

"There are people alive today who remember a world without plastics,"  
Jenna Jambeck (UGA)



R. Geyer at University of California, Santa Barbara in Santa Barbara, CA et al., "Production, use, and fate of all plastics ever made," *Science Advances* (2017). [advances.sciencemag.org/content/3/7/e1700782](https://advances.sciencemag.org/content/3/7/e1700782)

Read more at: <https://phys.org/news/2017-07-billion-metric-tons-scientists-total.html#jCp>

# Modern equivalents



# Why are we here?

Macromolecular Jargon	What it Means
Random coil	
Persistence length	
Polydispersity index	
Radius of gyration/Hydrodynamic Radius	
Loss modulus	
Free-draining	
Structure factor	
Partial specific volume	
Binodal/Spinodal	
ATRP	
Kramers-Kronig relationship	
Auxetics	

# Define molecule.

$\text{Na}_{5333333888}\text{Cl}_{5333333888} \text{ ???}$

$\text{C}_2\text{H}_4 \text{ ???}$

$m(\text{C}_2\text{H}_4) \rightarrow [\text{C}_2\text{H}_4]_m \text{ ???}$

# Why big?

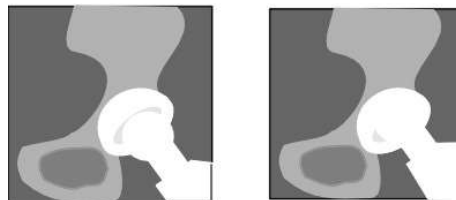
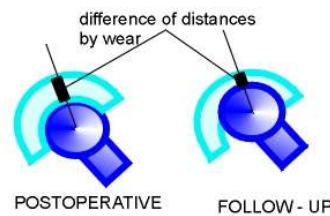




PE Images: a railcar full of PE (polyethylen) leaves a small Louisiana plant about every hour. The “Gret Stet” has many plants.



The ExxonMobil plant just north of the Baton Rouge airport makes the PE for 40% of all milk cartons in the US.



X - RAY PICTURES



**PE/PP production fills this stadium every 9 days...40 times a year. About 80% winds up in oceans.**



**BuzzPoints for anyone who checks this number!**



Dow is one of America's largest producers.

\$550 million purchased from Louisiana  
companies

\$340 million payroll

\$58 million state & local taxes

\$1.8 million donations

Tons of polyethylene

Methocel



Living.  
Improved daily.

Image: <http://www.unitedwaysb.org/Ice%20Cream.jpg>



# Some fun links: metals vs polymers

<https://www.productiveplastics.com/2017/04/13/metal-vs-plastic-5-key-comparisons/>

<https://phys.org/news/2017-07-billion-metric-tons-scientists-total.html>

The DNA to copy a lungfish has a molecular weight of 69,000,000,000,000 g/mol.



What's that in tons per mole?

Do it without your calculator!



# History belongs to the victors.

(this history from Elias' book, Megamolecules)



~1300 BC

Egyptian mummification  
reaches its zenith. (First  
mummy is from approx.  
5000 B.C.???)

# 1839

"Styrax liquidus" (a resin used by the Egyptians as embalming fluid, isolated from a tree) produces a clear liquid, "styrol", when distilled.

Styrol solidifies when heated. Everyone knows that pure substances melt sharply on heating. Melting points are a classic way organic chemists use to ascertain purity. Stuff that doesn't melt on heating can't be very pure. Why bother with gunk?

It is assumed that the gunk is oxide of styrol, called "styrene oxide".



~1845

It is learned that the gunk contains no oxygen atoms and, in fact, has the same empirical formula before and after solidifying (actual formula is under debate since relative masses of C and H are not known at this time).

Name is changed to metastyrene.

"Polymerization" coined as a word meaning that many parts had joined without changing.

# The big debate!

Right then and there, the argument began-- chemistry often involves change, so could polymerization just be aggregation?

# Not only styrol

Ethylene oxide also polymerizes this way  
(no change of formula)

Graham (of effusion law fame?) notes that diffusion of crystalline substances dispersed in solutions is fast, while that of noncrystalline substances is slow. Polymers diffuse slowly, hence probably not crystalline, hence probably not pure.

Again, why measure gunk?

# ~1888 to ~1925

Thermodynamic methods are applied to polymers, basically adapting the ideal gas law to solutions. It is found that the polymers have enormous masses--e.g., tens of thousands. But the doubters again raised objections:

- poor reproducibility, even within the same research group
- answers depended a lot on concentration and method
- chemical methods for crystallizable compounds did not have these problems--maybe thermodynamics doesn't work?



