The New England Green Chemistry Consortium

Shaw Ling Hsu, Tom McCarthy, Alan Lesser & Todd Emrick

May 31 2006

Green materials and processes, bio-based materials, polymer-wood composites, supercritical carbon dioxide, water purification – polymer membranes

Green Chemistry Efforts at UMass Amherst

***Shaw Ling Hsu*: reduction of aromatic isocyanates in polyurethanes; increased use of biodegradable polymers in everyday materials; spectroscopic characterization and impact on morphology**

***Tom McCarthy*: use of supercritical CO_2 to prepare composite materials; synthetic chemistry for surface modification; polymer-wood composites**

***Alan Lesser*: preparation and mechanical characterization of composite materials using supercritical CO_2; understanding the impact of small molecule, nanoparticulate and polymeric additives to polymers over a variety of length scales.**

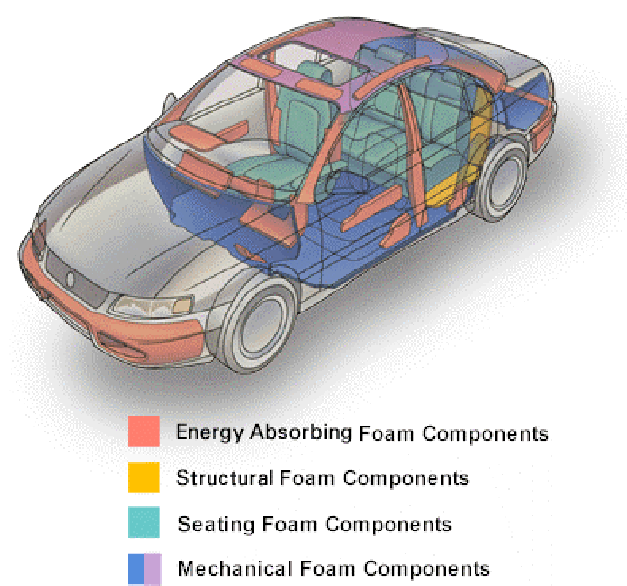
***Todd Emrick*: synthetic organic/polymer chemistry; polymer membranes for water purification; non-halogenated anti-flammable polymers; solar cells**

Beijing Olympics 2008
100% of food containers will be made from biodegradable polymers

Polyurethane applications

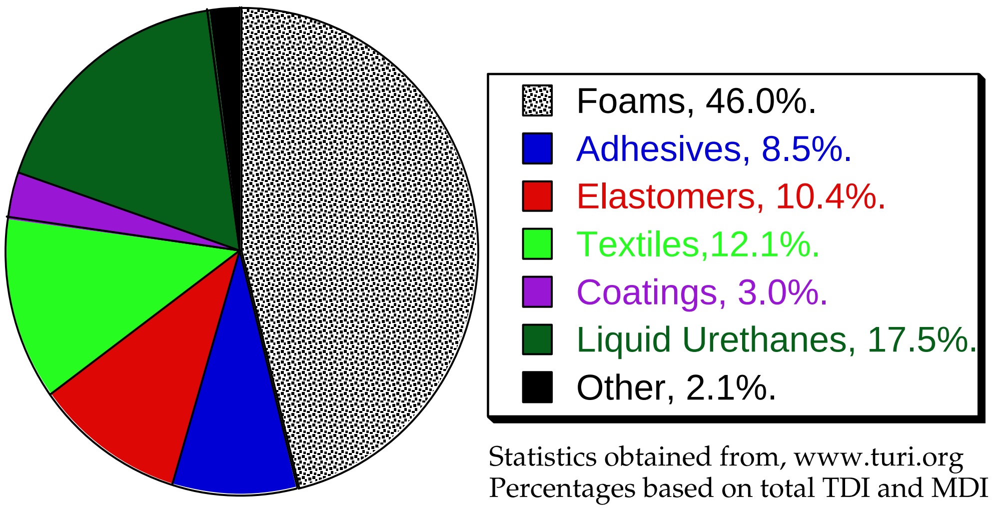
Typical Foam Formulation:

37% Aromatic diisocyanate
60% Polyether soft segments
3% Water, surfactants, other additives

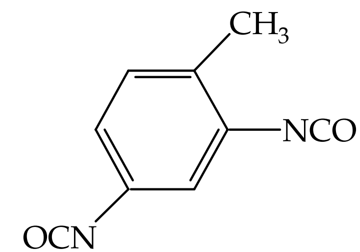


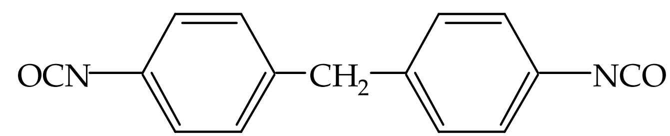
Aromatic Diisocyanates

Isocyanate Useage in Massacusetts (1998)



Statistics obtained from, www.turi.org
Percentages based on total TDI and MDI usage reported in 1998.





2 billion pounds of isocyanates were used in the US production of polyurethanes in 1996

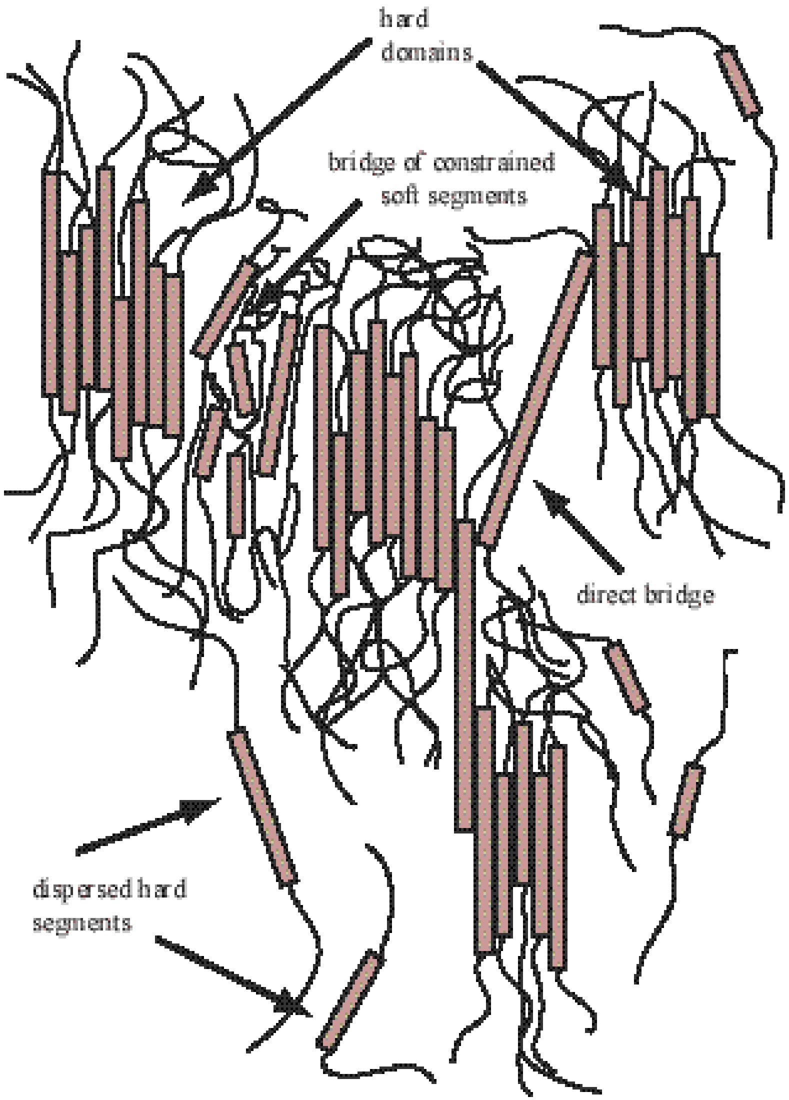
Toxicological effects of aromatic diisocyanates:

- sensitizer: respiratory, gastrointestinal, and central nervous system
- long term effects: asthma, memory loss, or genetic changes
- possible carcinogen

Exposure can occur in:

- those who work with formulations containing isocyanates
- the public through residual amounts left unreacted in the products
- environment through release to the air and to landfills

Polyurethane Foams: Isocyanates Provide Interconnected Morphology



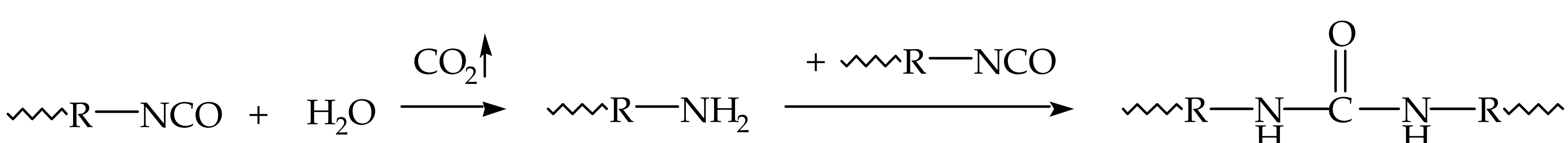
Isocyanates Provide Interconnected Morphology

Increasing the isocyanate index gives higher modulus

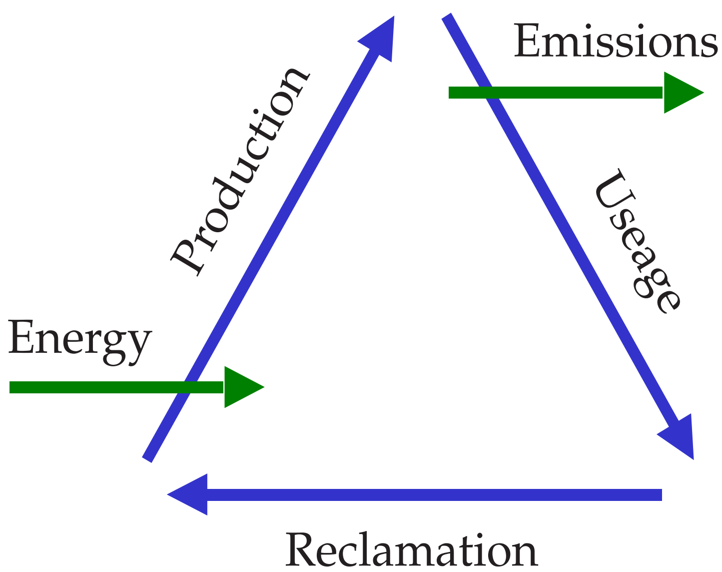
Relationship between competing factors

- polymerization of hard segments
- phase separation
- chemical crosslinking

Interconnected morphology is one of the most important factors in determining mechanical properties



Approach to Reducing Aromatic Isocyanates



Consider whole life cycle

- reduce isocyanate needed initially
- reduce unreacted isocyanate
- reclaim used isocyanate

