International Conference and Exhibition on
Biopolymers and Bioplastics
August 10-12,2015 San Francisco, USA

Bioadvantaged thermoplastic elastomers at Iowa State University

Eric W. Cochran
R. Chris Williams Nacu B. Hernandez Mengguo Yan Austin D. Hohmann
Michael J. Forrester

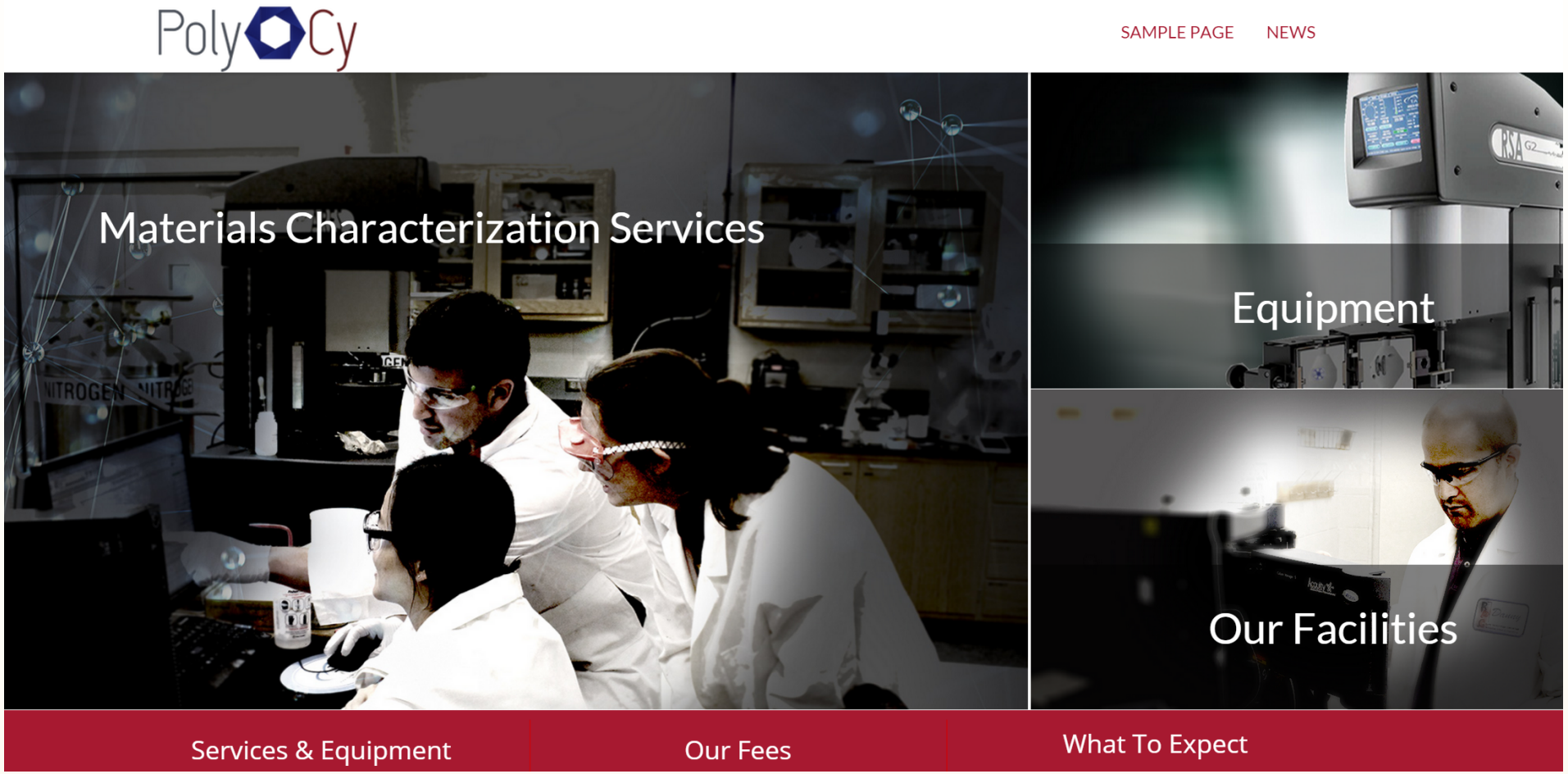
August 10, 2015

Iowa State University
of Science and Technology
Chemical & Biological Engineering

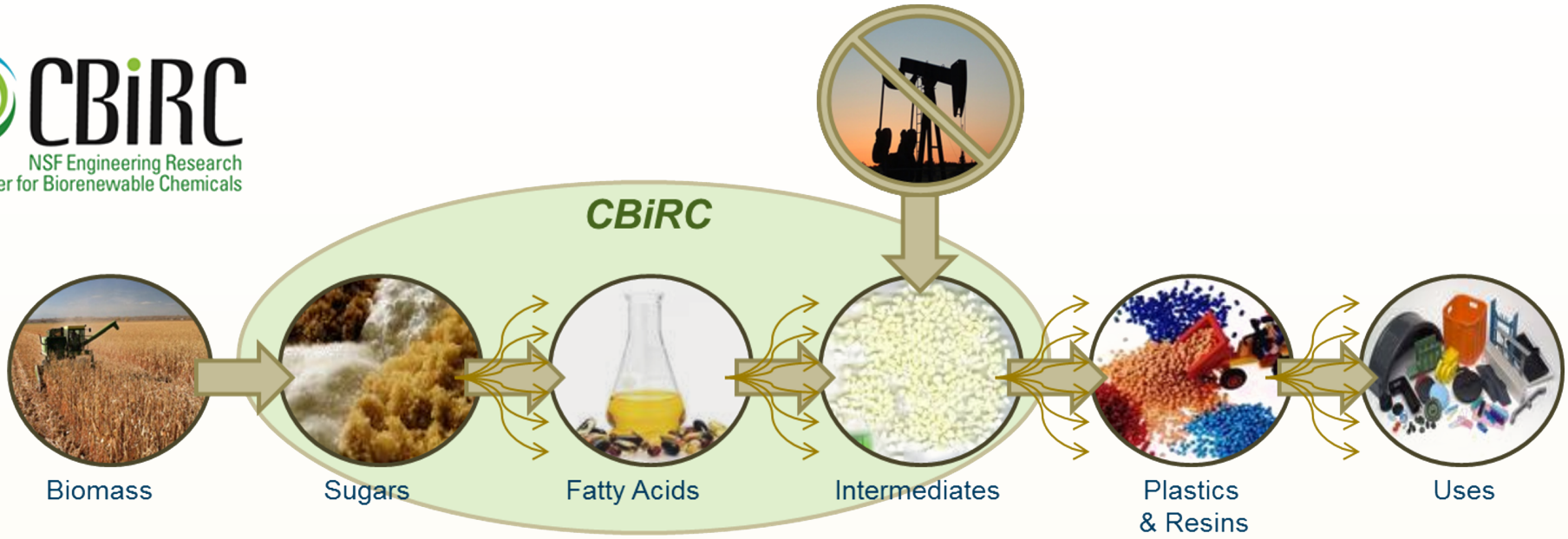
Outline

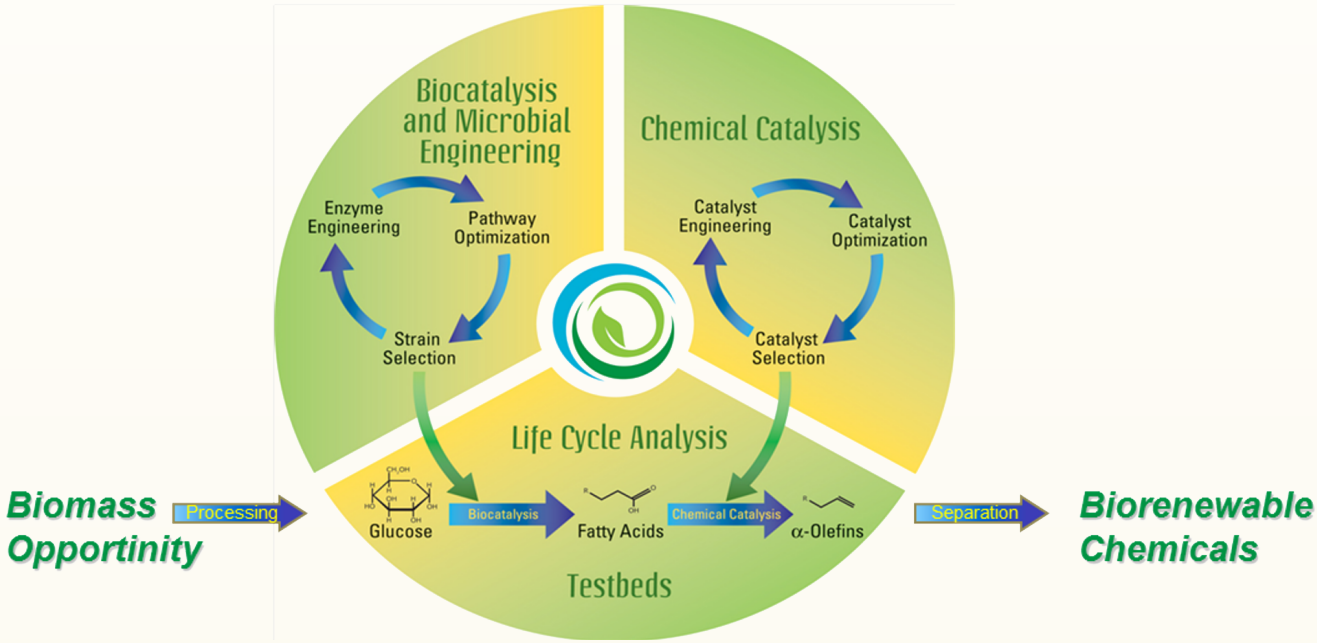
1. About my home institution…
2. The partnership…
3. The problem the technology solves…
4. The Technology…
5. Putting the technology to work…

