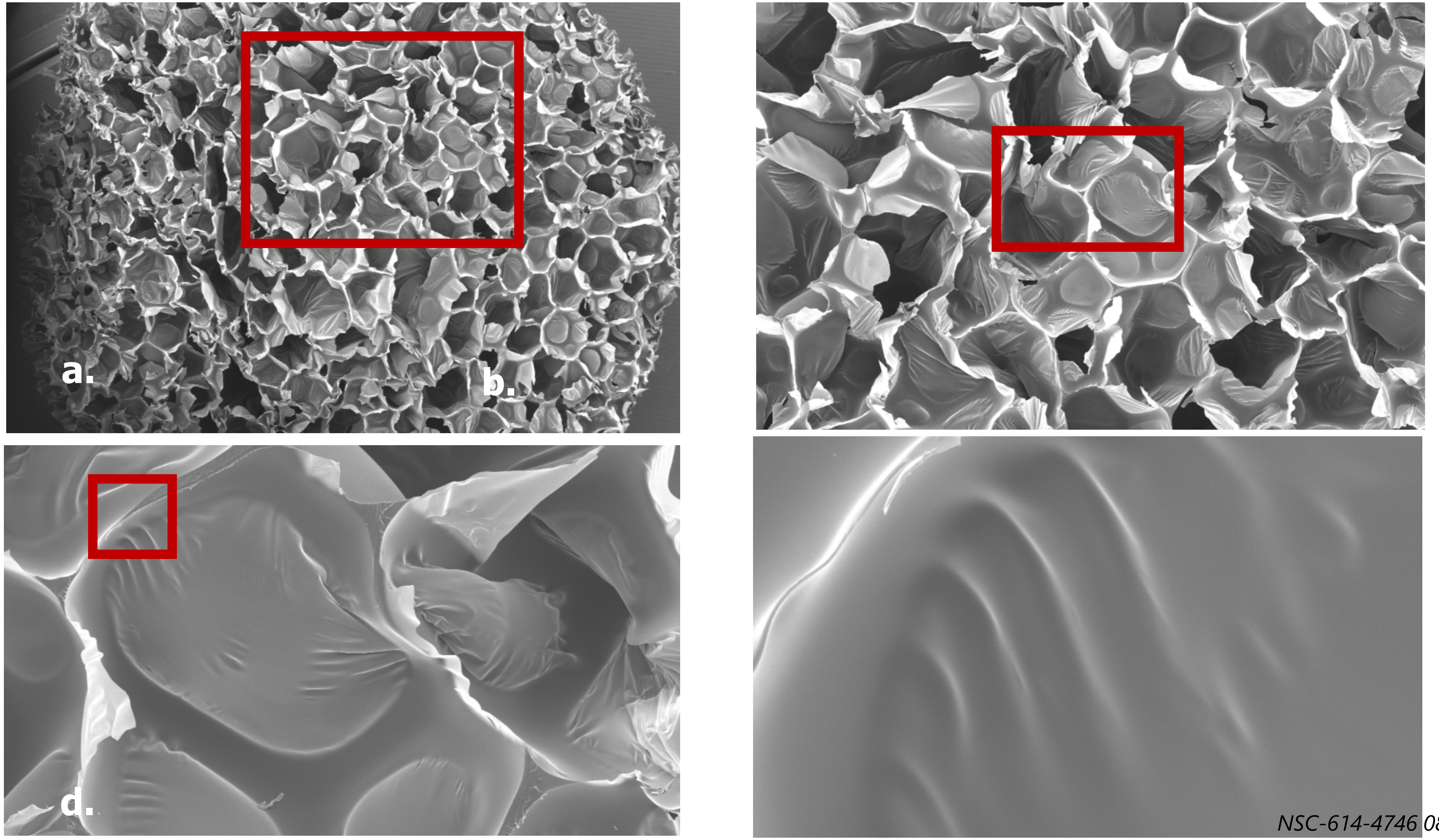


JEOL JSM – IT500HR SEM and Cressington Sputter Coater 208HR with Au/Pd

TADE-based PU foams contain closed-cells and unique pore structures

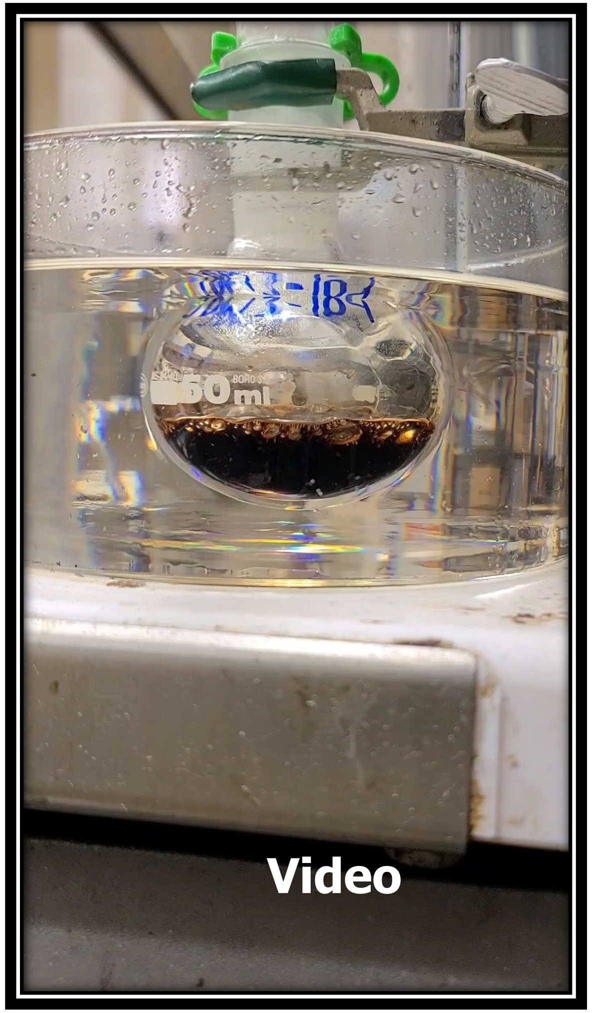
BBCI-TADE + 2.8 wt % Dabco DC193



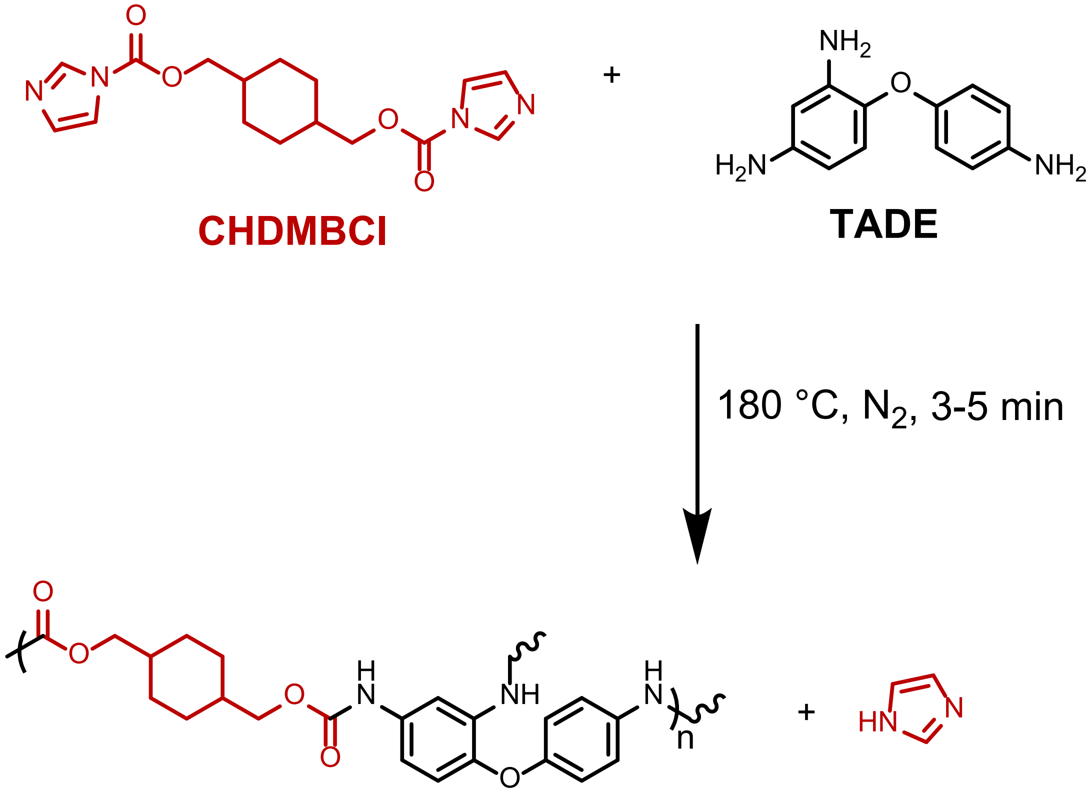


JEOL JSM – IT500HR SEM and Cressington Sputter Coater 208HR with Au/Pd

Partially aromatic, high T_g PU foams from 2,4,4'-triaminodiphenylether (TADE)



Video starts ~ 4 min after reaction start.



- CHDMBCI and TADE melted at 180 °C under N_2
- Reaction is homogeneous
- Curing reached after **~ 4-5 min**

T_g = 111 °C
(From TMA)

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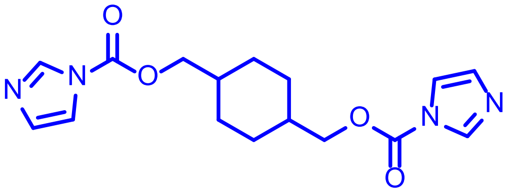
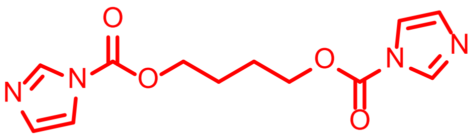
Aryl amines effectively increase T_g, allowing use in high performance applications