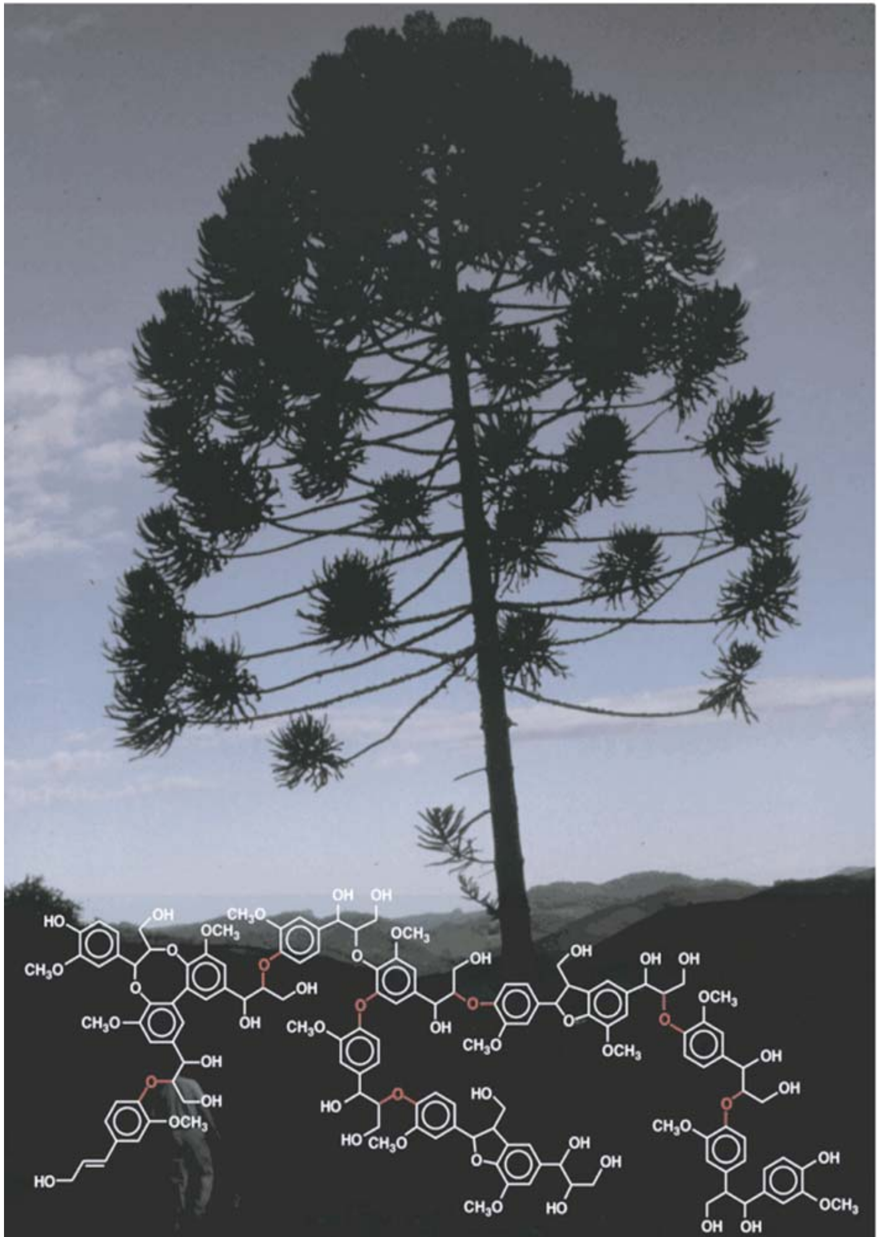
Approach

- Improve miscibility between reactants and water
- Add reinforcements
- Learn relationship between processing variables, chemistry, and morphology

Incorporate bio-based additives

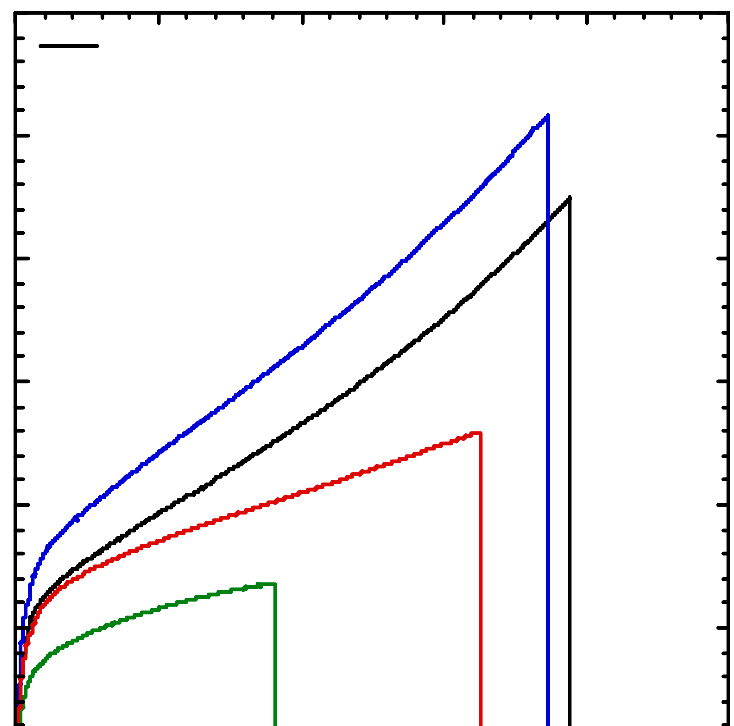
- lignin - one of the most abundant natural polymer after cellulose.
- polyesters - renewable feedstock; biodegradable.

Lignin-reinforced polyurethanes



	Modulus (MPa)	Tensile Strength At 100% Strain (MPa)	Elongation (%)
6-50 Sample	108	9.7	388
6-50, 5% Hwdlgn Direct Mix	65	5.8	182
6-50, 5% Hwdlgn Heat **Covalently integrated lignin**	160	12.1	373

Critical issue: dispersion of the lignin in the formulation

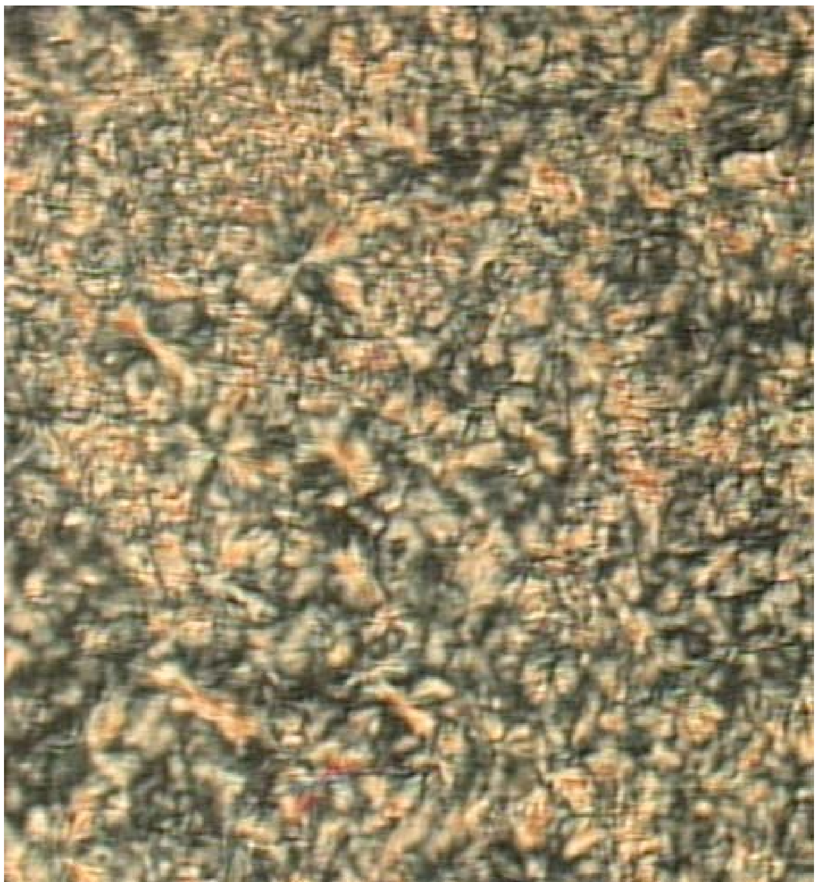


Polyester Reinforced Polyurethanes

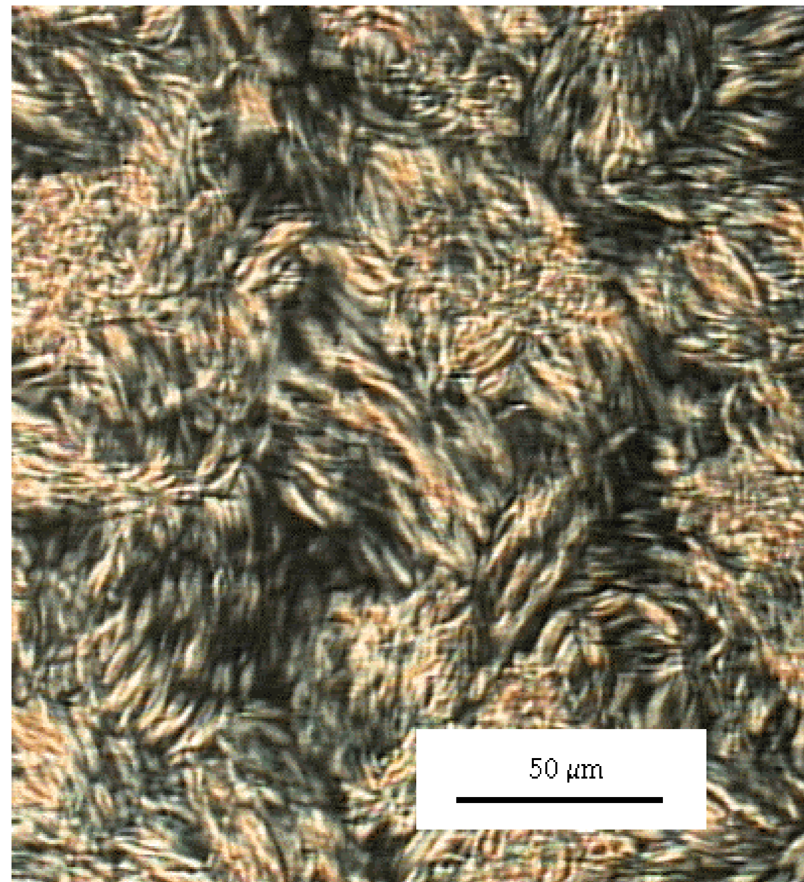
Incorporating 10 weight percent or less of a crystallizable polyol enhances the modulus of foams

Hysteresis may be attributed to phase separation of the polyester

10 weight percent poly(hexamethylene sebacate) in Voranol Polyether



quenched rapidly to 25 °C



isothermally crystallized at 50 °C

High value applications

Current technology

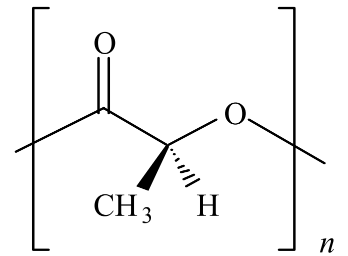
- Metallic stents coated with polymer/drug formulation
- Drug to be delivered at 37 °C (body temperature) and pH 7.4

Problems

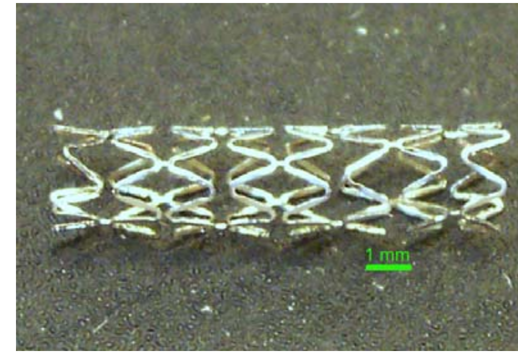
- Lack of control over release
- Stent removal difficult

Solutions

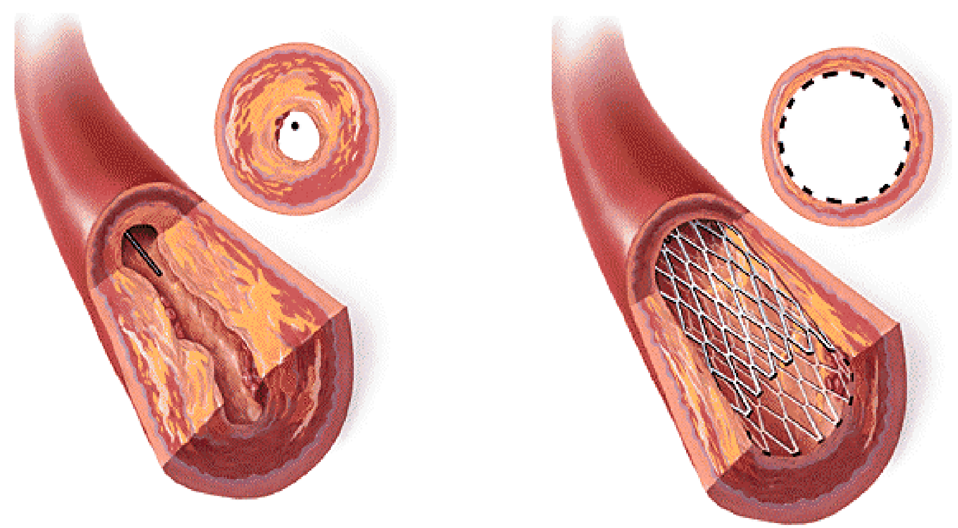
- Many problems are materials, not physiology, based
- Biomass-based stents are needed (low volume, high value)
- New polymer/drug formulations are needed



