



Functional Polymers From Renewable Resources

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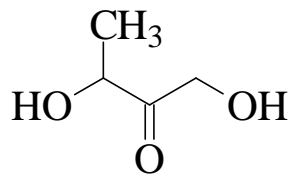
Polymers based on renewable resources

crops, grasses, agricultural byproducts

- Raw materials are sustainable;
- Polymers can be designed to be biodegradable

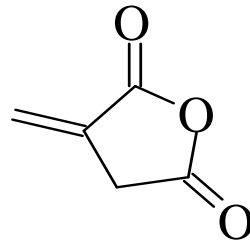
Monomers From Renewable Resources

Lactic Acid



Fermentation of agricultural by-products (carbohydrates), e.g., corn starch

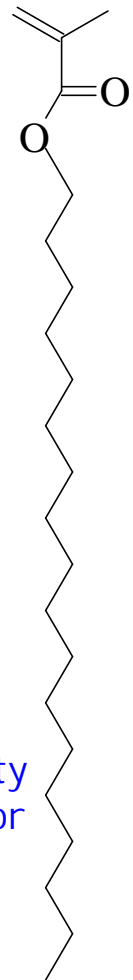
Itaconic Anhydride



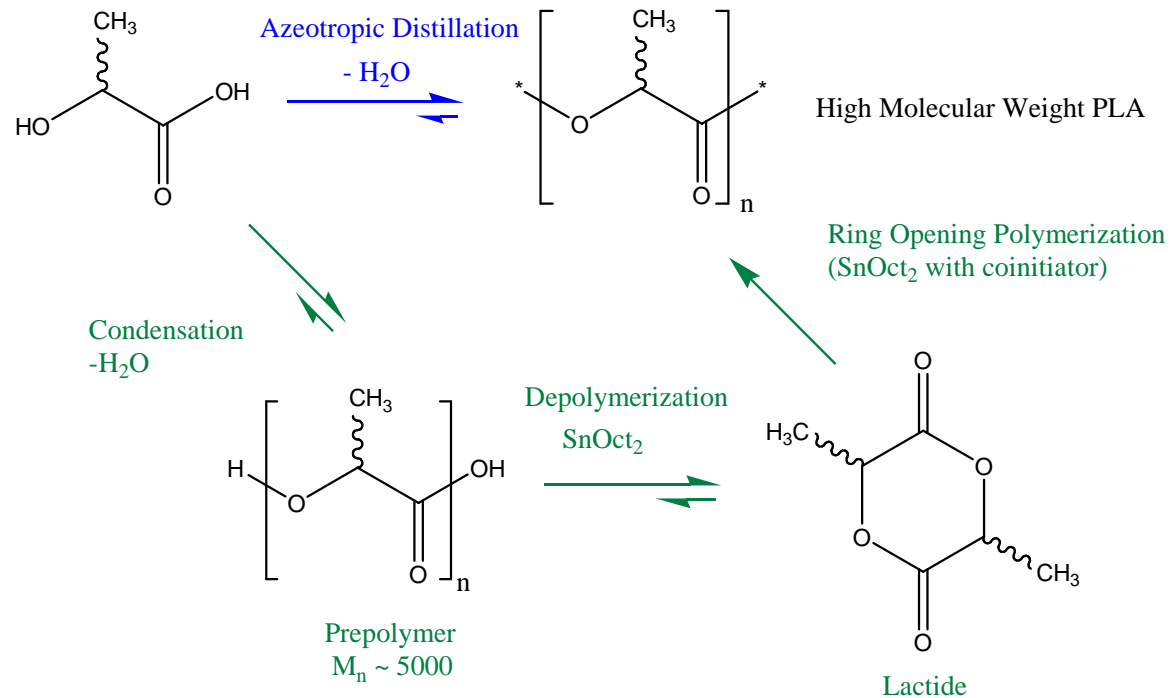
Pyrolysis of citric acid, or Fermentation of carbohydrates to form itaconic acid, followed by dehydration

Stearyl Methacrylate

Derived from fatty acid from animal or vegetable fats or oils



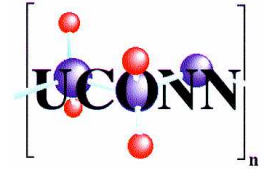
Poly(lactic acid), PLA



Drumwright, R. E.; Gruber, P. R.; Henton, D. E. Adv. Mater. 2000. 12. 1841.

Applications: Fibers, films, moldable thermoplastics ($T_m \sim 175^\circ\text{C}$), sutures

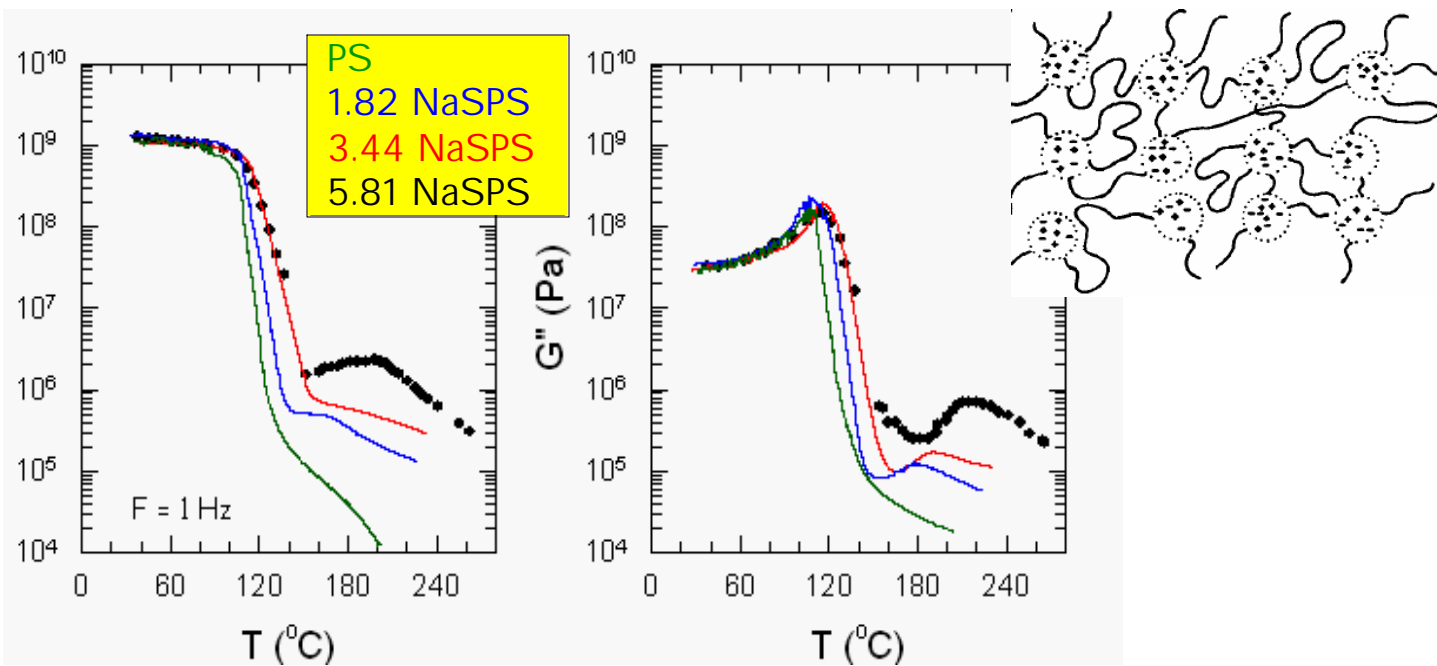
Deficiencies: Low T_g ($\sim 60^\circ\text{C}$), Narrow melt processing window, Brittle plastic, hydrophobic; incompatible with other polymers (blends)



Ionomers

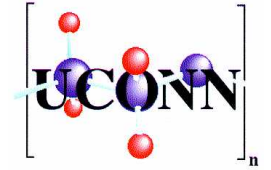
Predominantly hydrophobic polymers that contain modest amounts of bonded acid or salt groups (~ 15 mol%)

Interchain association of salt groups significantly alters thermal properties, mechanical properties and rheology.



