Rubber: History, Properties and Structure

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Physical Chemistry of Macromolecules

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Definition of Rubber/Elastomer

- "A material that can be stretched to at least twice its original length and will retract rapidly and forcibly to substantially its original dimensions upon release of the force."

Rosen; p389

Natural Rubber: Where?

- *Hevea brasiliensis*
  - Most common source
  - Responds to wounding by producing more latex
  - Produces cis-1,4-polyisoprene
  - Native to Amazon Rainforest
- Gutta-Percha
  - Produces trans-1,4-polyisoprene
  - Native to Malaysia
- Rubber Plantations in Malaysia

Pictures: http://en.wikipedia.org/wiki/Natural_rubber

Rubber in Prehistory

- 60 million BC – Europe - rubber-producing plants
- First millennium BC – Mexico – First evidence of the Mesoamerican ballgame
- 6th century – Mexico and Central America – Aztecs/Mayans
  - Balls
  - Dipped Feet to make shoes
  - Coated Fabrics

Pictures: http://en.wikipedia.org/wiki/Mesoamerican_ballgame

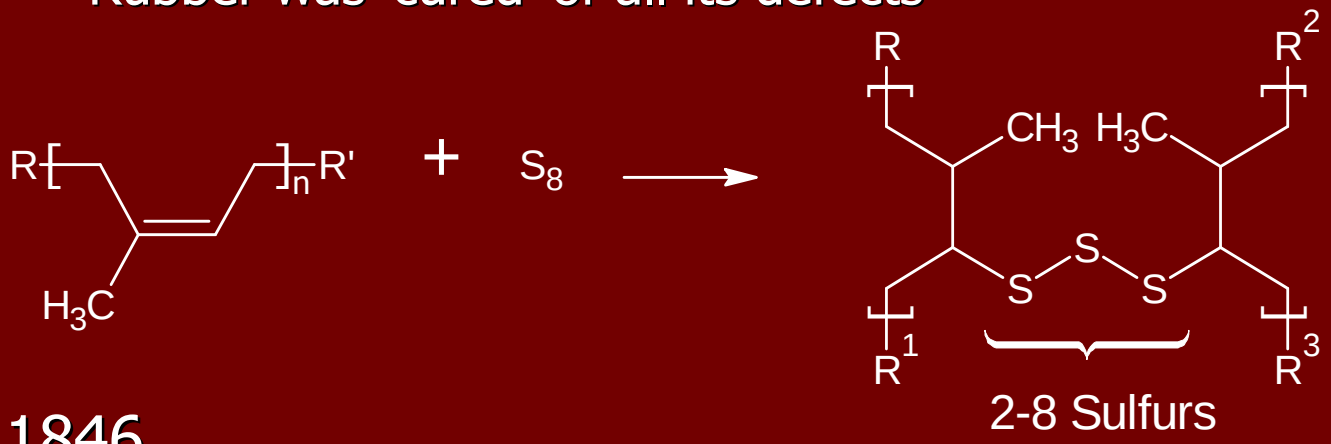
Rubber and Europe

- First European exposure
  - Columbus supposedly watched a Mesoamerican ballgame
  - Early explorers learned native waterproofing techniques
- Charles Marie de la Condamine and Francois Fresneau
  - Popularized rubber in France starting mid 1730's
  - Discovered first solvents
  - Wrote about properties

Picture: http://en.wikipedia.org/wiki/Charles_Marie_de_La_Condamine

Vulcanization

- 1839
  - Goodyear and Hancock
  - Mixed natural rubber, sulfur and white lead on a hot stove
  - Rubber was ‘cured’ of all its defects

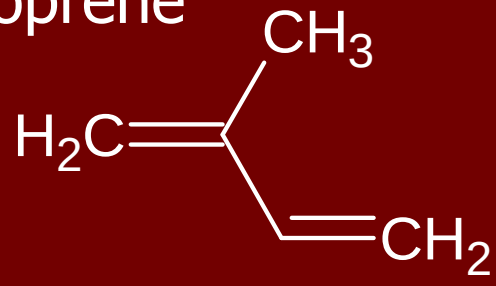


- 1846
  - Alexander Parkes invented a cold-cure process using sulfur chloride gas in solution

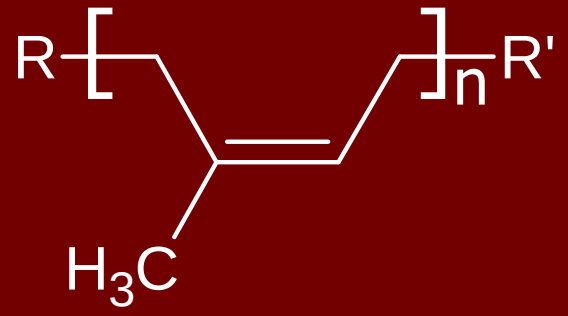
Natural Rubber the Real Story

- 1860 - Williams (UK)
  - Decomposed natural rubber to isoprene
- 1879 - Bouchardat (France)
  - Repolymerized isoprene to make rubber
- 1910 – Pickles
  - Rubber is made of long chains of isoprene