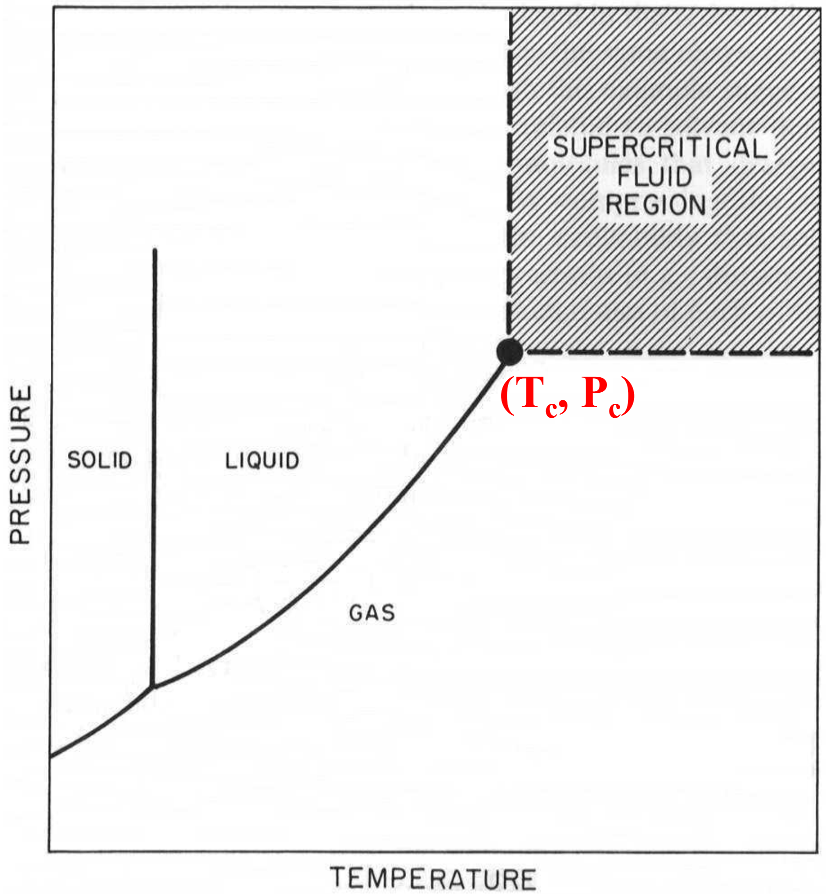
Poly(L-lactic acid)



Drug-Releasing Cardiovascular Stent



Carbon dioxide



Green aspects of SC CO_2

- Non-toxic, non-flammable, readily available, inexpensive, environmentally benign

CO_2

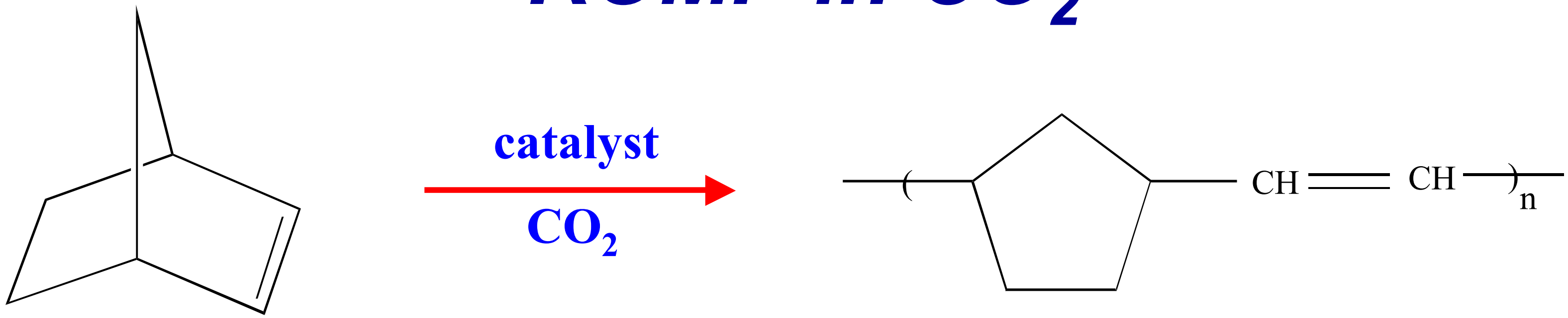
T_c = 31.1 °C

P_c = 73.8 bar

Advantages of SC Carbon Dioxide for Composites

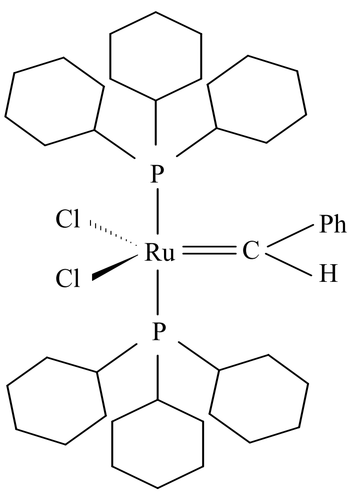
- **For semicrystalline polymers, CO_2 only swells amorphous phase.**
- **Many small organic molecules (i.e., catalysts!) are soluble in CO_2.**
- **Most polymers are insoluble in CO_2:**
  Swell amorphous phase w/o dissolving the polymer
- **CO_2 diffusivity in polymers is high.**
- **Post-treatment, by degassing, is clean and easy.**

ROMP in CO_2

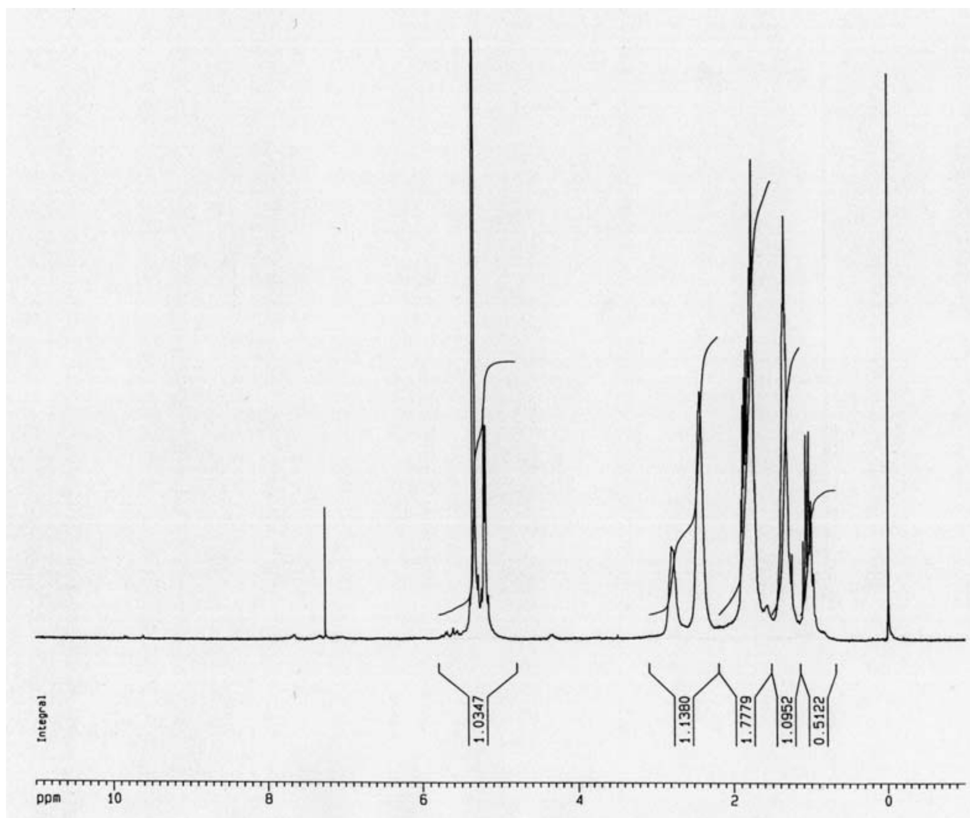


norbornene

polynorbornene (PN)



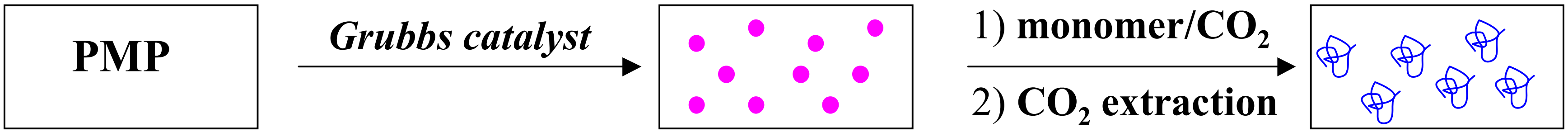
Grubbs' catalyst



ROMP in CO_2
- Mw ~ 4M
- PDI = 3.0
- cis = 30%
- yield ~ 90%

ROMP in CH_2Cl_2
- Mw = 178K
- PDI = 2.6
- cis = 21%
- yield ~ 80%

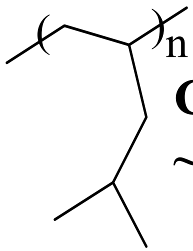
Reaction scheme



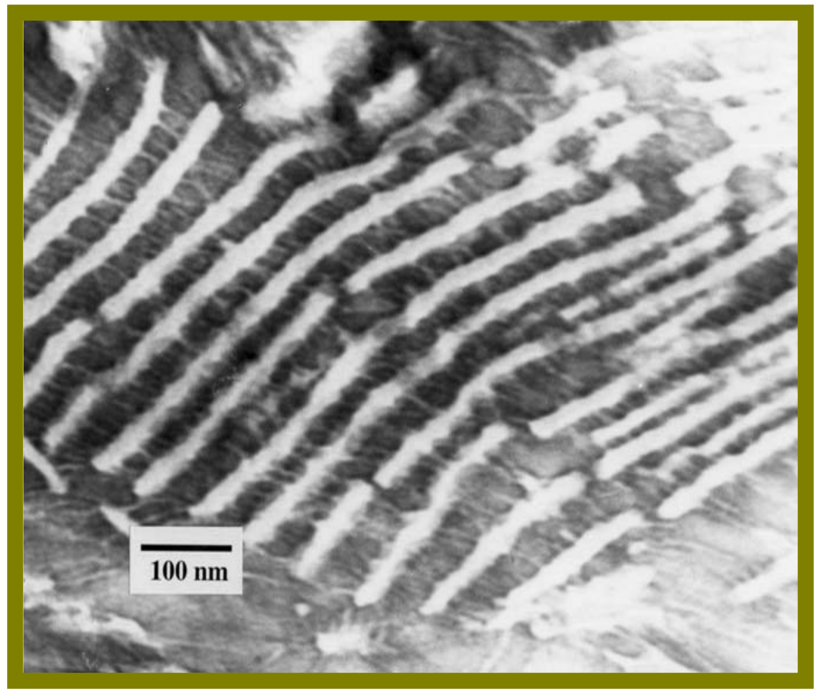
poly(4-methyl-1-pentene) (PMP)

Polymer blends

(& nanocomposites)



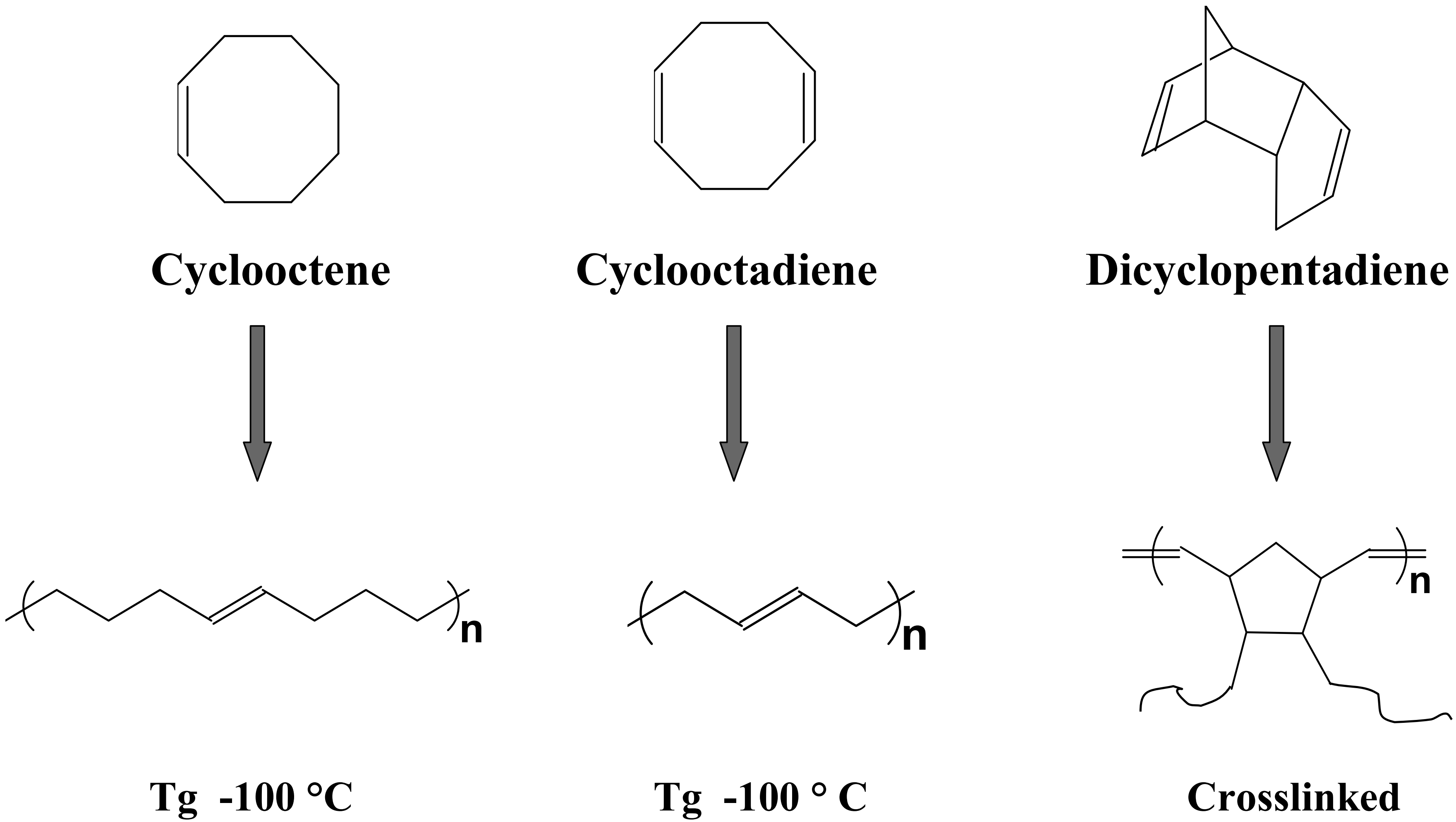
Crystallinity ~70 % (DSC)