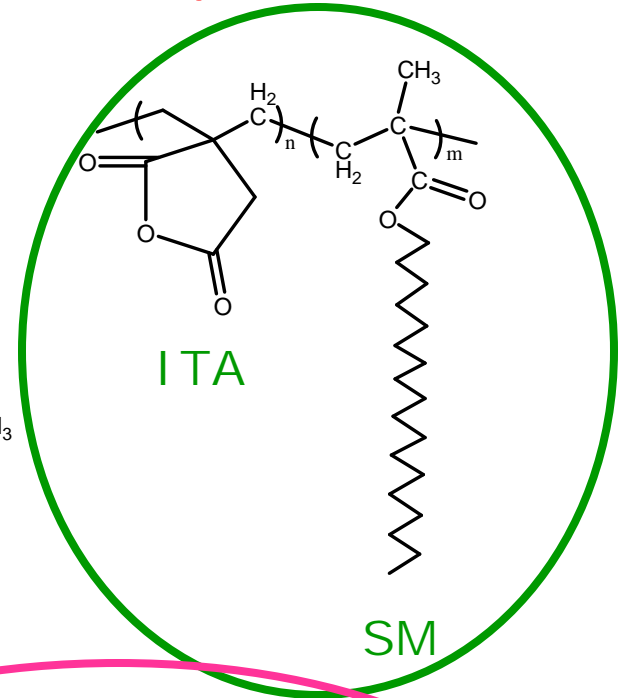
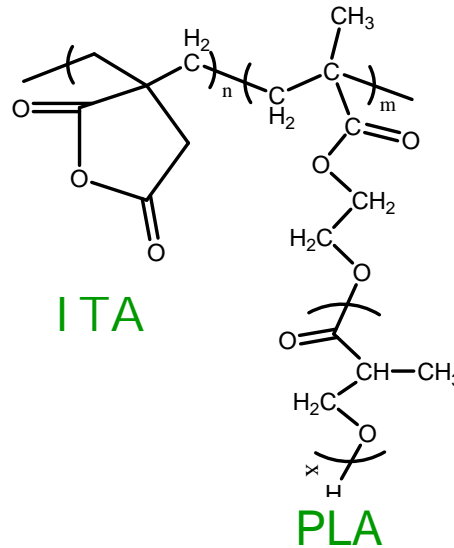
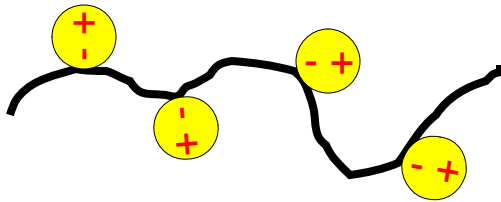
Applications: coatings, fibers, thermoplastics, adhesion promoters, compatibilizers, viscosifiers, permselective membranes, hydrogels...

Research Goals

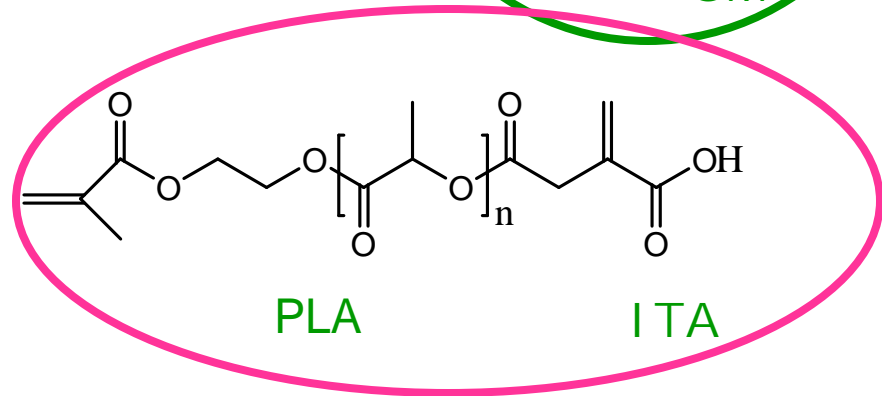
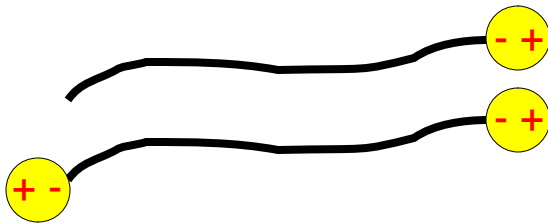


Synthesize and Characterize Ionomers Derived from Lactic Acid, Itaconic Anhydride and Stearyl Methacrylate

