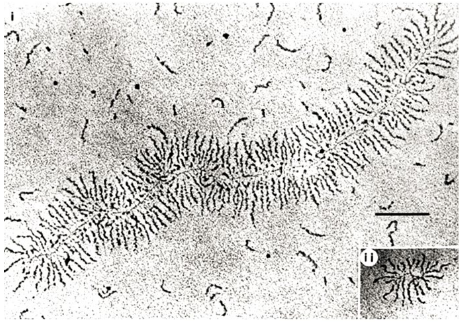
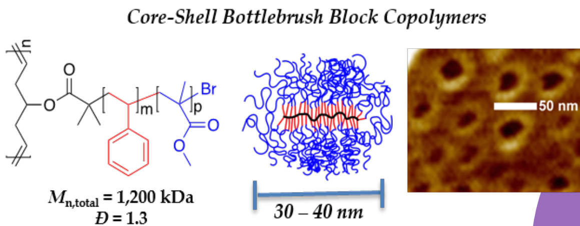
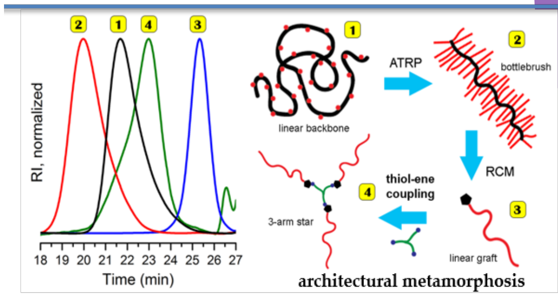
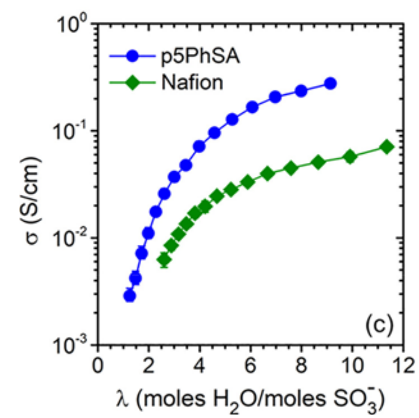
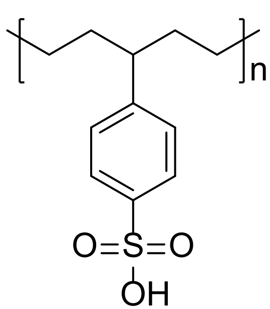
KEnEMUR GROUP

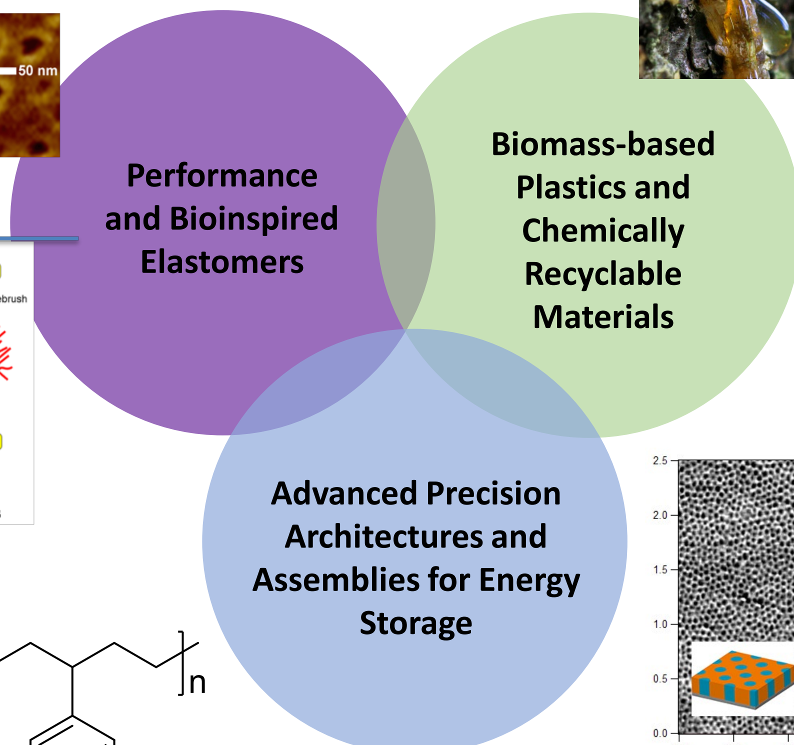


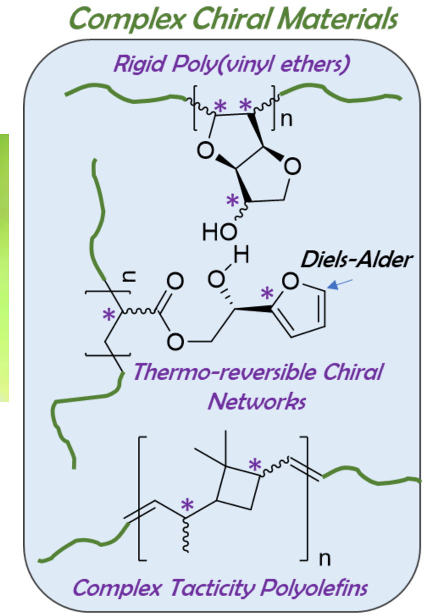


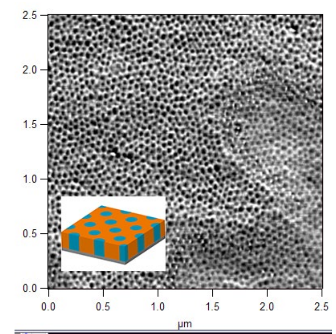


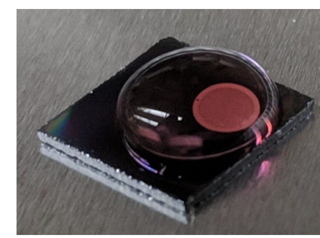






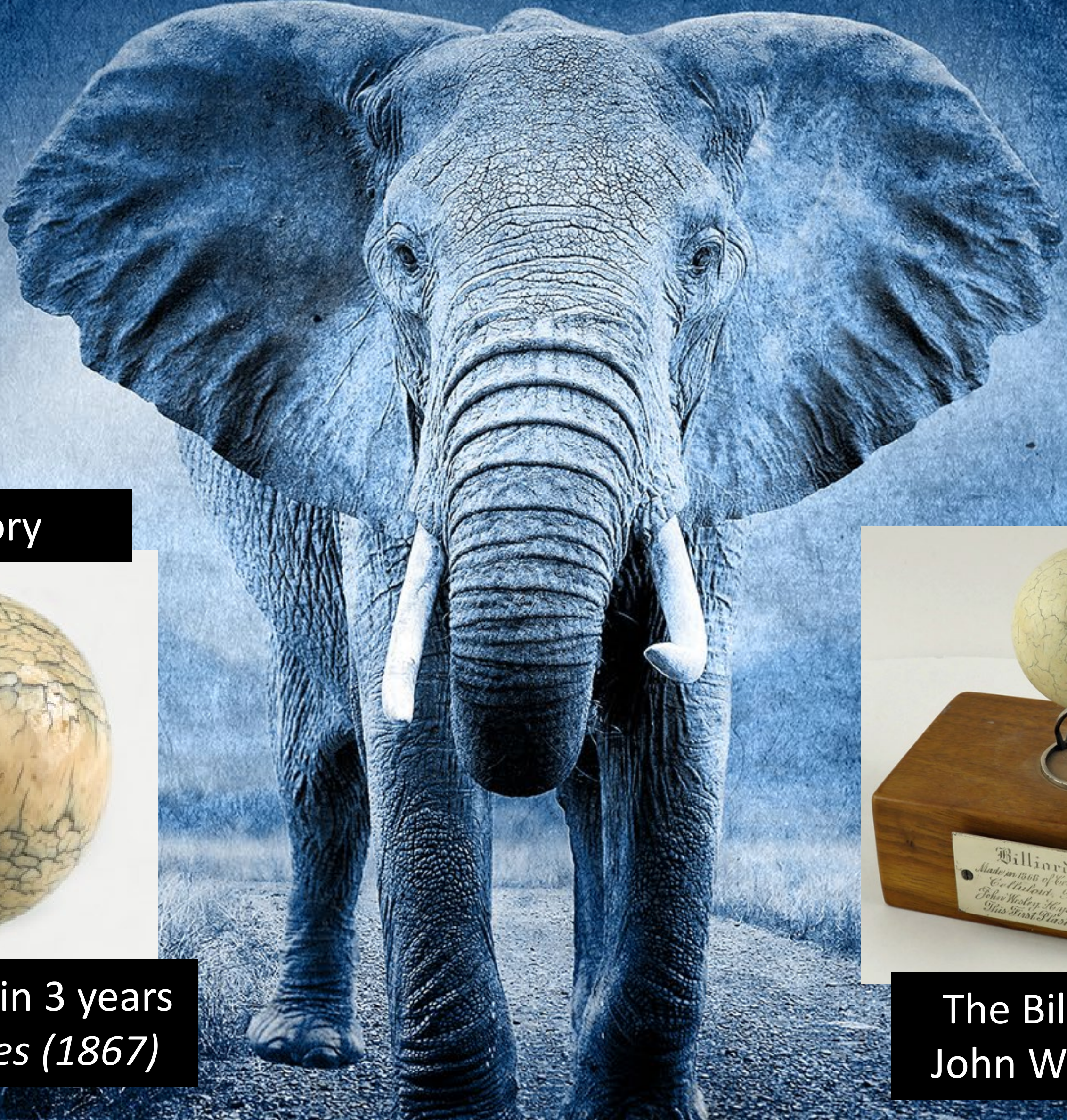




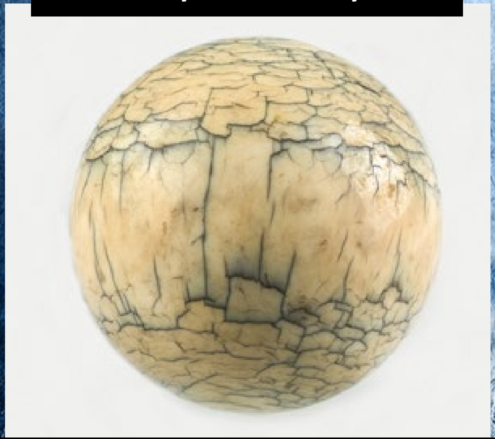


FSU REU Photochemistry Café
July 7, 2023

"As petroleum came to the relief of the whale," so "has celluloid given the elephant, the tortoise, and the coral insect a respite in their native haunts; and it will no longer be necessary to ransack the earth in pursuit of substances which are constantly growing scarcer." ~J. W. Hyatt

