TEXAS A&M UNIVERSITY

Completely Alternating Copolymerization of CO_2 and Epoxides to Polycarbonates

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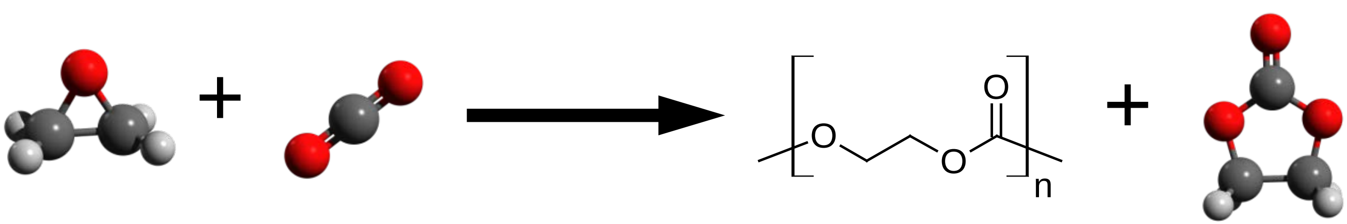

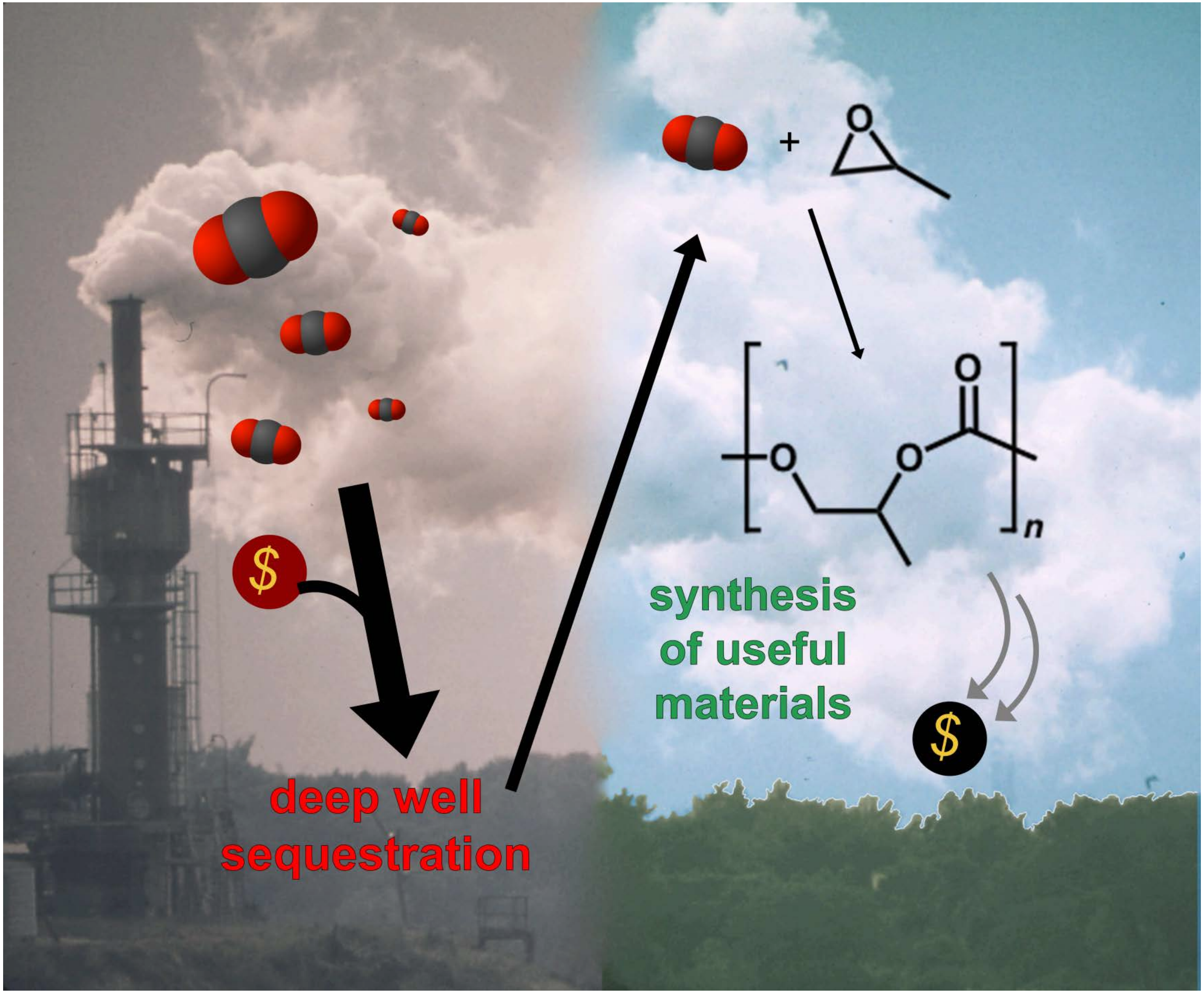

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synthesis
of useful
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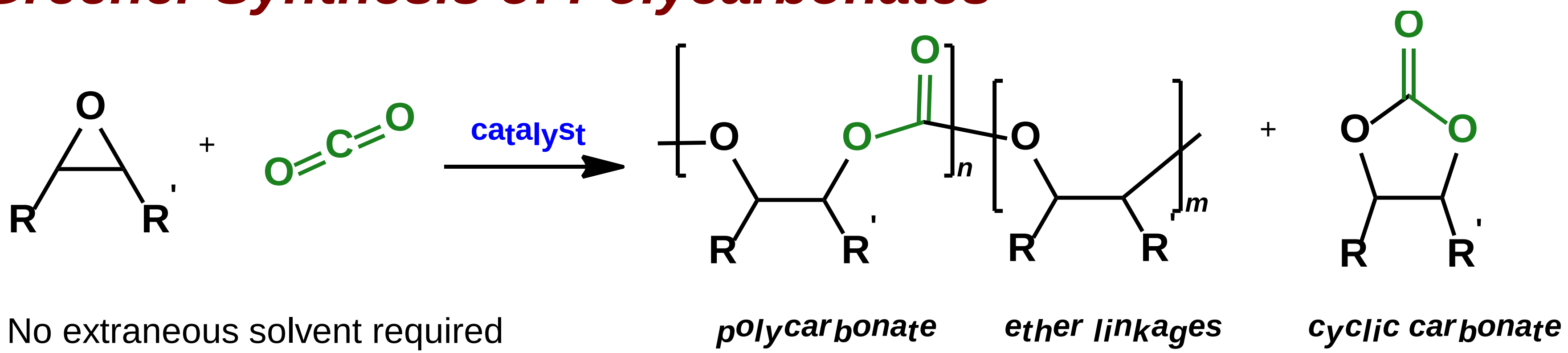
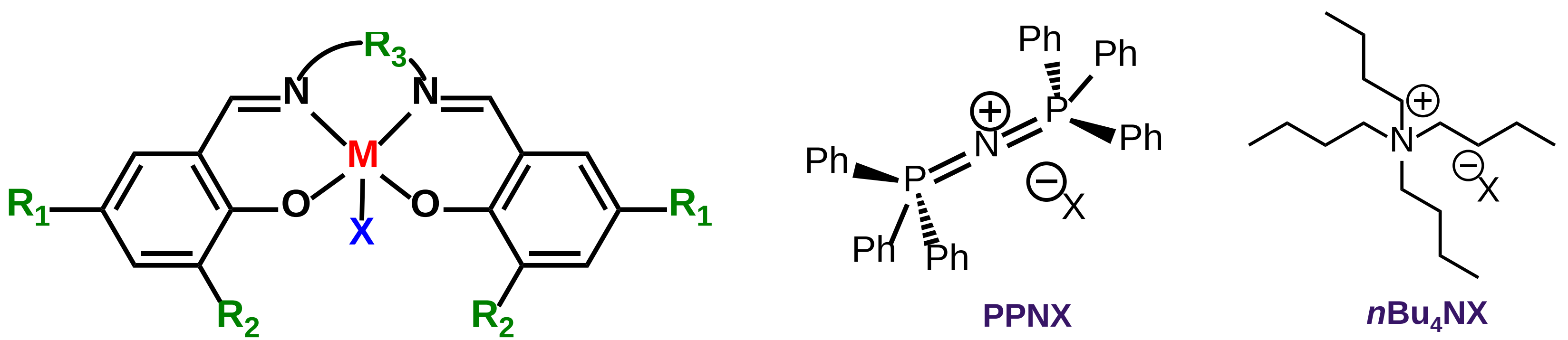
deep well
sequestration

Greener Synthesis of Polycarbonates



- No extraneous solvent required
- 100% atom economy
- Constructive use of abundant “waste” C1 feedstock
- Living polymerization

Typical Catalytic System: (salen)M(III)X with onium salt cocatalyst



- Robust, tetradentate* ligand
- Activity/Selectivity tunable by altering R_1, R_2, R_3, M, X