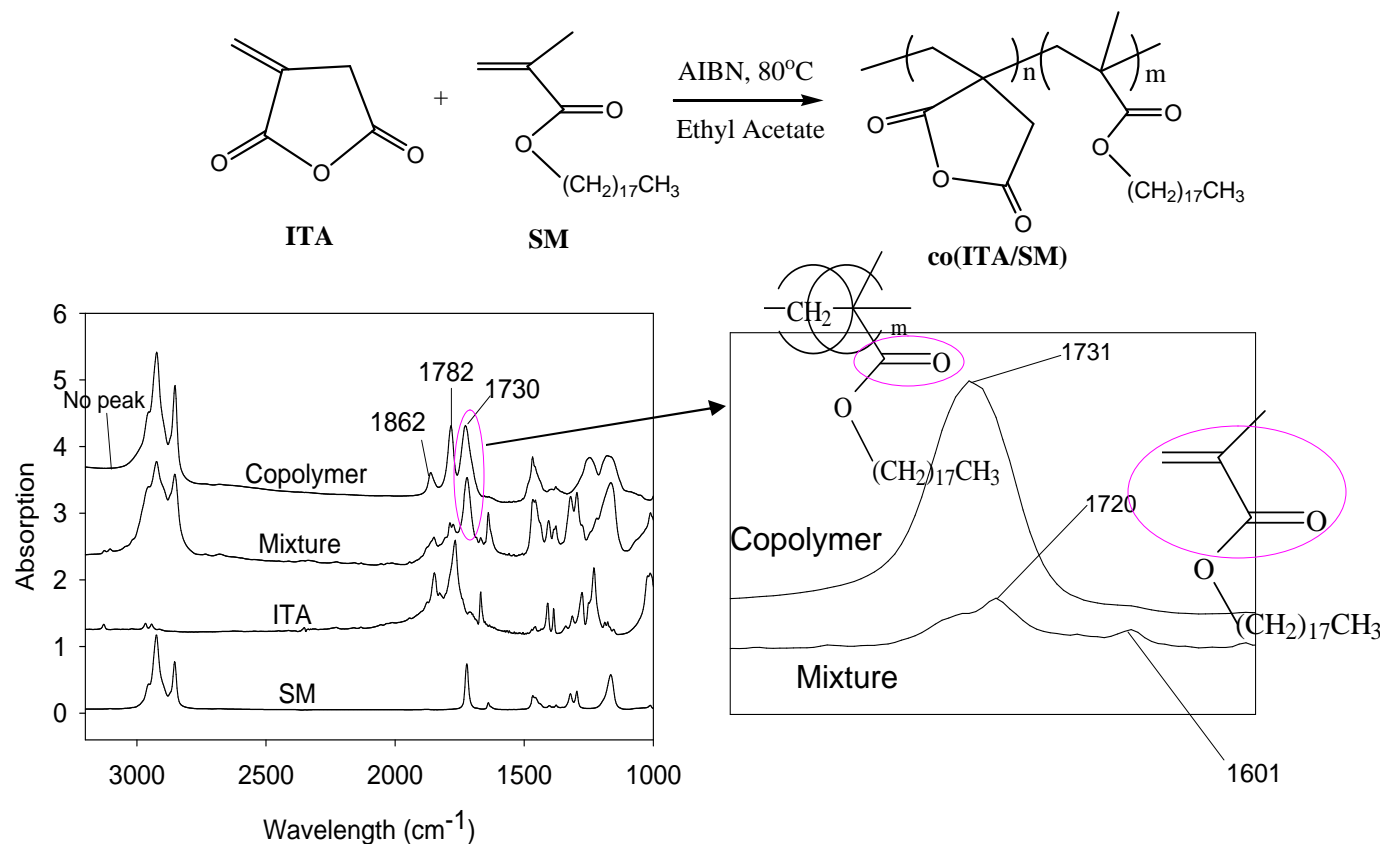
Random Ionomer



Telechelic Ionomer



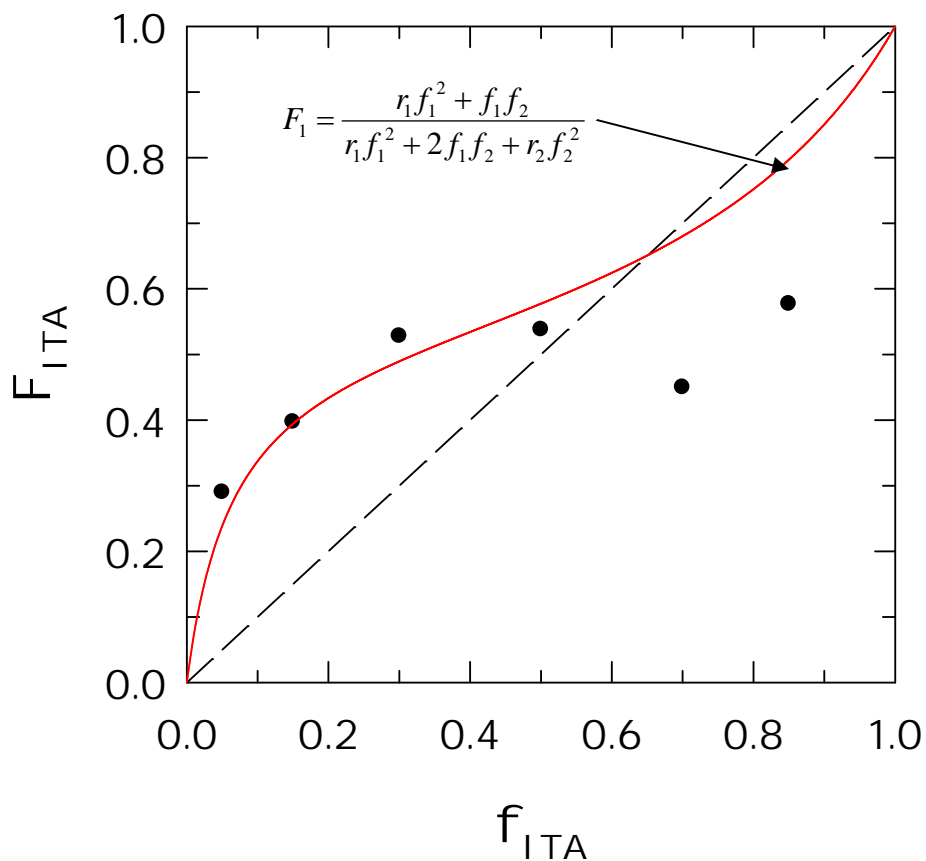
Radical copolymerization of ITA and SM



IR evidence for copolymerization:

- ✓ 1862, 1782 cm^{-1} : ITA (anhydride) 5 member ring
- ✓ shift of C=O in SM from 1720 to 1731 cm^{-1} indicating reaction of C=C
- ✓ disappearance of peak at 1601 cm^{-1} : reaction of C=C

Copolymerization of I TA and SM



$$r_{ITA} = r_1 = 0.53$$

$$r_{SM} = r_2 = 0.12$$



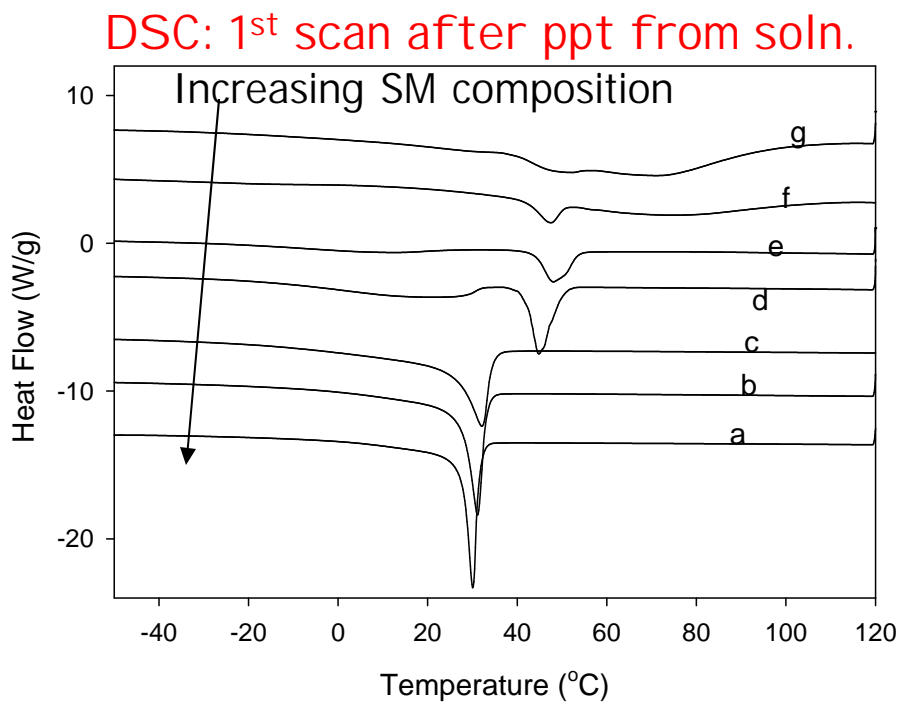
Random
Copolymers

J. Wallach, PhD Dissertation,
Univ. Conn., 2000

M_n (25k - 60kDa) decreased with increasing f_{ITA}



Thermal behavior of I TA-co-SM copolymers



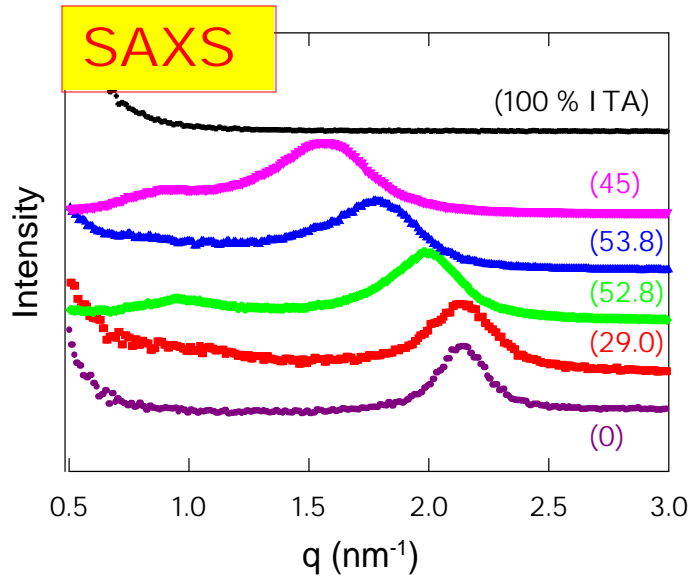
f_{ITA}	M_n (kDa)	T_m (°C)	ΔH (J/g SM)
0	57.1	30.2	62.8
0.29	45.1	31.2	83.0
0.40	33.0	32.1	77.0
0.53	34.8	44.7	87.9
0.54	29.1	48.2	50.9
0.45	24.1	45.6	21.3

Crystallinity is due to the SM side chain packing

- Melting temperature **increased** with increasing I TA content!
- Effect of I TA on crystallinity was complicated.