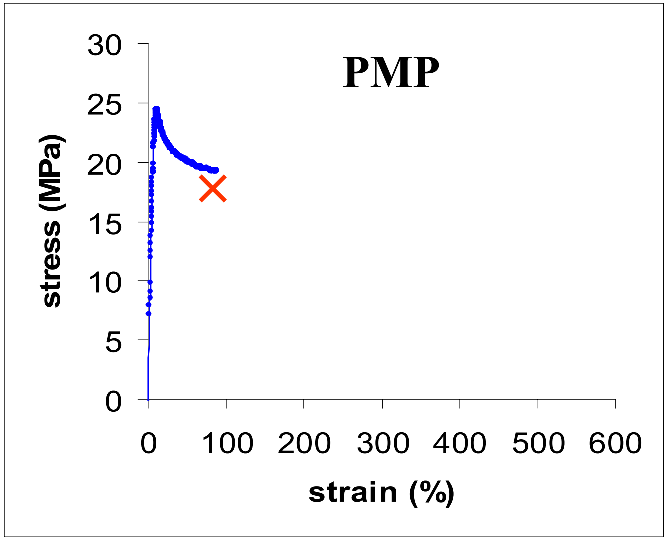
Microtomed

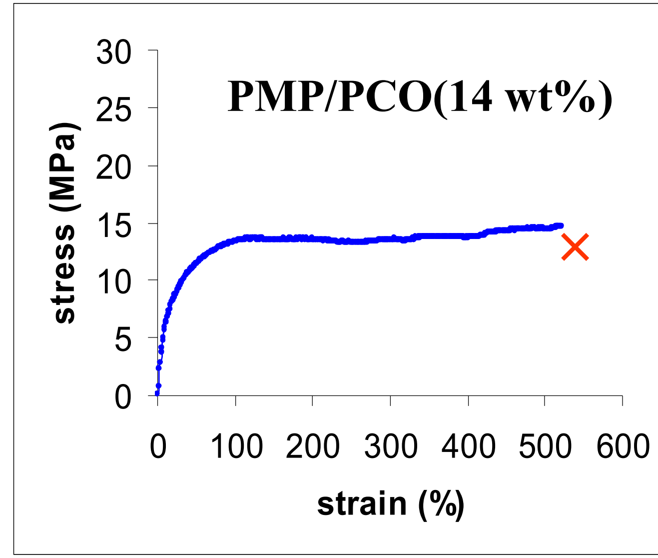
Stained with osmium tetroxide

Many monomers applicable to ROMP/composite formation

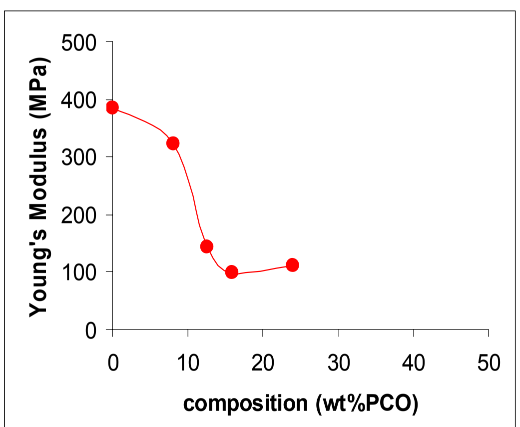


PMP/PCO composites

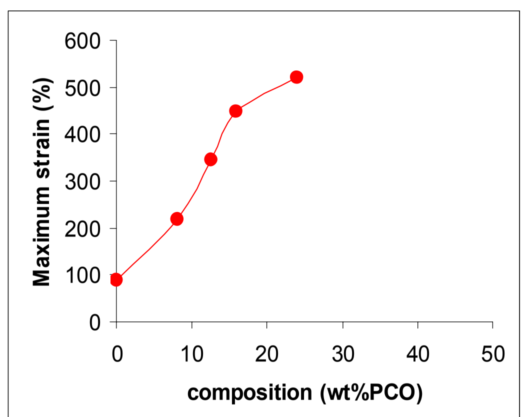




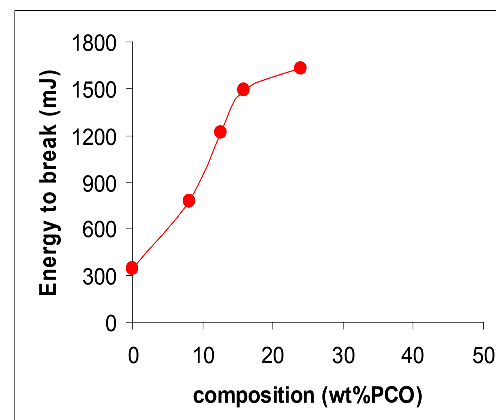
Tensile modulus (E):



Maximum strain (λ):

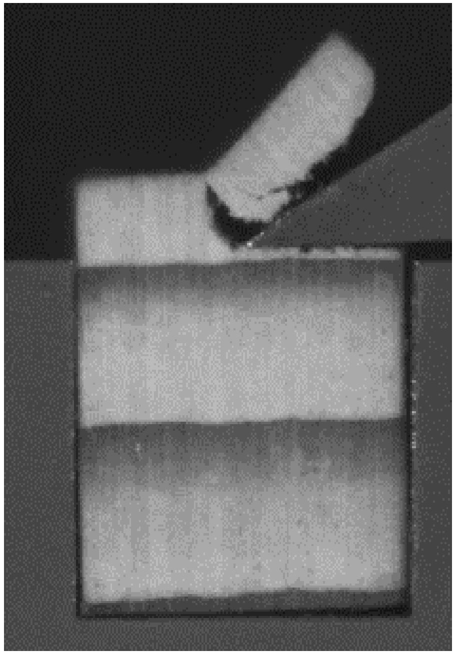


Energy to break (En):