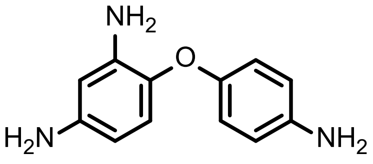
CHDMBCI

OR



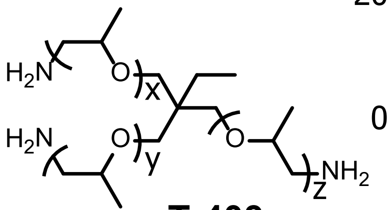
BBCI

+

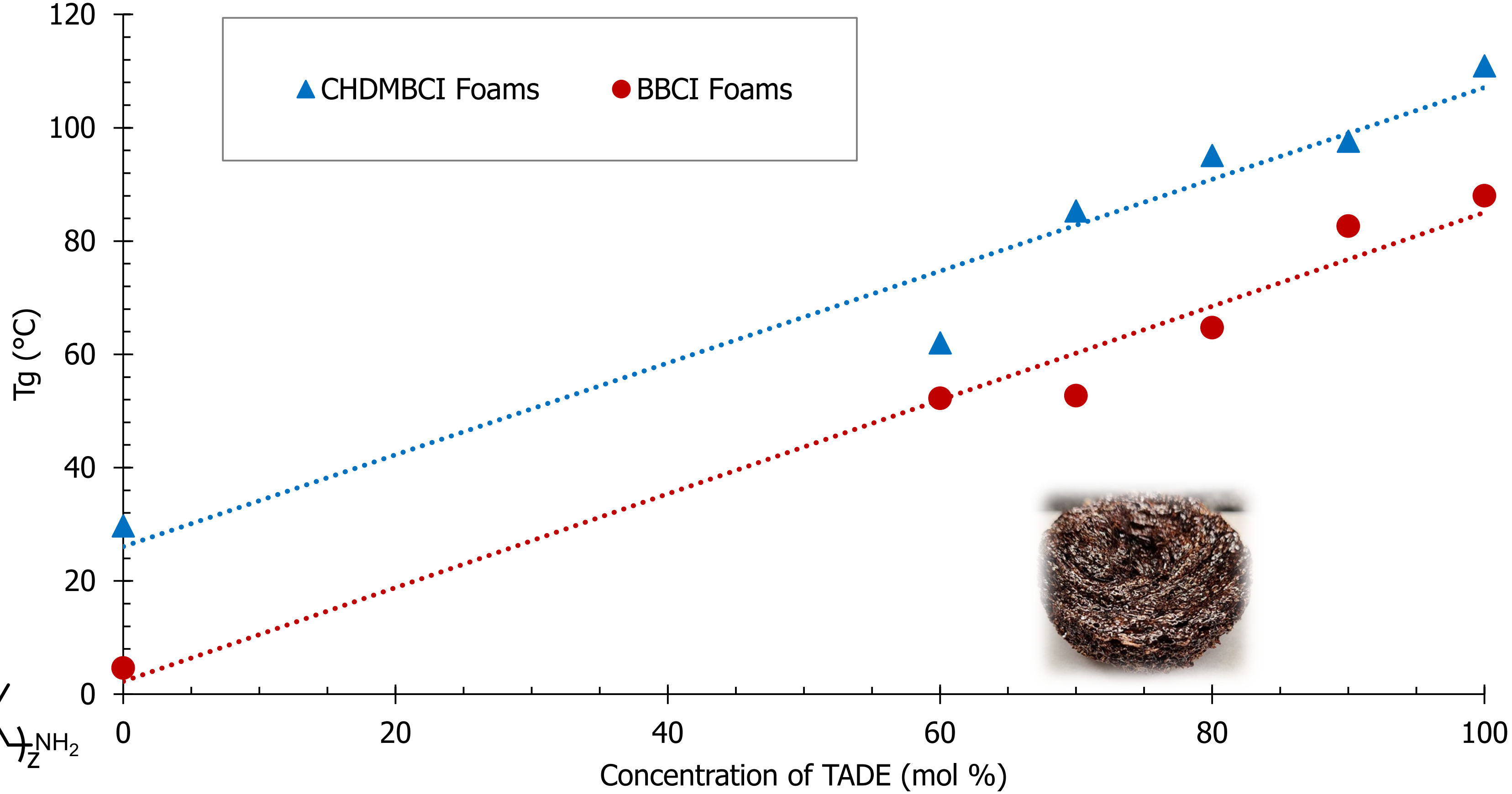


TADE

AND/ OR



T-403