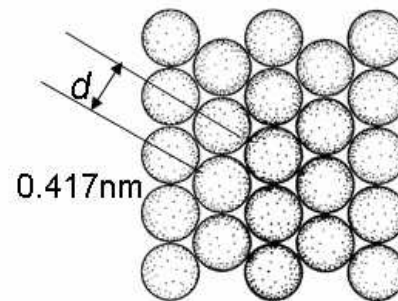
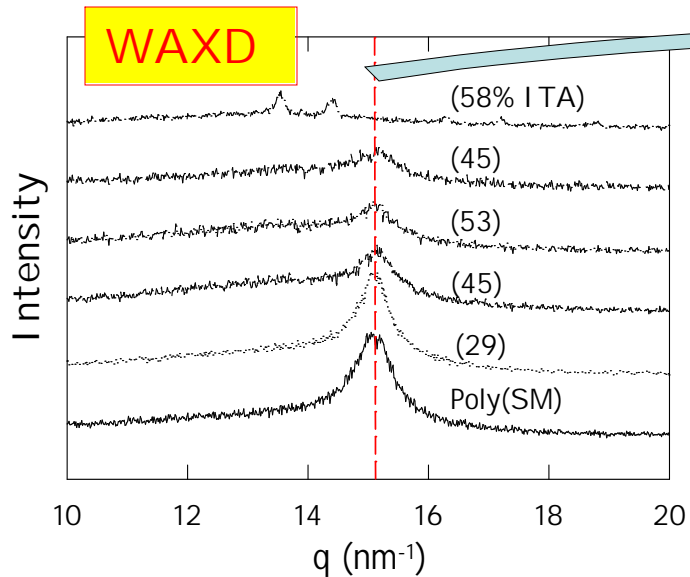
No glass transition was observed ($T_{g(I TA)} \sim 130^\circ\text{C}$).

Crystalline structure of I TA-co-SM



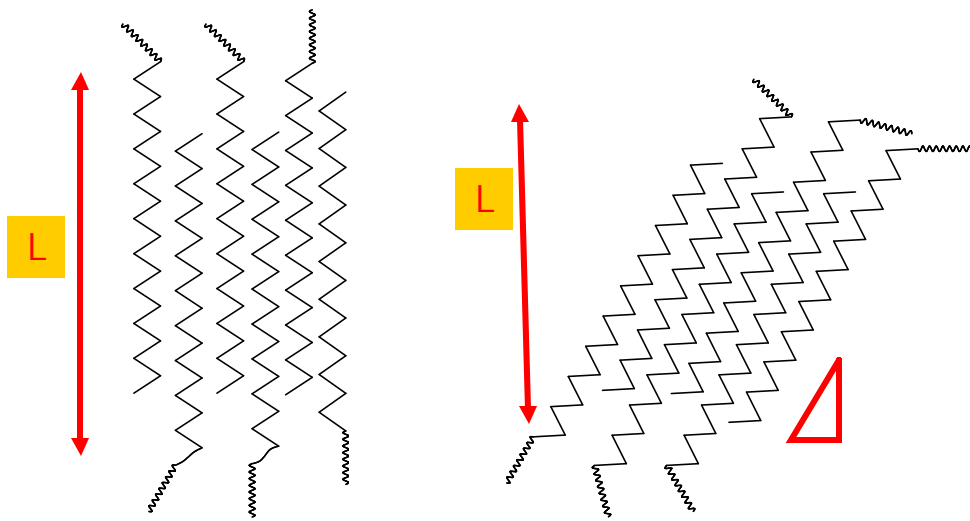
Composition (mol% I TA)	d (nm)
0	2.95
29.0	2.96
45	3.98
52.8	3.18
53.8	3.55
100	--

Length of alkyl side chain = 2.5 nm

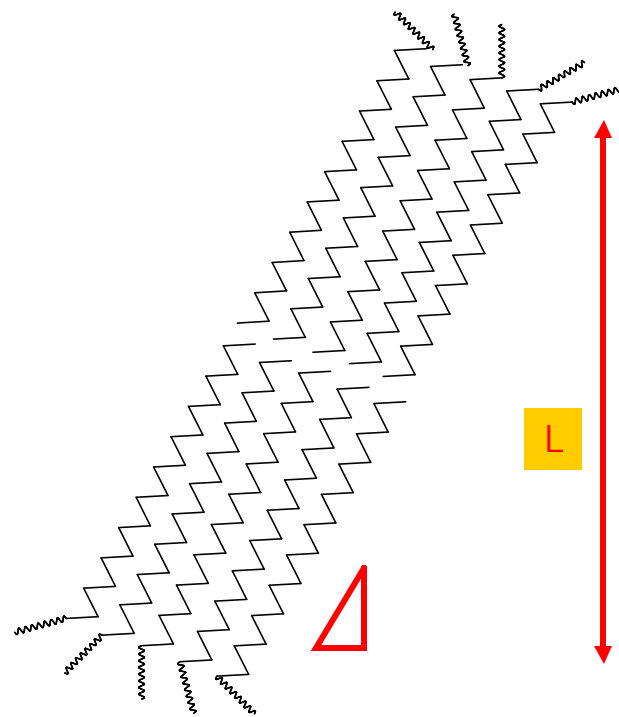


0.417 nm
characteristic of n-alkyl
hexagonal packing,

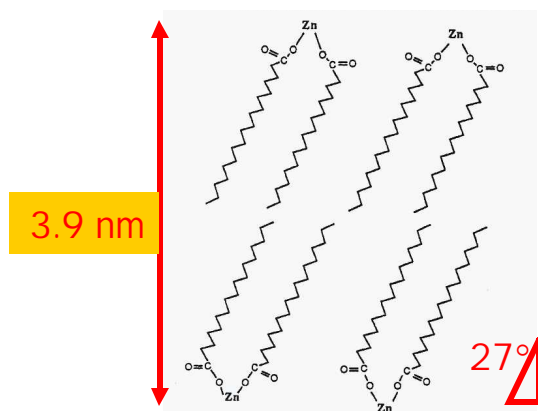
Side-Chain, Stearyl Methacrylate Crystals