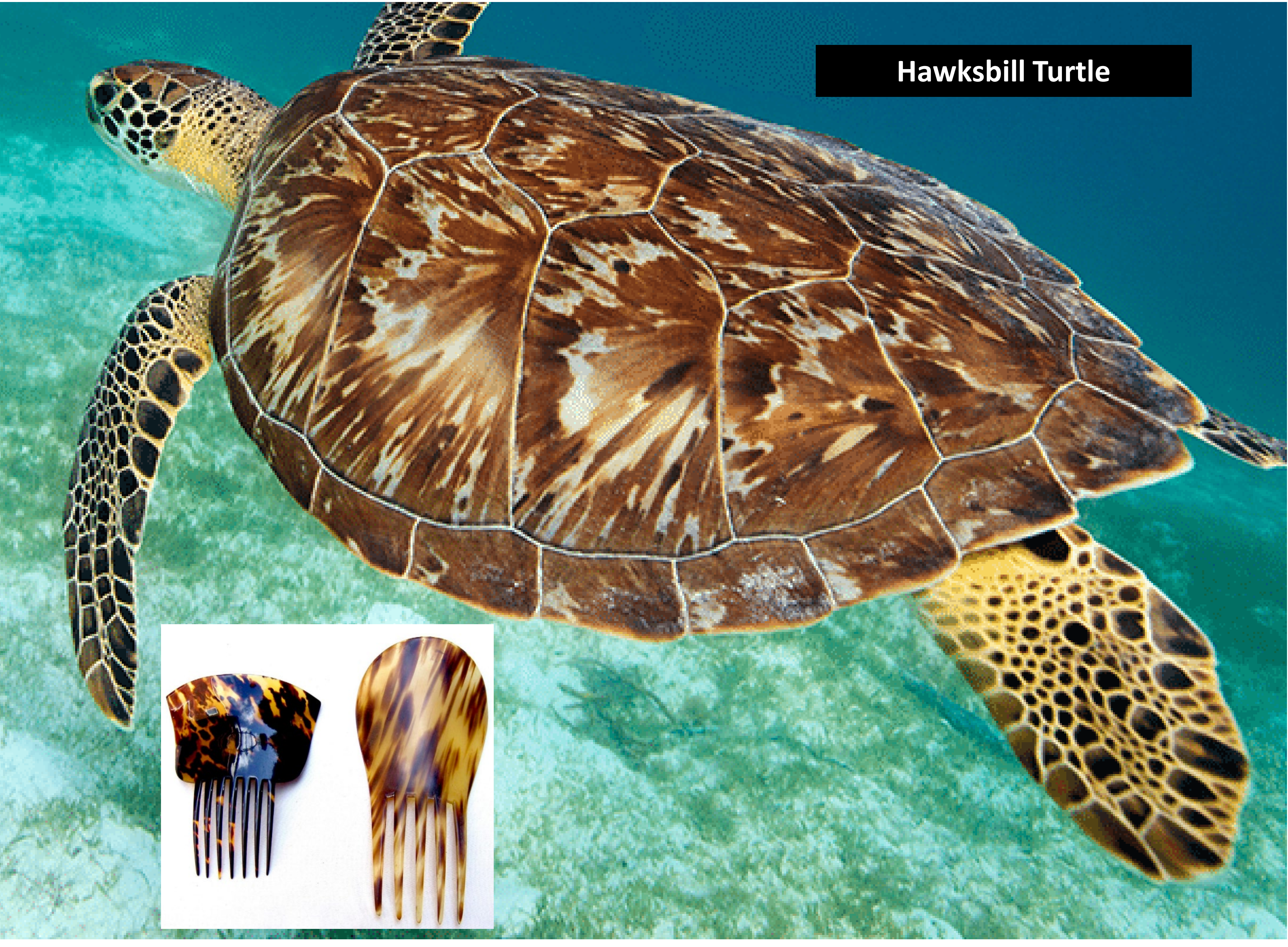


Ceylon Ivory

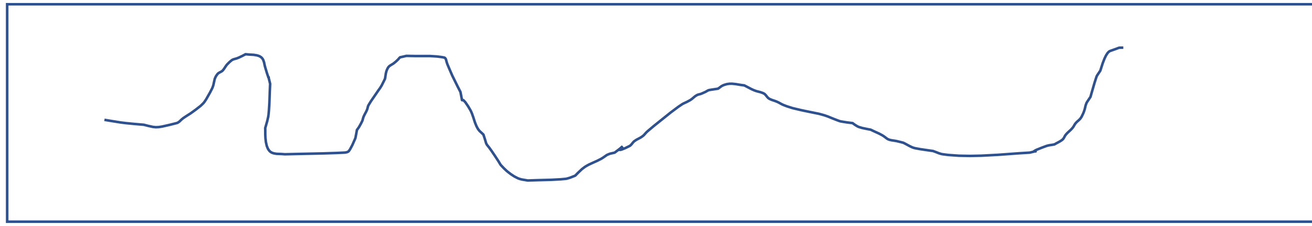


3,500 elephants in 3 years
~ *New York Times (1867)*

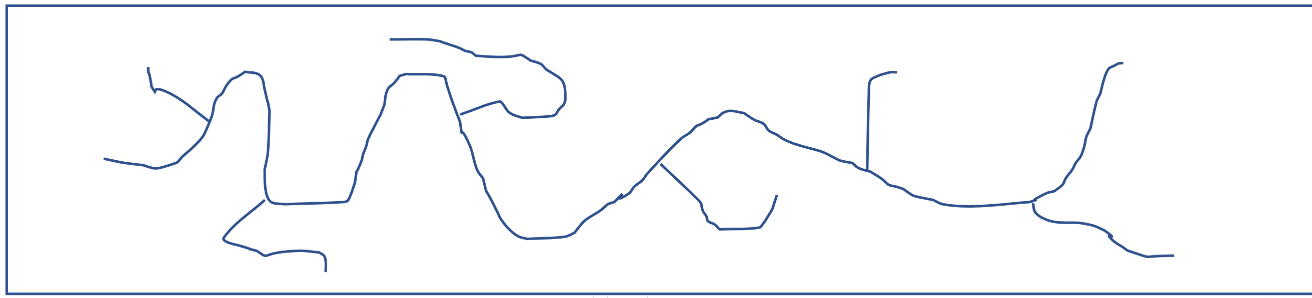
The Billiard Prize
John Wesley Hyatt


Hawksbill Turtle

Humans have found utility in polymers since the beginning



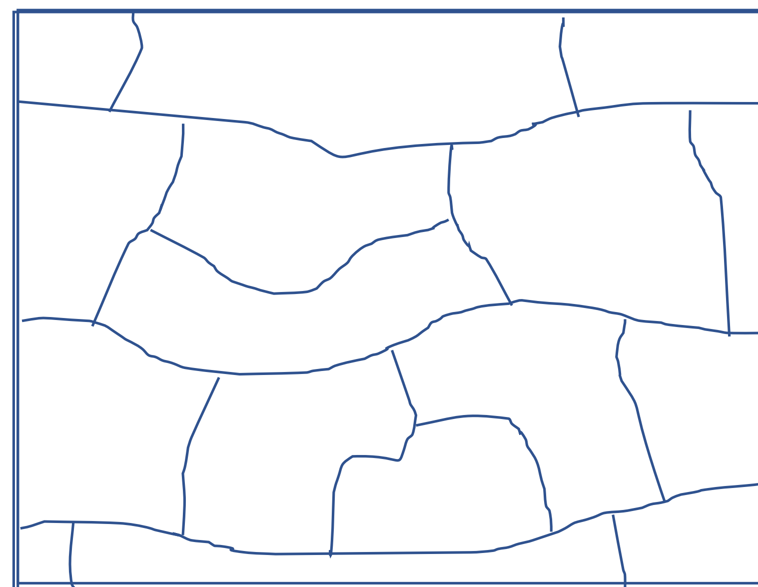
Cellulose – the most abundant organic polymer



Hemicellulose – many isomers (one example)

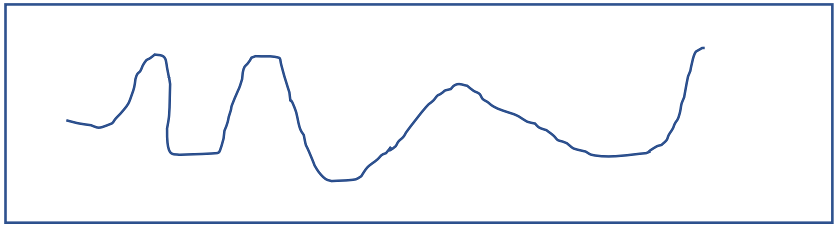
Lignin

- in hardwood (~28 ± 3%)
- in softwood (~20 ± 4%)
- "n" = infinity (network)
- extremely strong
- crosslinked
- hydrophobic



The first "man-made" polymers were modifications to natural polymers

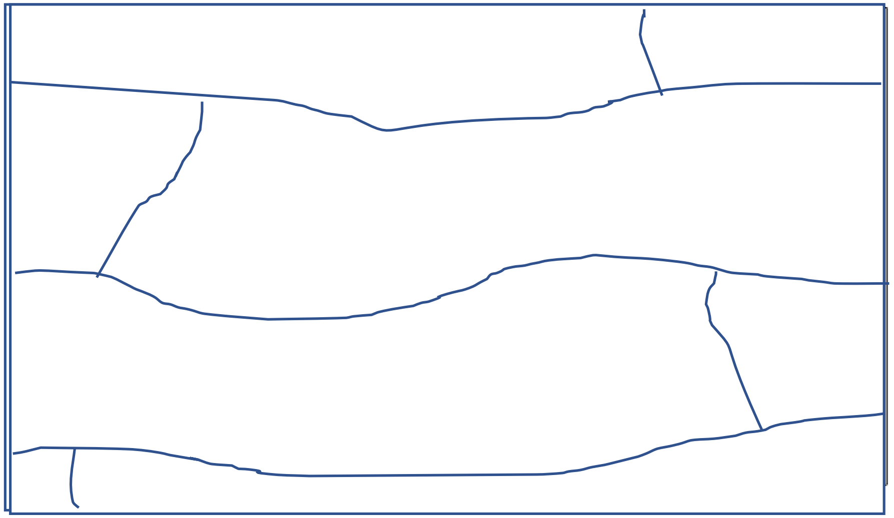
Natural Rubber (NR)



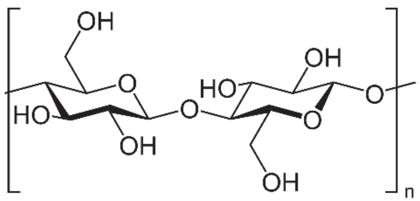
Note* - <u>100%</u> *cis* conformation

Vulcanized NR (sulfur treated) ~1839

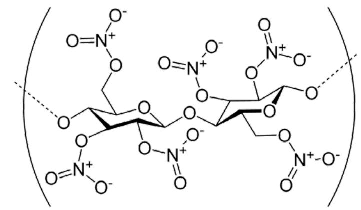
Utilizing the chemistry of olefins, Charles Goodyear treated NR with sulfur and temperature/pressure, creating a network polymer therefore stronger than NR.



The nitration of cellulose



Nitric Acid →



ignition → CO_2, CO, N_2, H_2O

all gases!!

cellulose trinitrate (gun cotton)

KNO_3, H_2SO_4 → cellulose mononitrate (celluloid) more stable

- industrial use (movie films, pool balls)

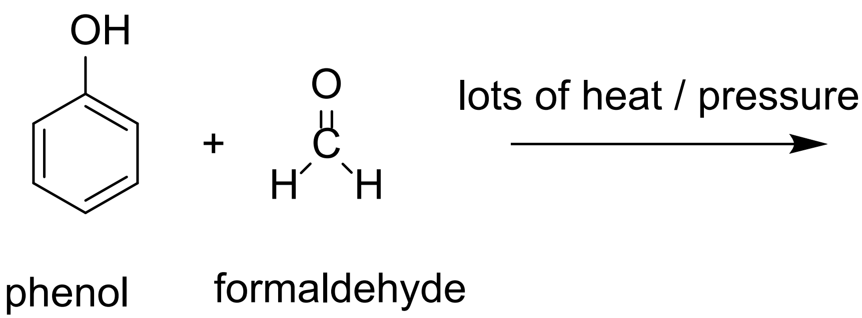
“smokeless” gun powder

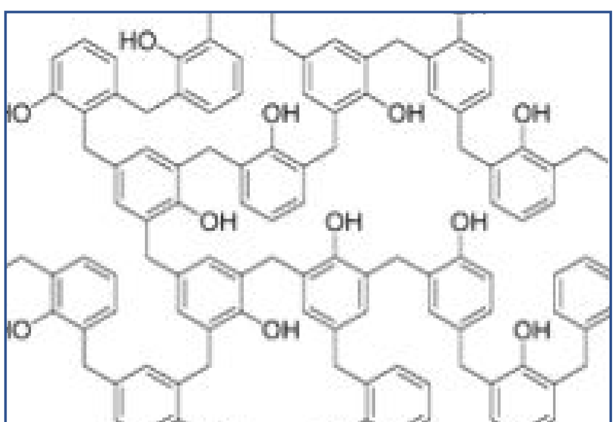
nitrate film (early movies)

The first synthetic polymer - Bakelite

Leo Baekeland - 1910’s (only a century ago)

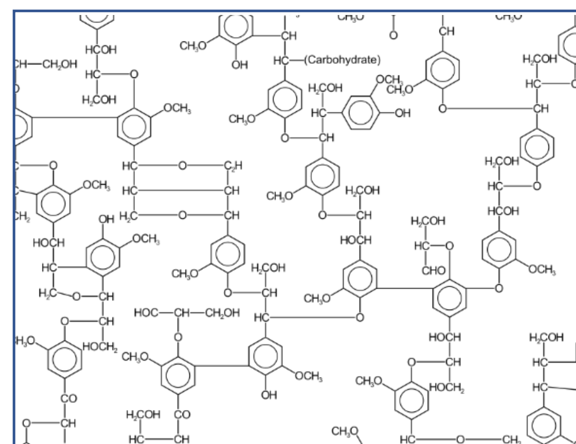
“Bakelite” – Phenolic Resins





Bakelite

remind you of anything you just saw?



Lignin!

Hermann Staudinger

Born: 23 March 1881 (Worms, Germany)
Died: 8 September 1965

1920: First predicted that polymers (rubber, cellulose, starch) were long chains of **covalently bonded** repeating units

"macromolecules"

Nobel Prize Chemistry 1953

WATER	METHANE
mol. mass = 18	mol. mass = 16
boils at 100 °C (212 °F)	boils at -162 °C (-258 °F)