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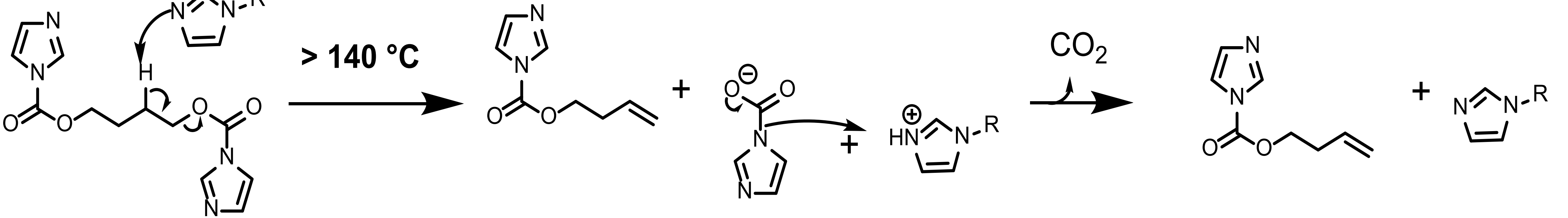
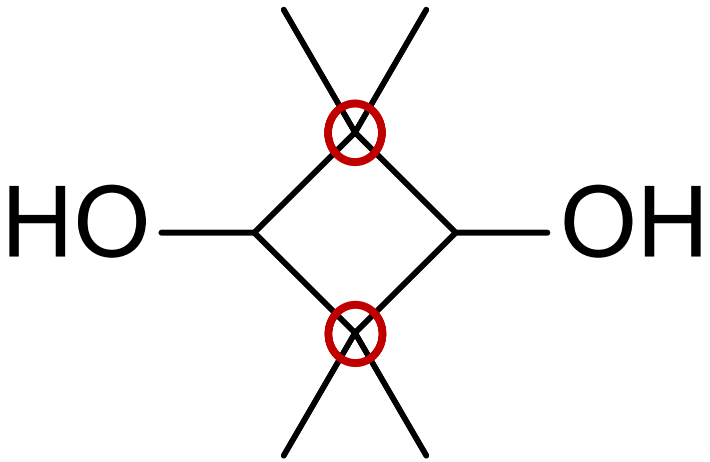
Design of new BCI monomer with no β-hydrogens allows for tunable CO_2 generation