Intercalated Crystal



Bilayer Crystal

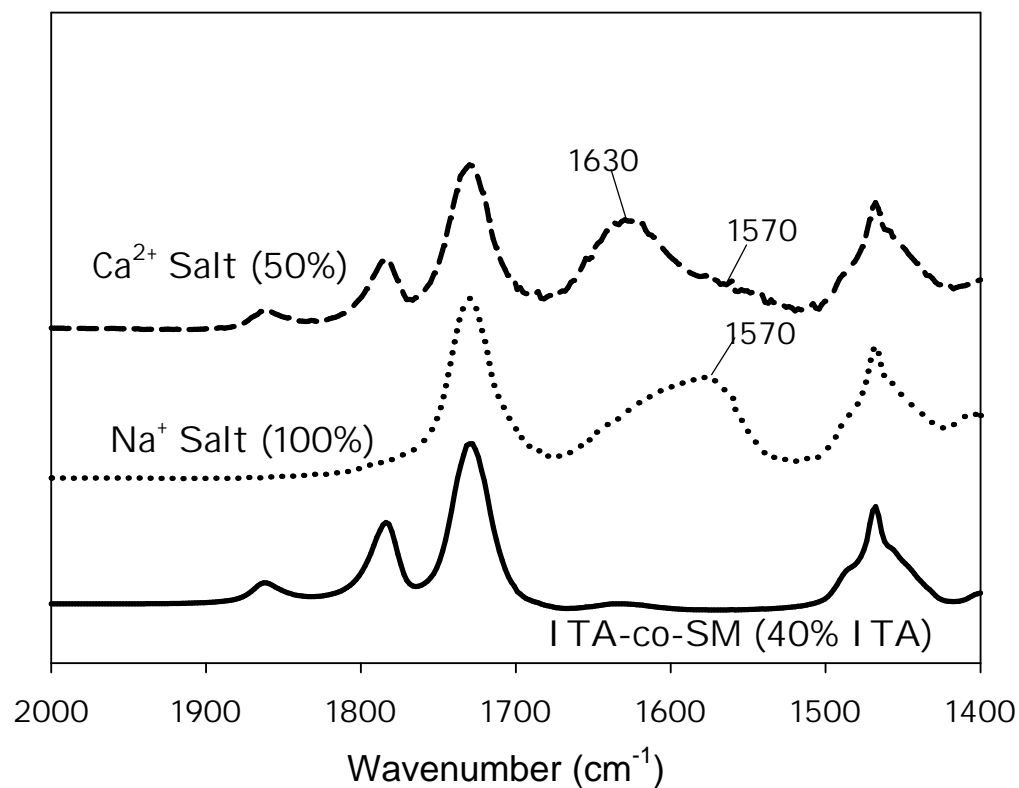


Zn-Stearate Bilayer Crystal



ITA-co-SM Ionomers

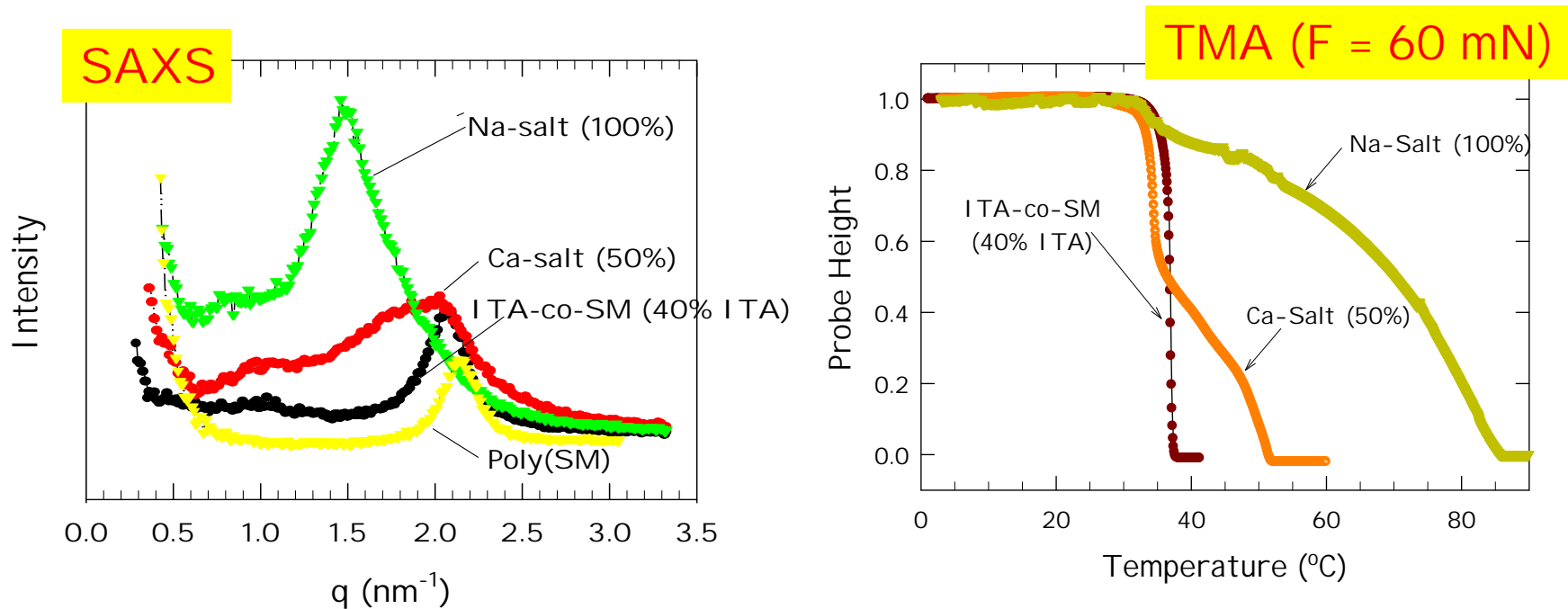
($M_n=33$ kDa; 40 mol% ITA)



IR evidence of neutralization

Peak ~ 1550-1650 cm⁻¹ due to COO⁻

Ionomer Structure and Properties



- Ionic aggregation was observed
- Long spacing of SM crystals increased upon neutralization
- Neutralization increased the elasticity of the polymer.

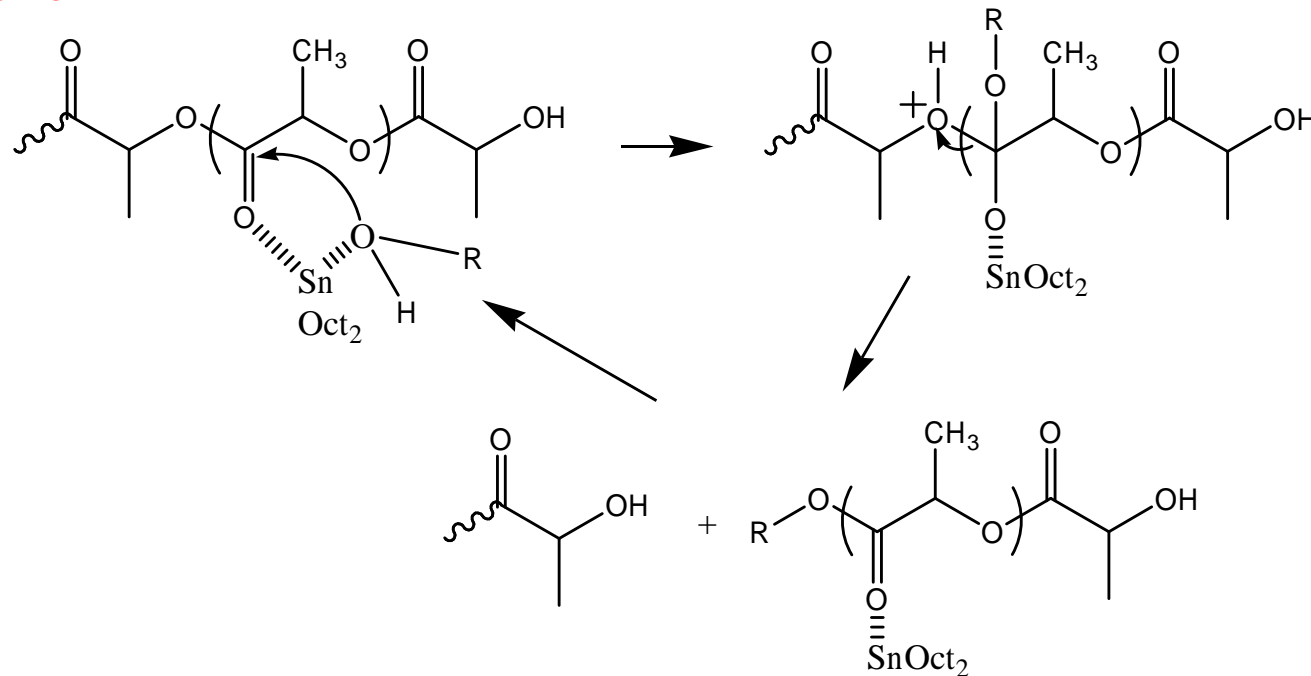
Chemical Recycling of PLA by Transesterification



Transesterification

- ❖ Uncatalyzed - slow process, reaction temperature 250-300°C.
- ❖ Catalyzed - lower time and temperature (J. Wallach, PhD Dissertation, Univ. Conn., 2000).
 - SnOct₂. FDA approved.

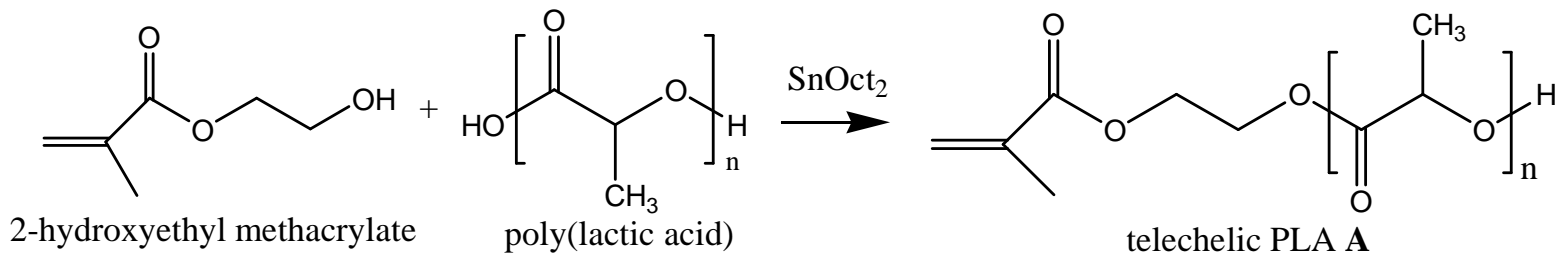
Mechanism



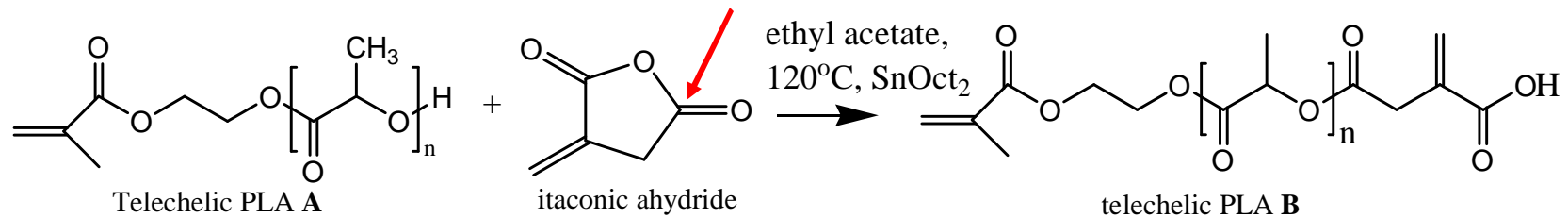
Synthesis of α -carboxylate functionalized PLA