World War II & the Birth of the Polymer Enterprise

Synthetic Rubbers

Polyesters

Polystyrene

Nylons

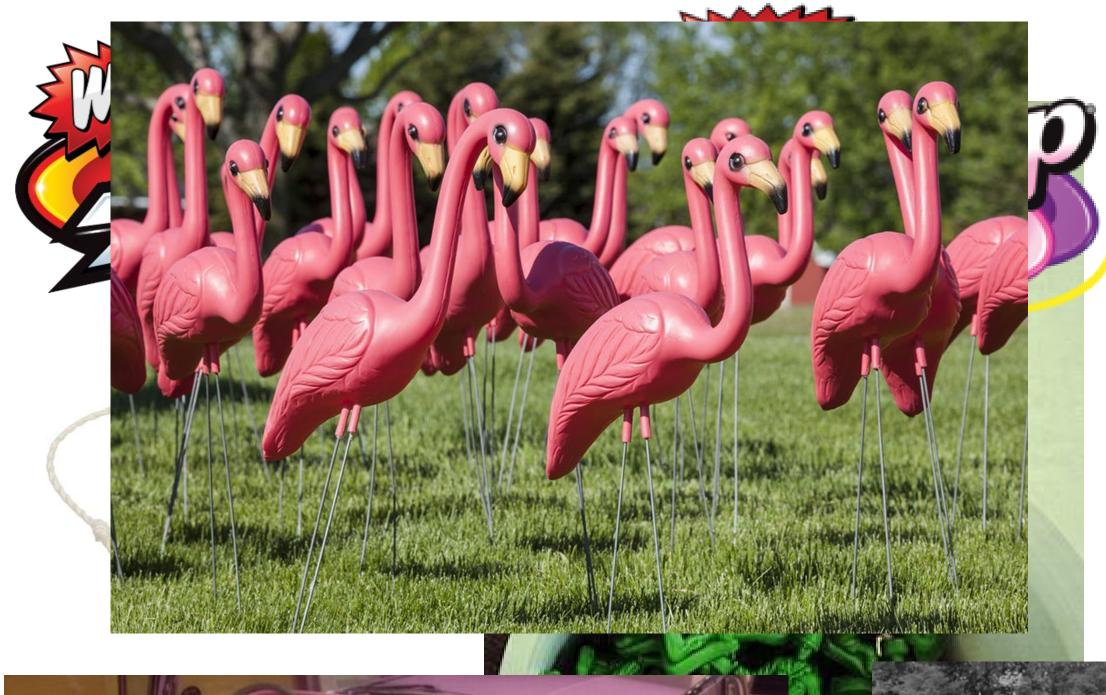
Vinyl

Acrylics

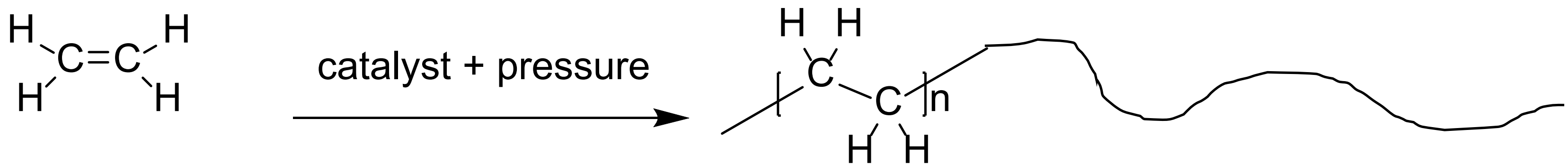
Saran

POLYETHYLENES

Post-war Era – Rebranding of Plastics

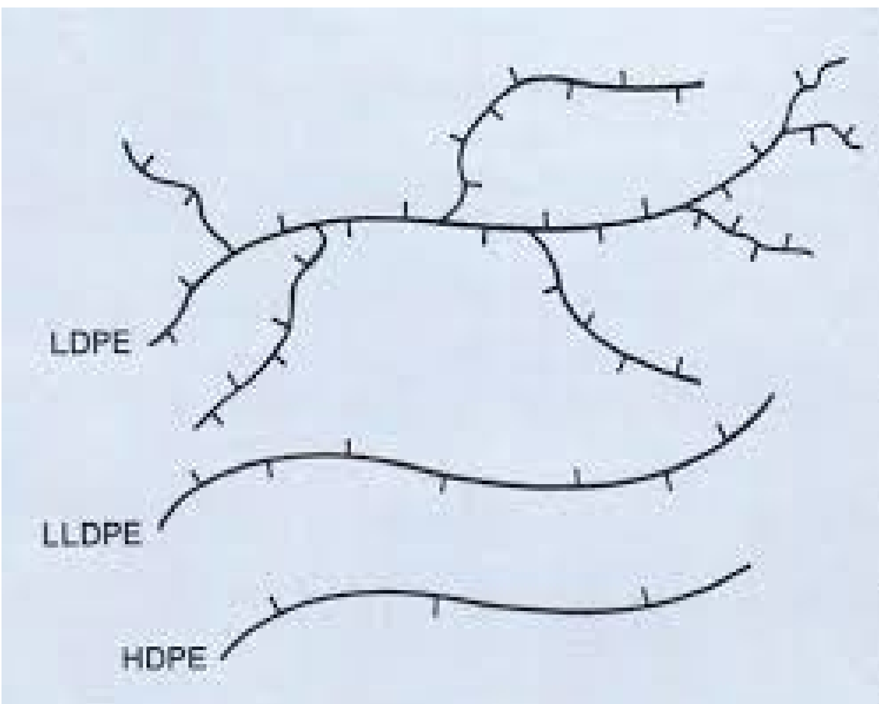


The World of Polyethylenes



ethylene

polyethylene



4
LDPE

e ... he
c ... :ular
arc
wi ... ties
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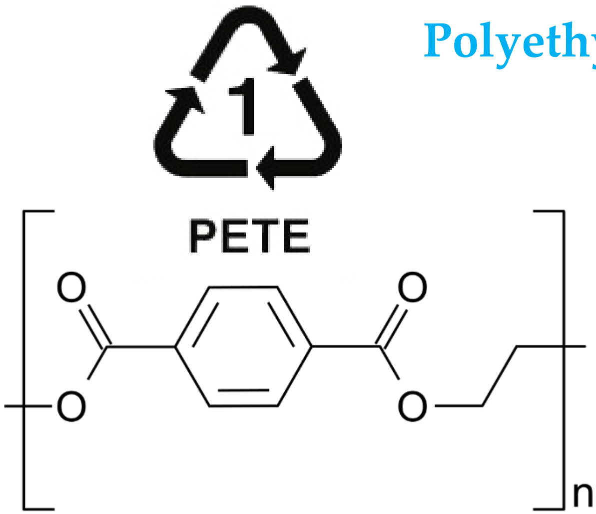
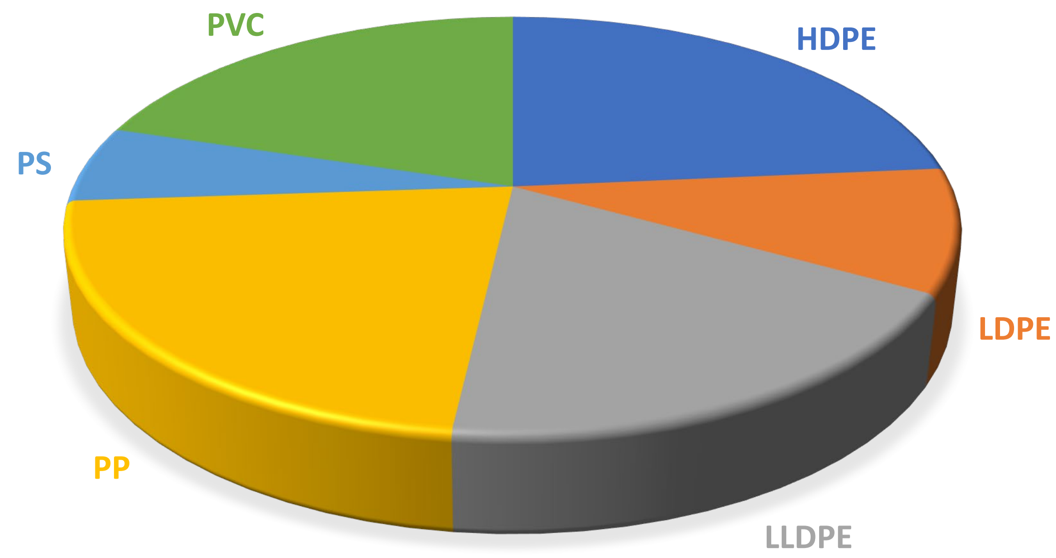
2
HDPE

Polyethylene Terephthalate (PET or PETE)



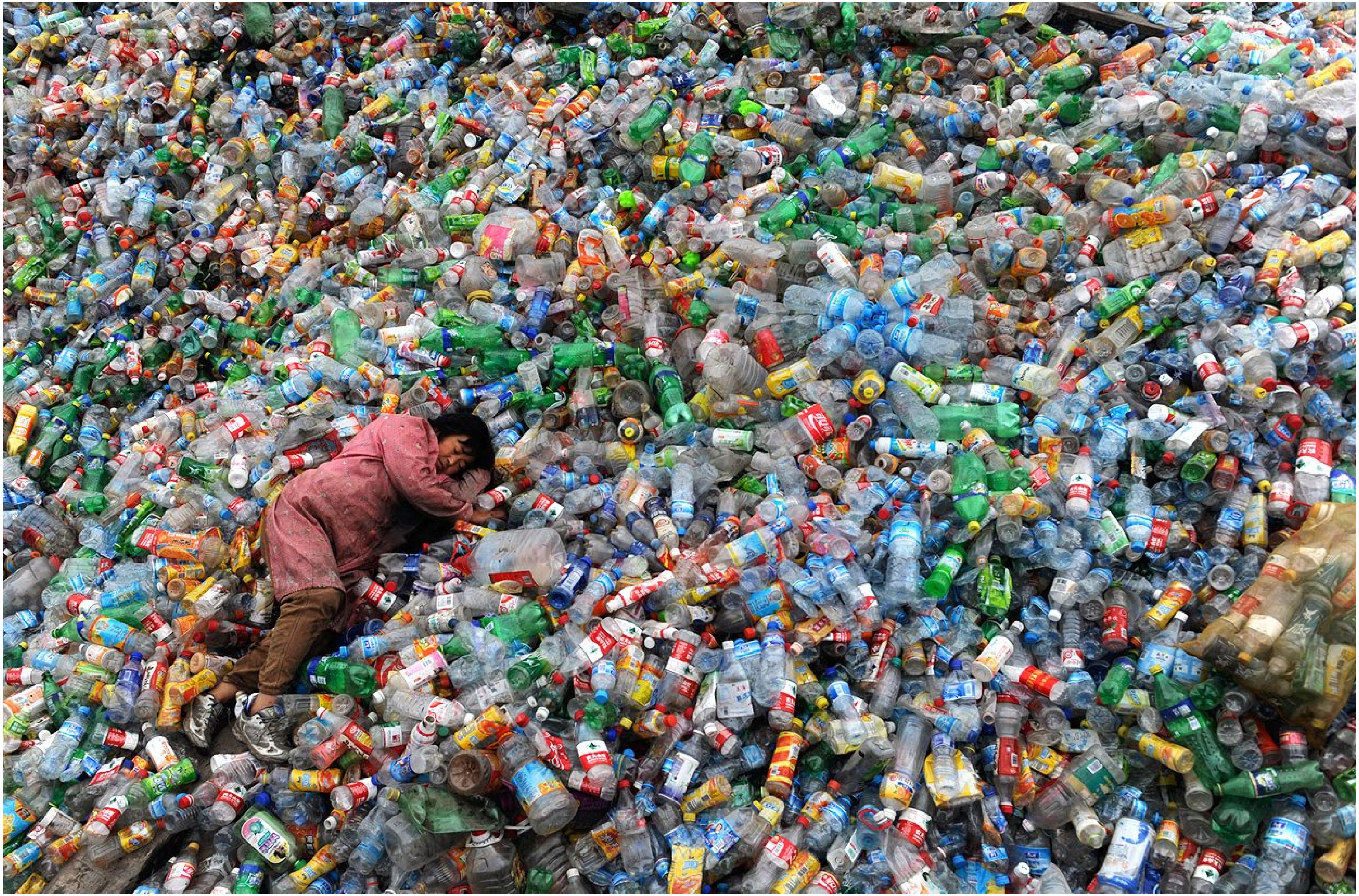
2013 NAFTA* PRODUCTION OF MAJOR COMMODITY POLYMERS – 74.3 BILLION POUNDS



Doesn't include PETE, which comprises most of your beverage bottles.

*North American Free Trade Agreement (includes Mexico, US, and Canada)

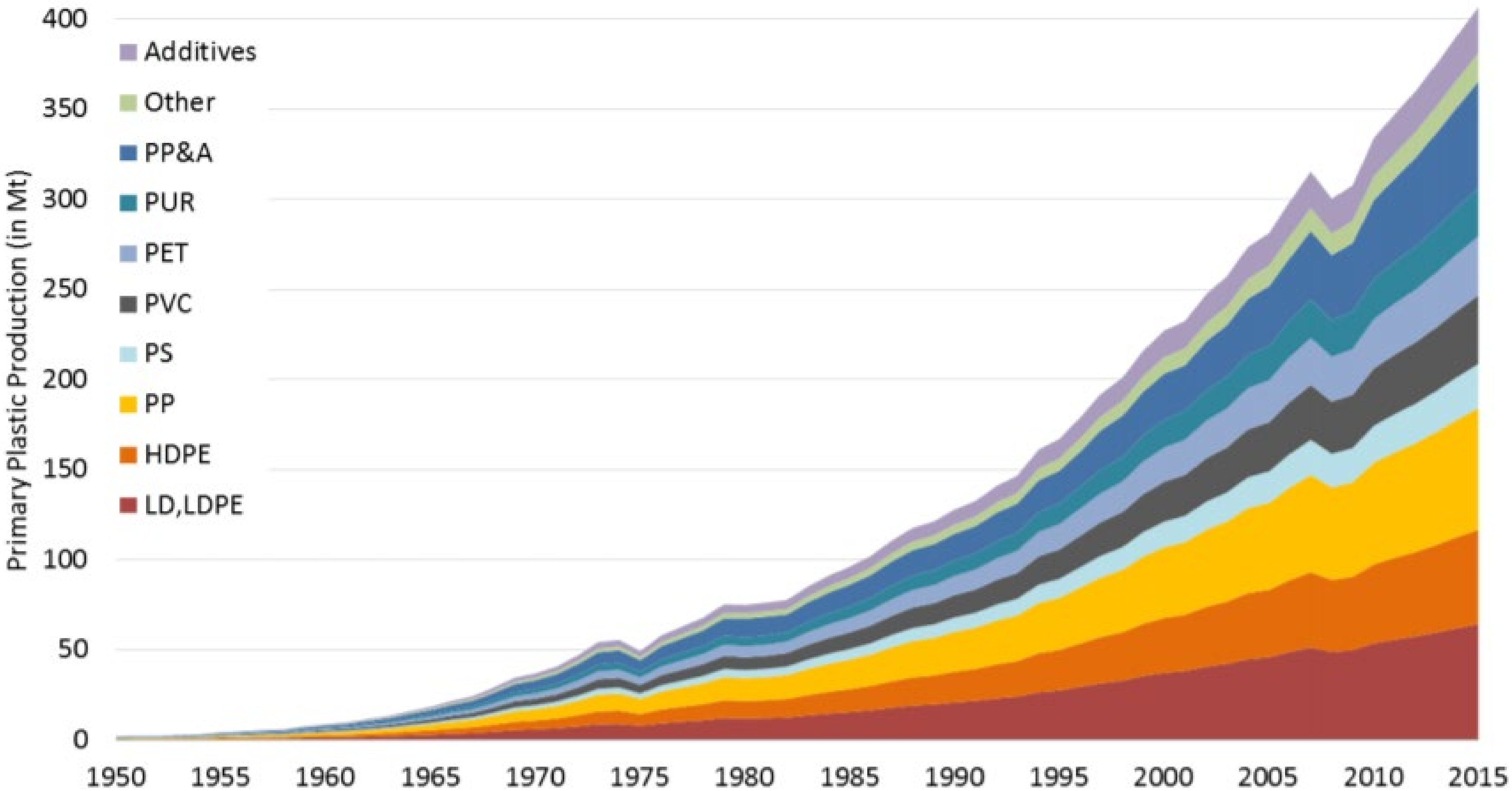
The growing realization that polymers are a bit TOO popular...