Accepted mechanism for CO_2 production in the BCI system

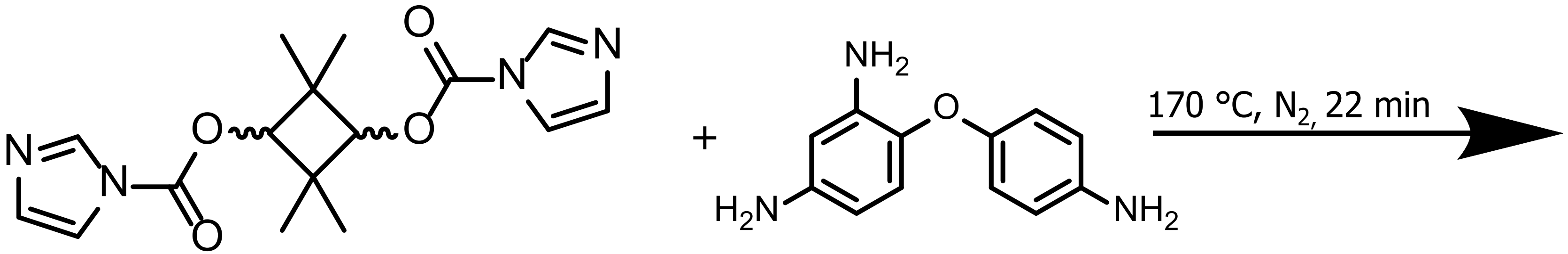


- Monomer for Eastman's Triton® polyester
- Provides good impact resistance and rigidity
- No beta hydrogens, so no CO_2 generation expected
- Could replace aromatic BCI monomers



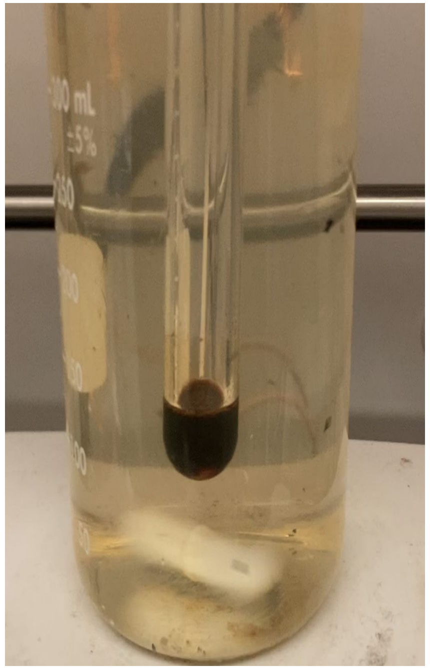
2,2,4,4-tetramethyl cyclobutenediol (CB)

Reacting TADE with CBBCI results in porous structure



CBBCI

TADE

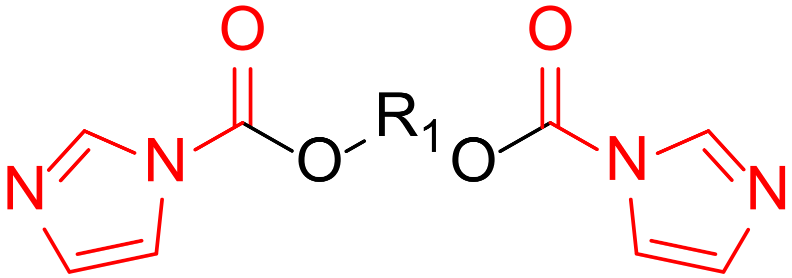


- Crosslinked product still achieved porous structure
- Volatile imidazole could serve as the blowing agent, eliminating need for CO_2 generation

T_g of 115 °C

Conclusions

CDI Chemistry allows for non-isocyanate polyurethane synthesis



BCI monomers are capable of synthesizing PU foams and thermoplastics

Imidazole as can be used as a circular, green route for polyurethane foam blowing

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