We offer a full suite of polymer synthesis and characterization services



CBiRC
NSF Engineering Research Center for Biorenewable Chemicals







David Grewell
Professor
Iowa State University
515-294-2036
dgrewell@iastate.edu



Michael Kessler
Berry Family Director & Professor
Washington State University
509-335-8654
michaelr.kessler@wsu.edu

http://www.cb2.iastate.edu

Bio plastics at ISU

Some key players…







Natural Soy Products, LTD



































National Center for Agricultural Utilization Research





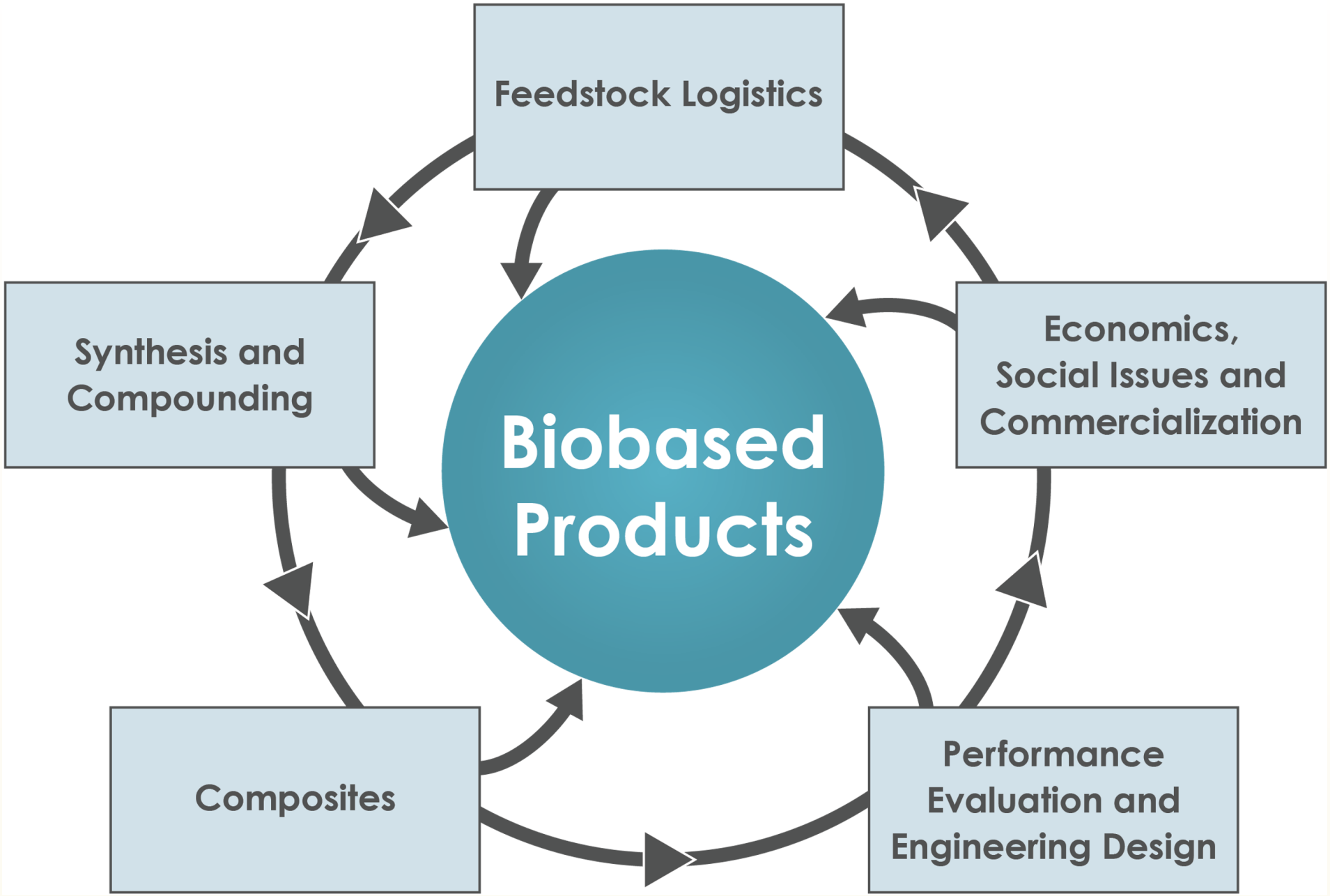


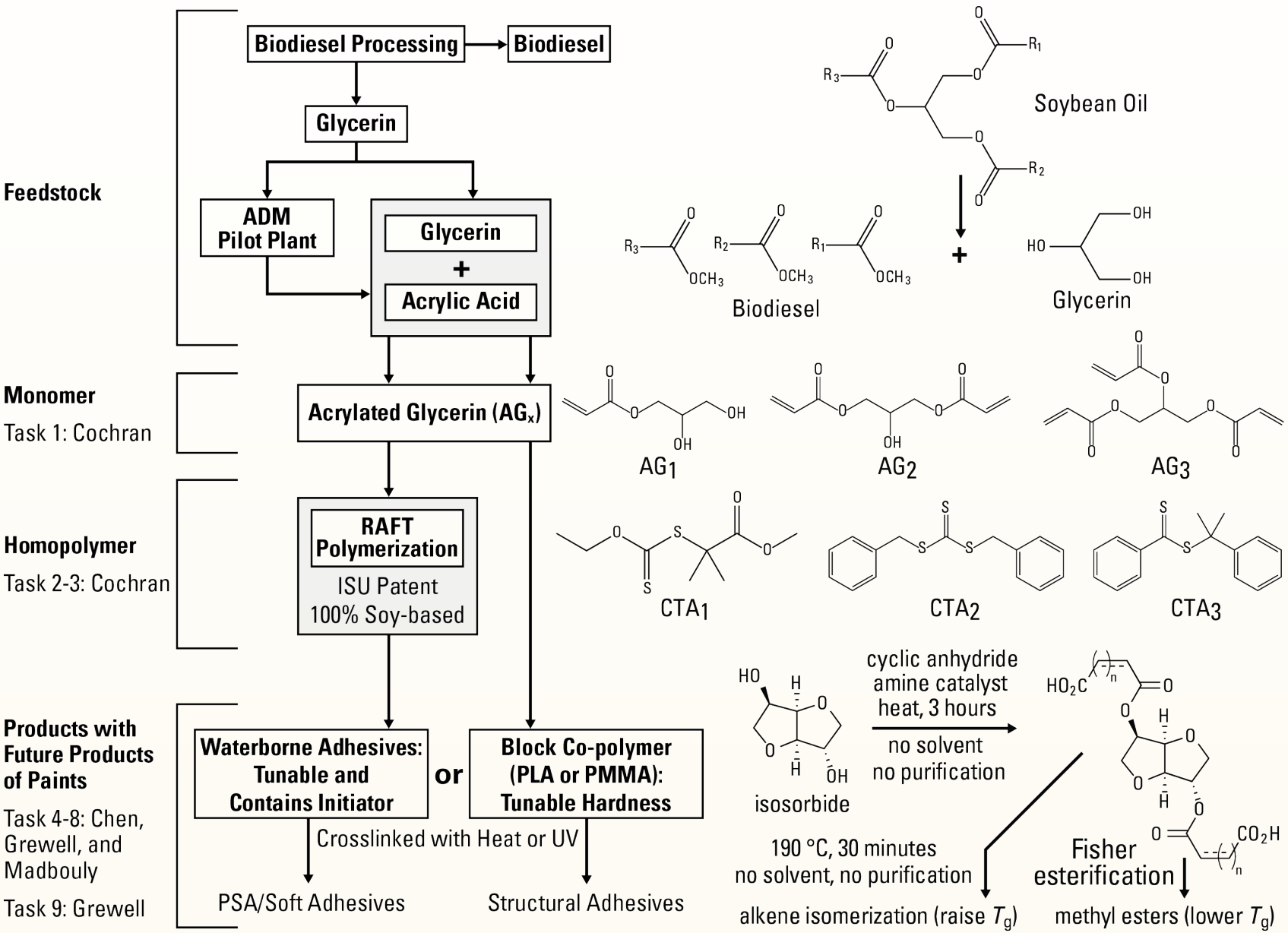









Feedstock Logistics
Economics, Social Issues and Commercialization
Performance Evaluation and Engineering Design
Composites
Synthesis and Compounding
Biobased Products