SC CO_2 to make Polymer-wood composites

Tom McCarthy & Scott Eastman

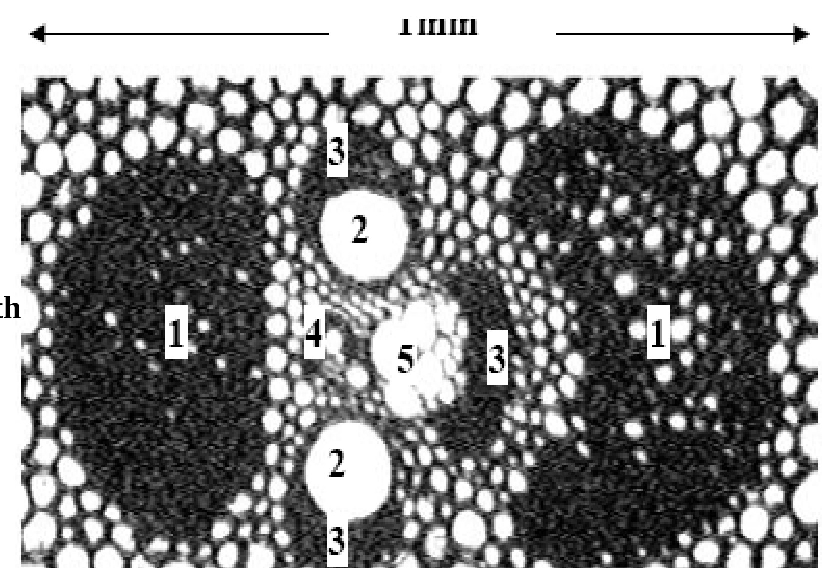


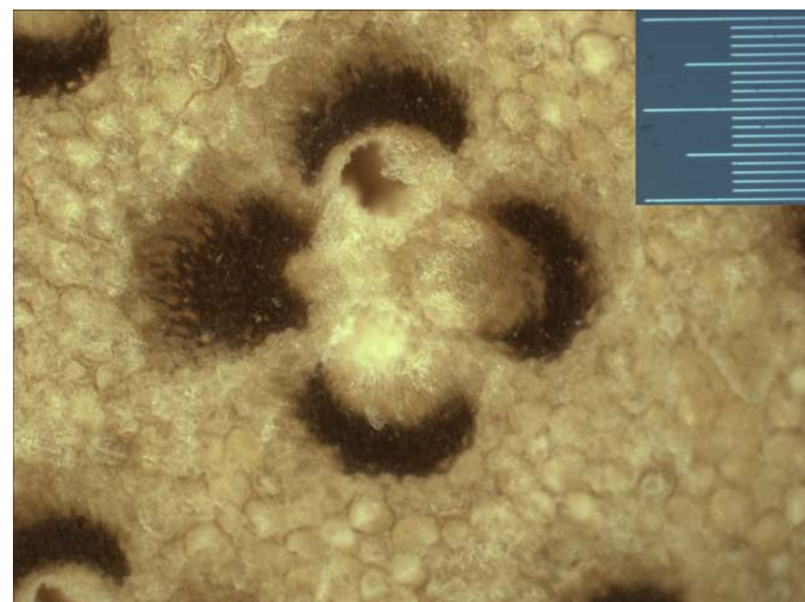
Polybutadiene to prevent splitting

Polystyrene to improve strength

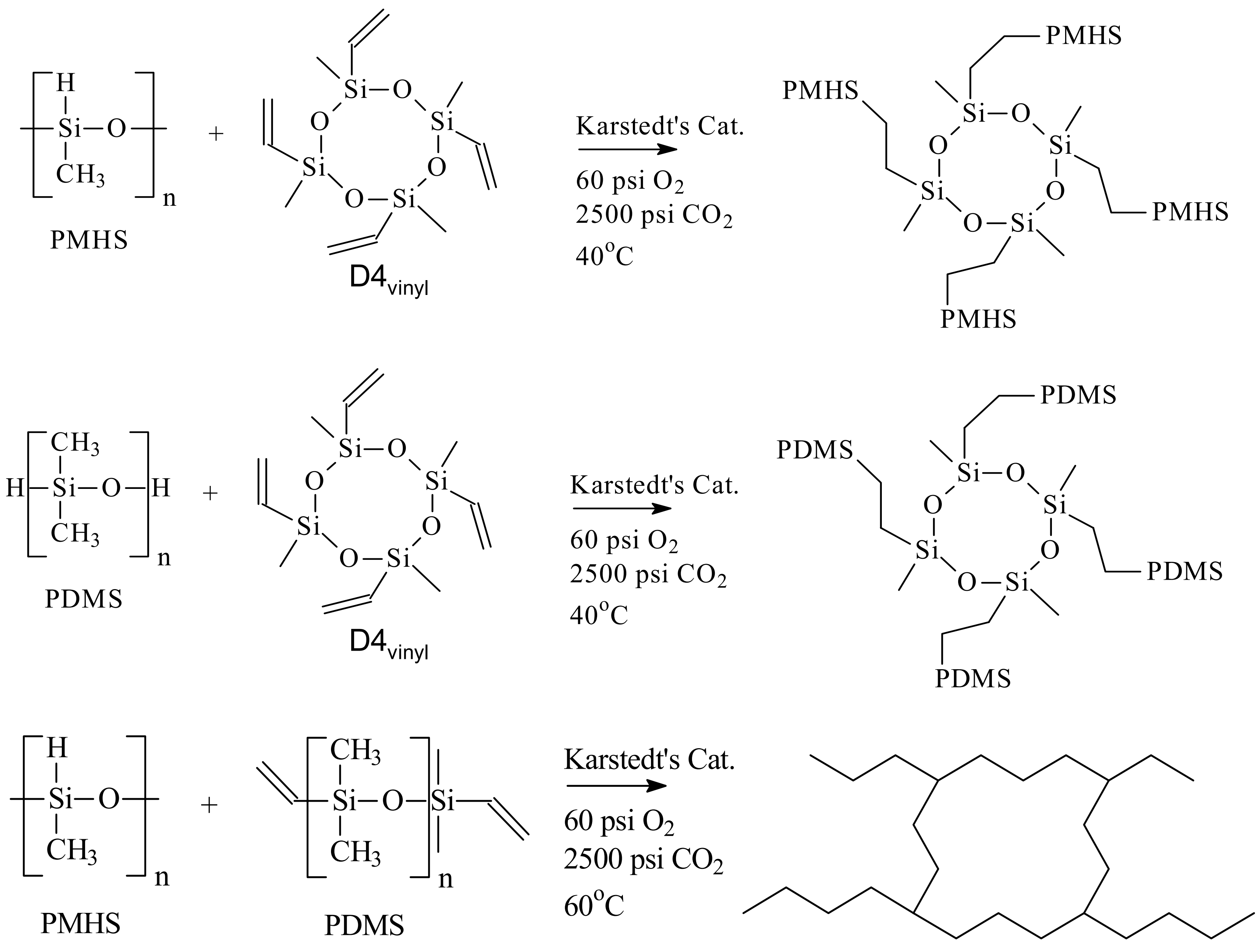
Poly(dimethylsiloxane) to prevent splitting, improve fire resistance, and slow decomposition by increased water resistance

- fiber bundles
- metaxylem vessel
- sclerenchyma sheath
- intercellular space
- phloem

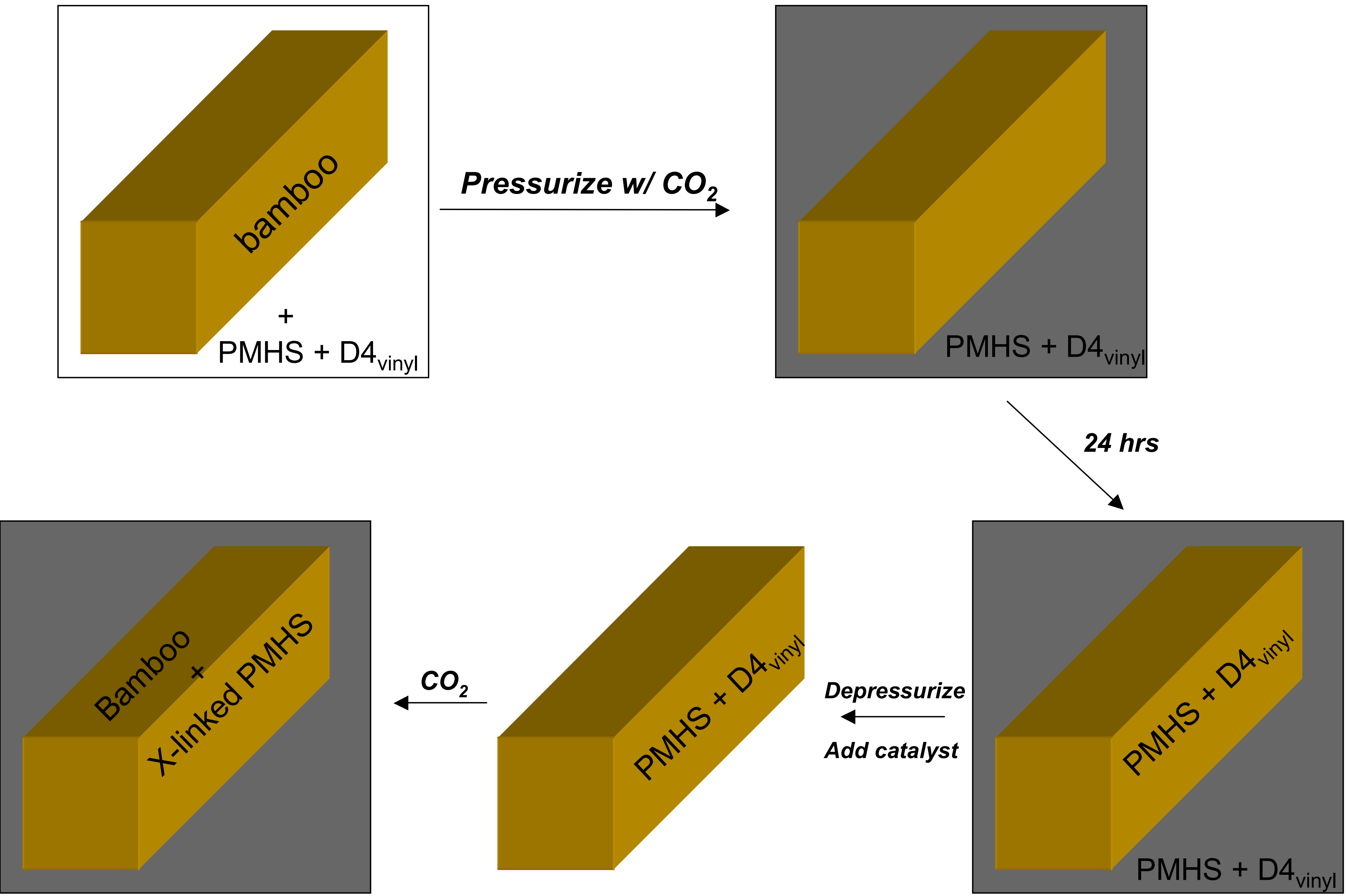




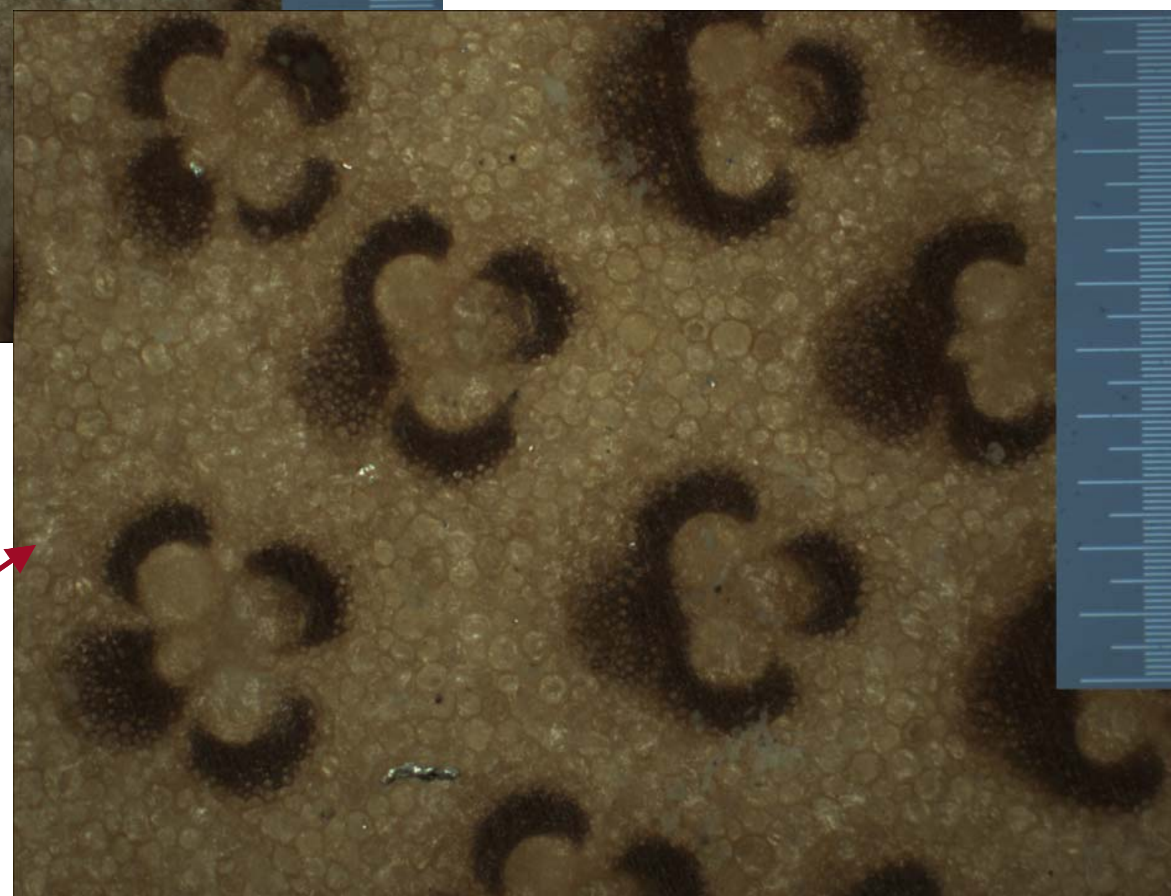
Siloxane polymer -Bamboo Composites



Composite Preparation



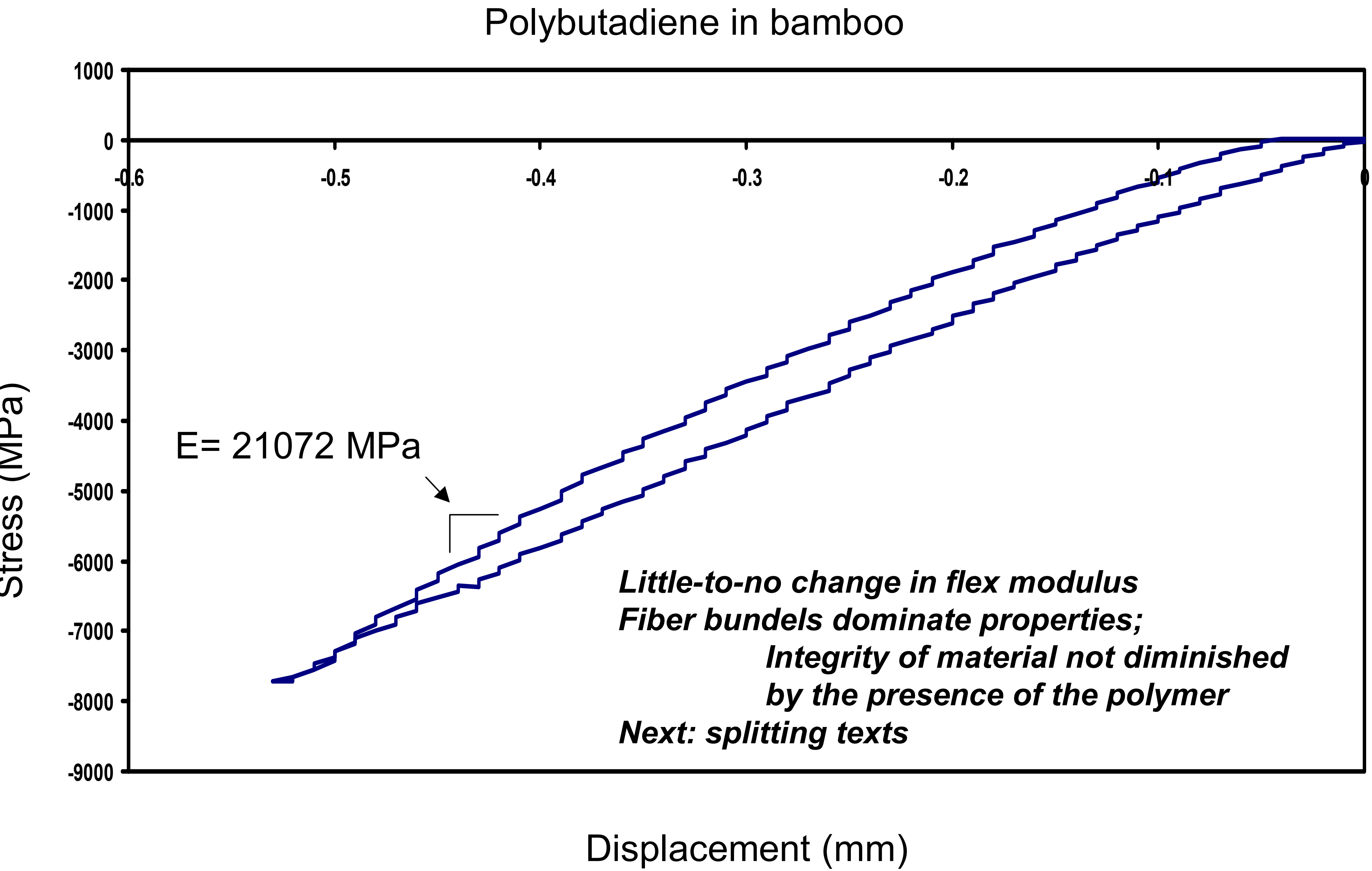
Soxhlet extracted bamboo 5X mag.