Isoprene

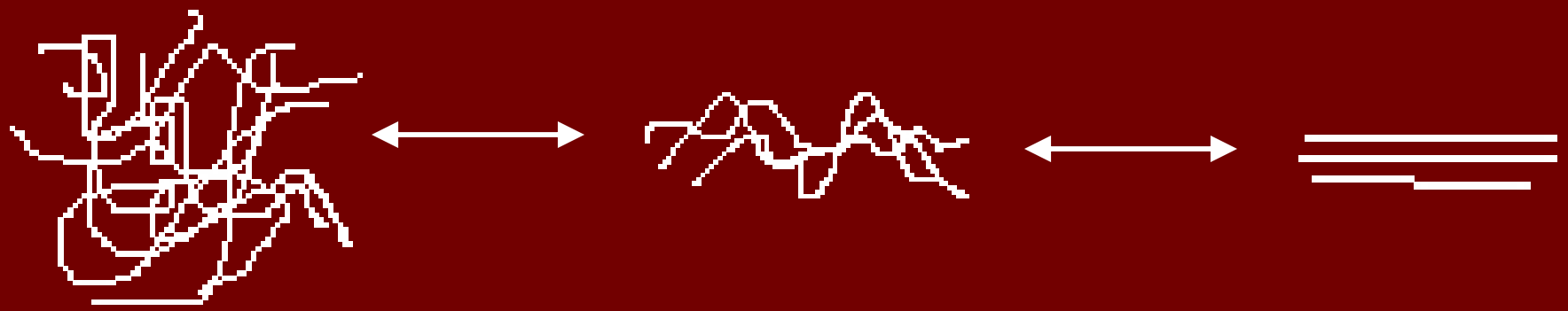


cis-Polyisoprene



Origins of Rubber Elasticity

- Energy elasticity – elongation resulting from rotation around single bonds and the straining of bond angles and lengths



Statistics of Ideal Rubber Elasticity

- Ideal rubber
- Slope of the stress-strain curve or Young's Modulus

$$E = \frac{\rho RT}{Mc}(2\alpha + \alpha^{-2})$$

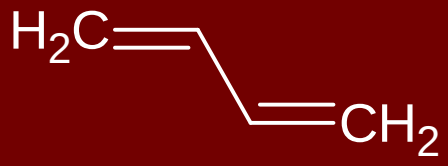
  - ρ = density
  - R = Gas Constant
  - T = temperature
  - Mc = number average molecular weight of the network chains
  - α = extension ratio, l/l_0
  - l/l_0 = current length/unstretched length