Laborer rests at a recycling plant in Jiaxing, China

http://www.theatlantic.com/infocus/2011/11/recycling-around-the-world/100186/

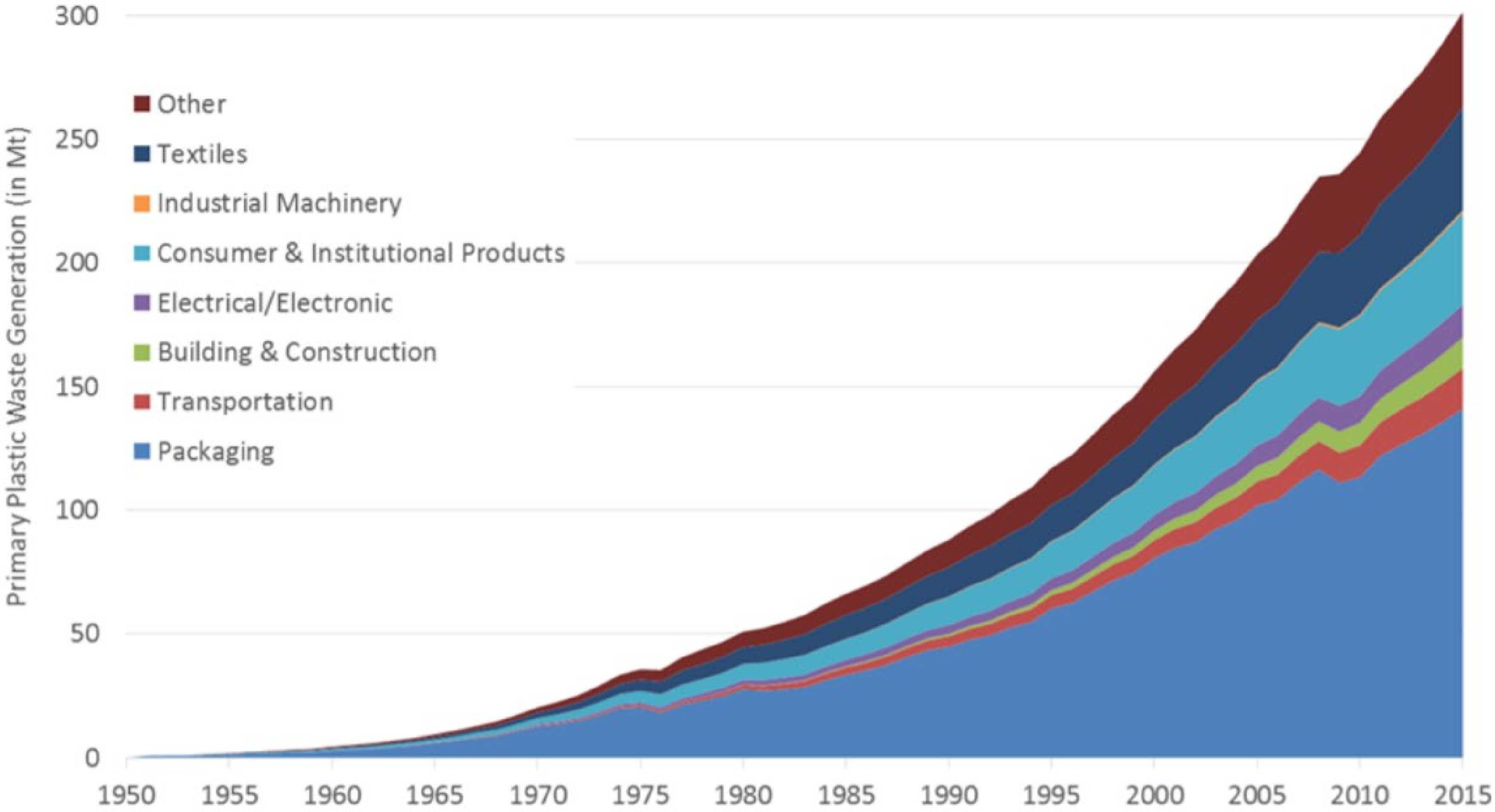
A Graphical Perspective by Type of Plastic



Geyer, R.; Jambeck, J. R.; Law, K. L., Production, use, and fate of all plastics ever made. *Science Advances* **2017,** *3* (7), e1700782.

400 Mtn = 882 BILLION POUNDS

A Graphical Perspective of Waste by Application

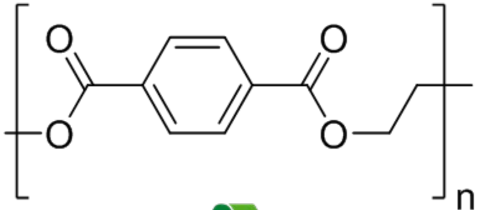


Geyer, R.; Jambeck, J. R.; Law, K. L., Production, use, and fate of all plastics ever made. *Science Advances* **2017,** *3* (7), e1700782.

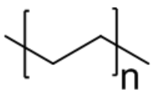
330 BILLION POUNDS of plastic packaging waste

Equivalent to 10,000 adult blue whales

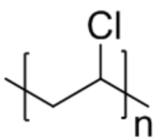
A Positive Trend: Recycling



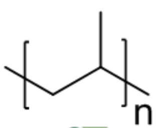
PETE



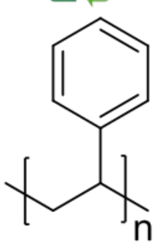
HDPE, LDPE



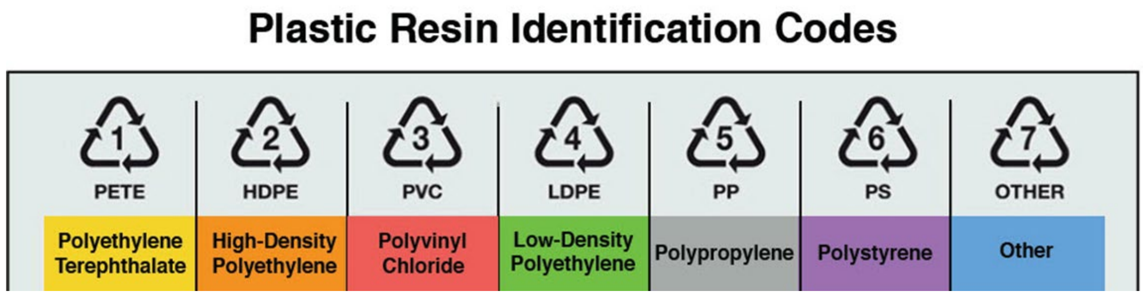
PVC

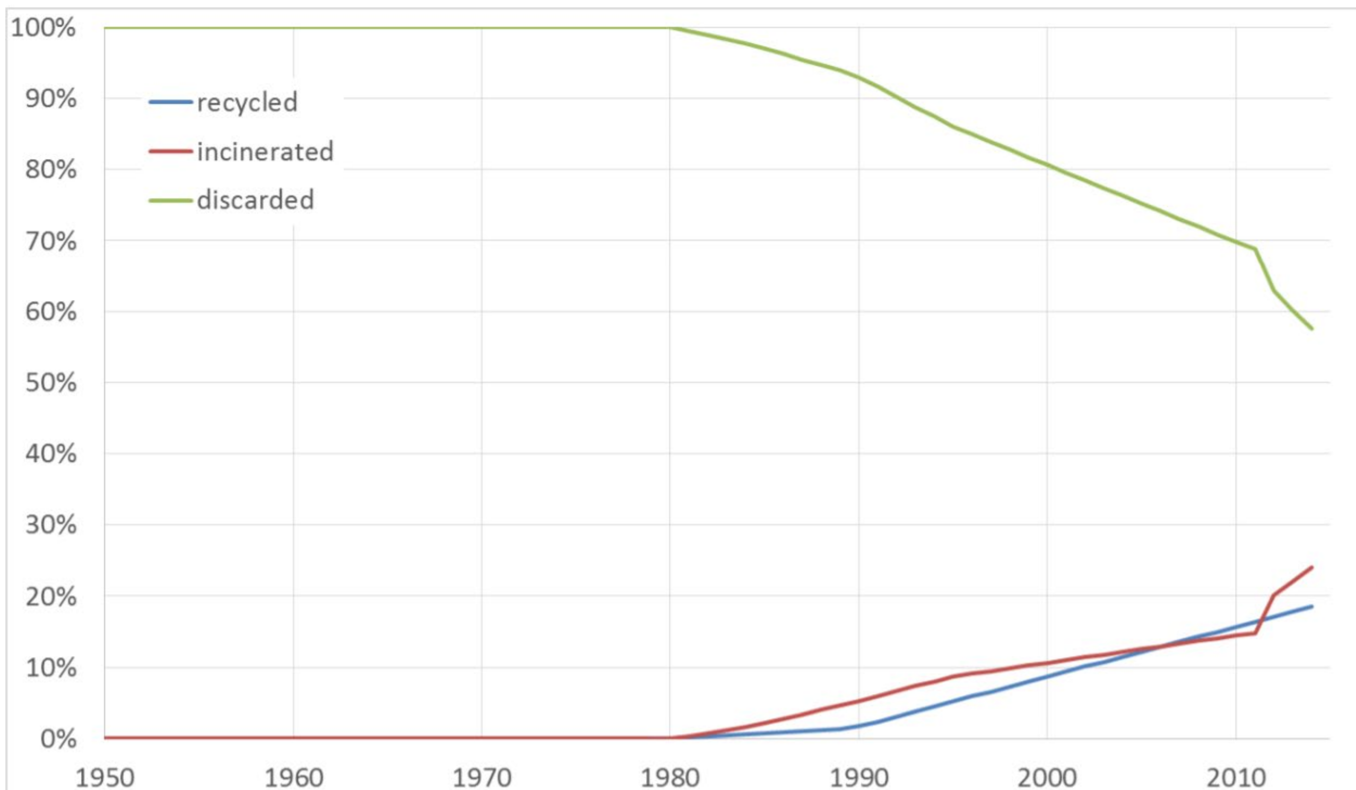


PP



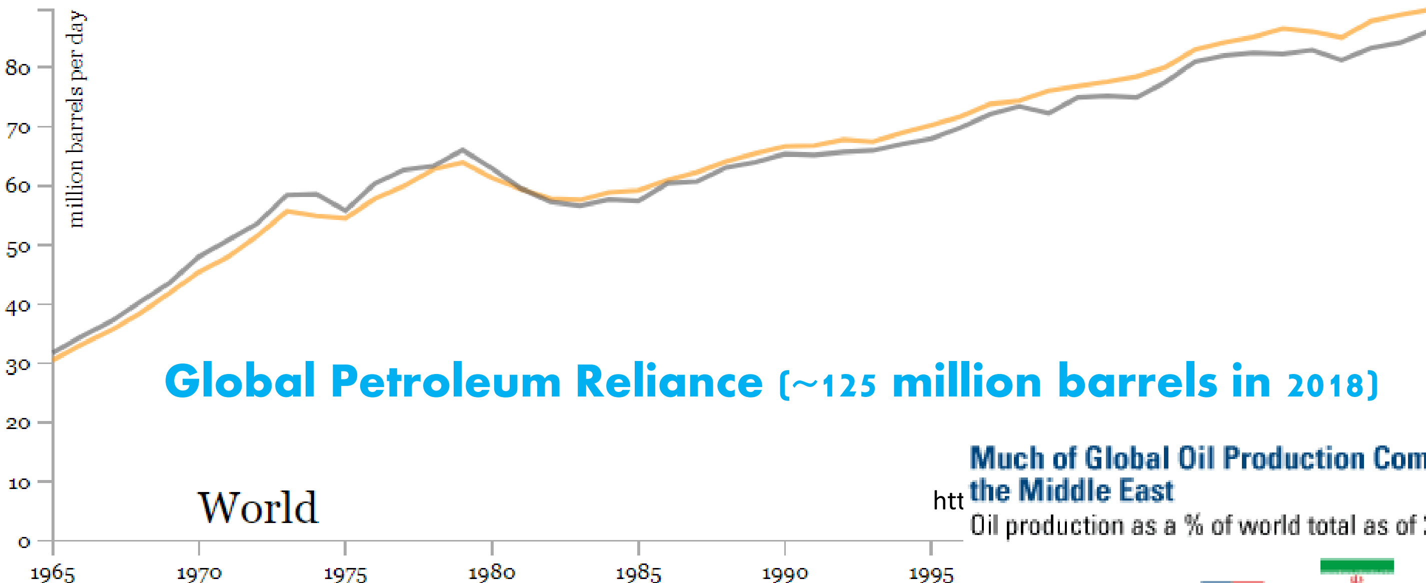
PS





Geyer, R.; Jambeck, J. R.; Law, K. L., Production, use, and fate of all plastics ever made. *Science Advances* **2017,** *3* (7), e1700782.

Our Increasing Dependence on Fossil Fuels

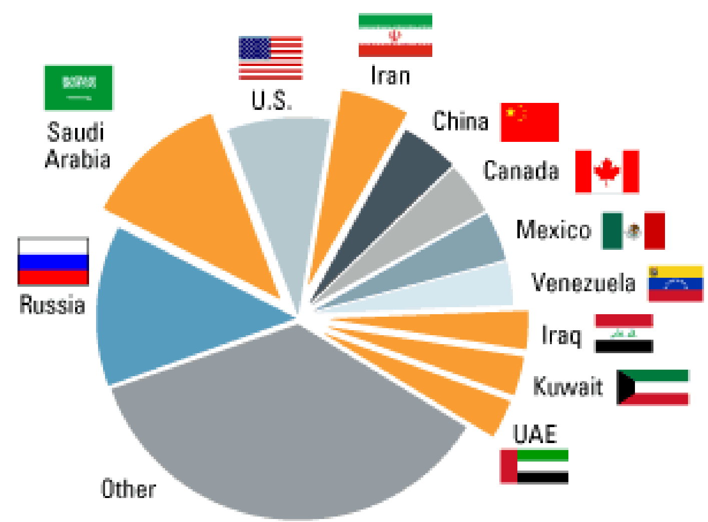


Global Petroleum Reliance (~125 million barrels in 2018)

htt

Much of Global Oil Production Comes from the Middle East

Oil production as a % of world total as of 2009



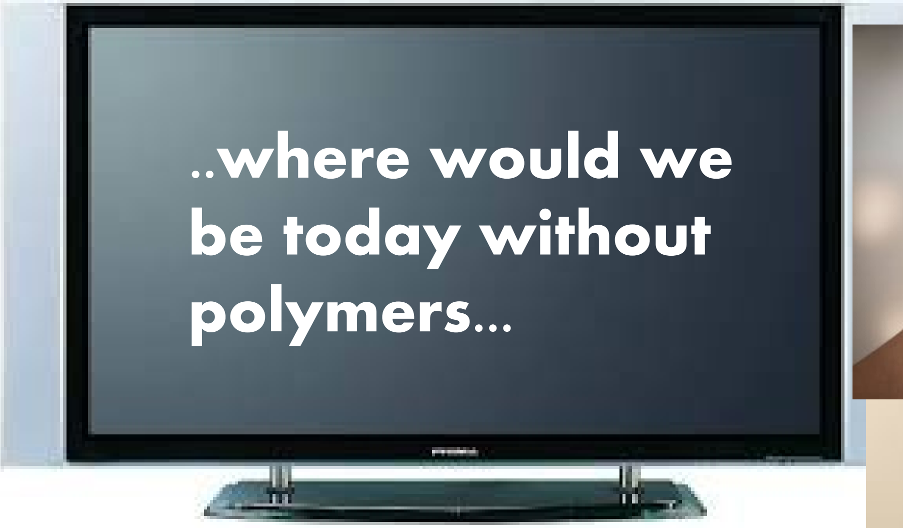
Source: BP (Statistical Review of World Energy, 2010), Barclays Capital

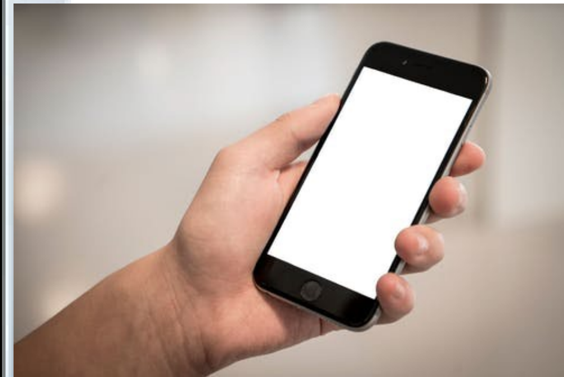
harder to get locations…

limited geographic availability…

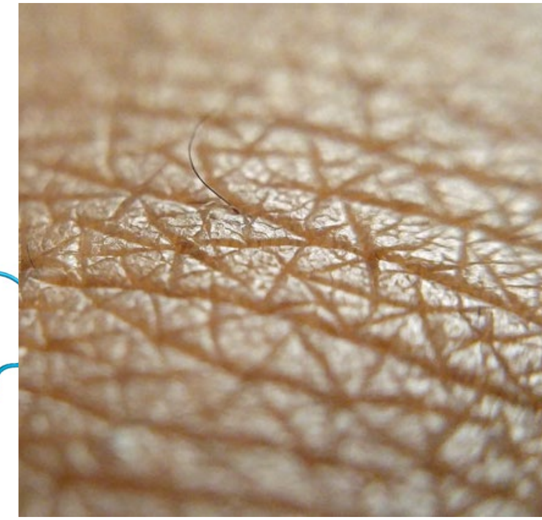
...and...of course, this!