Silicon content increased

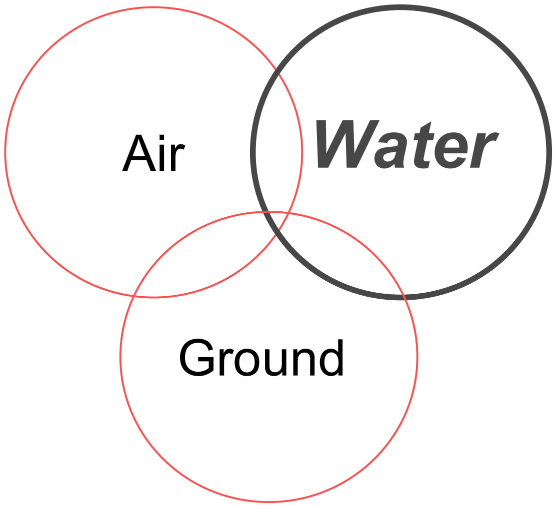
PDMS + $D4_{vinyl}$ + bamboo 5X mag.

3-Point Bend Test

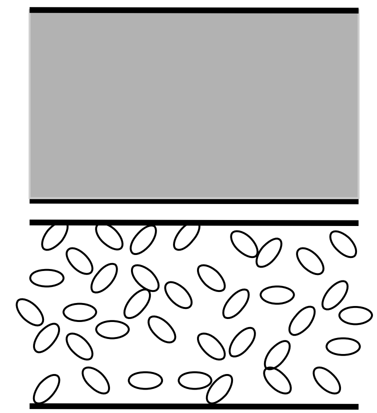


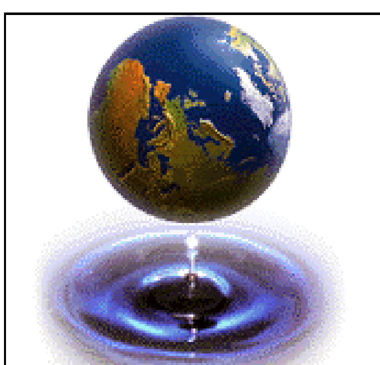
Polymer Membranes as Solutions to Aqueous Environmental Problems

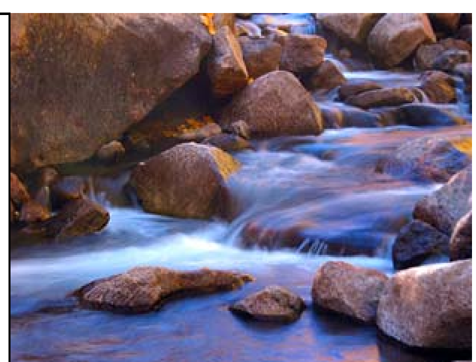
Problem: environmental contaminants



Solution: membranes

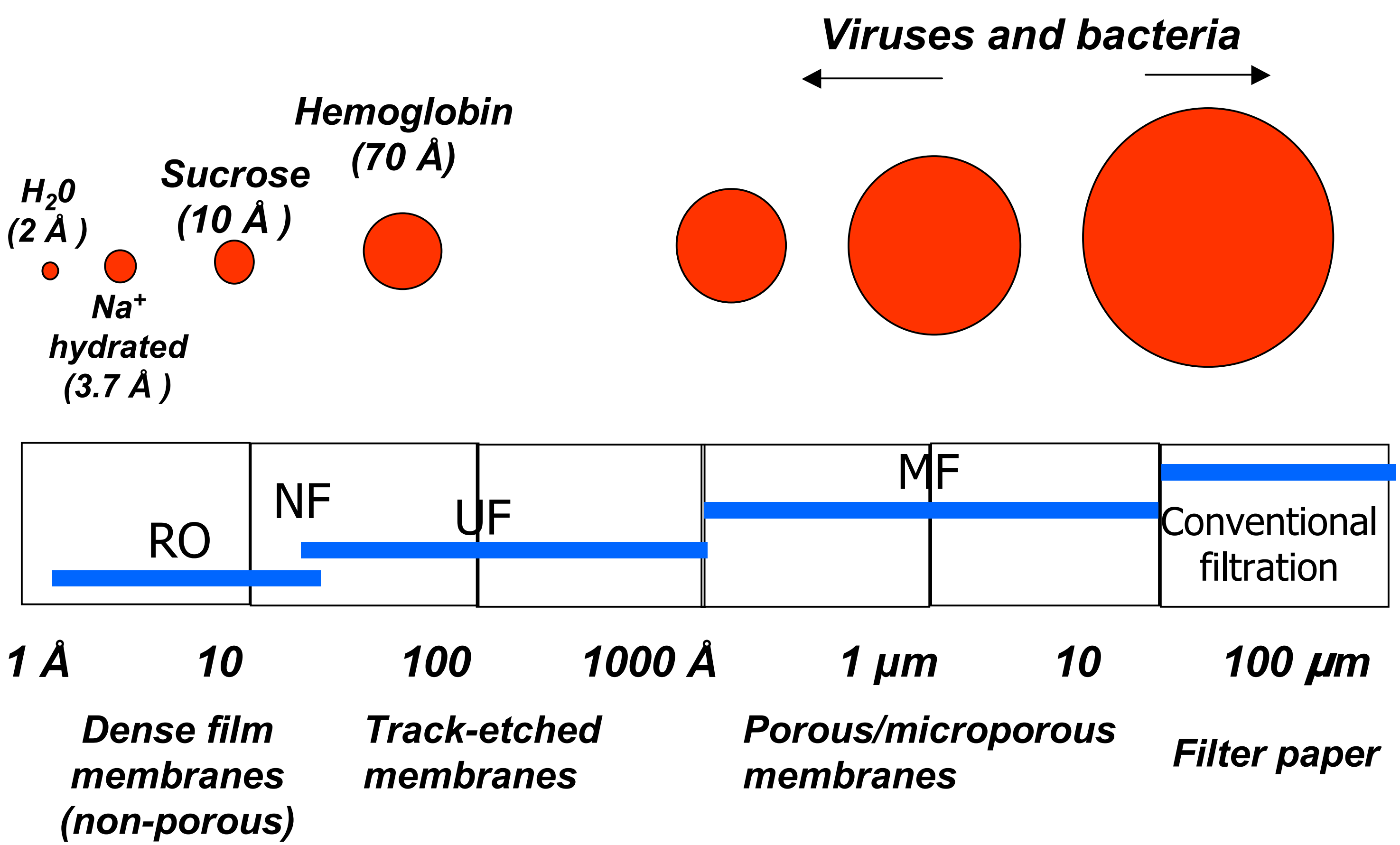






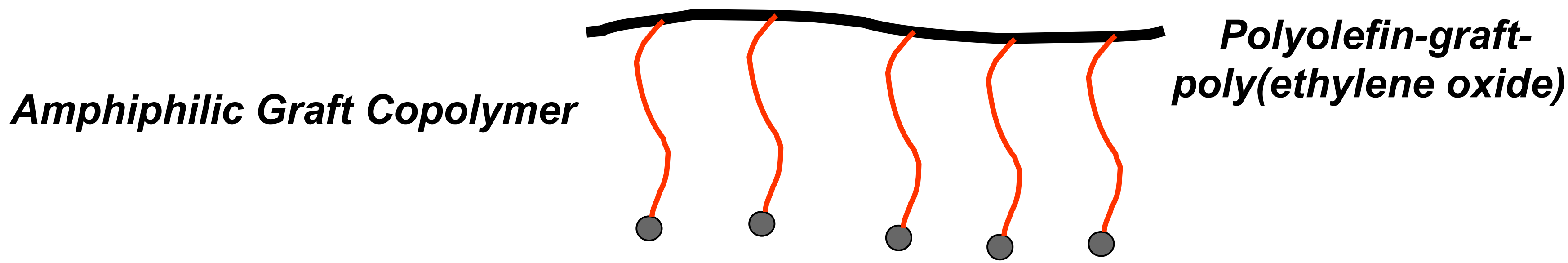
Membrane technology as a solution to multiple environmental problems in air, soil, and water

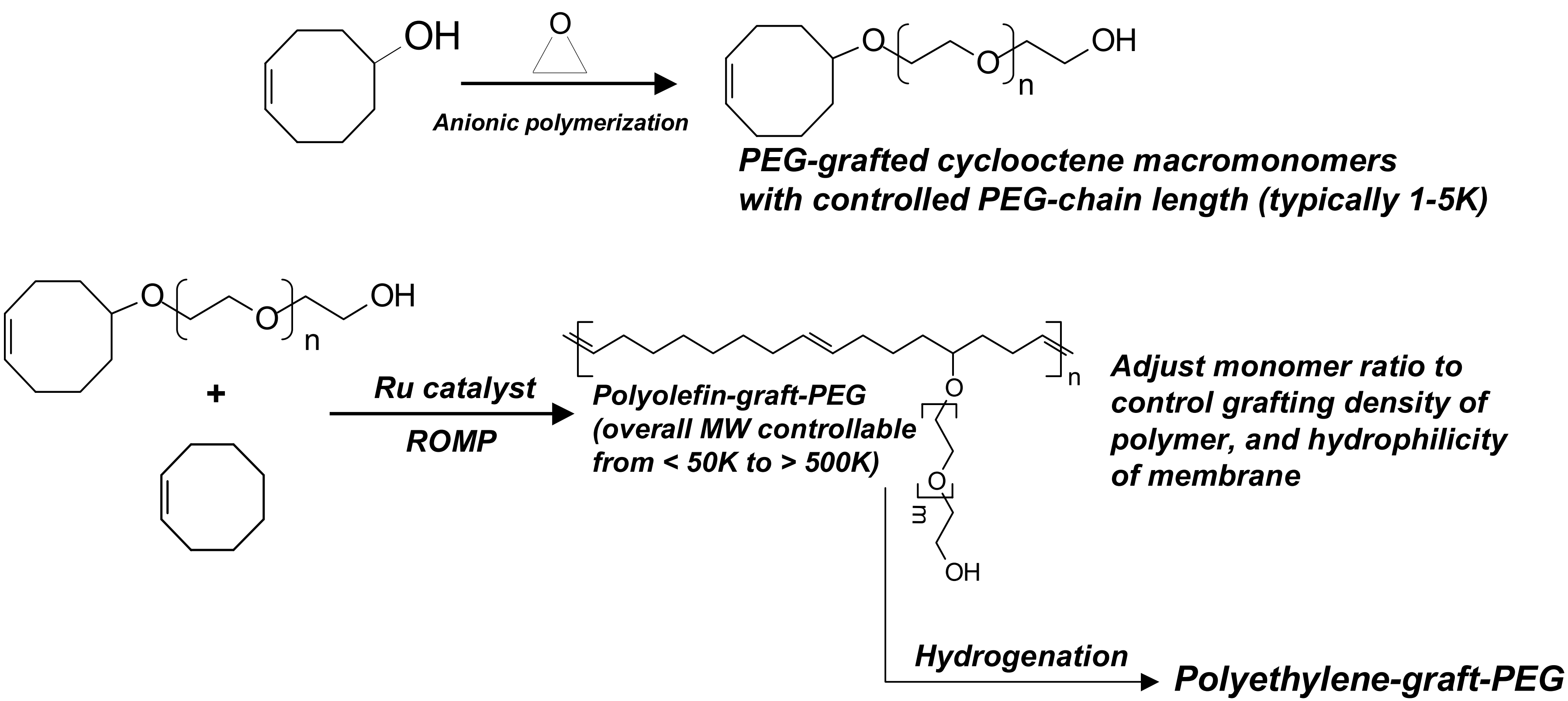
Pore Size Considerations in Membranes



Consistent problem across membrane science: surface & inner-membrane fouling

Amphiphilic Graft Copolymer Membranes





Dense Film Water Uptake as a Function of PEG Weight Percent

Membrane type	Composition* A:B:C (mole % monomer)	Weight % PEG	% water uptake
1	80:20:0	73	200-220
2	85:15:0	66	130-150
3	90:10:0	55	60-70
4	92:9:0	49	50-60
5	92:6:2	53	45-50
6	91:8:1	54	40-45