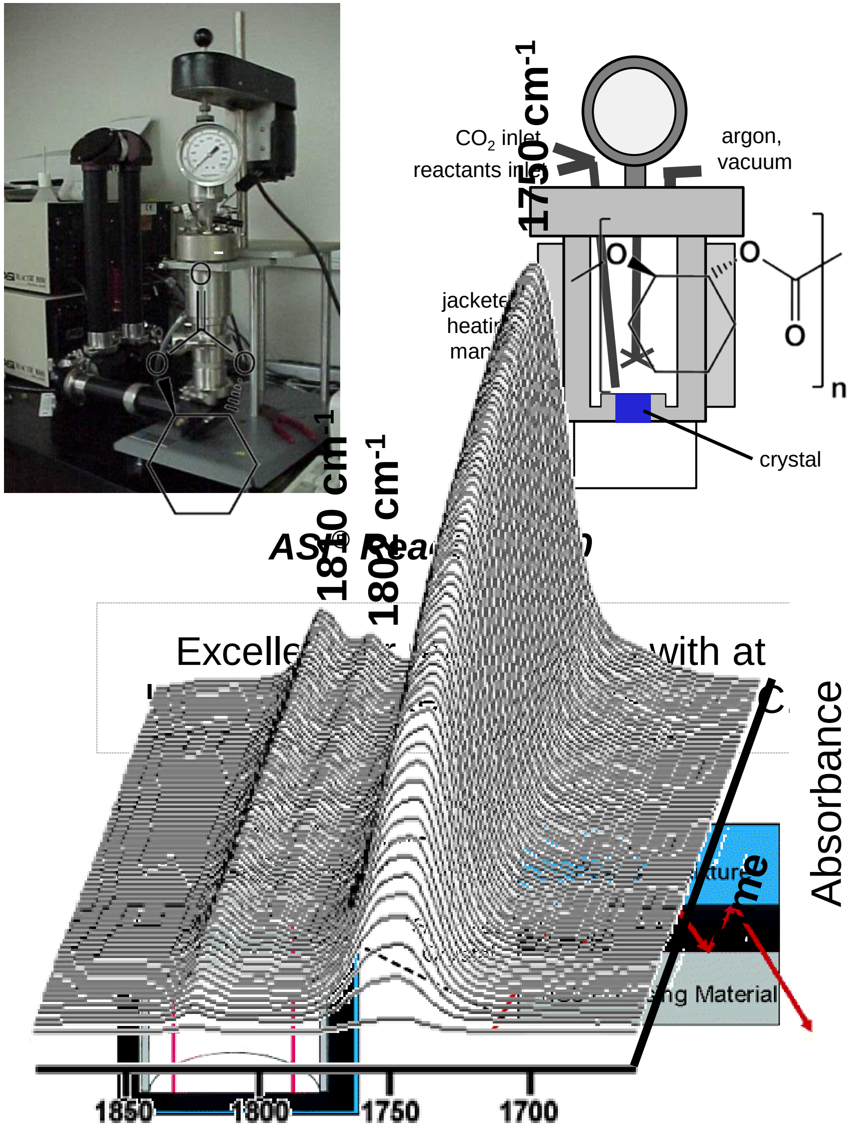
Typical System: M = Cr, Co

$R_1 = R_2 = {}^{t}Bu$

R_3 = $-C_2H_4-$, cyclohexyl

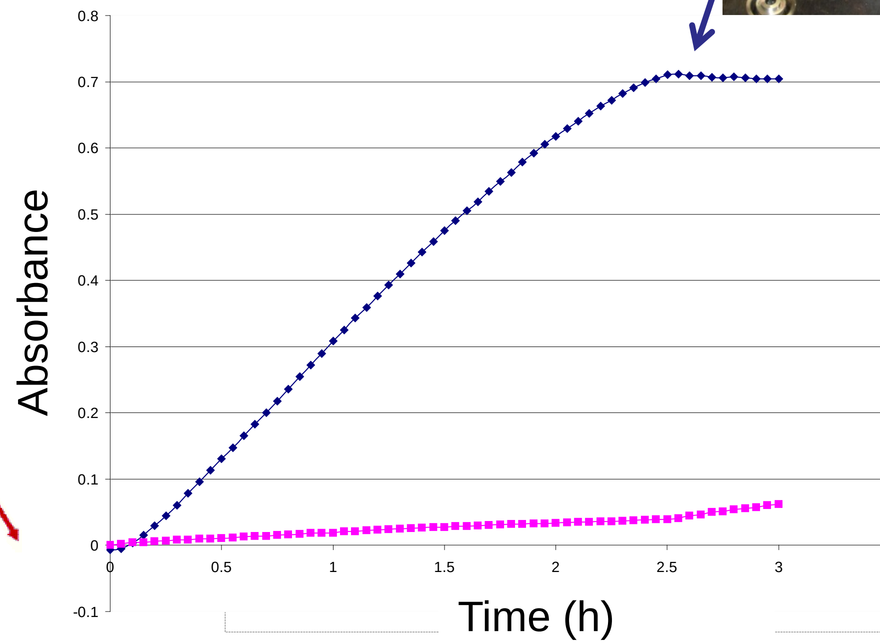
Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388-2410.
Darensbourg, D. J., Wilson, S. J. *Green Chem.* **2012**, *14*, 2665–2671..

Monitoring Polymerization Kinetics – in situ ATR FT-IR

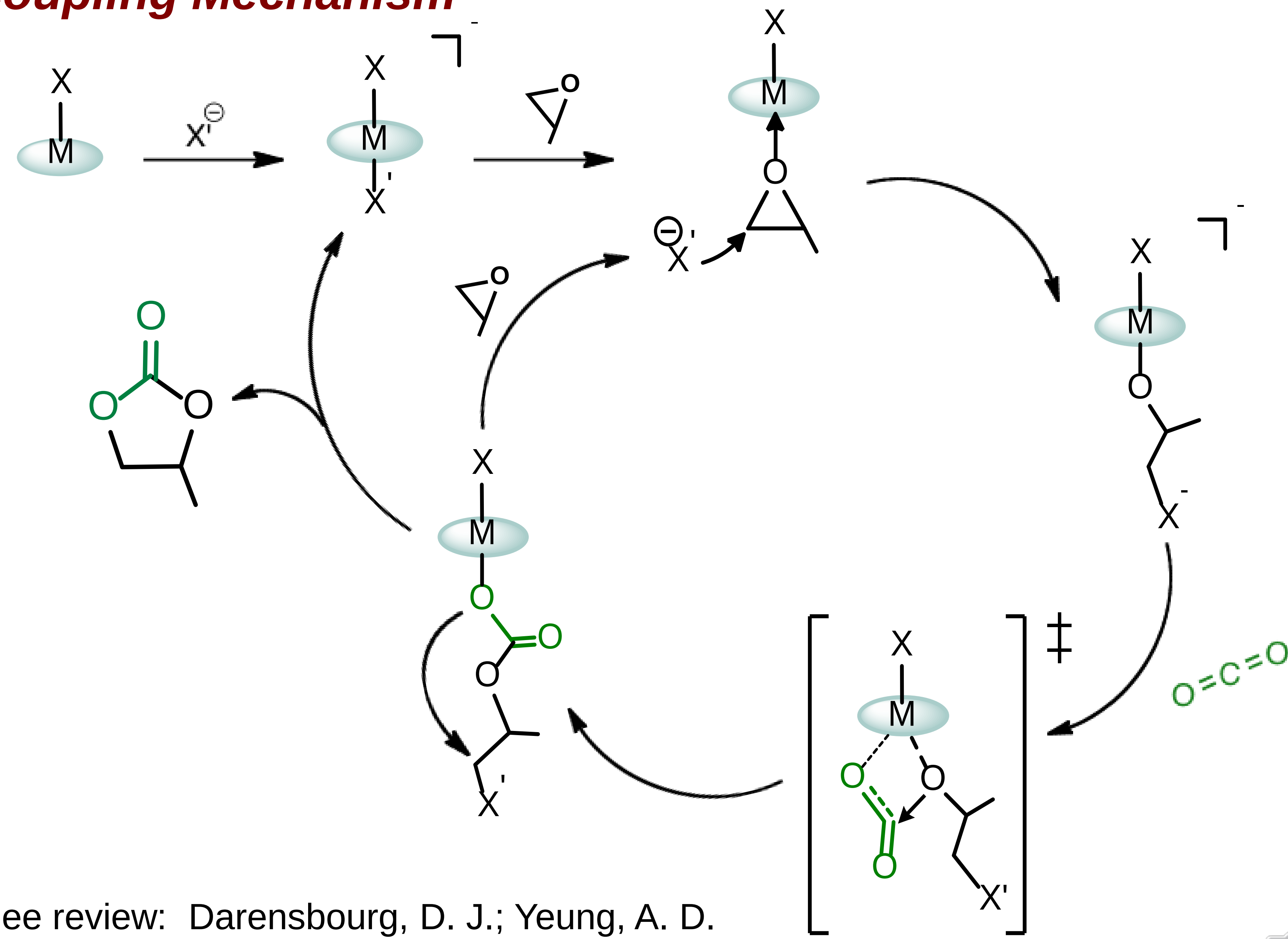


Attenuated Total Reflectance Infrared Spectroscopy

Solution becomes too viscous at this point.