OK, LETS TAKE A DEEP BREATH...

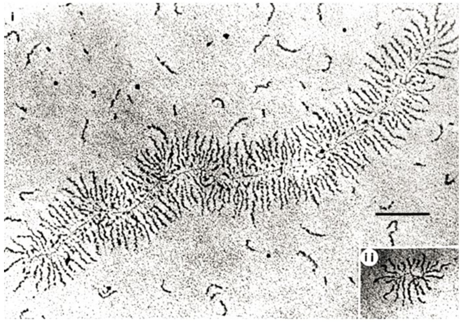

..where would we be today without polymers...



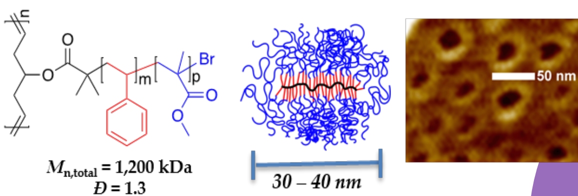

..we are
polymers...

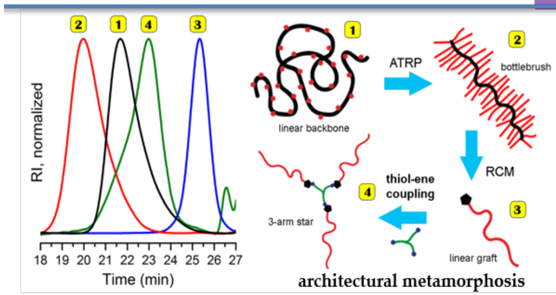


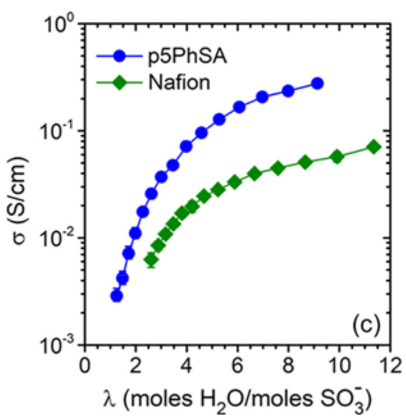
KEMUR GROUP

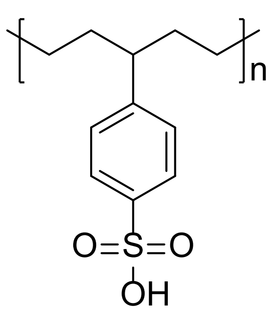


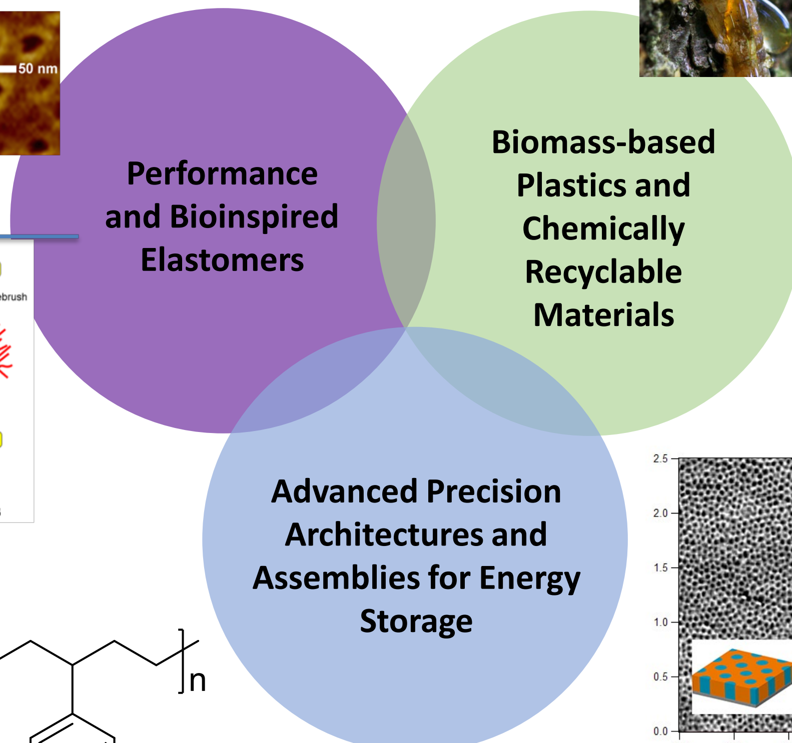
Core-Shell Bottlebrush Block Copolymers

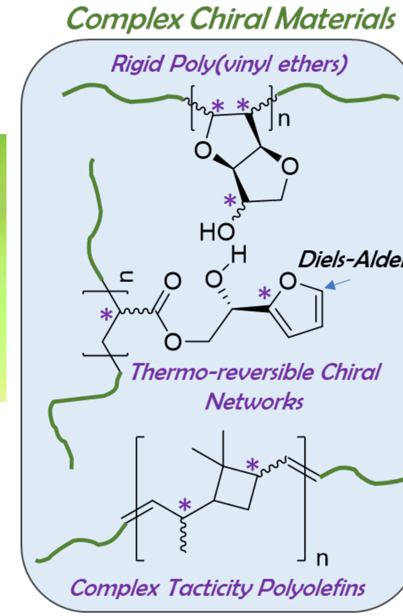


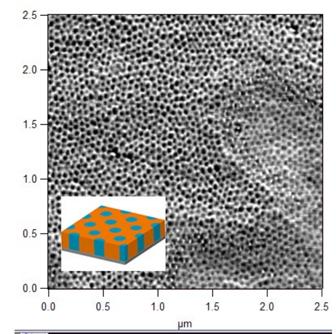


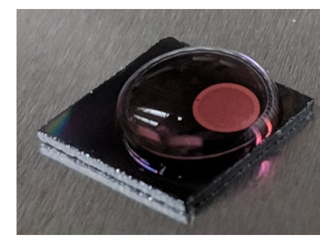












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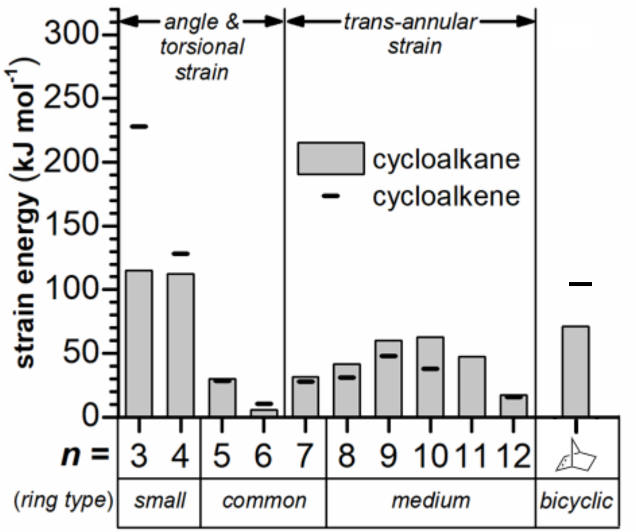
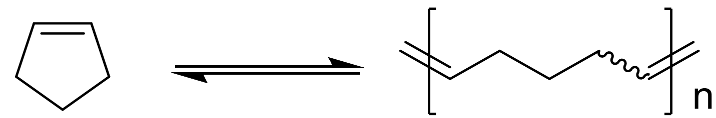
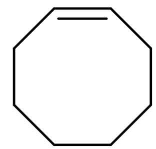
July 7, 2023

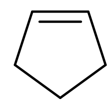
The Challenges of ROMP on Low Strain Rings



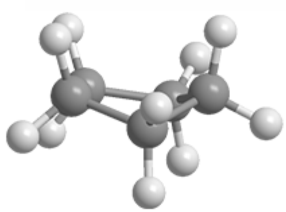




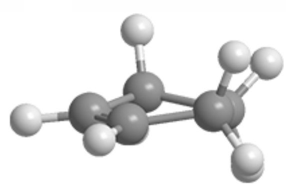
$-\Delta H$ = 31 kJ mol^{-1}
$-\Delta S$ = 9 J mol^{-1} K^{-1}



$-\Delta H$ = 28 kJ mol^{-1}
$-\Delta S$ = 70 J mol^{-1} K^{-1}



cyclopentane



cyclopentene

$$\Delta G_{pol} = \Delta H_{pol} - T\Delta S_{pol}$$

ring strain / *low strain*

molecular aggregation (-)
rot. degrees of freedom (+)

heightened sensitivity to temperature
- also $[M]_0$

Neary, W. J. & JGK. *ACS Macro Lett.* **2019**, *8*, 46

Cyclopentene ROMP

A need for:

- Better control - (dispersity, targeted molar mass, high conversion)
- Monomer development - More derivatives that undergo ROMP
- Material Properties - Especially on functionalized derivatives
- Advanced architectures - with control = block, gradient, or grafted polymers

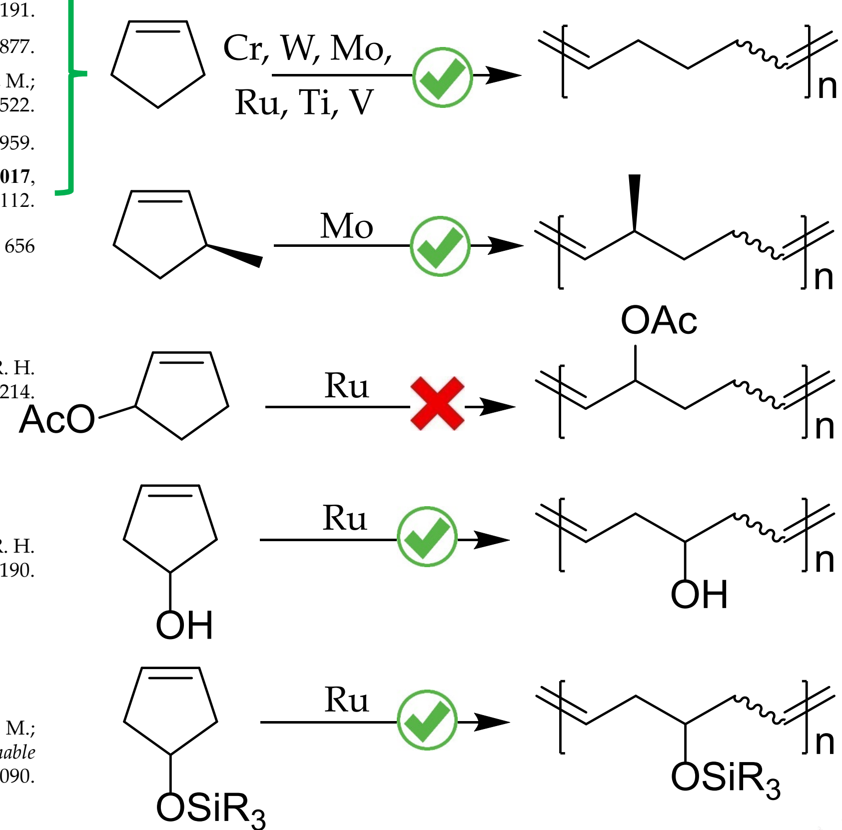
Eleuterio H. S. US Patent 3,074,098 **1963** (Du Pont)
Schrock, R. R. et al. *Macromolecules* **1989**, *22*, 3191.
Myers, S. B.; Register, R. A. *Polymer* **2008**, *49*, 877.
Herz, K.; Imbrich, D. A.; Unold, J.; Xu, G. J.; Speiser, M.; Buchmeiser, M. R. *Macromol. Chem. Phys.* **2013**, *214*, 1522.
Tuba, R.; Grubbs, R. H. *Polym. Chem.* **2013**, 3959.
Mulhearn, W. D.; Register, R. A. *ACS Macro Lett.* **2017**, 112.

Sita, L. R. *Macromolecules* **1995**, *28*, 656

Hejl, A.; Scherman, O. A.; Grubbs, R. H. *Macromolecules* **2005**, *38*, 7214.

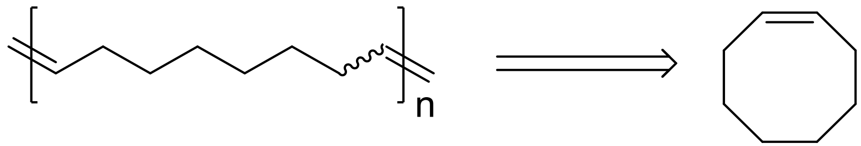
Tuba, R.; Al-Hashimi, M.; Bazzi, H. S.; Grubbs, R. H. *Macromolecules* **2014**, *47*, 8190.