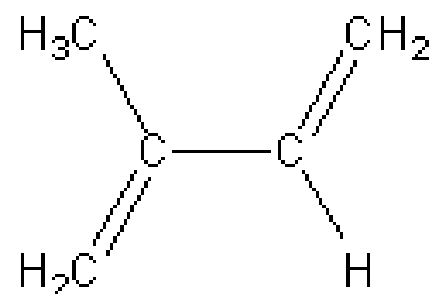
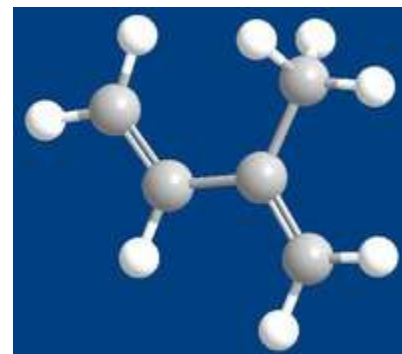
# ~1910

On the other hand....rubber is thought to be two units of isoprene joined in a circle.

The high viscosity is attributed to secondary forces grouping the circles into great aggregates.

If so, then brominating the isoprene should dramatically alter the viscosity.

It did not.



Examples of Consumer Products Which Contain Polyisoprene



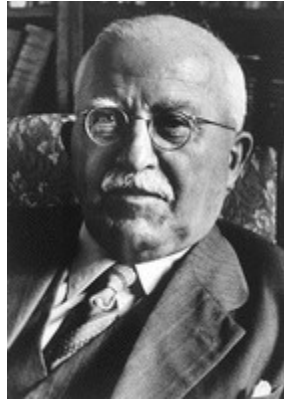
# Early 1900's

- Still people were not convinced...because where are the end groups if the chains are really linear?
- No one could find them, and no one could admit such a failure of chemical analysis...so linear polymerization was a mystery. Maybe polymers were large rings???
- (Leaping ahead for awhile: In fact, it *was* a failure of chemical analysis that the end groups were not found. On a polystyrene of  $M=104,000$  there are only 2 ends: Only 1 in 500 styrene units is different. Even today, end groups are hard to see. )

# 1920's onward

**Staudinger**

Nobel 1953



*If secondary, physical forces hold polymers together, they should eventually go away if we continually dilute the polymer solution and polymers would fall apart.*

*They did not.*

*Staudinger had the good luck to be poor. He could only afford a simple experiment that proved to be very precise: viscosimetry. He found that the viscosity increment per unit polymer did not go away.*

*Stein's law: the product of money and intelligence is a constant.*

Richard Stein →



# Alternate history: better “polymers” and more dollars make better history?



Theo Svedberg  
Nobel 1926

Diagram  
from  
Svedberg's  
Nobel Prize  
Lecture,  
showing  
the oil and  
hydrogen  
(yes,  
hydrogen!)  
circulation  
system for  
one of his  
AUC's

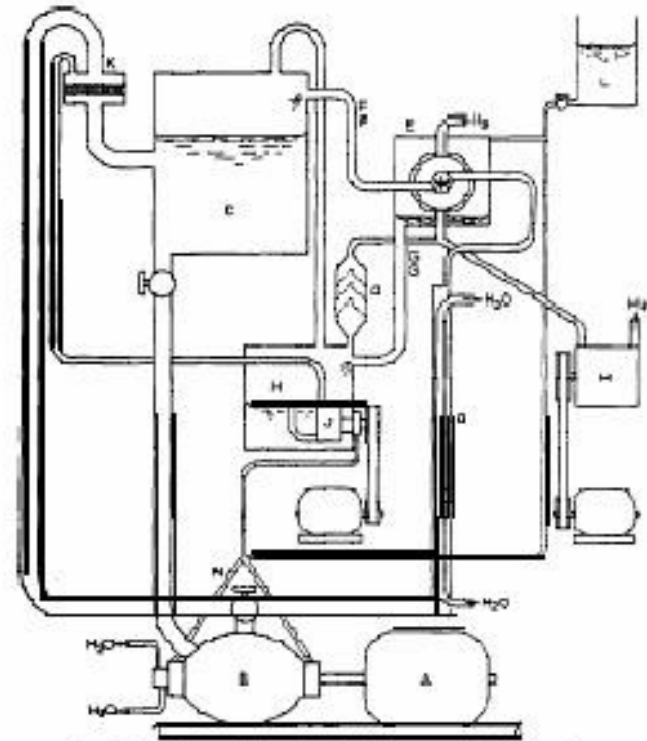


Fig. 4 The ultracentrifuge oil and hydrogen circulation system.

- |                                  |                      |
|----------------------------------|----------------------|
| (A) electric motor               | (H) oil tank         |
| (B) oil pump                     | (I) oil pump         |
| (C) oil tank                     | (K) oil filter       |
| (D) oil cooler                   | (L) sealing oil tank |
| (E) ultracentrifuge              | (M) vacuum pump      |
| (F) discharge pipe from turbines | (N) three-way cock   |
| (G) discharge pipe from bearings | (O) drip trap        |