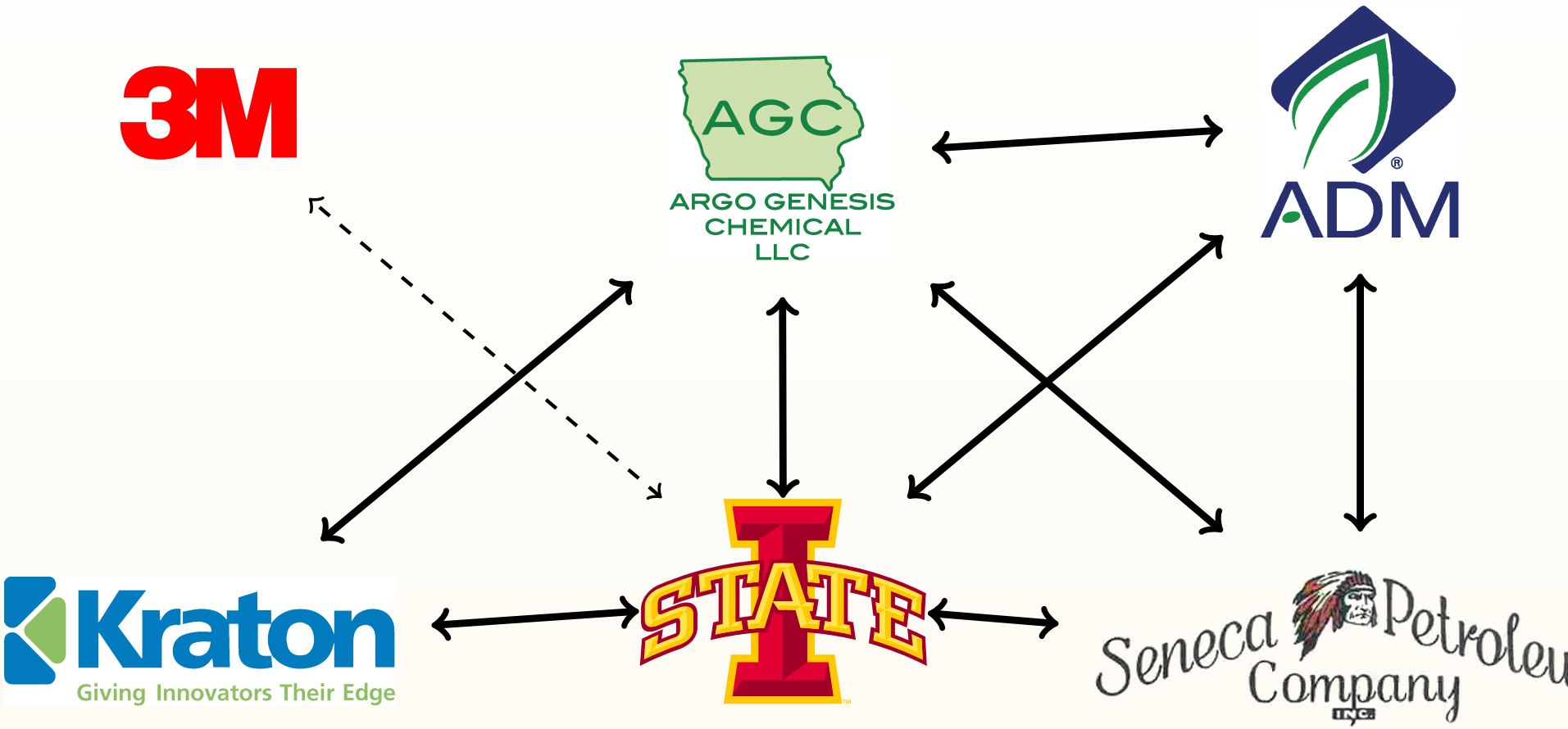

Feedstock
Biodiesel Processing
Biodiesel
Glycerin
ADM Pilot Plant
Glycerin
+
Acrylic Acid
Soybean Oil
Biodiesel
Glycerin
Monomer
Task 1: Cochran
Acrylated Glycerin (AGx)
AG1
AG2
AG3
Homopolymer
Task 2-3: Cochran
RAFT Polymerization
ISU Patent
100% Soy-based
CTA1
CTA2
CTA3
Products with Future Products of Paints
Task 4-8: Chen, Grewell, and Madbouly
Task 9: Grewell
Waterborne Adhesives: Tunable and Contains Initiator
or
Block Co-polymer (PLA or PMMA): Tunable Hardness
Crosslinked with Heat or UV
PSA/Soft Adhesives
Structural Adhesives
isosorbide
cyclic anhydride
amine catalyst
heat, 3 hours
no solvent
no purification
190 °C, 30 minutes
no solvent, no purification
alkene isomerization (raise Tg)
Fisher esterification
methyl esters (lower Tg)

Outline

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4. The Technology…
5. Putting the technology to work…

So how did we get here?
(Putting soybean-oil/glycerine based thermoplastic elastomers to work)




3M
AGC
ARGO GENESIS
CHEMICAL
LLC
ADM
Kraton
Giving Innovators Their Edge
STATE
Seneca Petroleum
Company
INC

Project Team

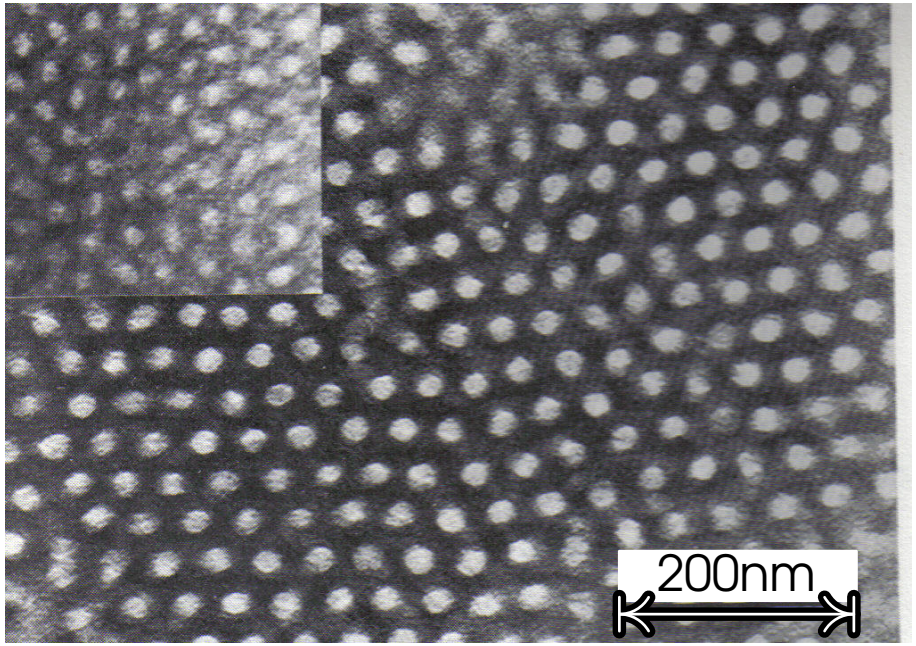


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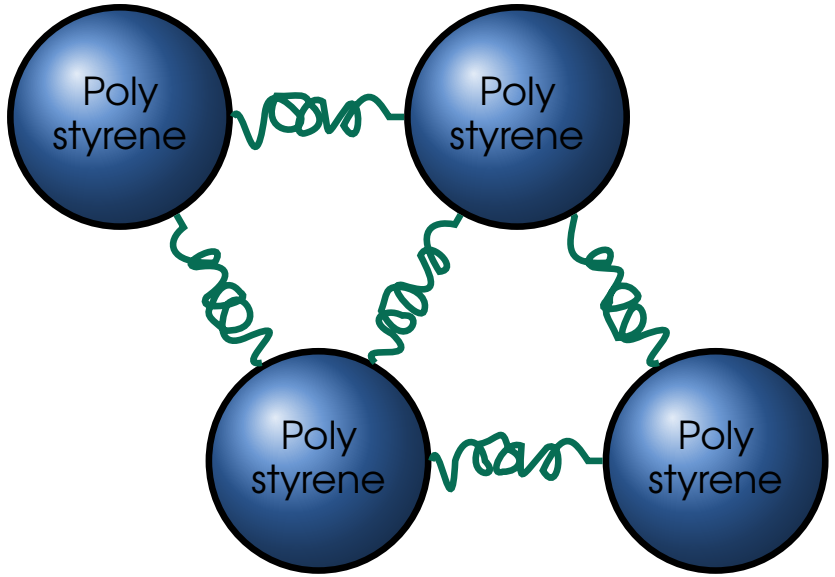
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Thermoplastic elastomers are *ordered* materials…
(a $14 bn industry)