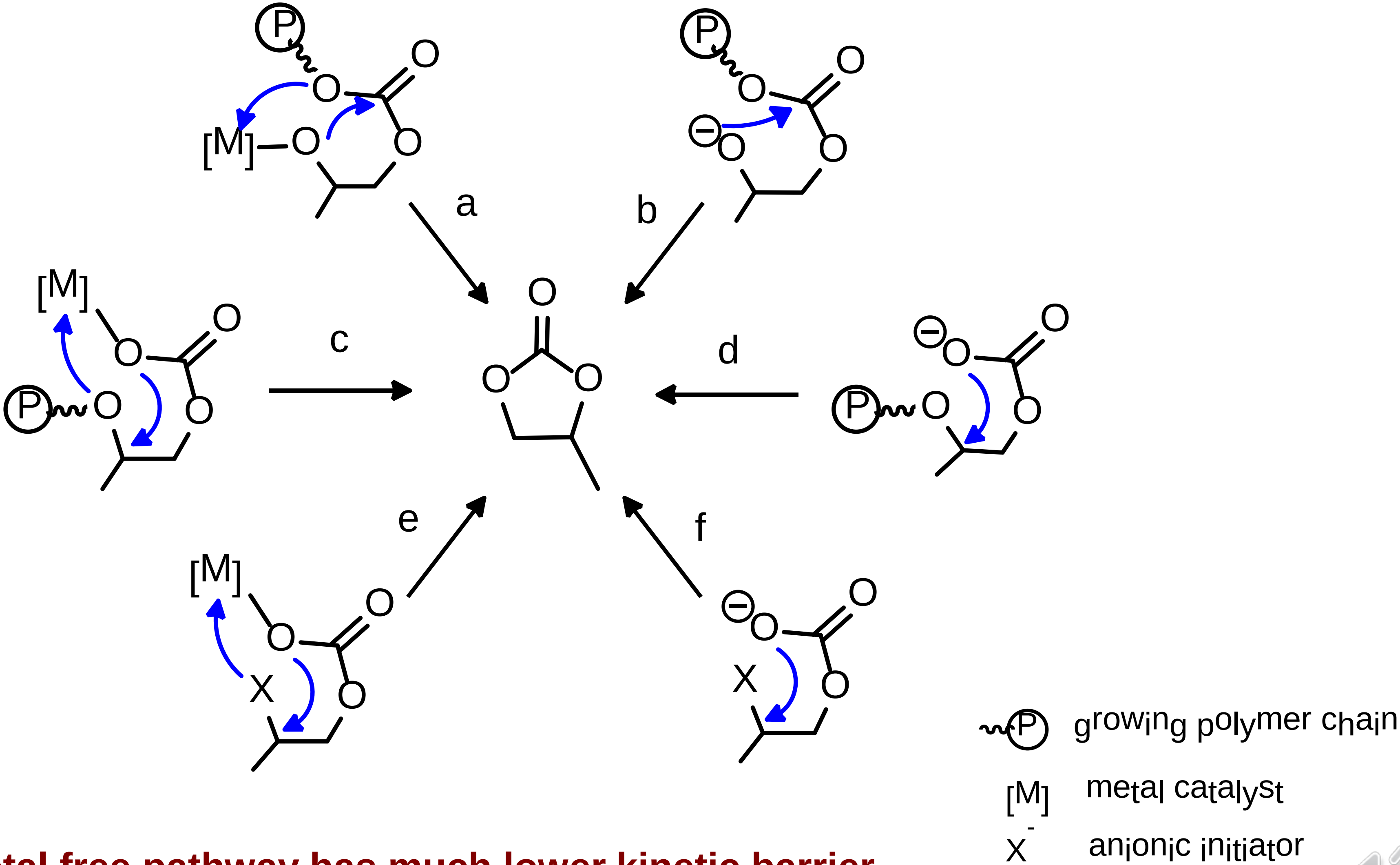


Coupling Mechanism



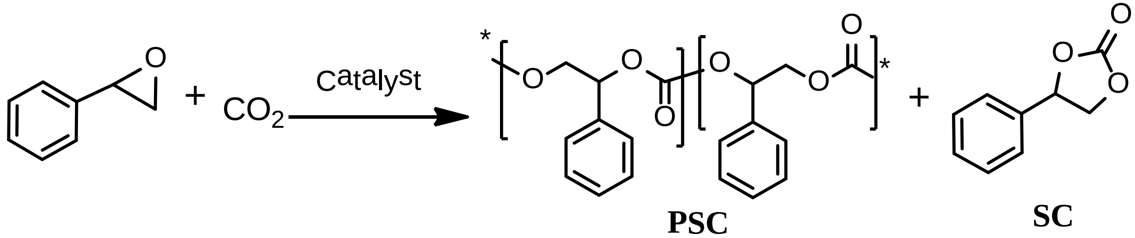
See review: Darensbourg, D. J.; Yeung, A. D. *Polymer Chemistry* **2014**, *5*, 3949—3962.

Routes to Cyclic Carbonates



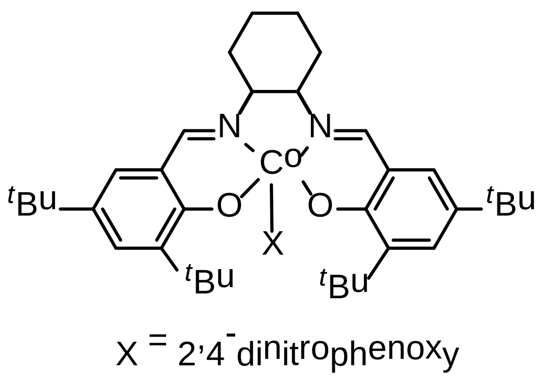
Metal free pathway has much lower kinetic barrier.

Copolymerization of Styrene Oxide and Carbon Dioxide

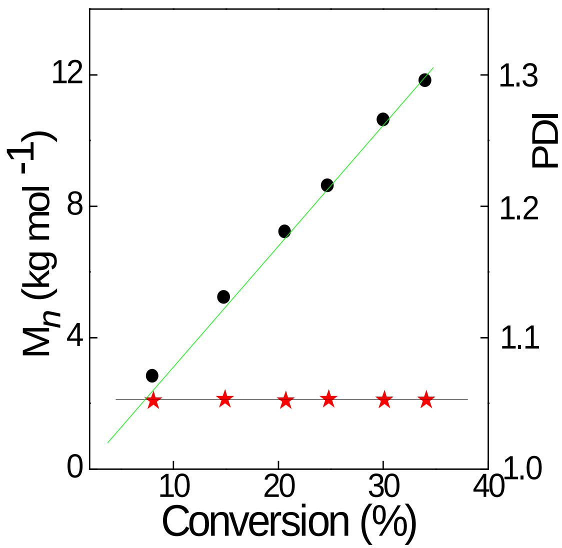


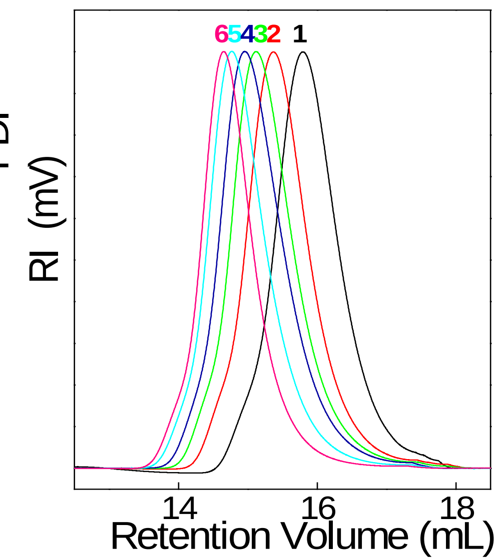
Thermal stability up to 300 ºC and Tg = 80 ºC

25 ºC, TOF = 75 h^{-1} @ 2.0 Mpa
CO_2 Selectivity PSC:SC of 99:1



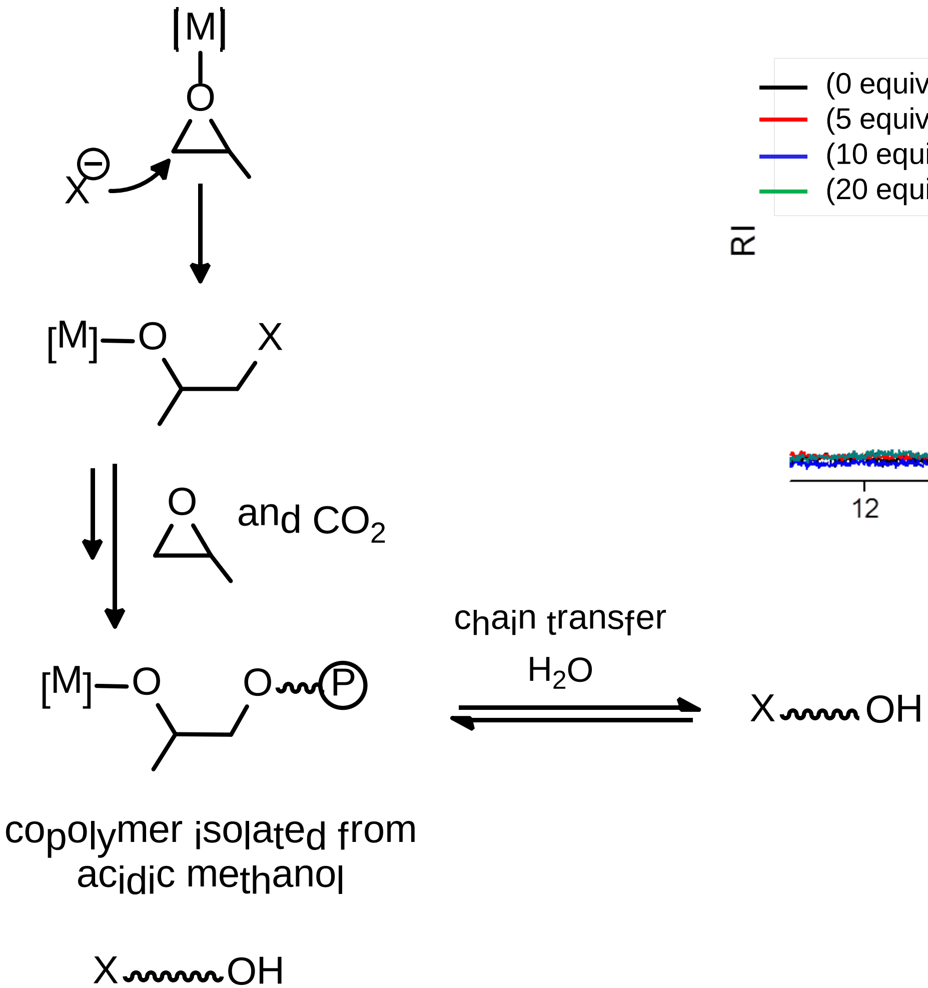
PPNX as cocatalyst

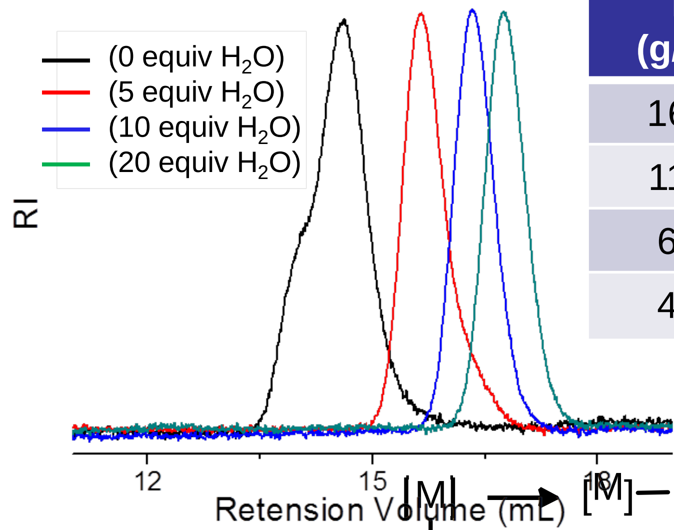




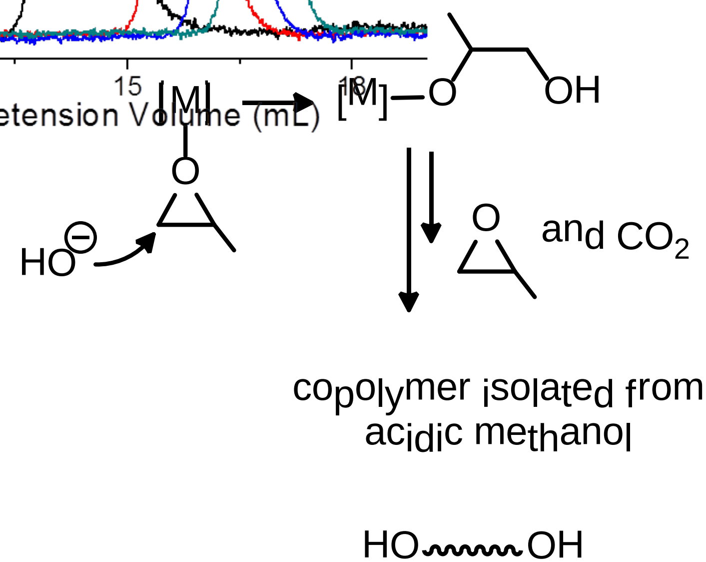
Wu, G.-P.; Wei, S.-H.; Lu, X.-B.; Ren, W.-M.; Darensbourg, D. J. *Macromolecules* **2010**, *43*, 9202.
Wu, G.-P.; Wei, S.-H.; Ren, W.-M.; Lu, X.-B.; Li, B.; Zu, Y.-P.; Darensbourg, D. J. *Energy & Environmental Sci.* **2011**, *4*, 5084-5092.