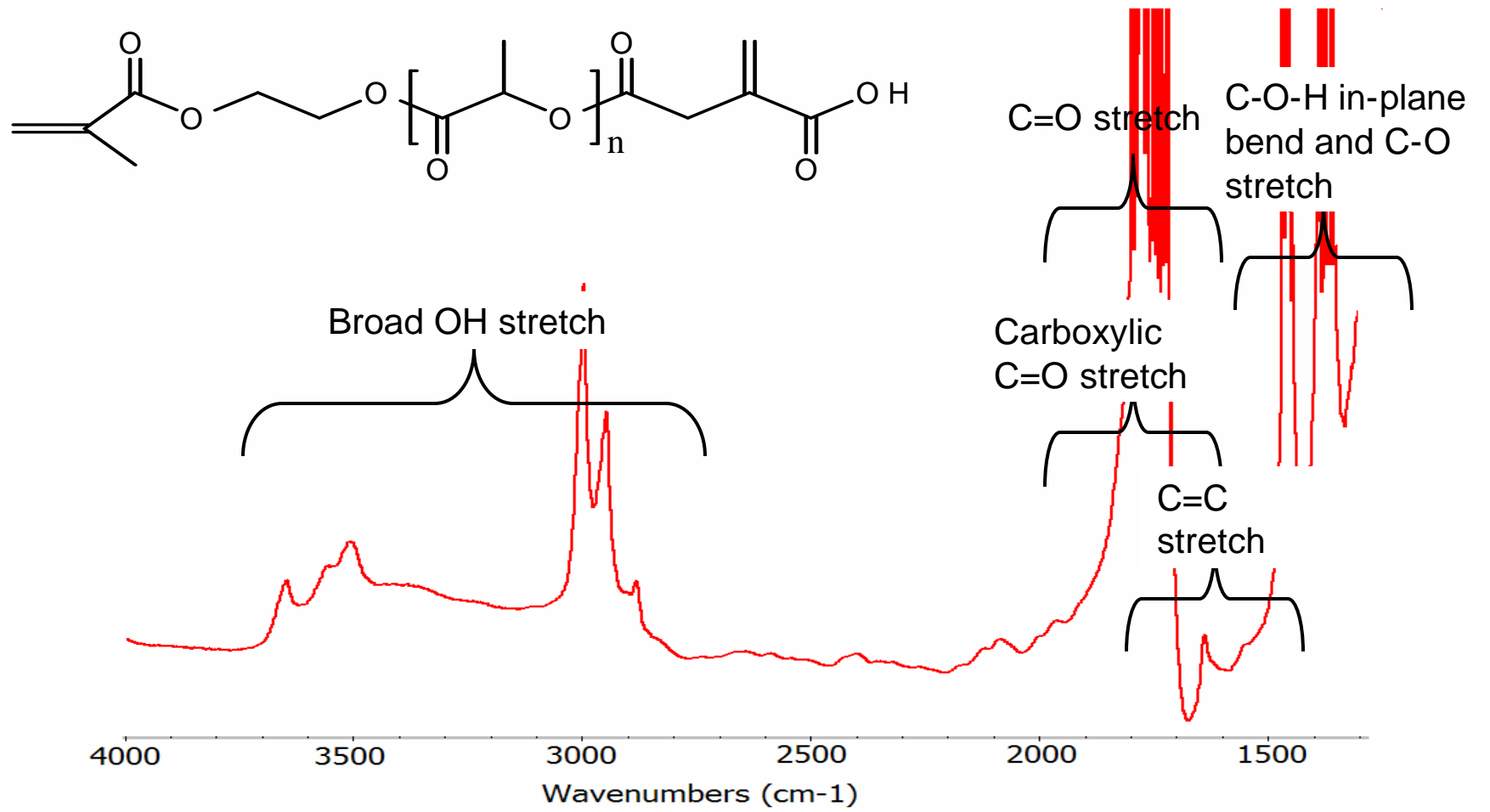


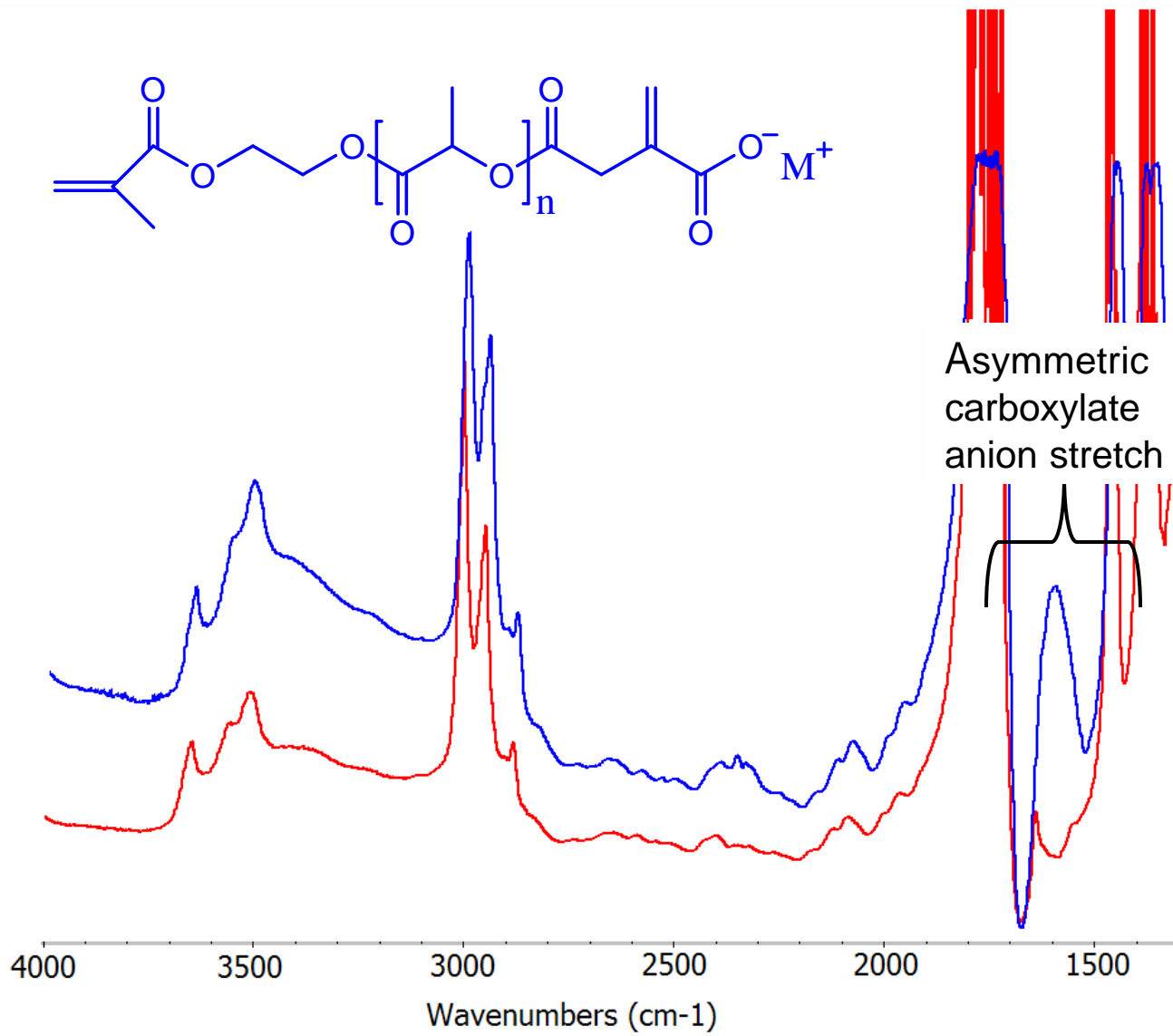
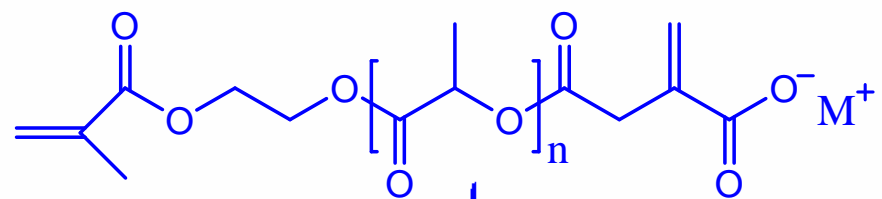
A. Synthesis of methacrylate-terminated PLA