Polymer, 13, 22 (1972)



An SBS (Kraton®) material



Softens at 100 °C

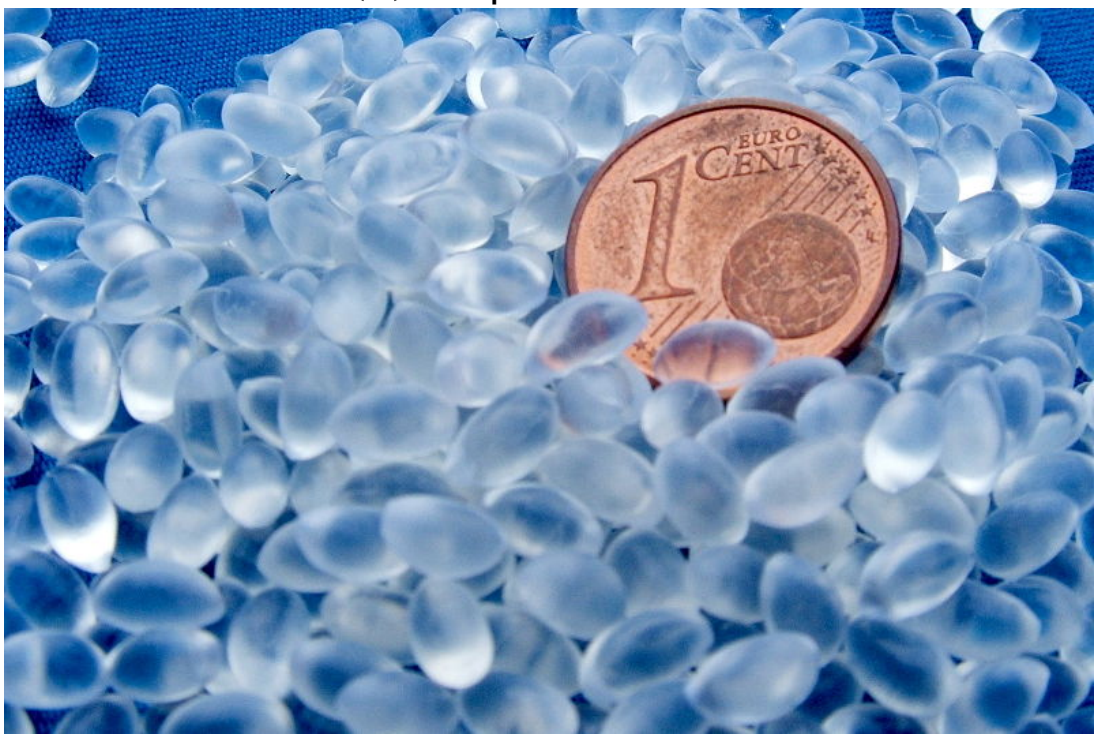




Soft and rubbery

…and can be processed into any shape

(1) Ship as Pellets



(2) Extrude



(3) Mold



Thermosets are processed much differently…

Start with liquid resin



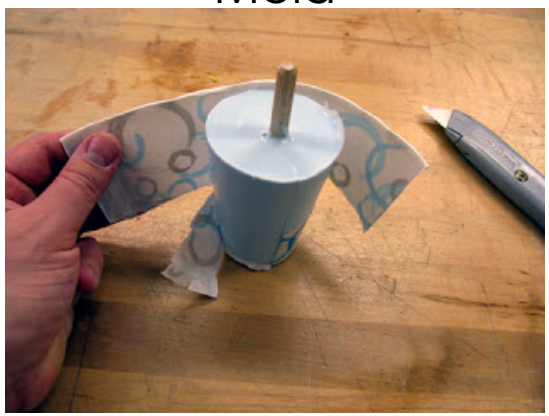
Mix



Cure



Mold



Side effects of shale gas…

A butadiene refinery



Ethylene can be produced from crude oil by *cracking* large oil molecules into smaller pieces.

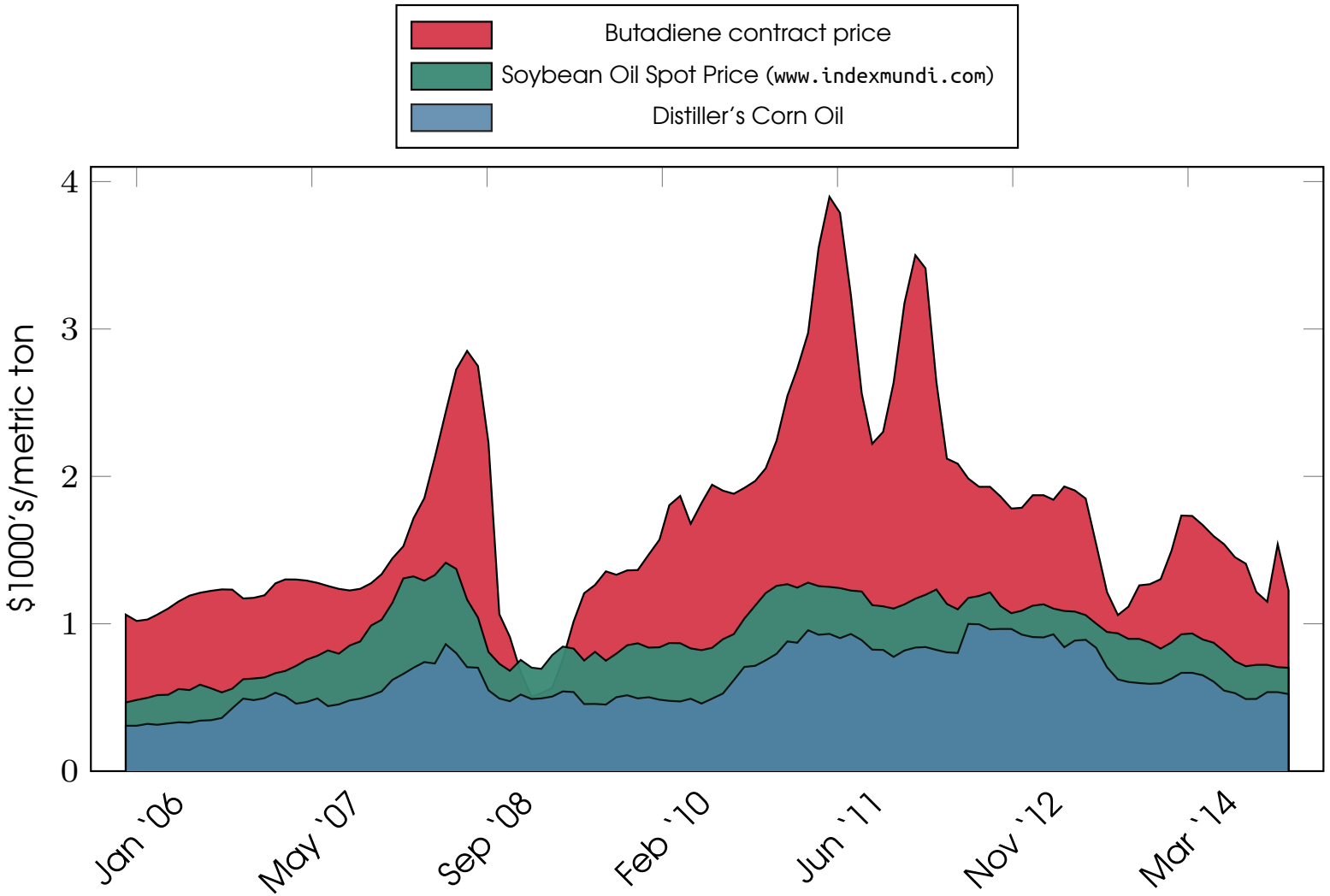
$$CH_2{=}CH_2$$

This is a high-temperature high-pressure catalytic process (high energy consumption)

Butadiene and isoprene are produced as byproducts.