Rapid and Reversible Chain Transfer Processes





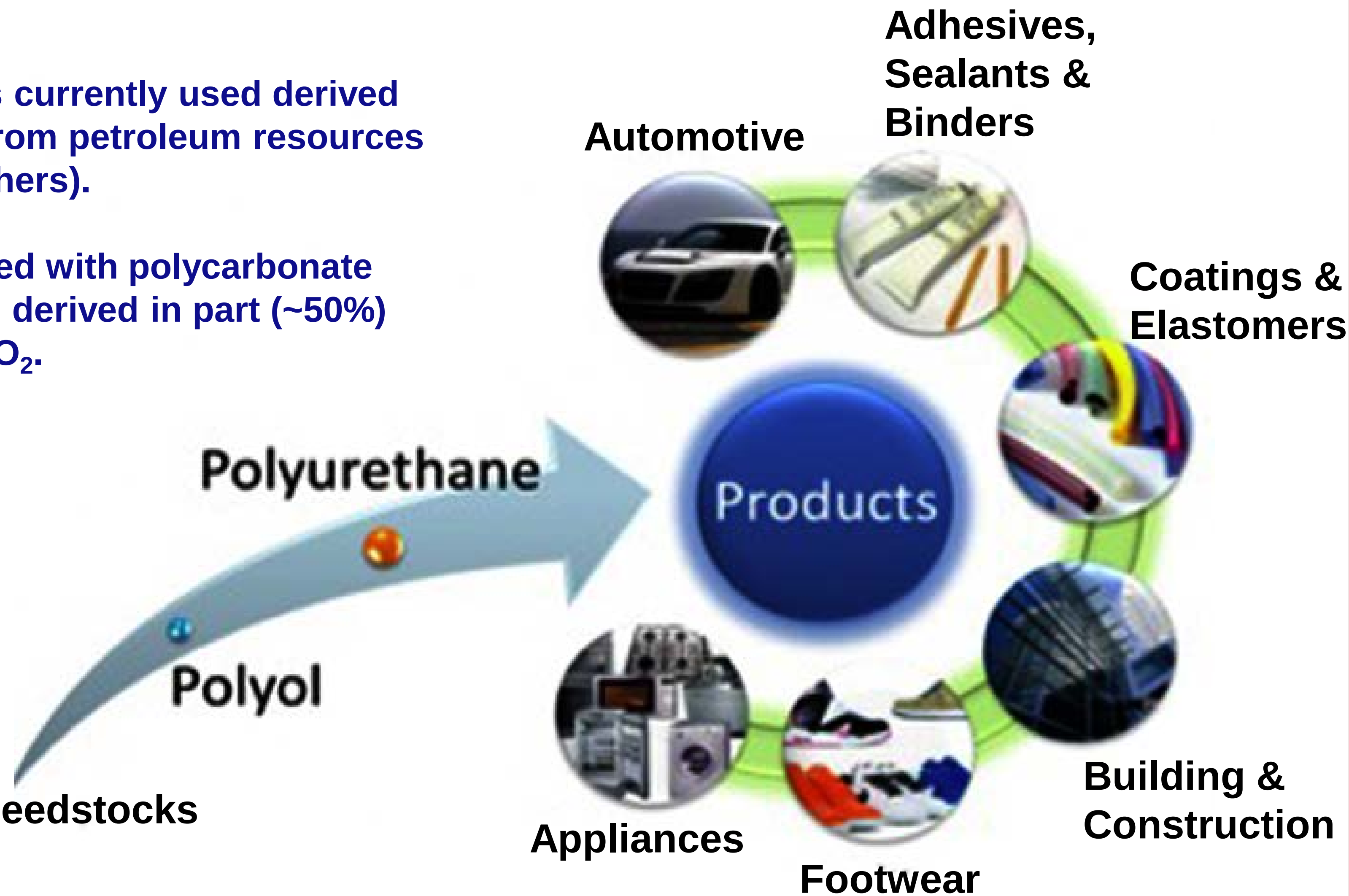
Mn (g/mol)
16800
11000
6800
4200



Bimodal Distribution of Molecular Weights

Polyether Polyols

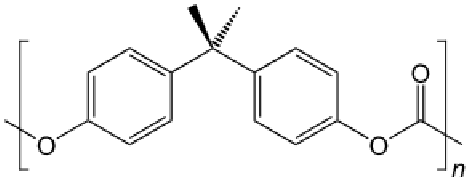
- **Polyols currently used derived 100% from petroleum resources (polyethers).**
- **Replaced with polycarbonate polyols derived in part (~50%) from CO_2.**



http://www.econic-technologies.com/technologies/products/polyols/

Desired Properties

?

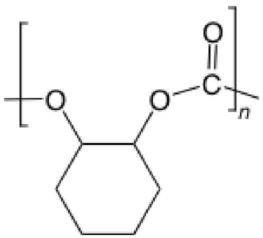


BPA Polycarbonate
Lexan®

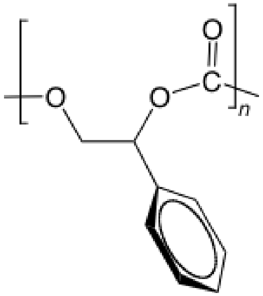
Industrial standard polycarbonate
T_g ≈ 150 °C
Amorphous, robust polymer
High M_n's achievable
Chain entanglement at low MW

What conditions can we use to produce polymers similar to that of BPA polycarbonate?

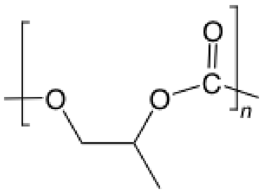
Our Focus:
high glass transition temperature (T_g)



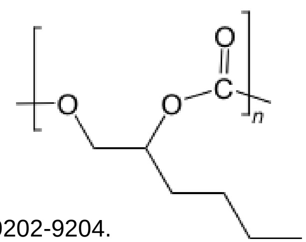
poly(cyclohexene carbonate)
T_g ≈ 115 °C
easy to polymerize
brittle polymer



poly(styrene carbonate)
T_g ≈ 80 °C
sensitive polymerization



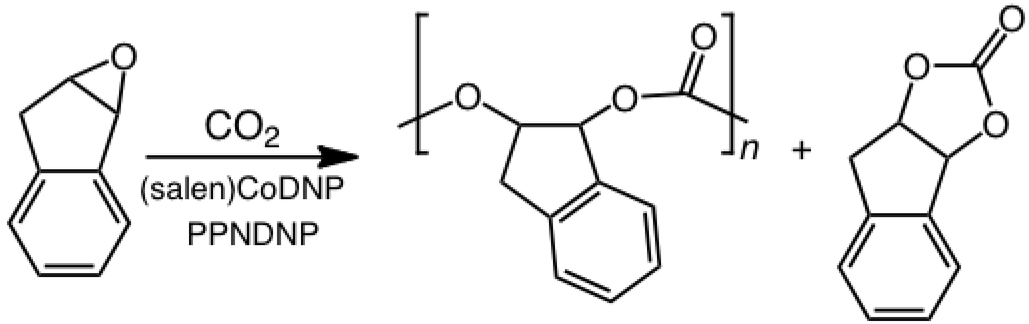
poly(propylene carbonate)
T_g ≈ 40 °C
excellent mechanical properties
industrially produced

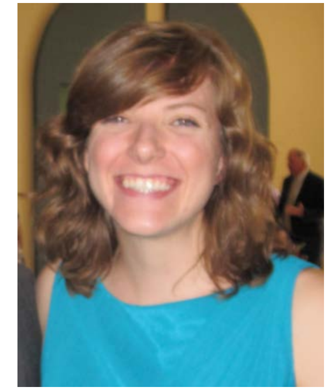


poly(1-hexene carbonate)
T_g ≈ -15 °C

Wu, G.-P.; Wei, S.-H.; Lu, X.-B.; Ren, W.-M.; Darensbourg, D.J. *Macromolecules* **2010**, *43*, 9202-9204.
Seong, J.E.; Na, S.J.; Cyriac, A.; Kim, B.-W.; Lee, B.Y. *Macromolecules*. **2010**, *43*, 903-908.