Tuba, R.; Balogh, J.; Hlil, A.; Barlóg, M.; Al-Hashimi, M. Bazzi. *ACS Sustainable Chem. Eng.* **2016**, *4*, 6090.

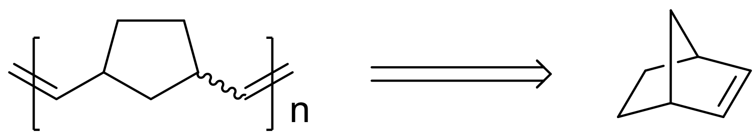


Reviewed in: Neary, W. J. & JGK *ACS Macro Lett.* **2019**, *8*, 46

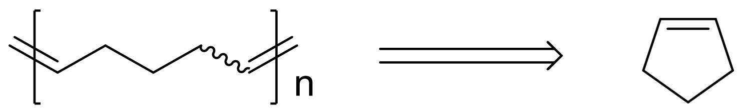
Why Go Through All the Trouble?



- *Even numbered ring*
- *Regioregularity required unless symmetric disubst.*
- *semi-crystalline*



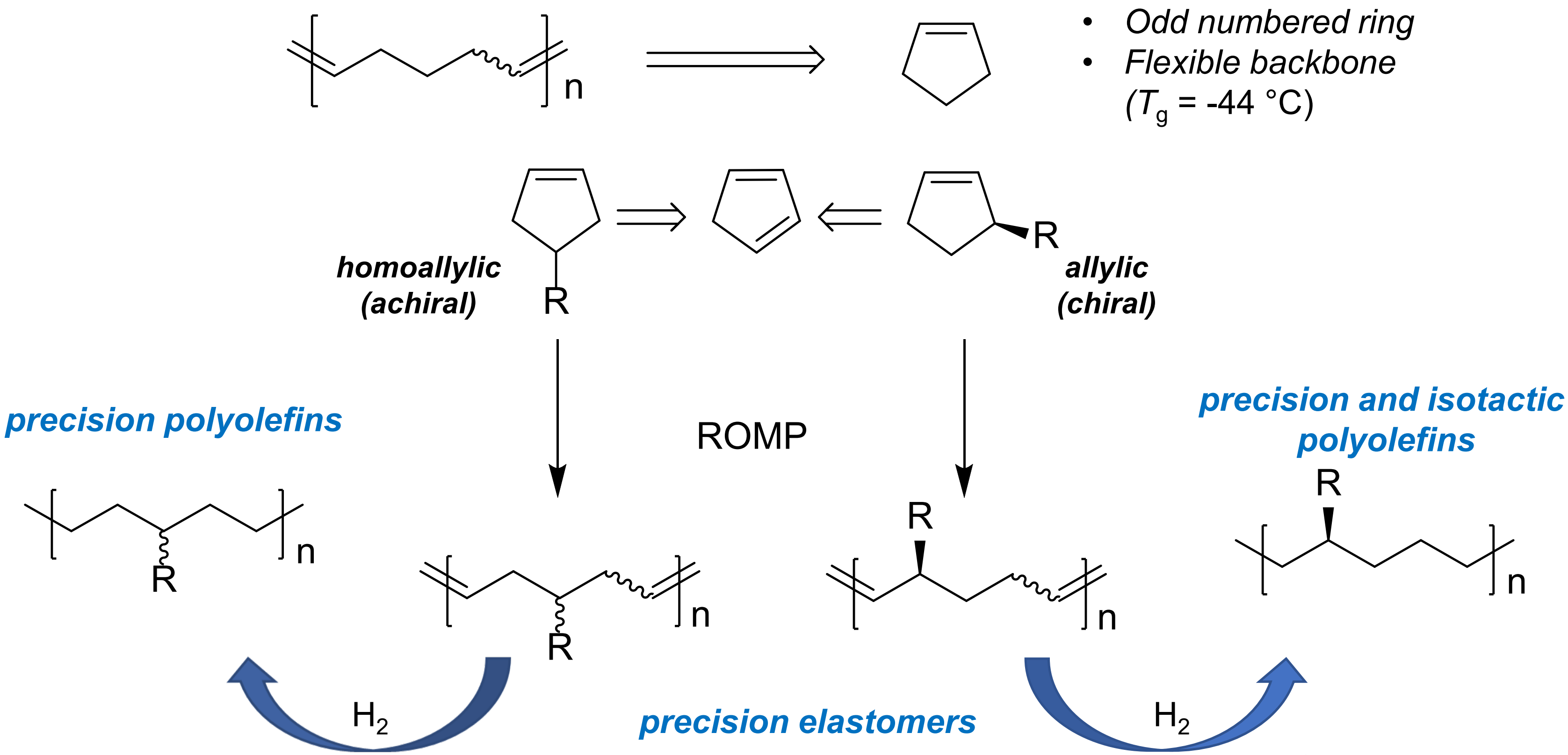
- *Cyclopentane-tethered backbone*
- *Enhanced rigidity* (T_g= 40 °C)



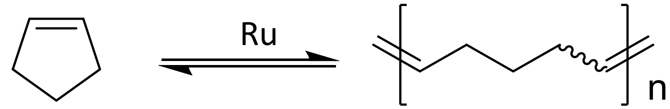
- *Odd numbered ring*
- *Flexible backbone* (T_g = -44 °C)

Divergent Possibilities from Cheap Starting Materials

- *Odd numbered ring*
- *Flexible backbone* *(T_g = -44 °C)*



Polypentenamers are Chemically Recyclable

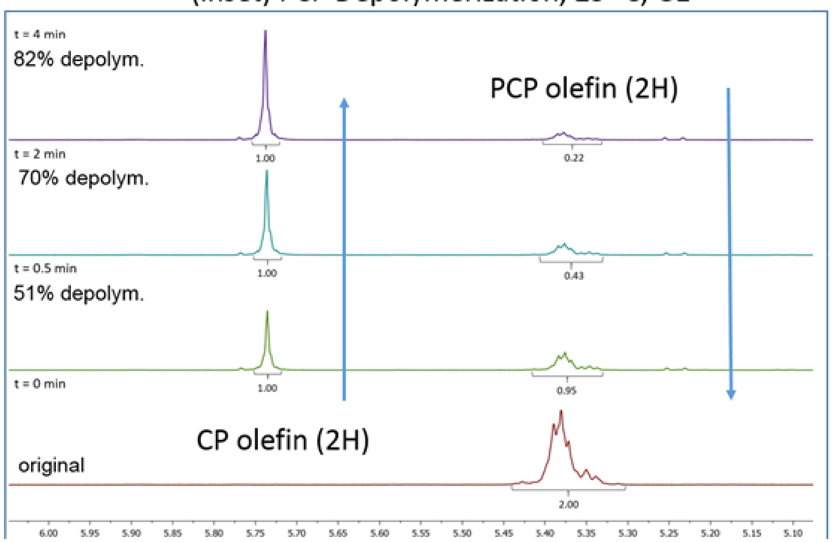


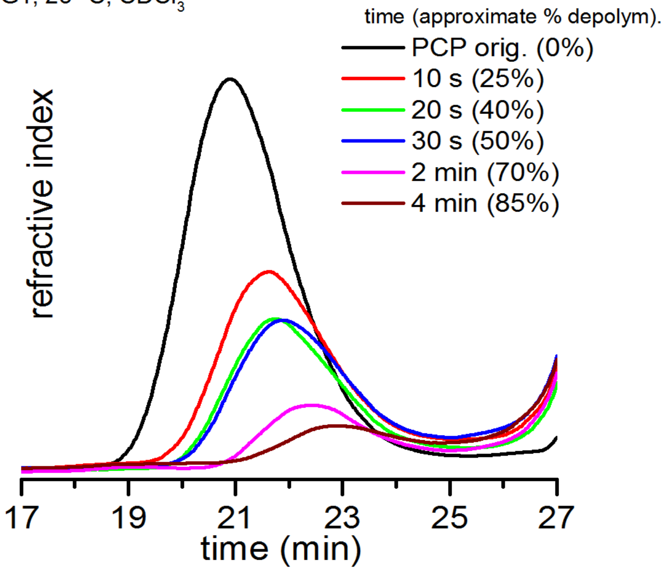
Monomer favored at high temp diluted

Polymer favored at low temp, concentrated

Due to the low ceiling temperature (T_c), depolymerization is possible under reverse conditions

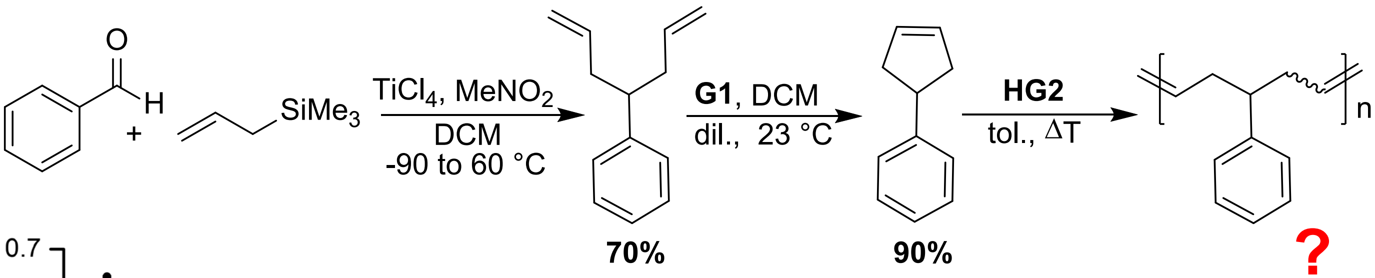
(inset) PCP Depolymerization, 25 °C, G1

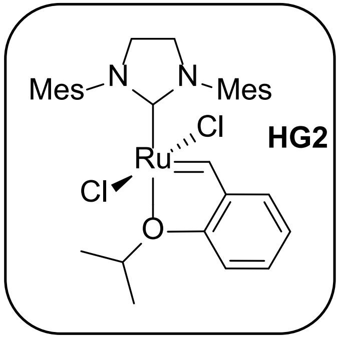


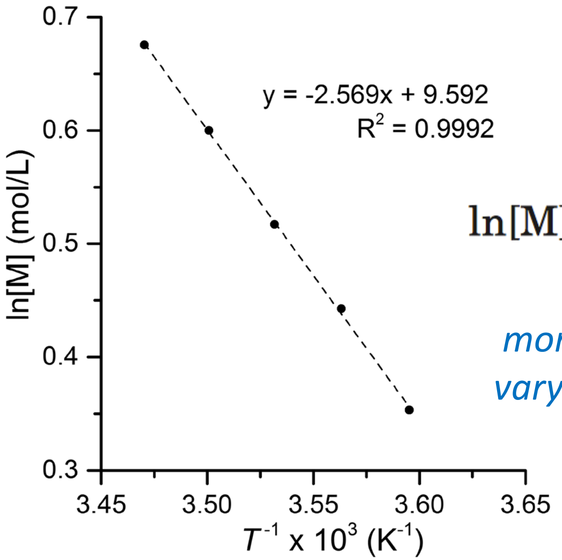


Neary, W. J.; Isais, T. A.;& JGK. *JACS.* **2019**, *141*, 14220.

Where to Begin?: 4-Phenylcyclopentene (4PCP)



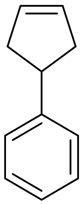




in toluene-d_8; $[M]_0$=2.50 M; 0.23 mol% HG2
(VT-^{1}H NMR; 5, 7.5, 10, 12.5, 15 °C)

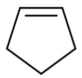
$$\ln[\mathrm{M}]_e = \frac{\Delta H_p}{RT} - \frac{\Delta S^\circ}{R}$$

monitoring $[M]_{eq}$ at varying T by ^{1}H NMR



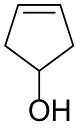
ΔH_p = -21.3 kJ mol^{-1}
ΔS_p = -79.5 J mol^{-1} K^{-1}

ring strain slightly less than CP



ΔH_p = -23.4 kJ mol^{-1}

Tuba, R.; Al-Hashimi, M.; Bazzi, H. S.; Grubbs, R. H. *Macromolecules* **2014**, *47*, 8190.



ΔH_p = -25.9 kJ mol^{-1}

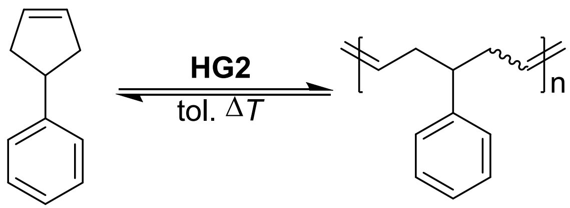
Tuba, R.; Grubbs, R. H. *Polym. Chem.* **2013**, *4*, 3959.

William Neary

THE FLORIDA STATE UNIVERSITY

Neary, W. J. & JGK *Macromol. Rapid Commun.* **2016**, *37*, 975
US Patent 10,640,587 (**2020**)

Effect of Temperature on Ru-based ROMP



$[4PCP]_0$ = 4.5 M
[cat] = 0.23 mol %
rxn time = 12 h

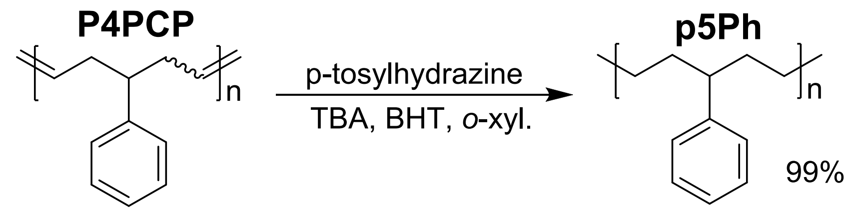
T (°C)	Conv. (%)[a]	$M_{n,theo}$ (kg mol^{-1})[b]	$M_{n,SEC}$ (kg mol^{-1})[c]	*Đ*[c]
10	62.3 ± 0.3	39.1	47.9 ± 2.7	1.51 ± 0.02
5	67.2 ± 0.3	42.1	47.6 ± 0.5	1.65 ± 0.03
0	72.2 ± 0.4	45.3	50.9 ± 0.6	1.63 ± 0.01
-5	75.0 ± 0.1	47.1	67.4 ± 1.4	1.60 ± 0.01
-10	78.9 ± 1.2	49.5	72.1 ± 0.5	1.60 ± 0.15
-15	84.6 ± 0.4	53.1	92.3 ± 3.3	1.63 ± 0.03

[a] determined by ^{1}H-NMR analysis ($CDCl_3$) following termination with ethyl vinyl ether.
[b] based on $[M]_0/[cat]_0$ adjusted for % conversion.
[c] determined by SEC analysis in THF.