$$CH_2{=}CH{-}CH{=}CH_2$$

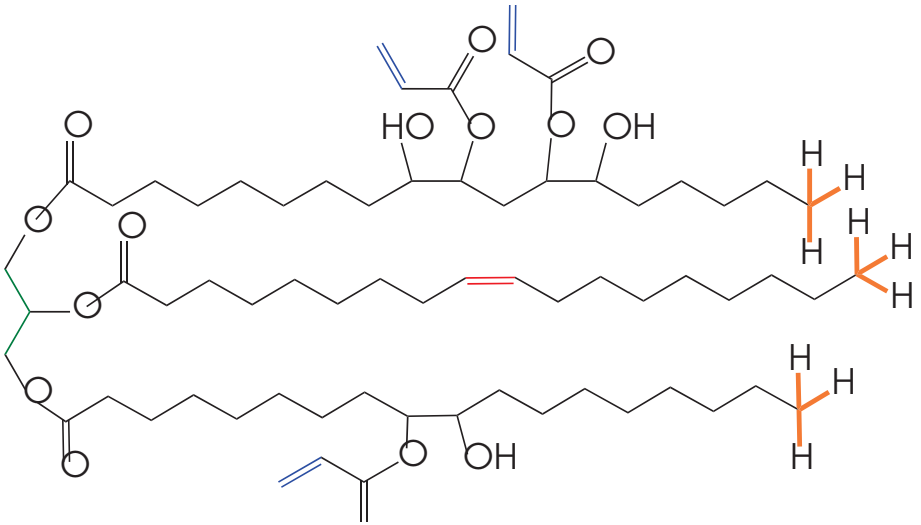
The Economics of Triglycerides



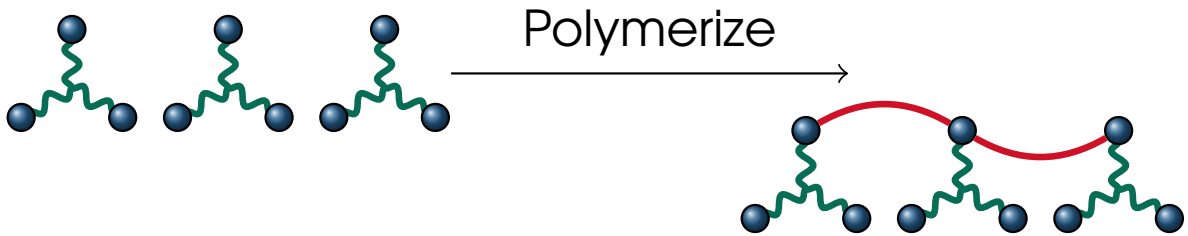
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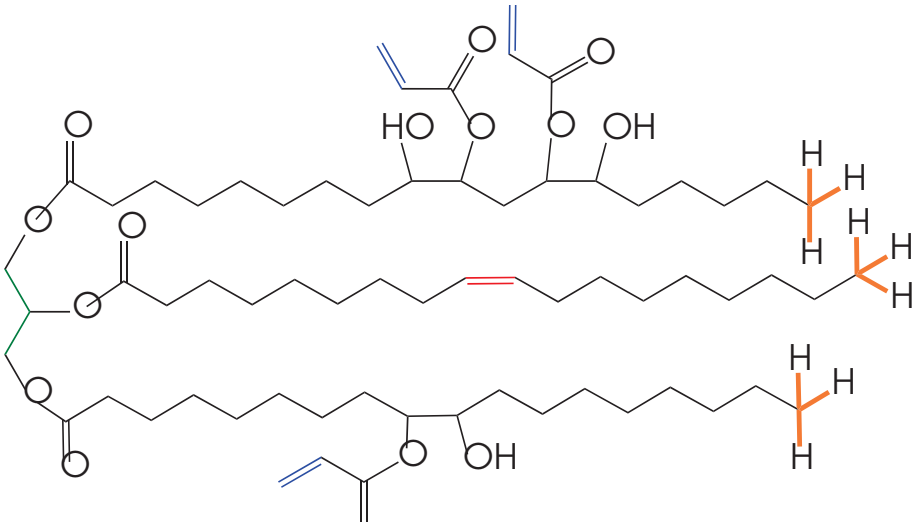
Too much of a good thing…



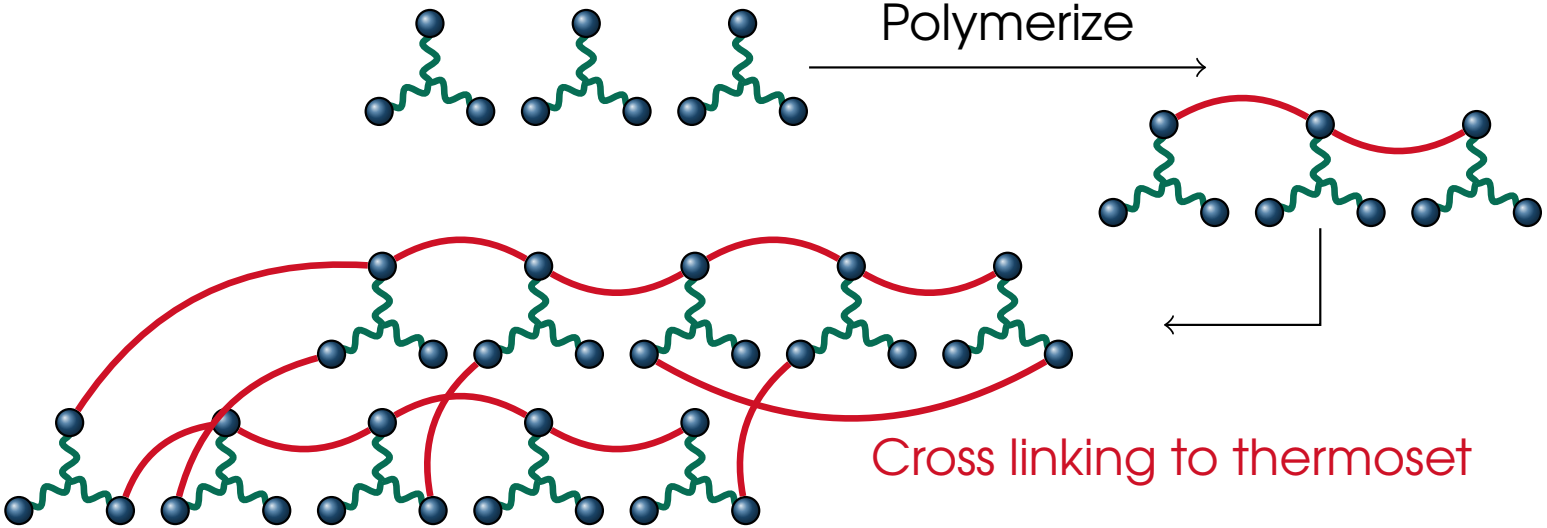
- A typical triglyceride has up to 6 double bonds
- The C=C bonds in natural oils are not reactive enough to polymerize
- The C=C bonds in **A**crylated **E**poxidized **S**oybean **O**il are *very* reactive



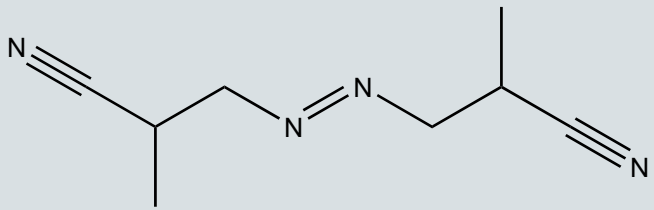
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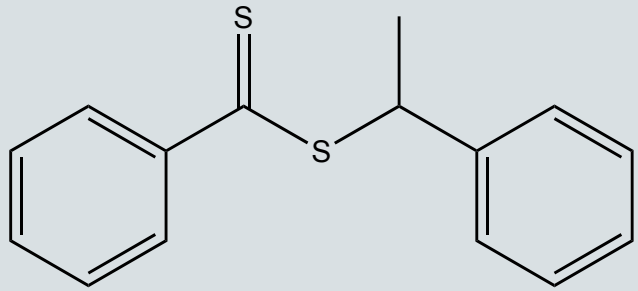
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Key Ingredients (Moad)



azo-*bis*isobutyronitrile



1-phenylethylbenzodithioate

- A small quantity of free radical initiator generates radicals and ititiates polymerization.
- Chain transfer agent (CTA) scavenges the growing radicals to form a stable intermediate
- The intermediate dissociates briefly to allow polymers to add a few units at a time.