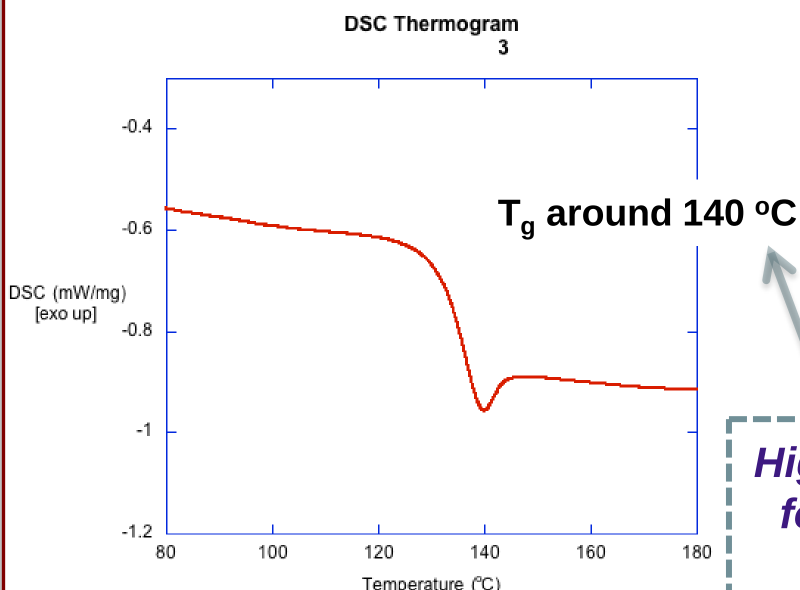
Coupling of CO_2 and Indene Oxide



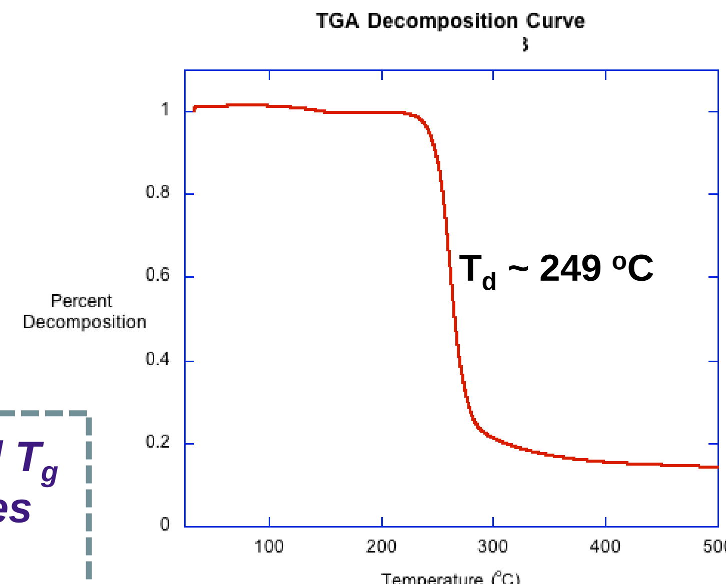


Stephanie Wilson

Poly(indene carbonate)



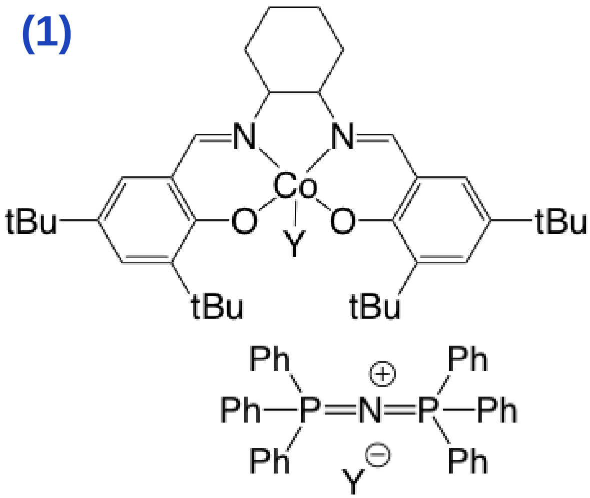
Highest reported T_g for CO_2/epoxides coupling!



Darensbourg, D.J.; Wilson, S. J. *J. Am. Chem. Soc.* **2011**, *133*, 18610-18613.

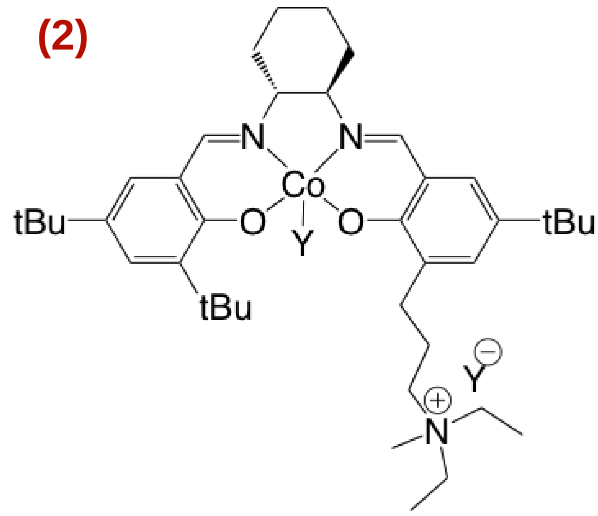
Binary vs Bifunctional Catalyst Systems

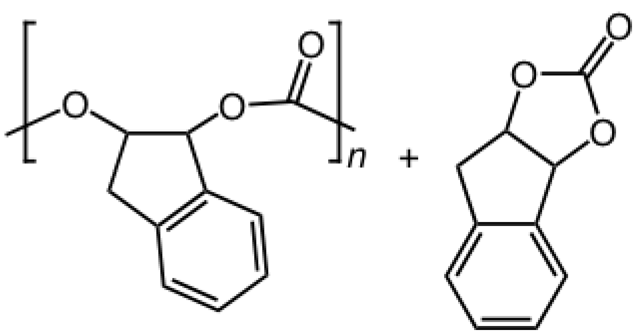
(1)



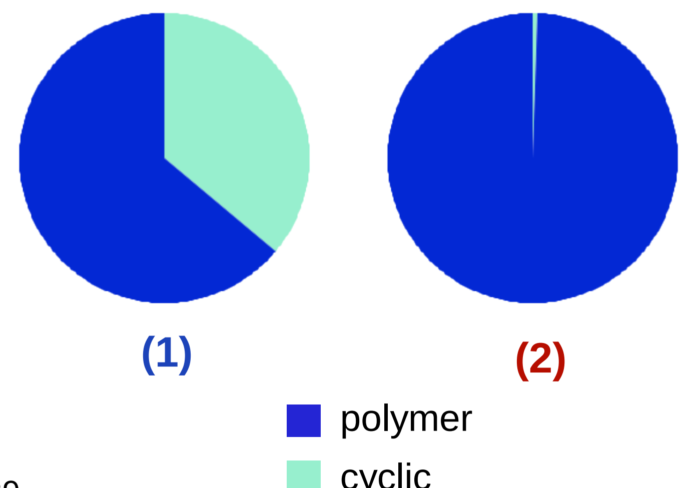
versus

(2)



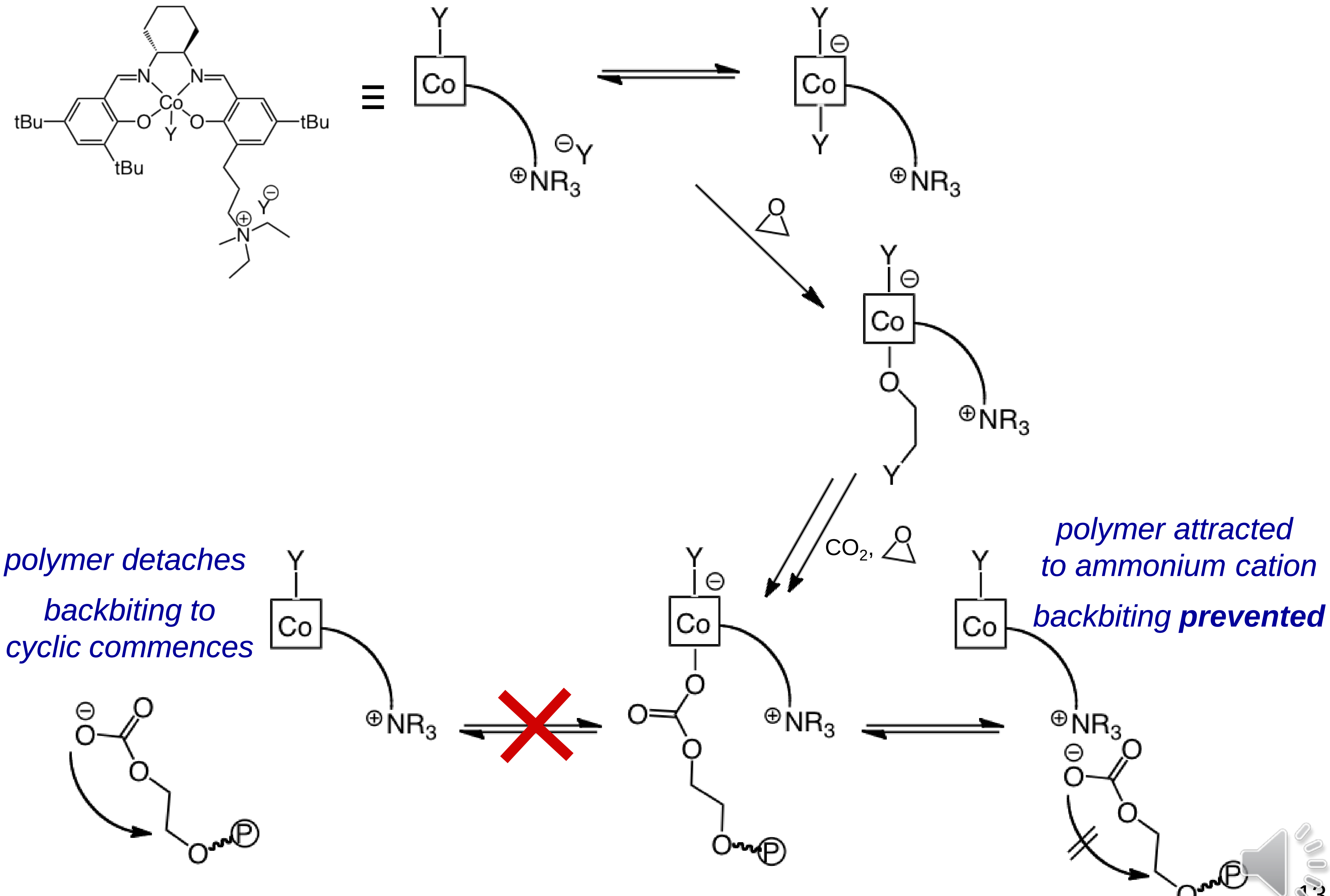


Selectivity for Polymer



Darensbourg, D.J.; Wilson, S. J. *Macromolecules* **2013**, *46*, 5929.