- colder temperature = higher conversion
  but loss of control
- standard deviation values represent duplicate trials (repeatable!)
- each material had 85 ± 3% *trans* olefins
- dispersities are consistent with previous Ru-ROMP reports

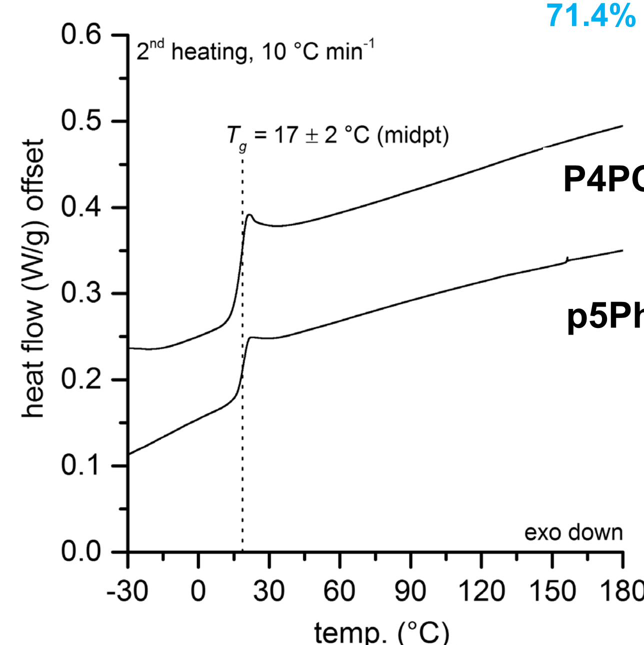
Neary, W. J. & JGK *Macromol. Rapid Commun.* **2016**, *37*, 975

A Precision Styrenic-Rubber → Precision ES Copolymer



71.4% w/w styrene

access to ES Interpolymers with varying %S (w/w)



Pros:

- large scope of material properties
- variety of applications: compatibilizers, packaging, foams, bitumen modifiers

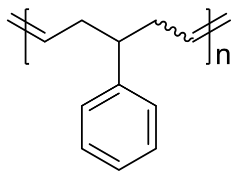
Cons:

- homopolymer formation
- aggressive reaction conditions
- batch repeatability

cons increase when higher S content targeted

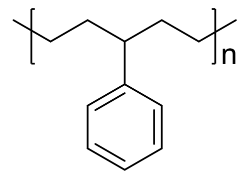
Klosin, J.; Fontaine, P. P.; Figueroa, R. *Acc. Chem. Res.* **2015**, *48*, 2004.
Rodrigues, A.-S.; Carpentier, J.-F., *Coord. Chem. Rev.* **2008**, *252*, 2137.
Chen, H.; Guest, M. J.; Chum, S.; Hiltner, A.; Baer, E. *J. Appl. Polym. Sci.* **1998**, *70*, 109.

Elucidating Precision Material Properties



M_n = 44 kg/mol
$Đ$ = 1.80

$\rho_{90°C} = 0.999\ g/cm^3$

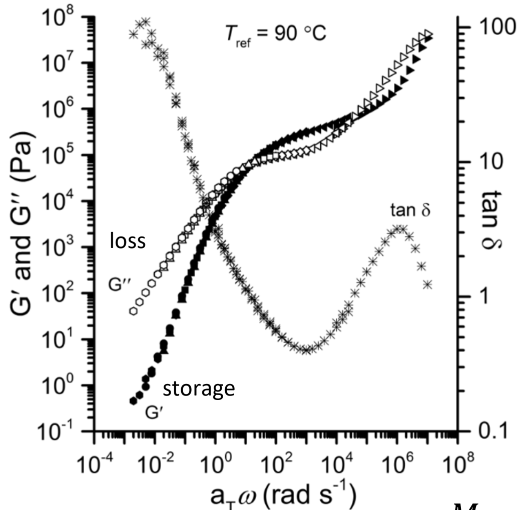


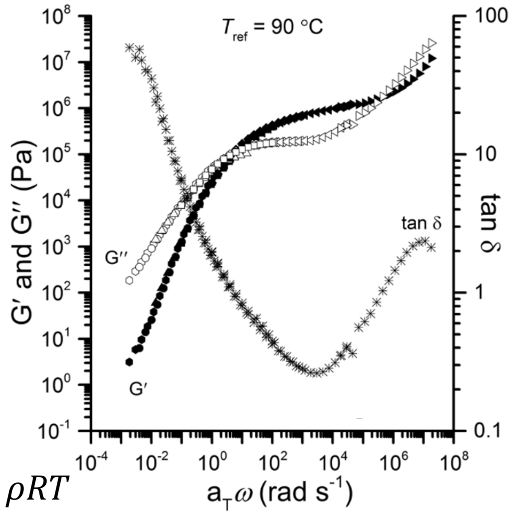
M_n = 51 kg/mol
$Đ$ = 1.68

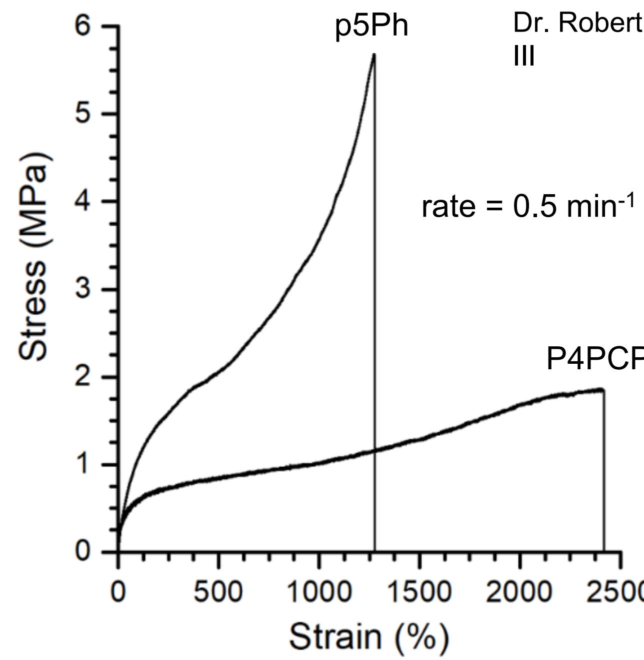
$\rho_{90°C} = 0.980\ g/cm^3$

Dr. Robert Kieber III

average of multiple specimens







$$M_e = \frac{\rho RT}{G_N^o}$$

$$G_N^o = G' at \min \tan \delta$$

***M_e* = 10 kg/mol**

***M_e* = 3.6 kg/mol**

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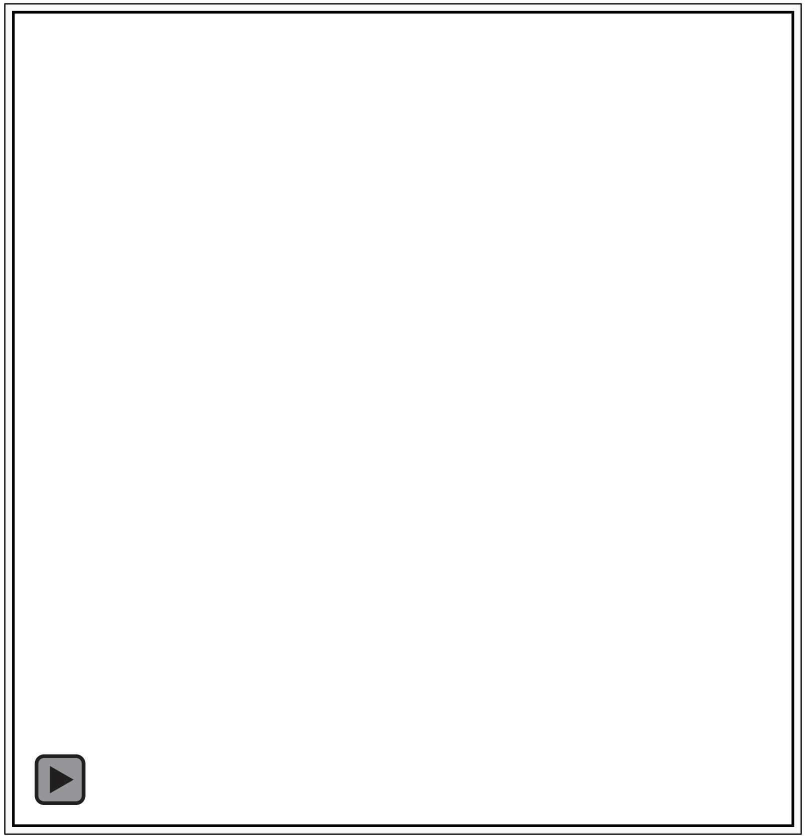
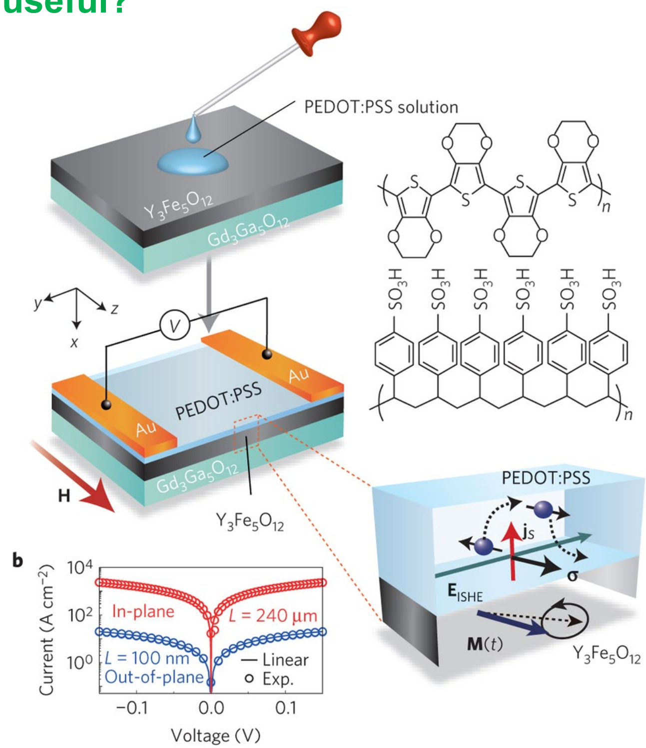
Kieber III, R. J.; Neary, W. J.; & JGK *Ind. Eng. Chem. Res.* **2018**, 57, 4915

Elastic at Low Strain Rate

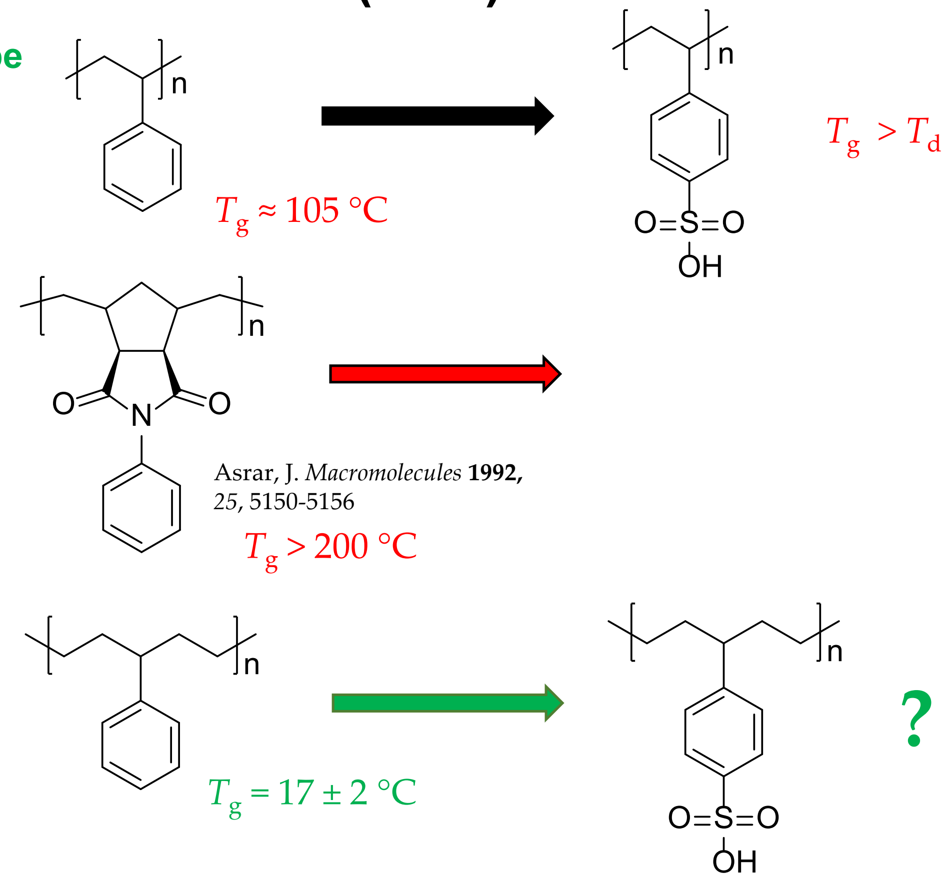


Polystyrene Sulfonate (PSS)

Where might more flexible versions of PS be useful?