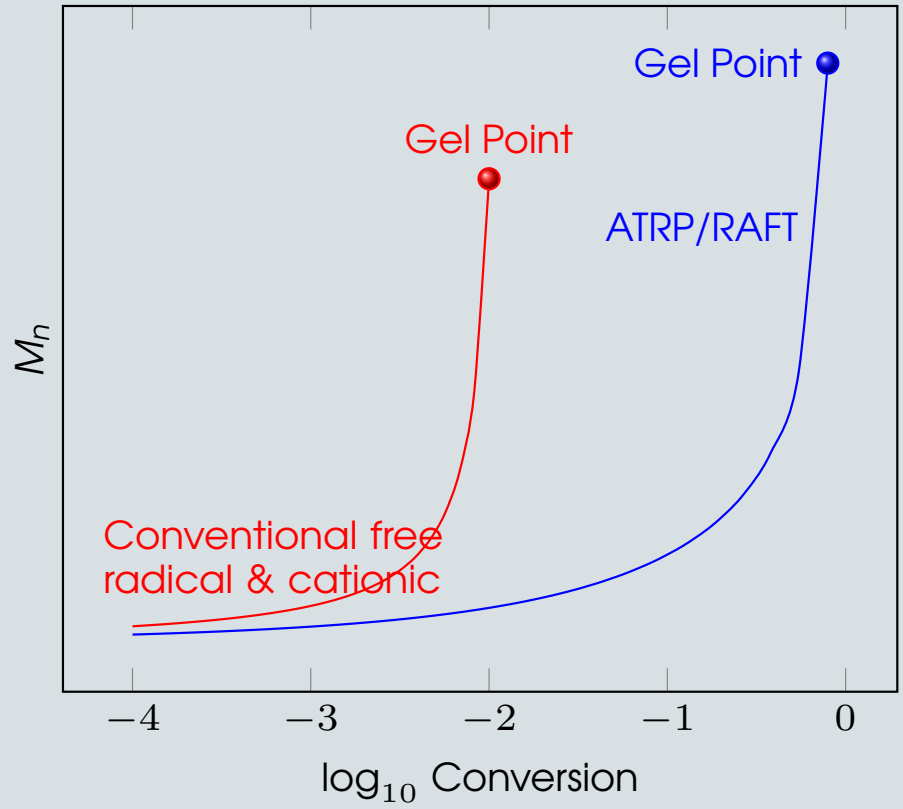
E. W. Cochran, **R. C.** Williams, **N.** Hernandez, and **A.** Cascione, *Thermoplastic elastomers via reversible addition-fragmentation chain transfer polymerization of triglycerides* (2014),

The key difference

Controlled vs. Not

- In a conventional polymerization chain transfer (crosslinking) reactions lead to gelation at low monomer conversion ($< 1\%$)
- With controlled polymerization, we can achieve high molecular weight polymers at 90% conversion and arrest the polymerization prior to gelation.

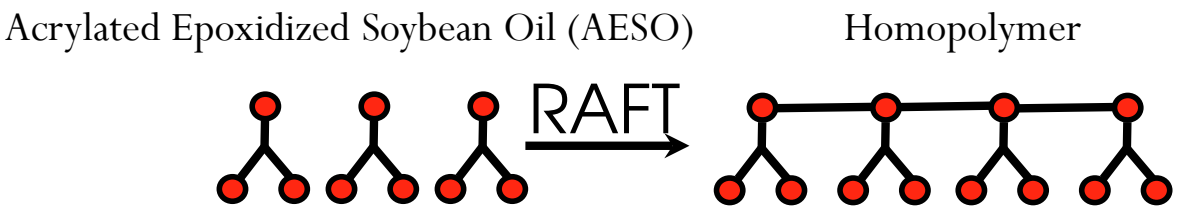
Molecular weight vs. conversion



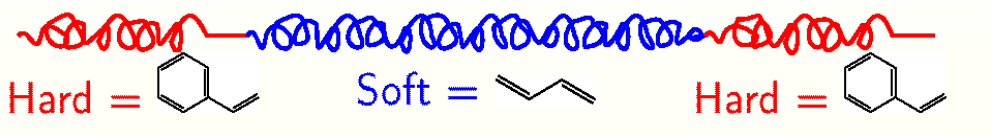
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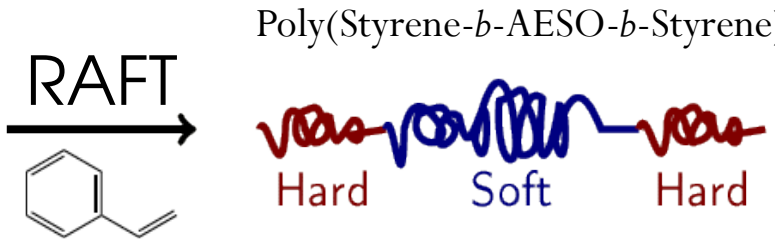
With RAFT/ATRP the path to thermoplastic elastomers is straightforward…in principle



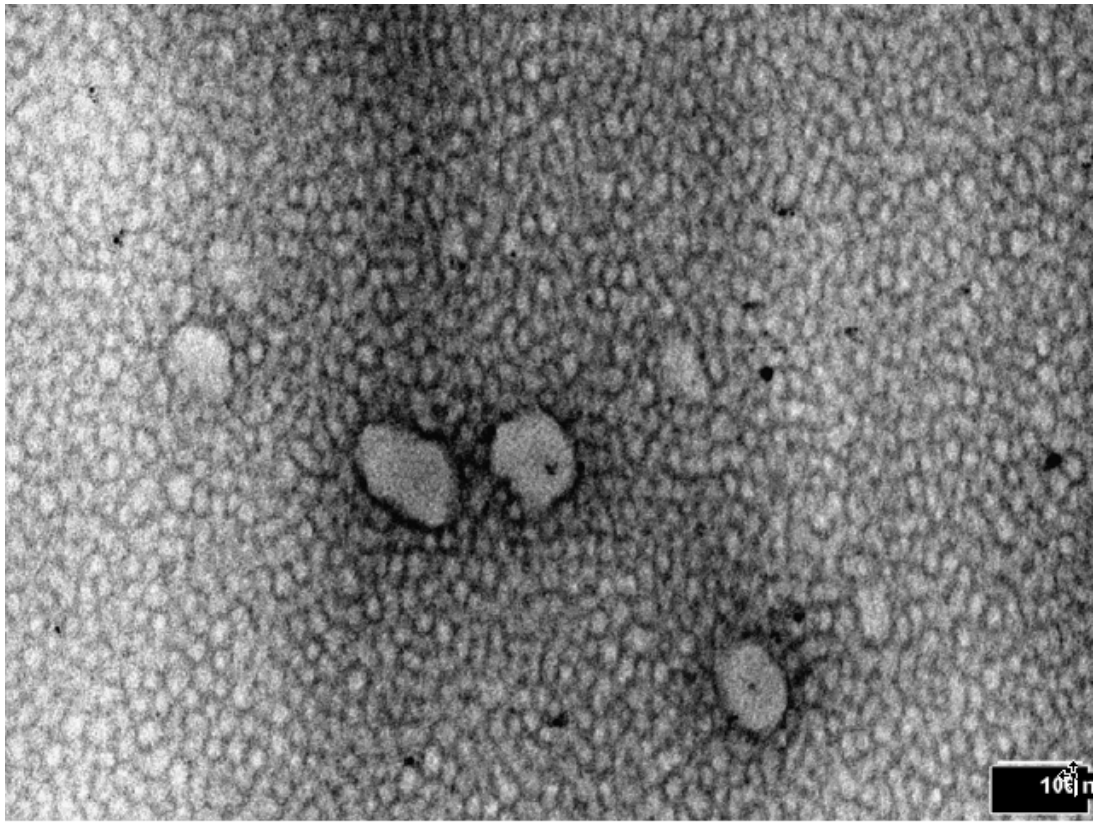
- Formation of elastomeric block copolymers
  - Analogous to, e.g. the PS-polybutadiene-PS (SBS) polymers of the Kraton® family.