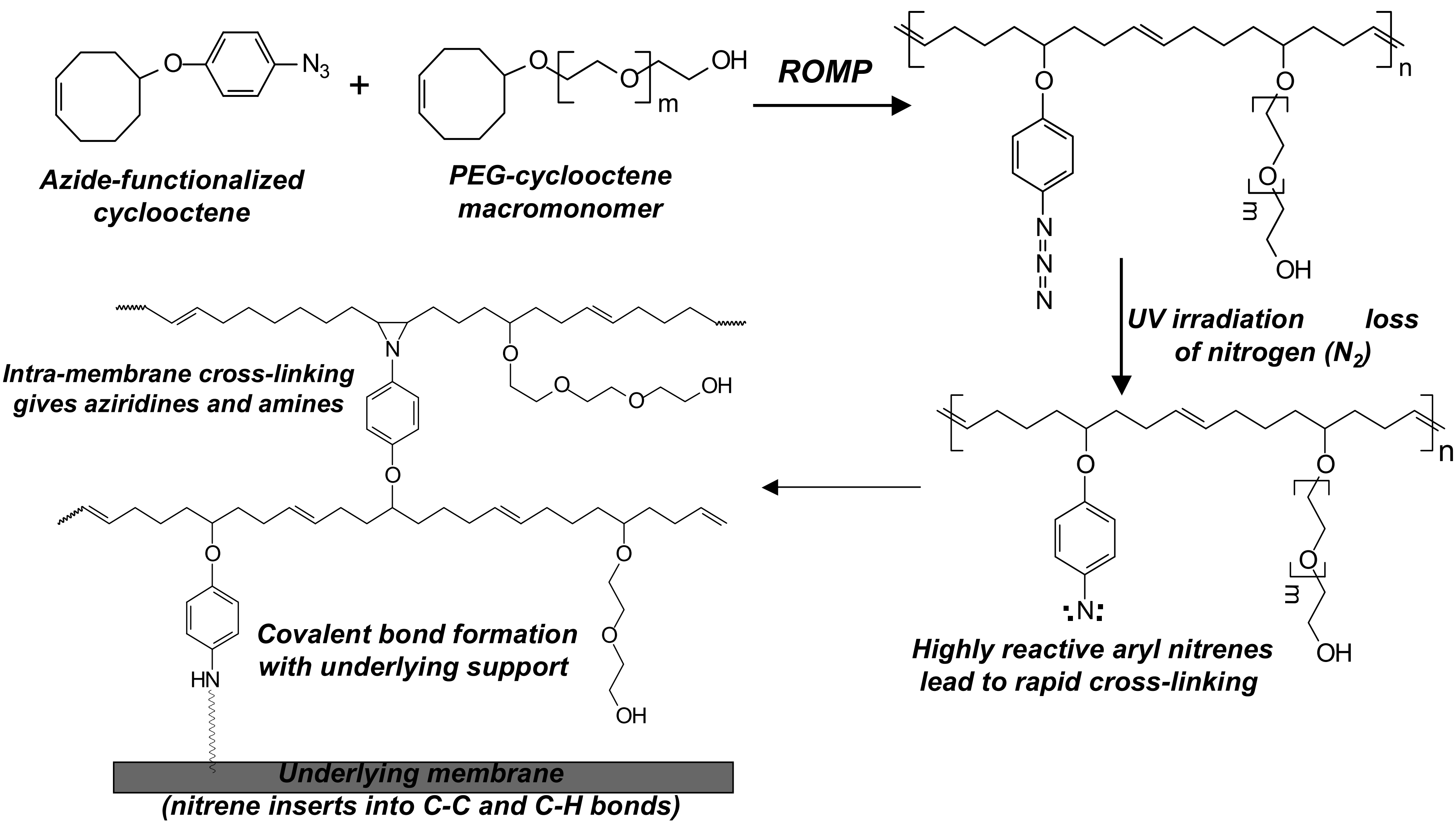
** A = cyclooctene; B = PEG-1200 cyclooctene macromonomer; C = PEG-2200 cyclooctene macromonomer*

All films are cross-linked using 2-3 mole percent bis-cyclooctene cross-linker

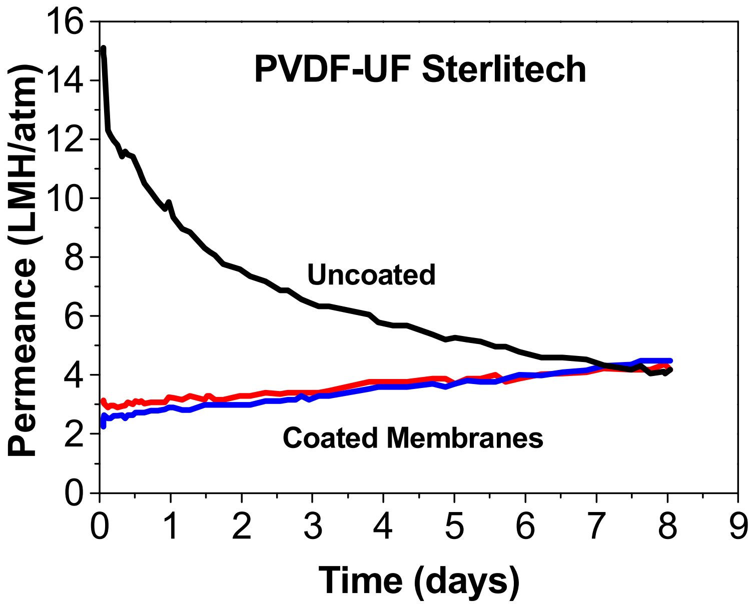
Membranes 1 and 2 are very hydrophilic!
Cross-linking improves mechanical integrity

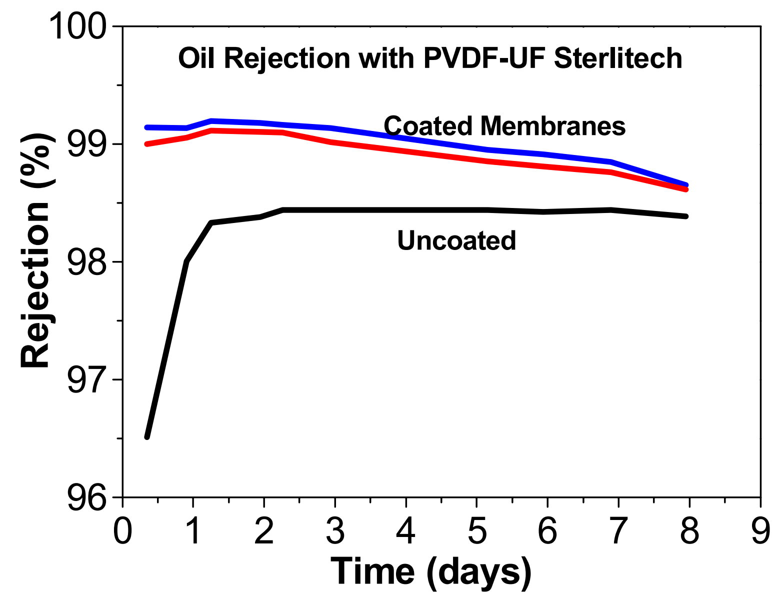
Membranes 3-6 are mechanically robust dense films that are handled easily as uncross-linked or cross-linked films

Improved cross-linking through aryl azide functionalized graft copolymers



Cross-Flow Experimental Results





Data collected by Bryan McCloskey and Dr. Ravindra Revanur in Benny Freeman's labs at UT Austin

Feed : 1500 ppm (9:1 by wt. soybean oil:Dow fluid 193) oil emulsion @ 150 psi

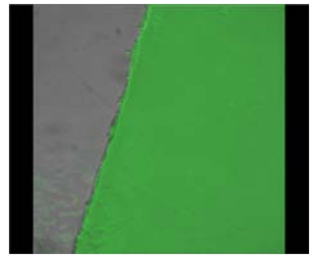
Support Membrane: PVDF-UF, **Coating polymer** : 5 wt% Arylazide functional PCOE-*g*-PEG4400 in ethanol, **UV crosslinking** : λ 302 nm

Outcome : Highly anti-fouling composite membranes with good water flux and good adhesion to underlying supports