Bifunctional Catalyst System – How They Work

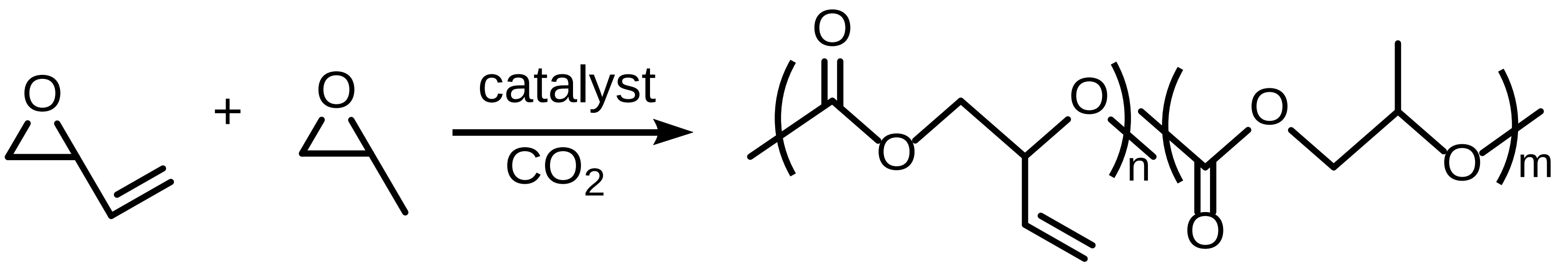


Design of New Polymeric Materials

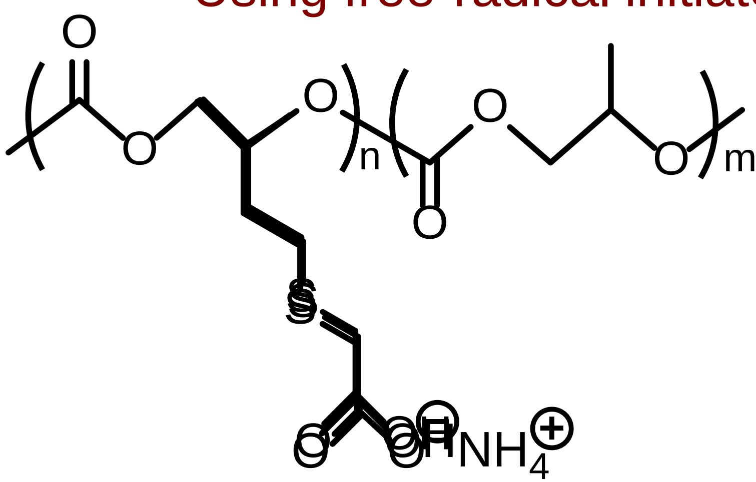
- Terpolymerization, addition of a second epoxide monomer.
- Postfunctionalization of copolymers.
- Diblock polymers incorporating ROP of other cyclic monomers, e.g., polycarbonate-polylactide

  (NOTE: polylactides are among the few biodegradable polymers with FDA approval for human clinical use. *Controlled drug delivery and tissue engineering scaffolds.)*

Terpolymerization with Postpolymerization Functionalization

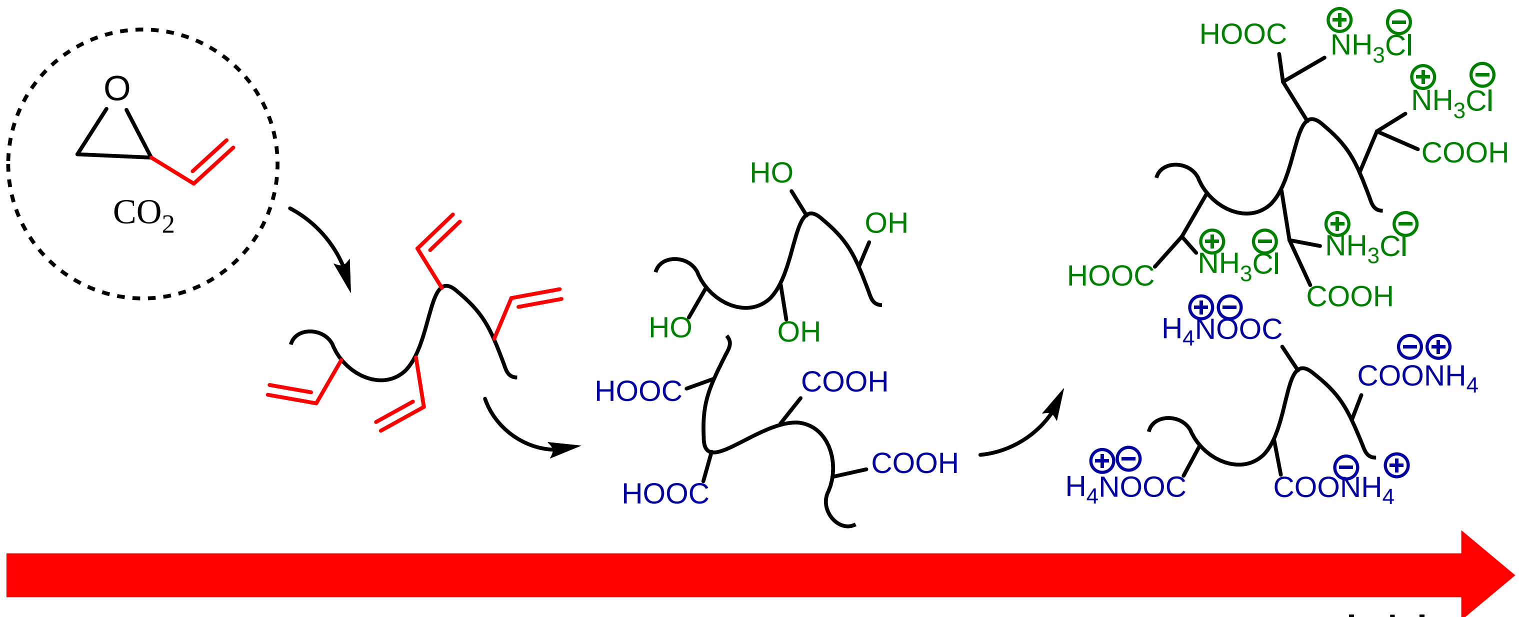


Using free-radical initiator (AIBN), add



- **HS-CH_2CH_2OH (2-mercaptoethanol)**
- **HS–CH_2–C(=O)OH (thioglycolic acid)**
- **Deprotonate latter ⟹ water-soluble polymer**

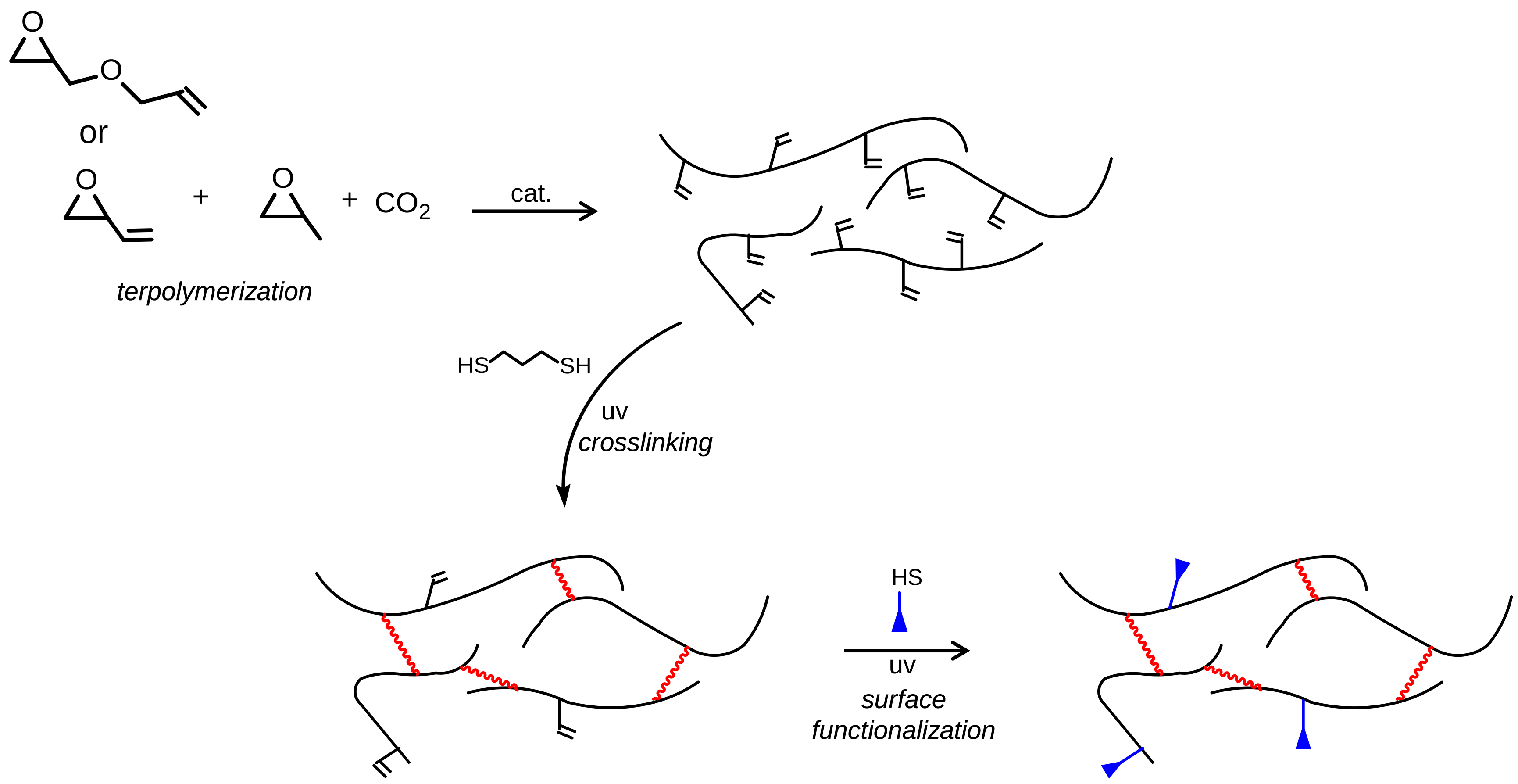
Postfunctionalization of Copolymers ⟹ Hybrid Polymers