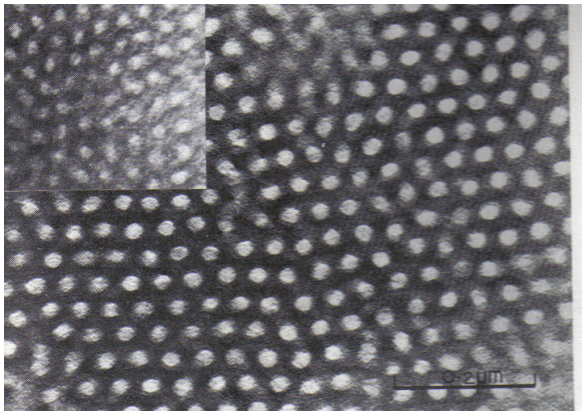


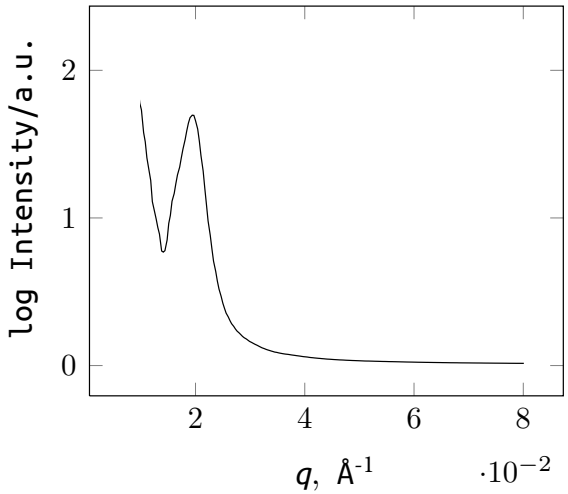


Our elastomers



SBS elastomers



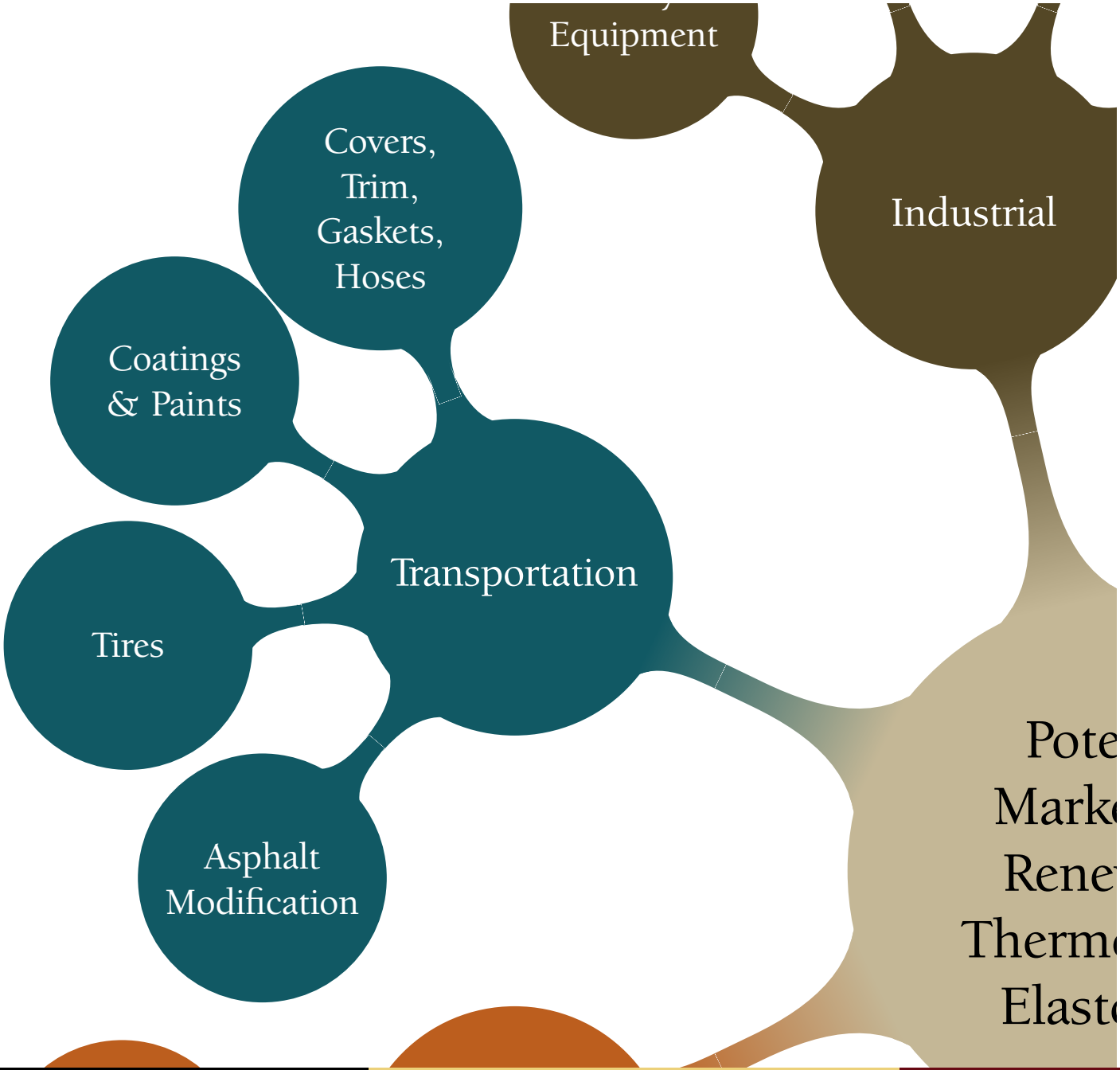


SAXS of Soy-based SBS

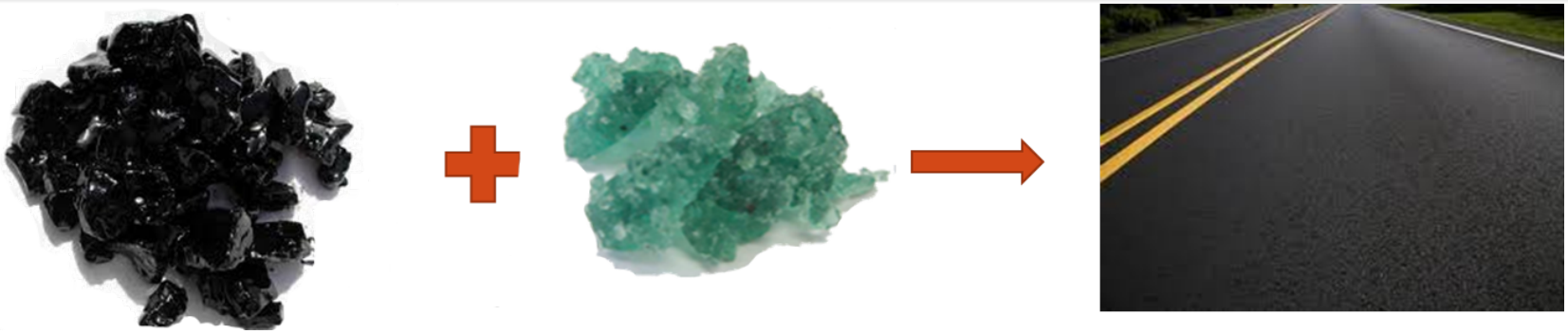
Hundreds of value-added market opportunities

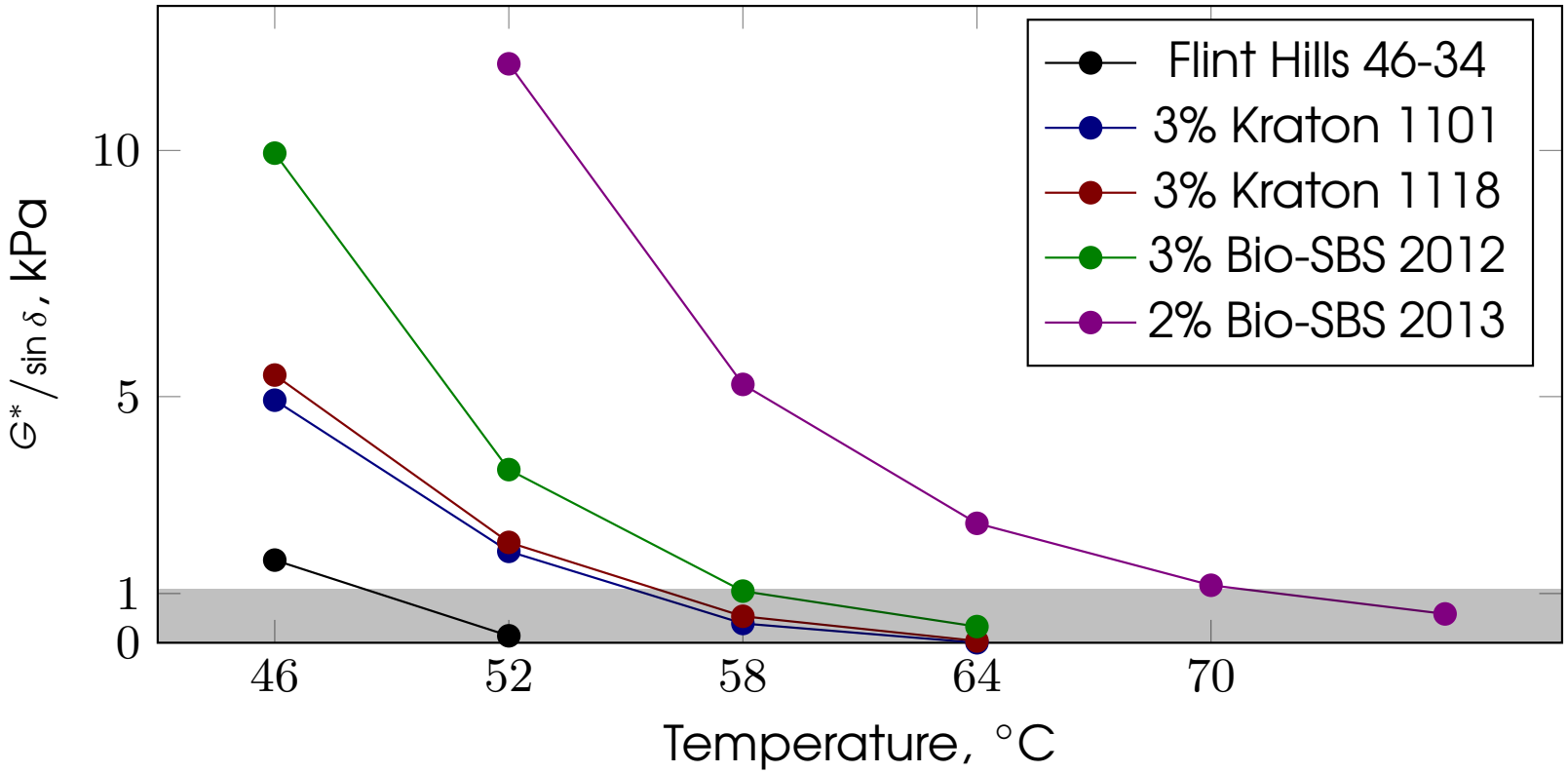


Hundreds of value-added market opportunities



Early promise as asphalt modifier





So is it worth it?
Back-of-the-napkin technoeconomic analysis…

What we're up against

- SBS for asphalt modification is around $1.35/#
- Cost per ton of asphalt is ≈$100–120
- Fully amortized capital in place, process optimized over 30 years