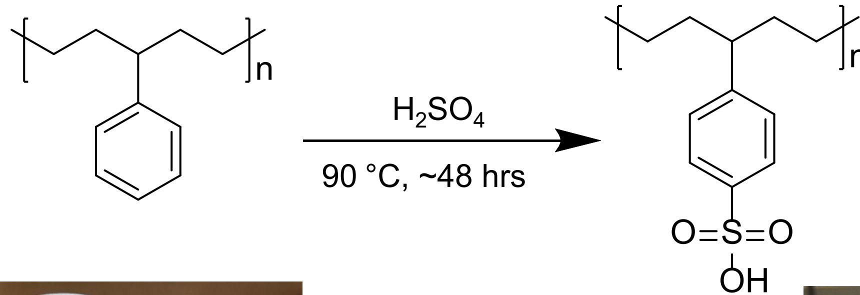
Ando et al. Nature Materials, *12*, 622–627, (2013)



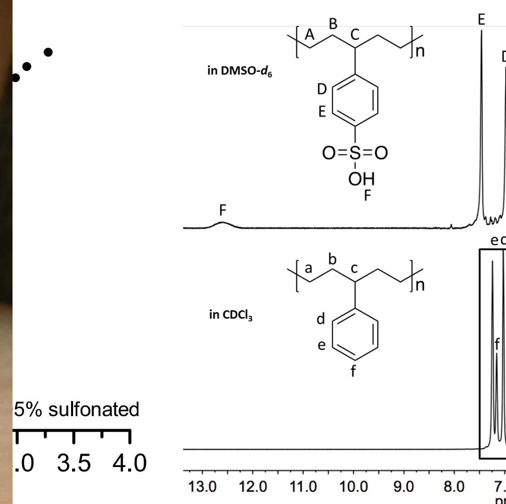
Asrar, J. *Macromolecules* **1992,** *25*, 5150-5156

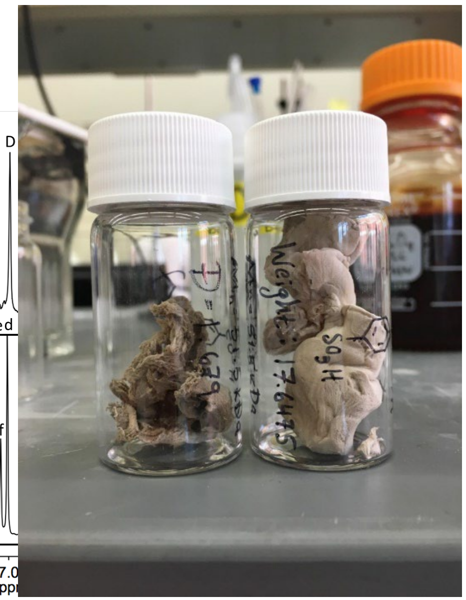
A Precise and More Flexible PSS Analog?

Aaron Kendrick



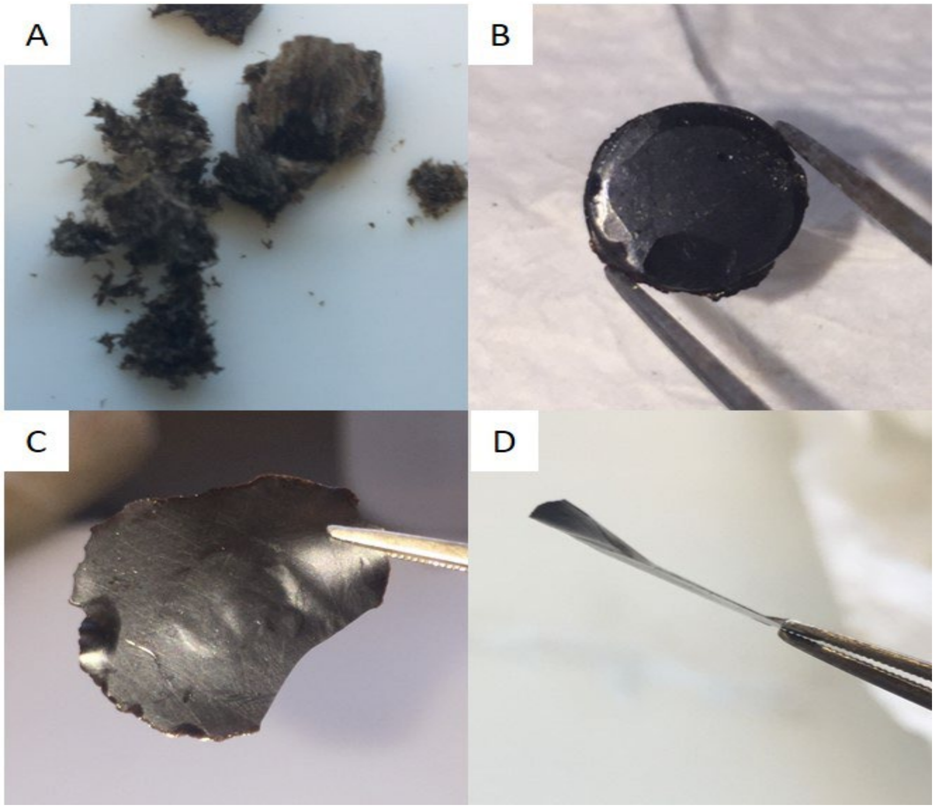
William Neary





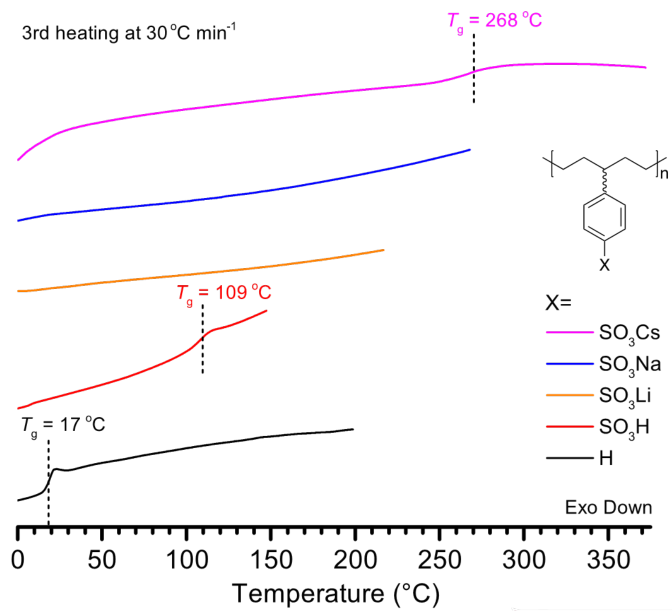
Kendrick & Neary et al. *MRC.* **2018**, *39*, 1800145.
US Patent 10,640,587 (**2020**)

Thermal Properties

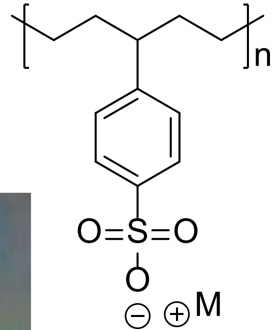


- **Increasing thermal stability with size of counter-cation**
- **Two-step loss of acid form suspected to be desulfonation**

DSC ANALYSIS



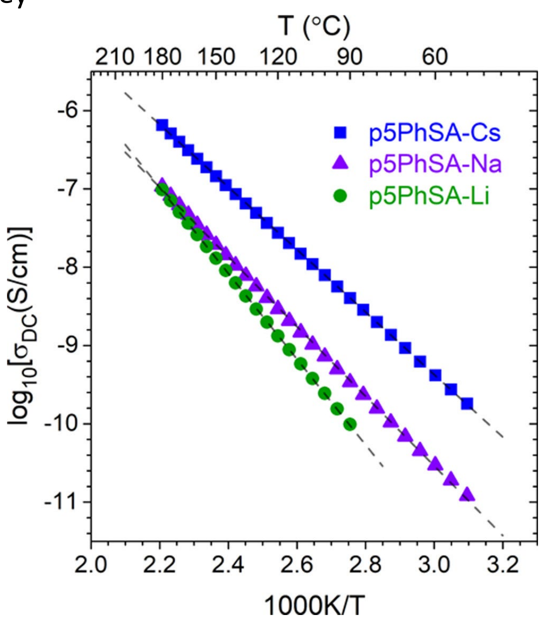
Kendrick & Neary et al. *MRC.* **2018**, *39*, 1800145.
US Patent 10,640,587 (**2020**)

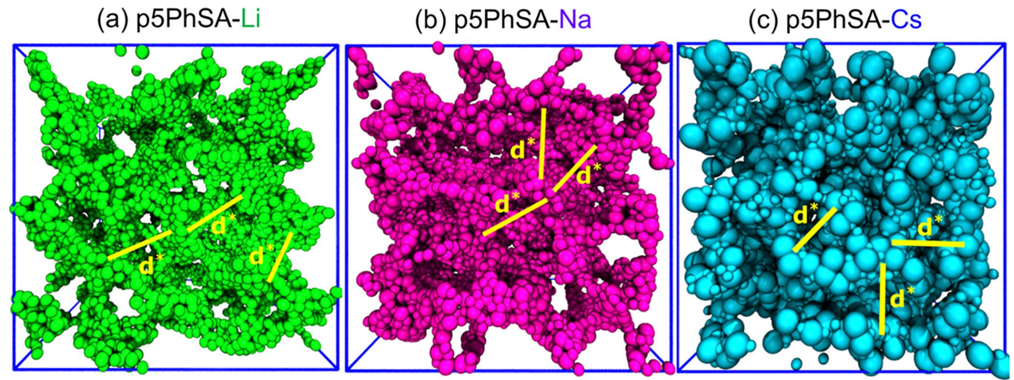


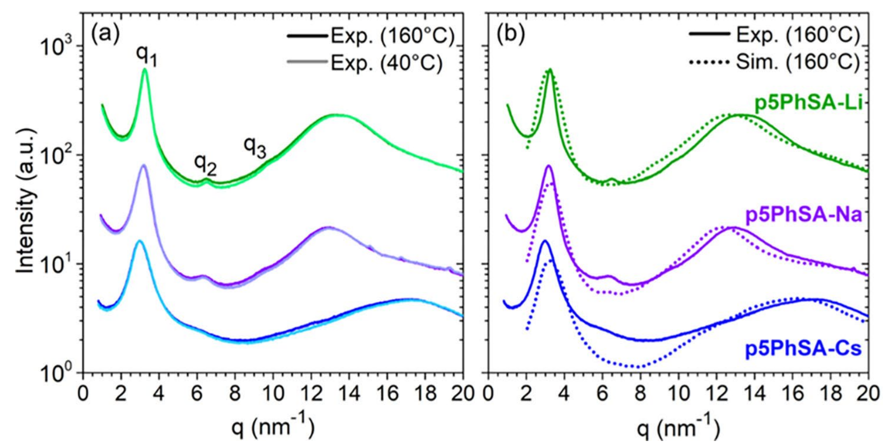
Collaboration: Percolated Ion Networks

Karen Winey

Amalie Frischknecht



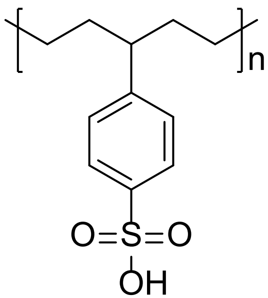




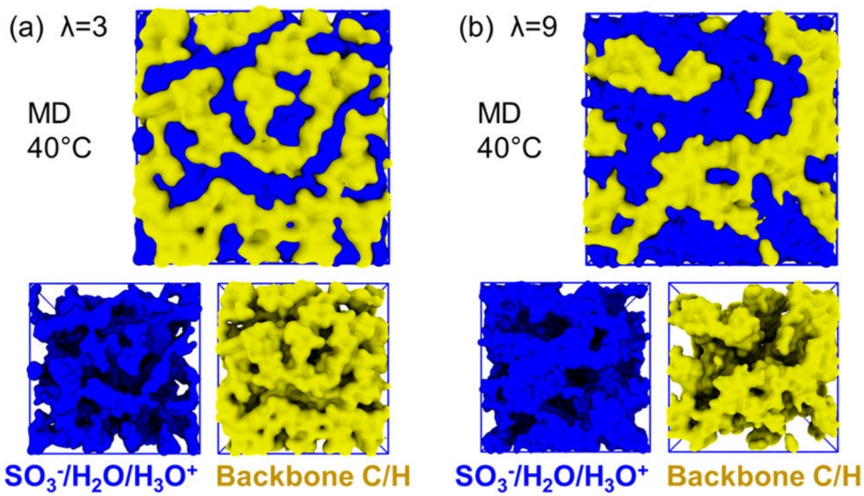
Paren et al. *Macromolecules.* **2020**, *53*, 8960

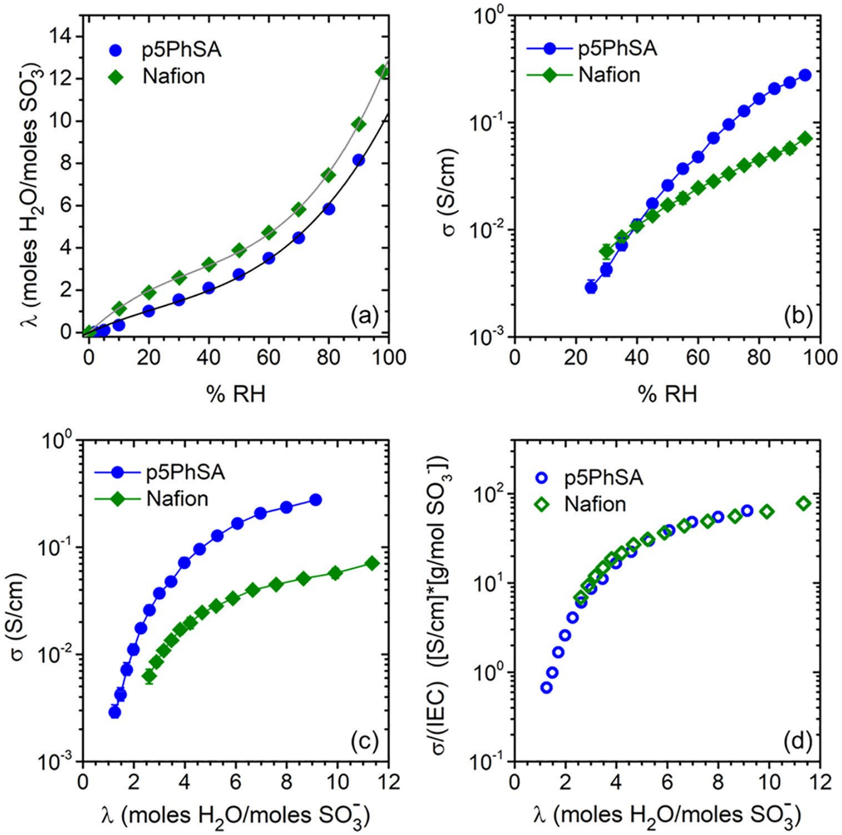
Collaboration: Fluorine-free PEMs

U.S. DEPARTMENT OF ENERGY



Lubrizol





Paren et al. *Chem. Mater.* **2021**, *33*, 6041

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