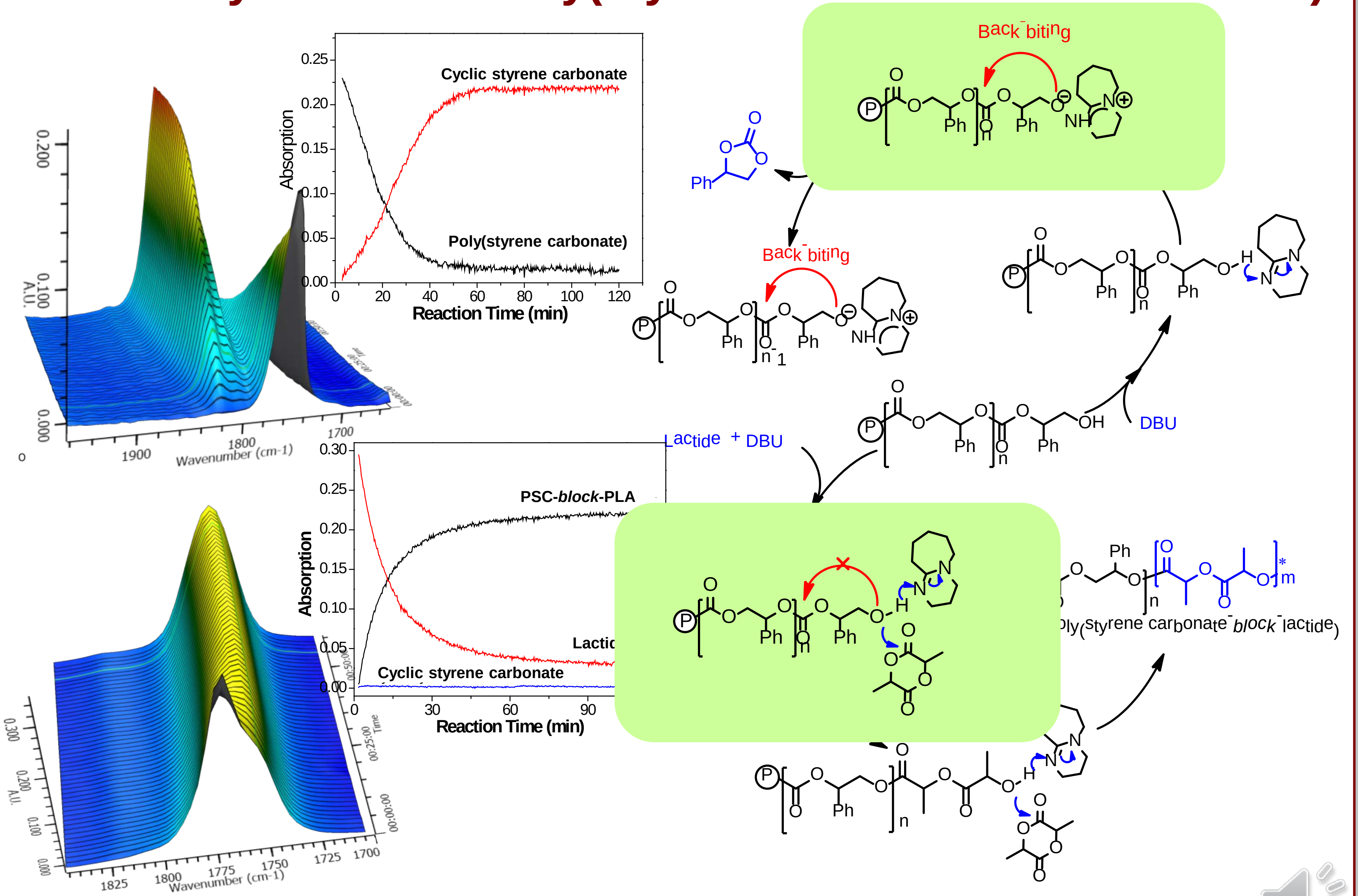
hydrophobic amphiphilic water-soluble

Darensbourg, D. J.; Tsai, F.-T., *Macromolecules*, **2014**, *47*, 3806—3813.

Functionalization of Polycarbonate Films

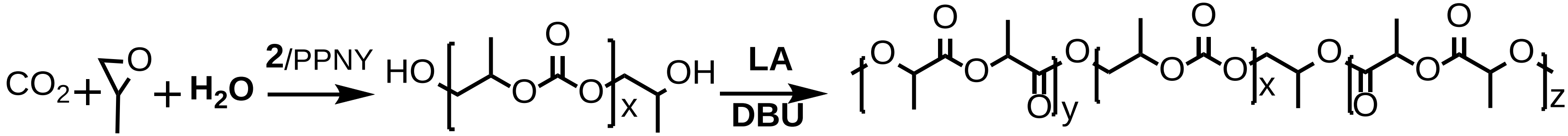


Tandem Synthesis of Poly(styrene carbonate-*block*-lactide)

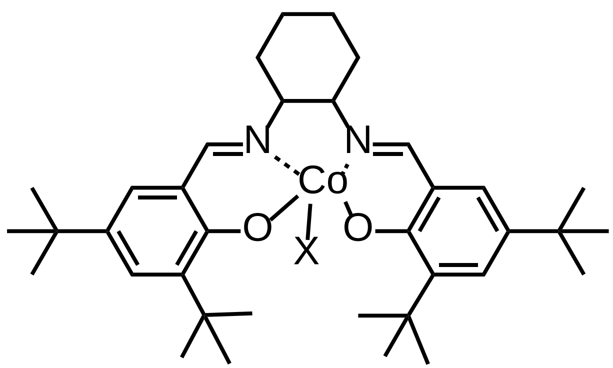


Wu, G.-P.; Darensbourg, D. J.; Lu, X.-B. *J. Am. Chem. Soc.*, **2012**, *134*, 17739-17745.

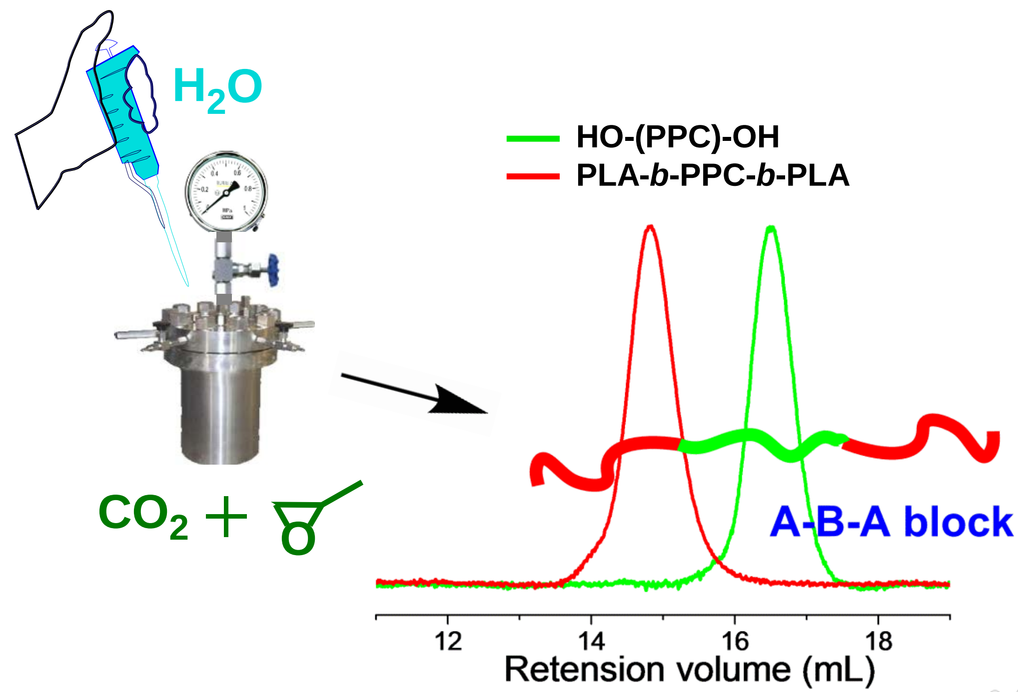
A One-Pot Synthesis of a Triblock Copolymer from PO/CO_2 and Lactides



poly(lactide-*b*-propylene carbonate-*b*-lactide)