What we have to offer

- Vegetable oil @ $0.37 per pound
- Epoxidation cost @ $0.35 per pound
- Acrylation cost @ $0.07 per pound
- CTA cost @ $0.03 per pound
- Solvent cost (95% recovery) @ $0.08 per pound
- Operating costs @ $ 0.25 per pound (at full scale)
- Capital costs @ $150M for 100,000 kt per year

Raw material + OPEX ≈ $1.15 per pound + CAPEX

(Looks close)

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- Veg
- Epo
- Acr
- CTA
- Solvent cost (95% recovery) @ \$0.00 per pound
- Operating costs @ \$ 0.25 per pound (at full scale)
- Capital costs @ \$150M for 100,000 kt per year

BUT…don't forget the ``bioadvantage''

Enhanced efficacy of PS-PAESO means asphalt modification requires only 50–75% of the polymer.

Economic opportunity.

Raw material + OPEX ≈ \$1.15 per pound + CAPEX

(Looks close)

A solid portfolio of protected IP



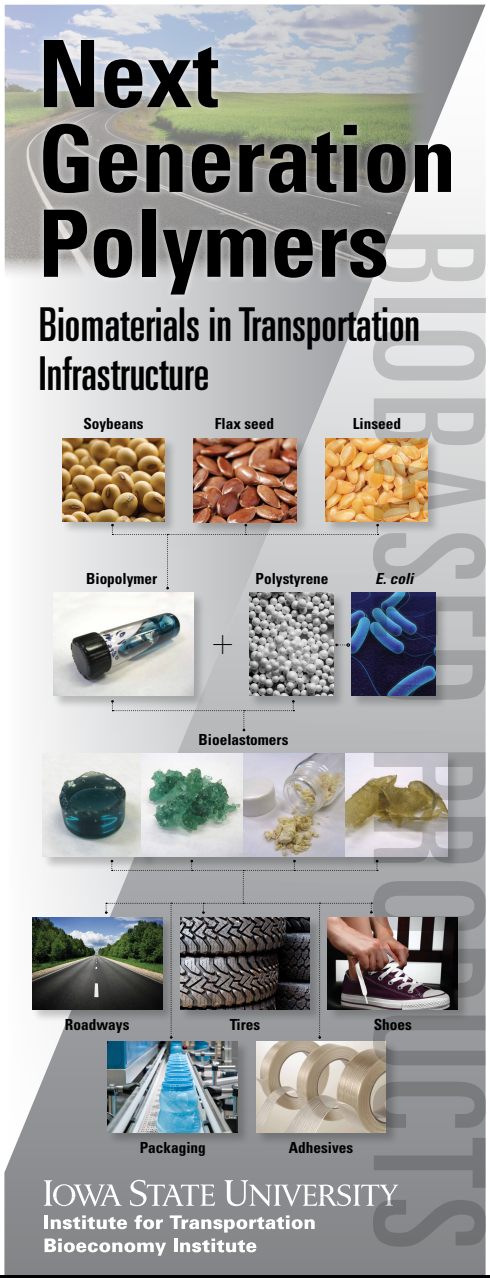
#03949 Thermoplastic Elastomers Via Atom Transfer Radical Polymerization of Plant Oil

#04064 Thermoplastic Elastomers via Reversible Addition-Fragmentation Chain Transfer Polymerization of Triglycerides

#04126 Poly(Acrylated Polyol) and Method For Making and Using Thereof as Asphalt Rubber Modifiers, Fracking Additives or Fracking Fluids.

#04255 Radical Polymerization Macro-Chain Transfer Agents and Initiators from Condensation Polymers

So where how did this partnership evolve?
(and continue to evolve)



A fortuitous relationship built on mutual trust and respect

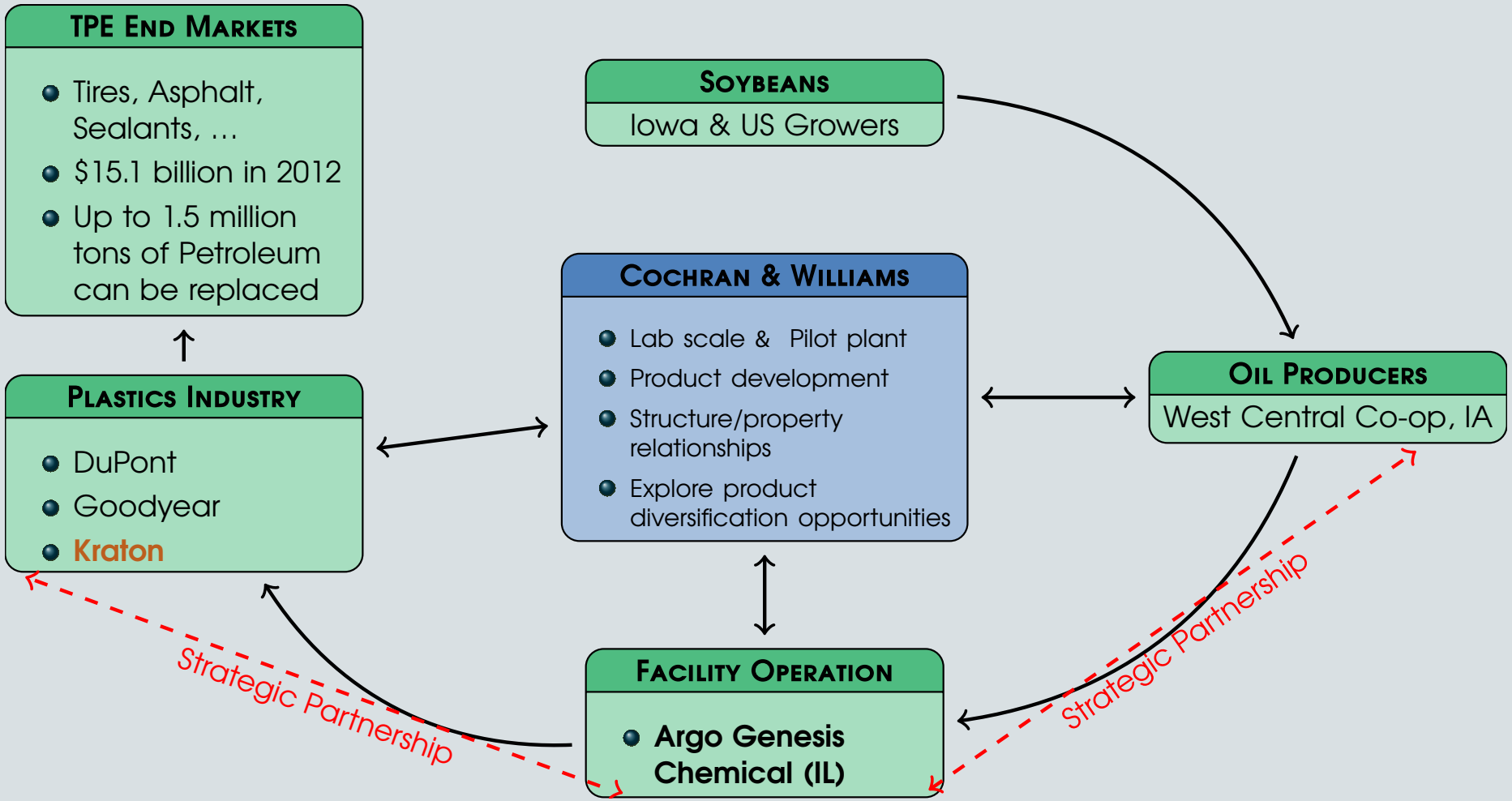


- Years of contract and fee-for-service research
- Leader in asphalt supply to the upper-midwest
- A privately held company with a history of forward thinking and strategic investing
- A shared vision → early licensing

Seneca Petroleum Company INC.

So where how did this partnership evolve?
(and continue to evolve)

Plans that evolve over time.



So where how did this partnership evolve?
(and continue to evolve)

Leverage amplifies the investment and distributes the risk.




THANK YOU!