B. Functionalization with itaconic anhydride

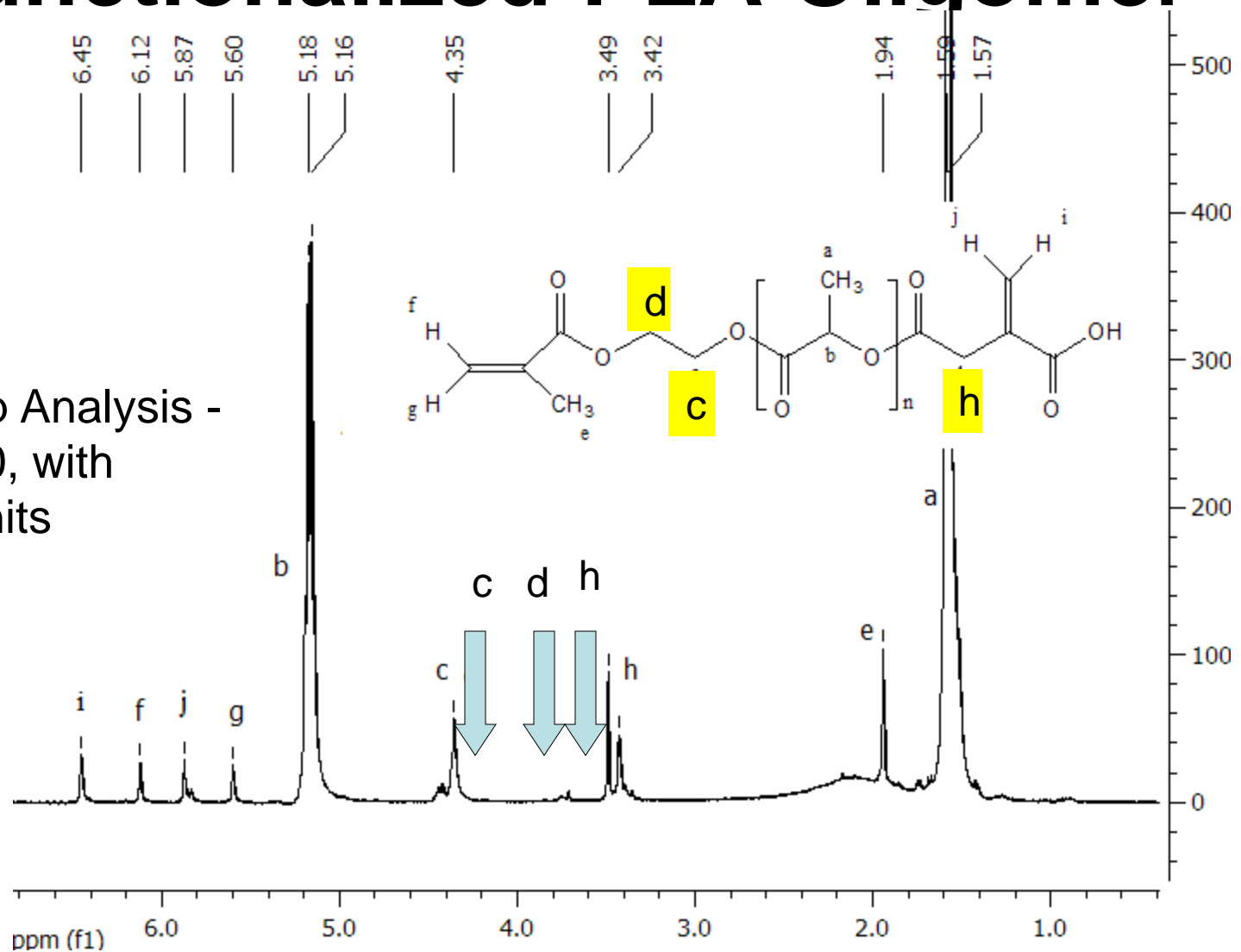






$^1\text{H-NMR}$ Spectrum of Functionalized PLA Oligomer

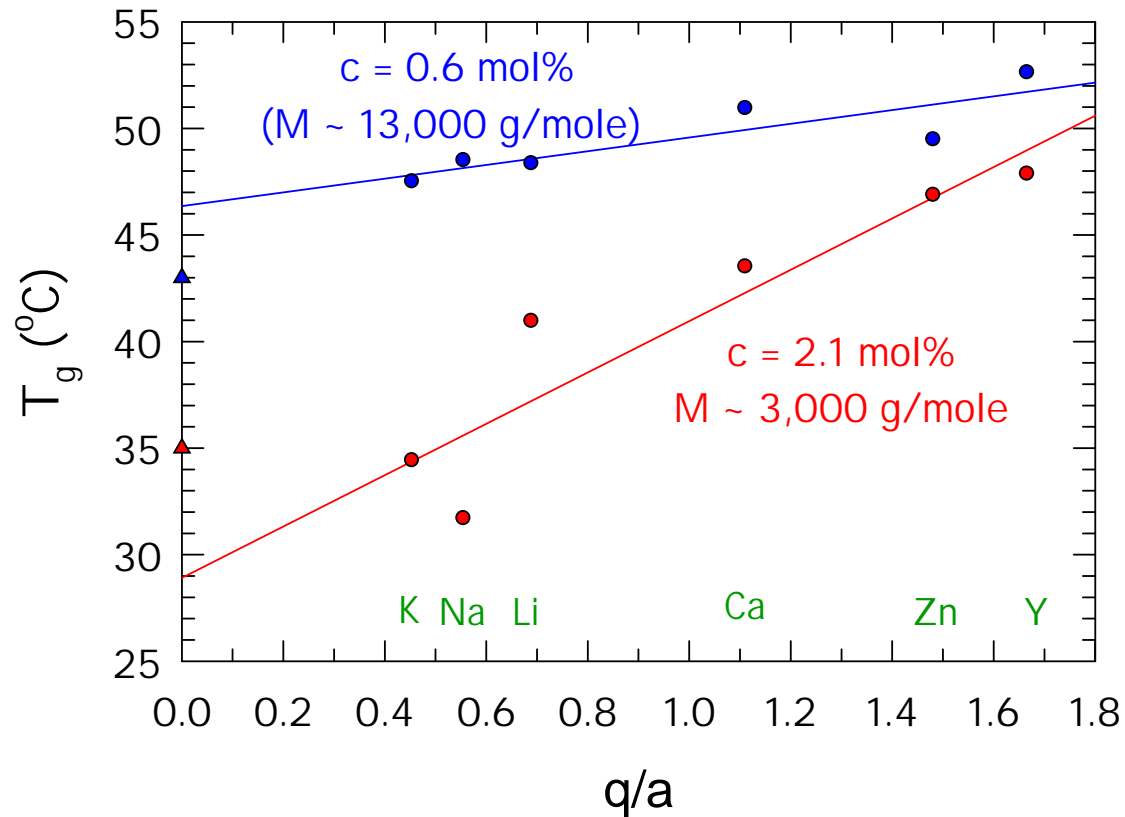
End group Analysis -
 $M_n = 1930$, with
 25 LLA units