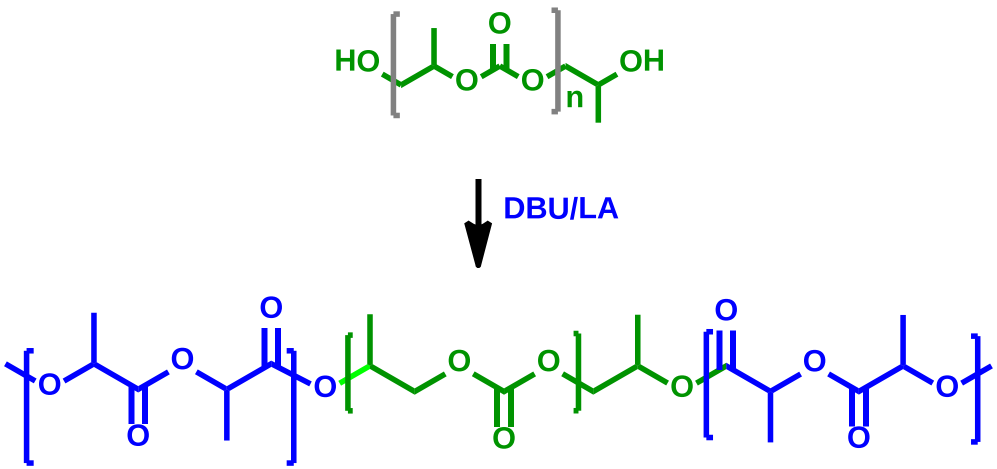


2 X = CF_3COO^-

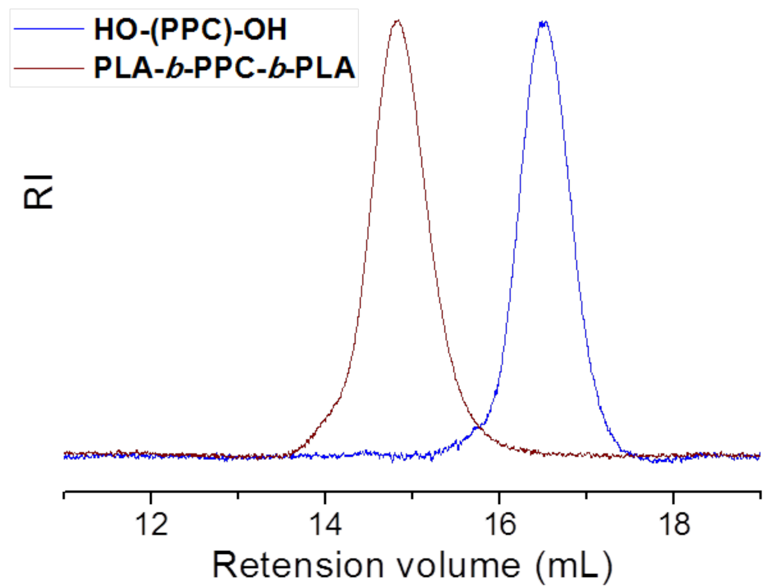


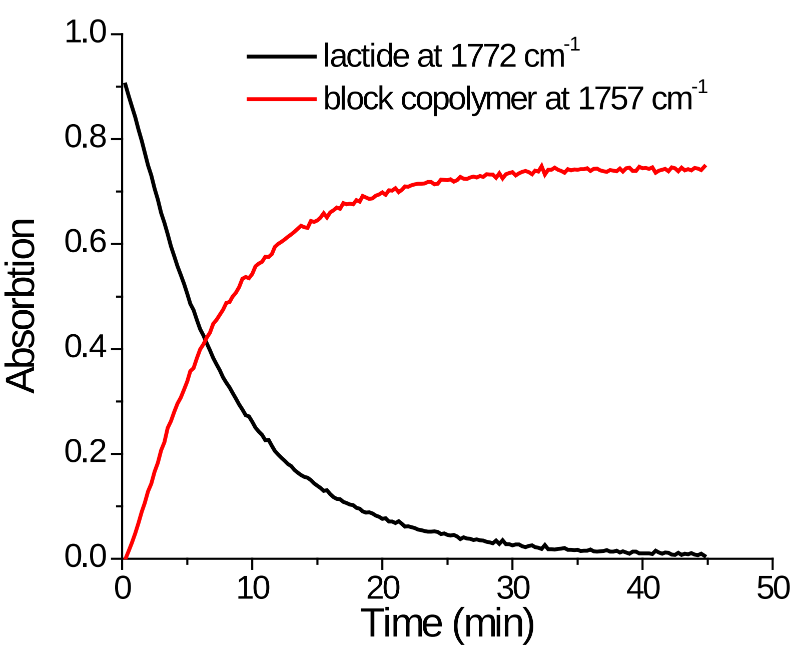
Darensbourg, D. J.; Wu, G.-P. *Angew. Chem. Int. Ed.* **2013**, *52*, 10602-10606.

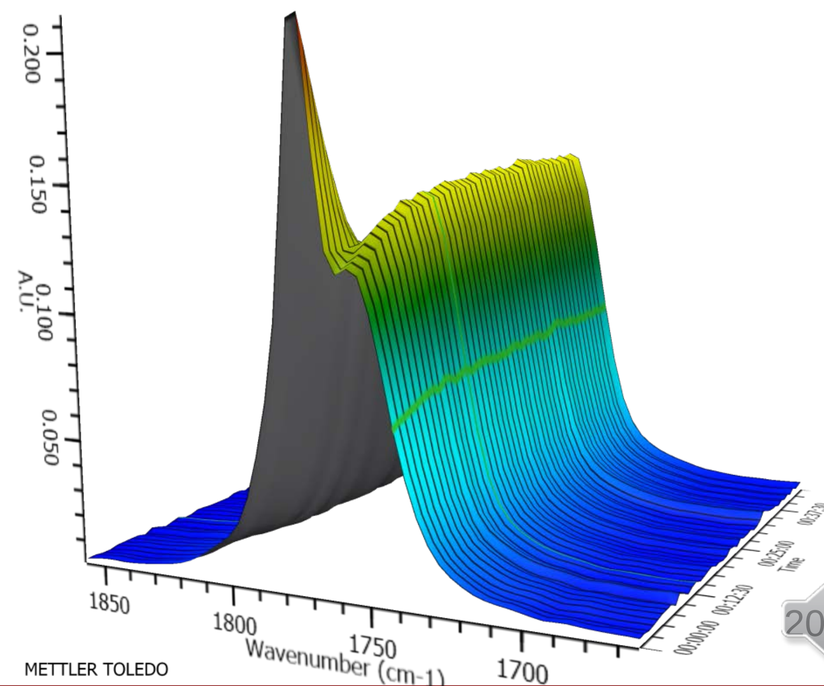
ABA Triblock Polymers

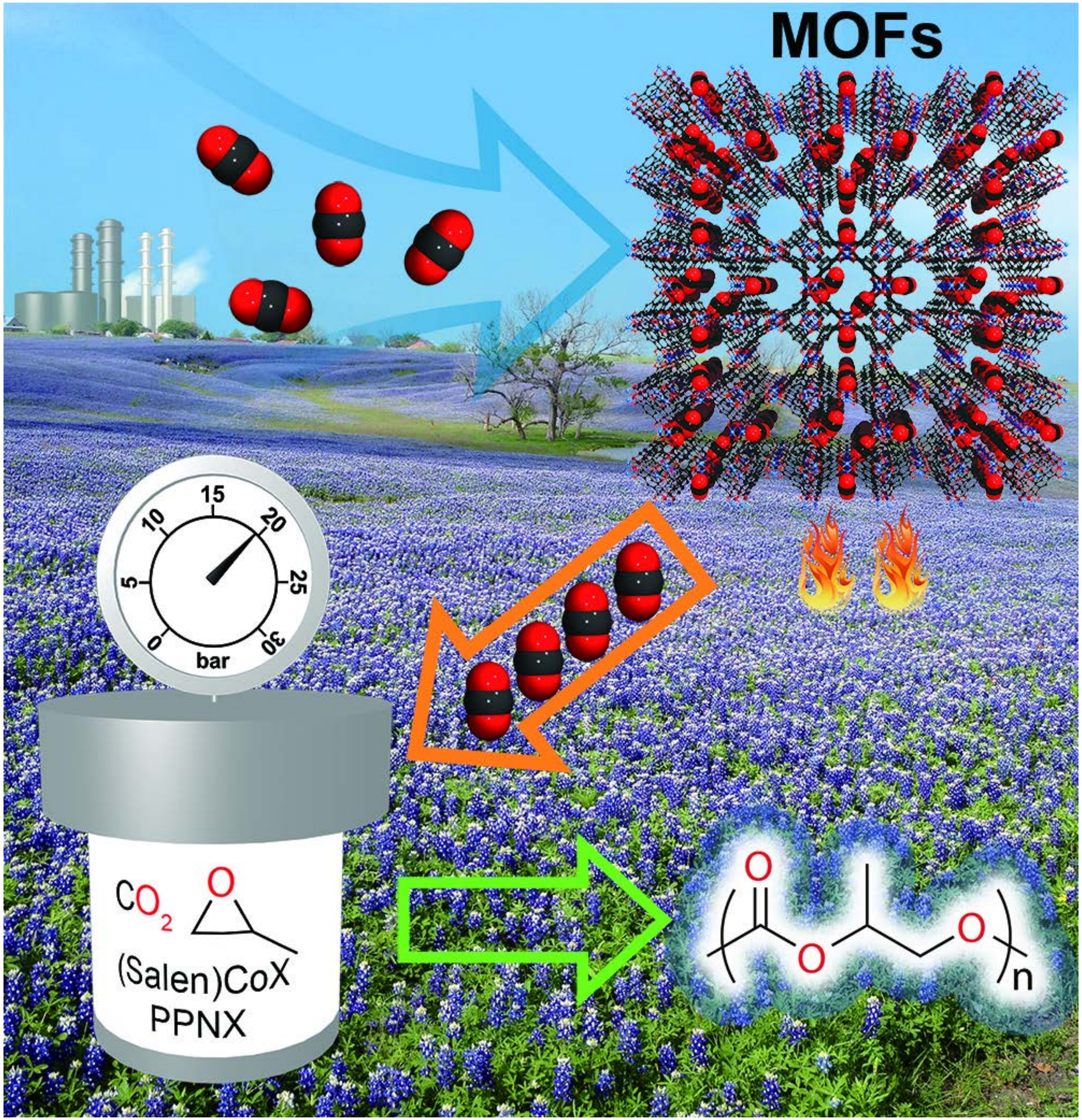


ABA block copolymer









Darensbourg, D. J.; Chung, W.-C.; Wang, K.; Zhou, H.-C. *ACS Catalysis*, **2014**, *4*, 1511–1515.

Acknowledgements

DJD Group Members:

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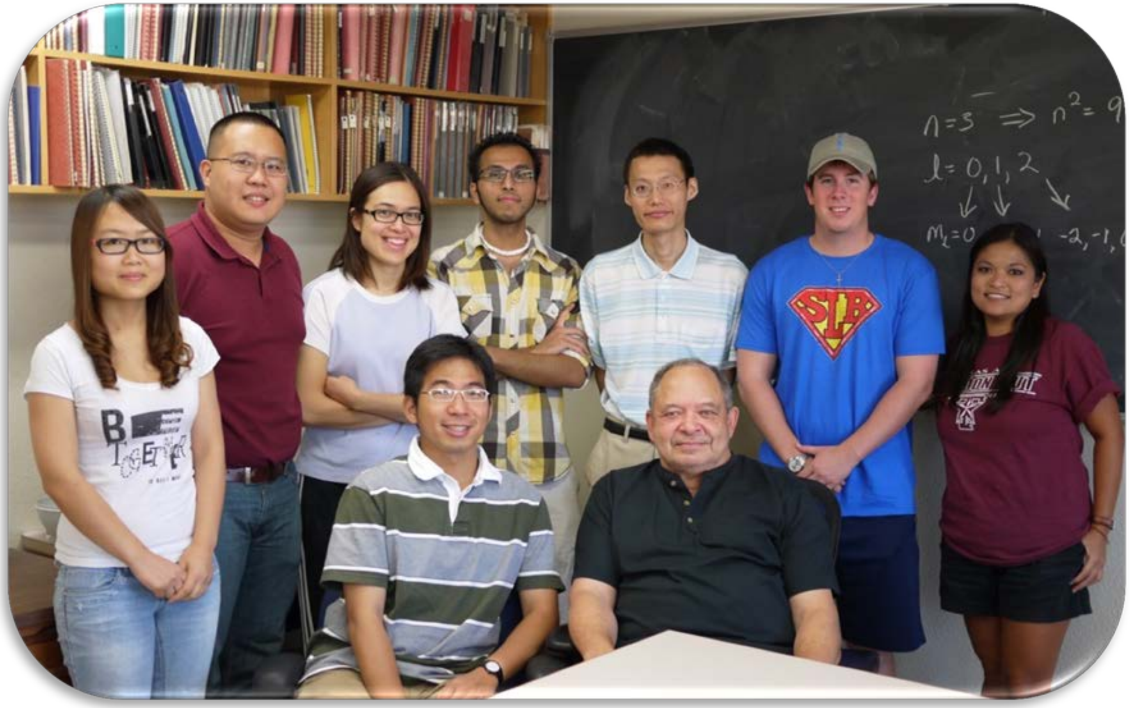
Dr. Guangpeng Wu



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