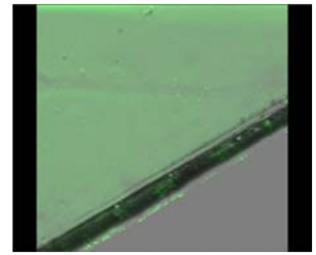
Protein Fouling Experiments

Polyamide treated thin film composite membrane

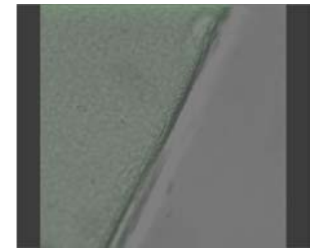
Cellulose acetate asymmetric membrane



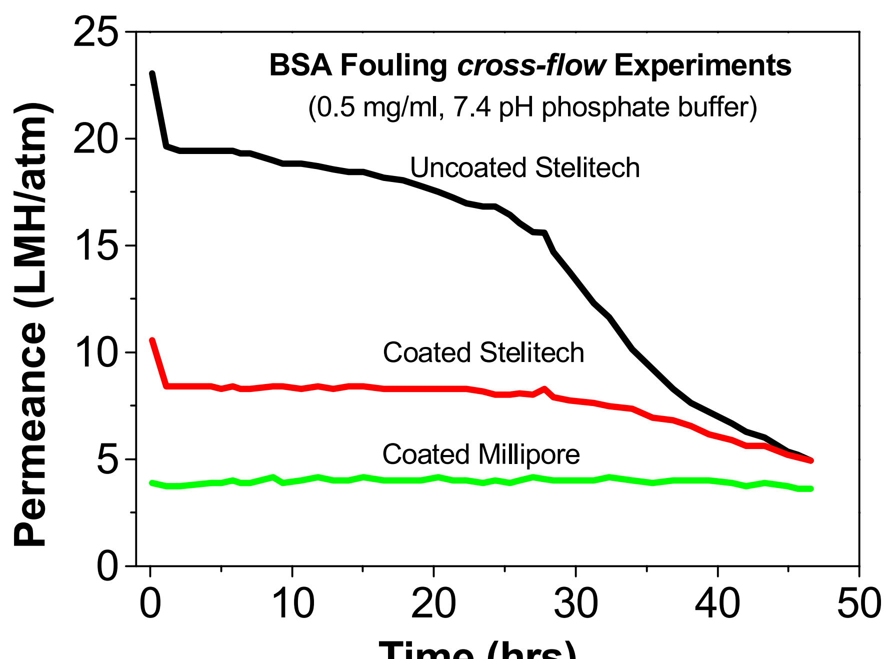
Polysulfone UF membrane



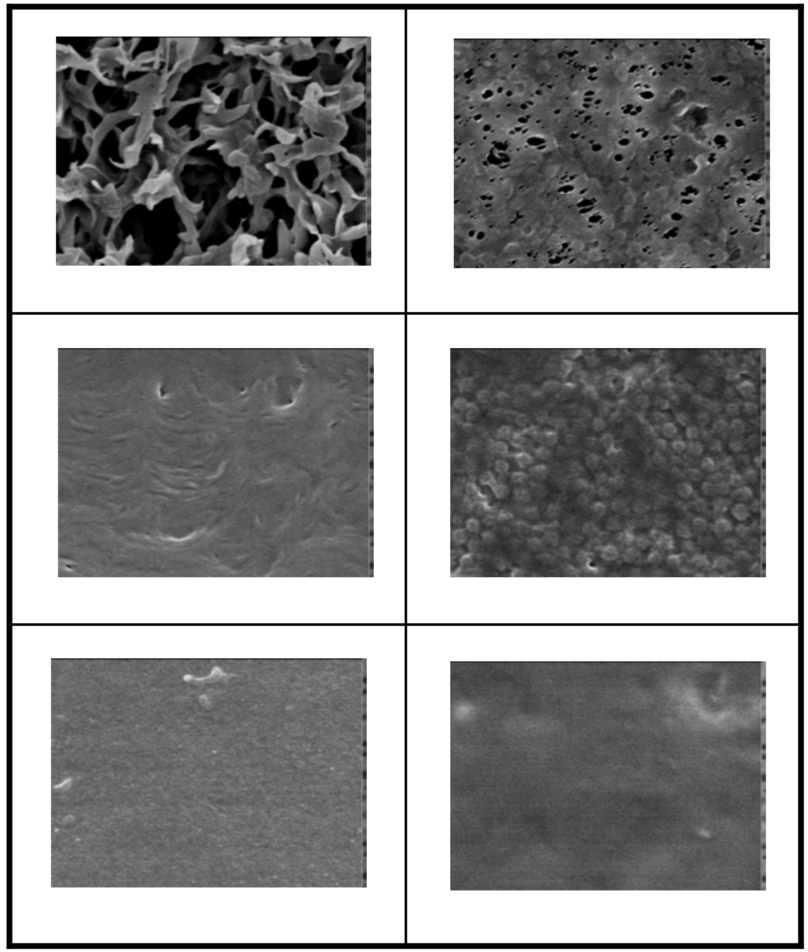
Polyolefin-graft-PEG dense film



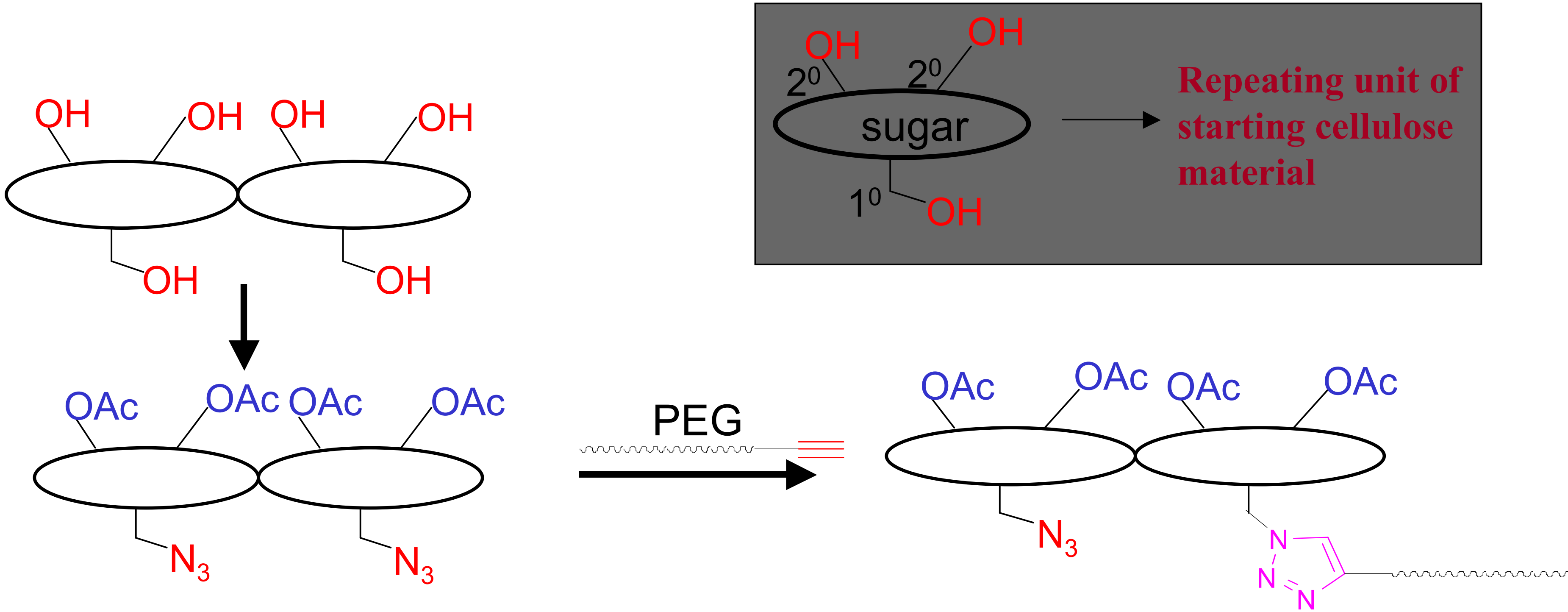
Fluorescence confocal microscopy images of protein adsorption (fluorescein-BSA in aqueous buffer solution at pH 7.4) on a dense film of polyolefin-*graft*-PEG (far right), and on commercial samples of polyamide, cellulose acetate, and polysulfone UF membranes. The intense green color arises from the fluorescently labeled protein, and the resistance to protein adsorption by the polyolefin-*graft*-PEG is evident.



SEM images before & after coating & cross-flow

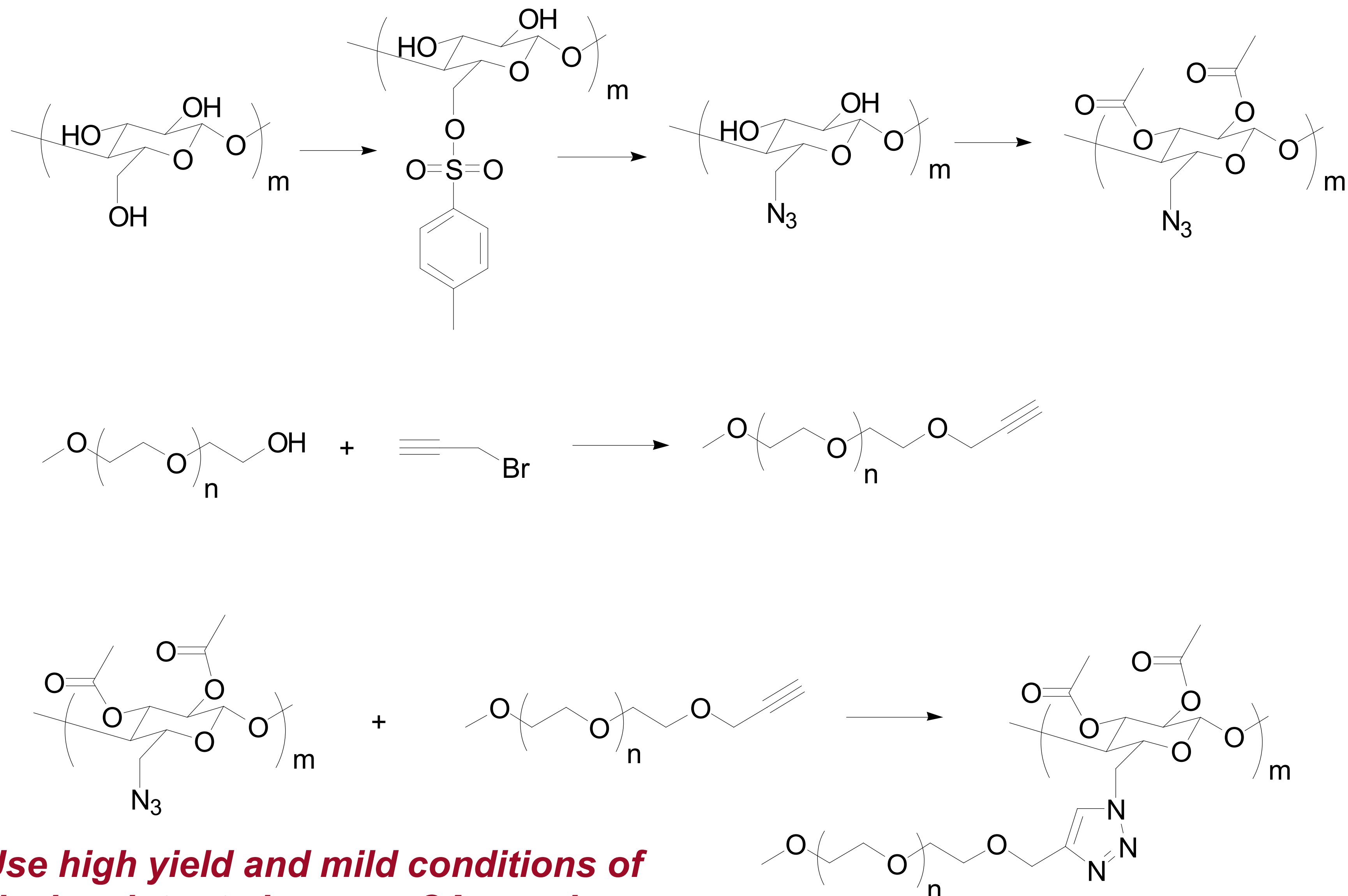


Improved cellulose acetate membranes



Xiongfei Zhang & Ravindra Revanur

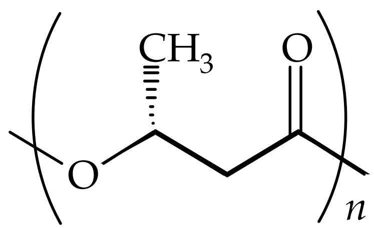
PEGylation of CA by Huisgen (click) cycloaddition chemistry



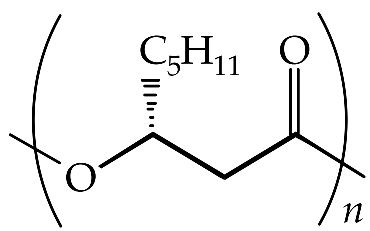
Use high yield and mild conditions of

Poly(hydroxy alkanoates) Incorporated as Blends or Copolymers

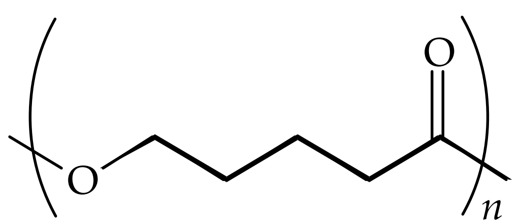
PHAs exhibit a broad range of Tg's and crystallinity depending on the structure.
Copolymers can improve compatibility between rubbery and crystalline polyols. Copolymer composition can be used to manage tune miscibility and use isocyanates efficiently.



Tg = 5 to -12 °C



Tg = -35 °C



Tg = -53 °C

Chemtech 1996

Conclusions

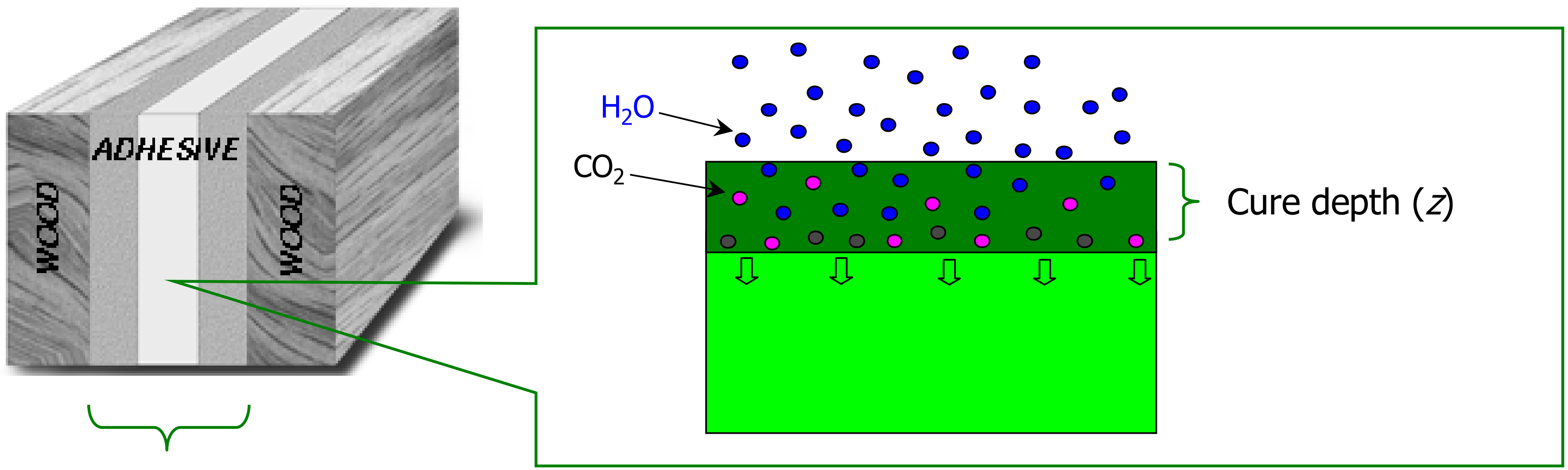
Lignin can be used as an additive to improve the modulus and elongation of polyurethane foams. Critical issues are:

- Dispersion of the lignin in the formulation
- Optimizing the catalyst package

Aliphatic polyesters, incorporated as blends, reinforce the polyurethane foam and increase the modulus.

- Hysteresis occurs upon phase separation of the polyester.
- Varying the crystallization conditions or incorporating the reinforcements as copolymers may eliminate the hysteresis.

Large volume applications



Reactive polyurethanes
- prepolymer
- usually ternary blends with polyester component

Morphology observed