Glass Transition Temperatures of PLA-ITA Telechelic Ionomers



Cations = Li^+ , Na^+ , K^+ , Ca^{2+} , Zn^{2+} , Y^{3+}



For higher molecular weight ($M \sim 15,000 - 900,000$), T_g was relatively insensitive to functionalization

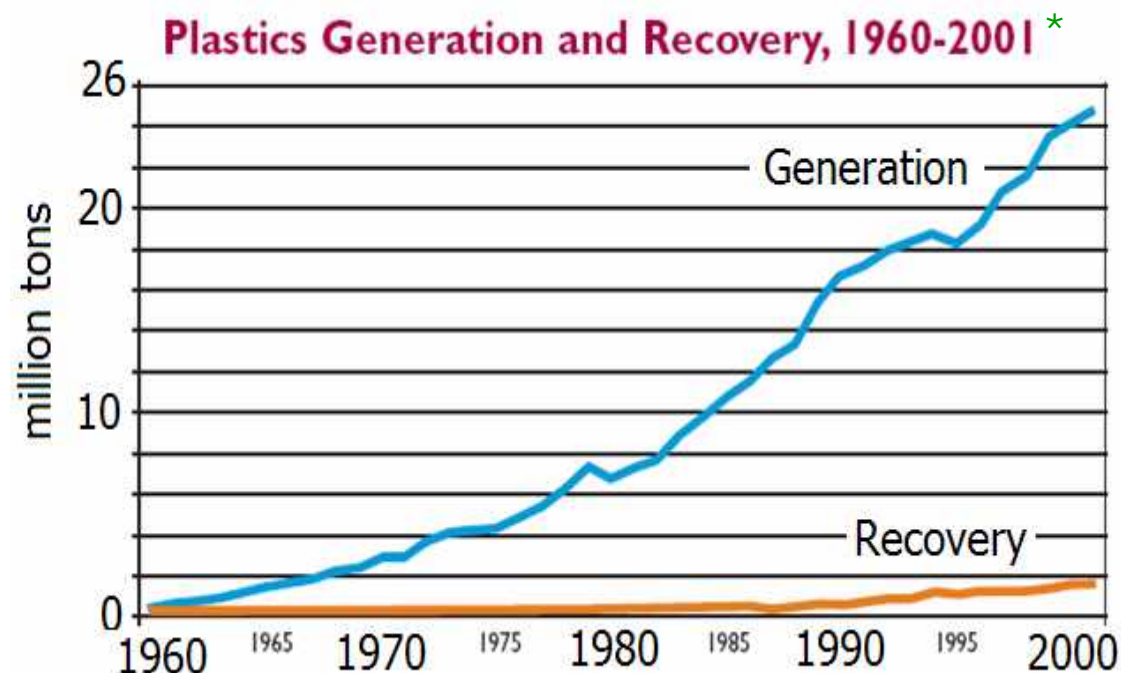


Acknowledgments

Funding by:

- New England Green Chemistry Consortium
- NSF/EPA

Petroleum-Based Polymers

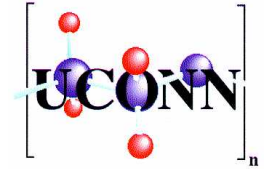


- Hydrophobic and resistant to biodegradation
- Escalating prices of petroleum (only ~ 2% of petroleum is used for polymers)

* Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2003, U.S. Environmental Protection Agency, 2003.

Tullo, Chem. Eng. News. 2005, 83, 19.

Environmental Concerns



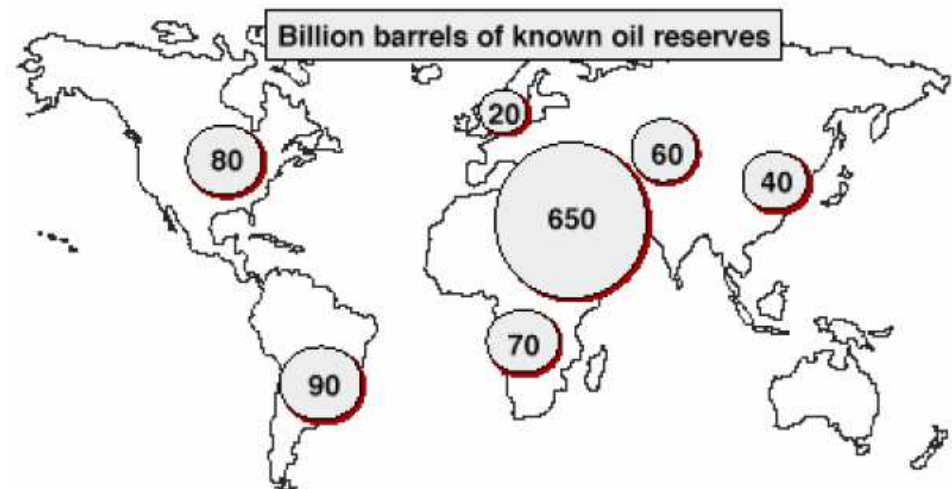
Plastics production has nearly doubled every 10 years for four decades.

Environmental Issue



Plastic are the largest volume component in U.S. landfills (~ 25%)

Sustainability Issue



Source: DOE-Energy Information Admin.

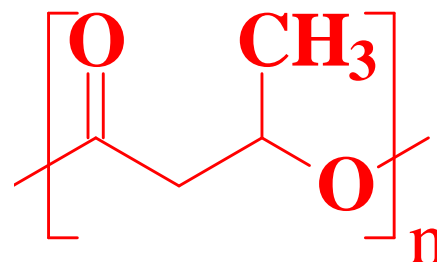
Existing petroleum resources are limited.

Biodegradable Polymers



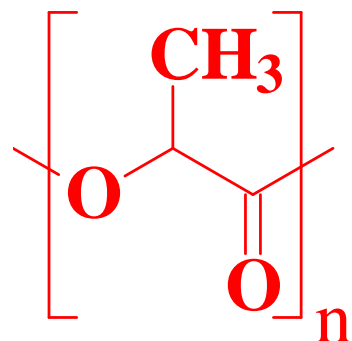
Aliphatic Polyesters from Hydroxyacids

Poly(3-hydroxybutyric acid)



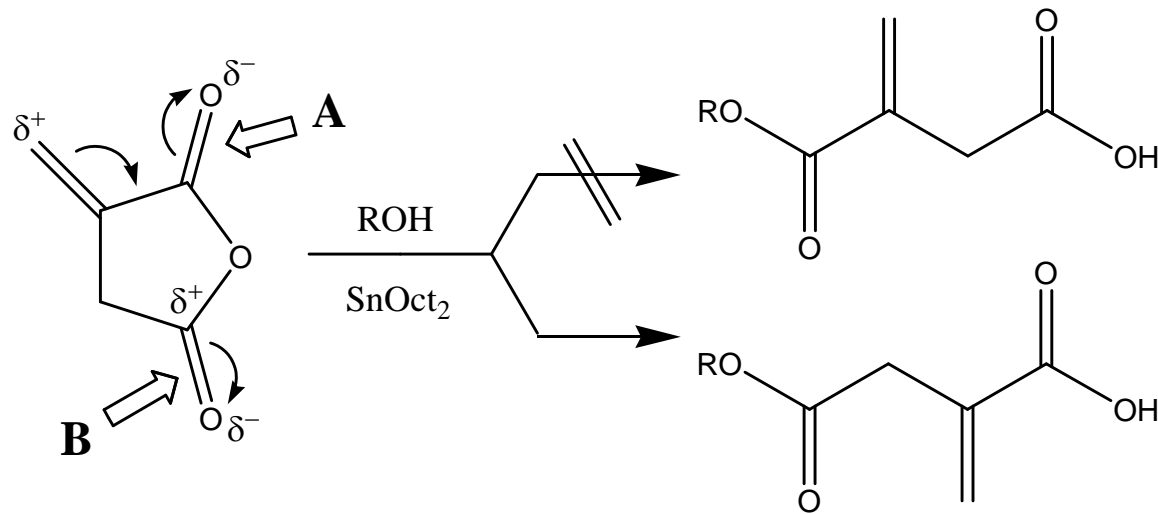
Poly(lactic acid)

NatureWorks LLC



Itaconic Anhydride

- Ramos – PEG functionalization



- Biocompatible – citric acid distillation, fermentation of carbohydrates (*Aspergillus terreus*)