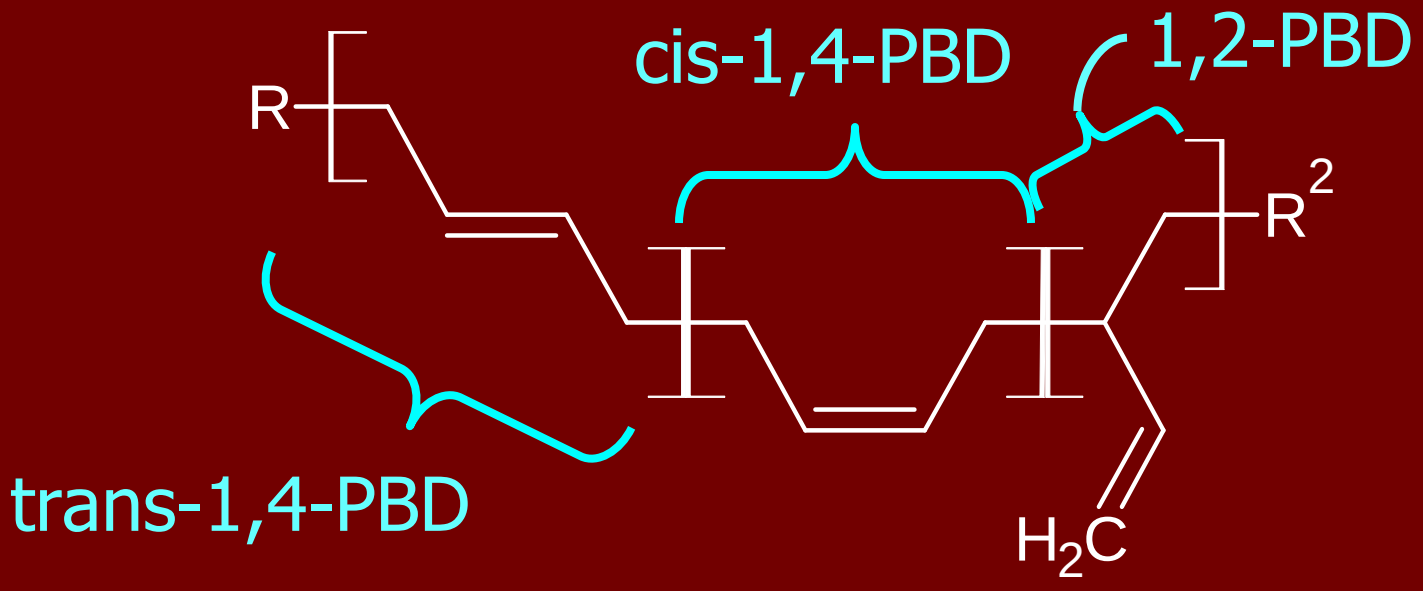
Deviations from Ideality

- Under predicts modulus for $\alpha > 1.5$
- Chain ends
- Stress induced crystallization

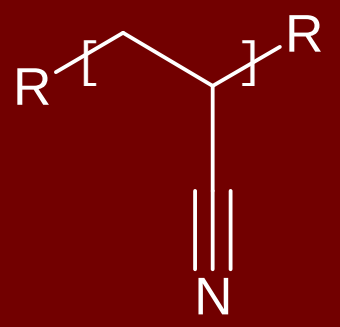
Butadiene Rubber

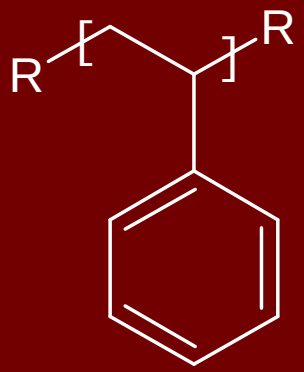
- Polybutadiene
  - First synthesized in 1910 by S. Lebedev
  - Very durable but cis/trans issues
  - Side walls of truck tires and golf balls
  - Modern day use is as copolymer





And its copolymers





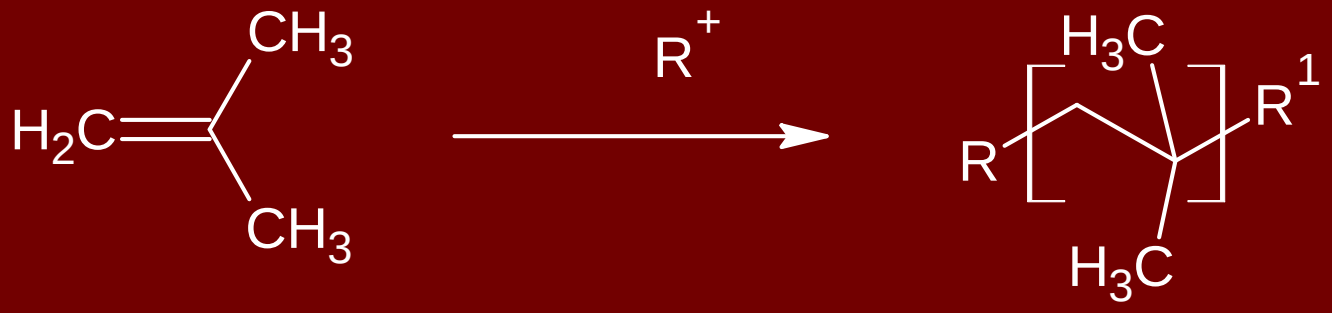
- Buna N/ Buna NN
  - Butadiene and acrylonitrile
  - Increased acrylonitrile increases stiffness and oil resistance
- Buna S
  - Butadiene and styrene
  - Increased styrene leads to stiffer rubber

The War Years

- Japan captured Pacific Rubber plantations
- US synthetic rubber
  - 1939 – 2000 tons/yr
  - 1945 – 830,000 tons/yr
  - Butyl rubber
- German synthetic rubber
  - Before – 22,000 tons/yr
  - Middle – 100,000 tons/yr

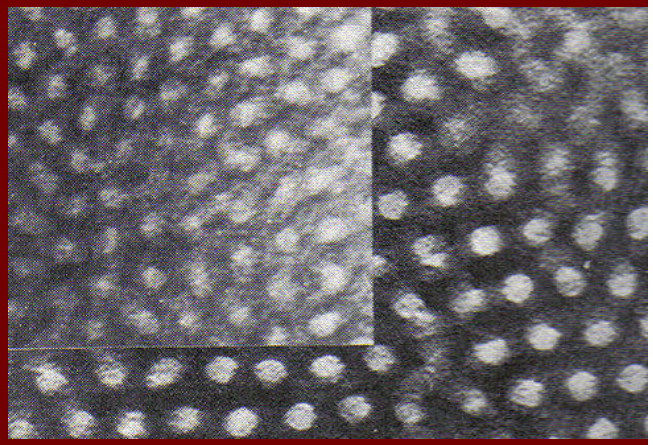
Butyl Rubber

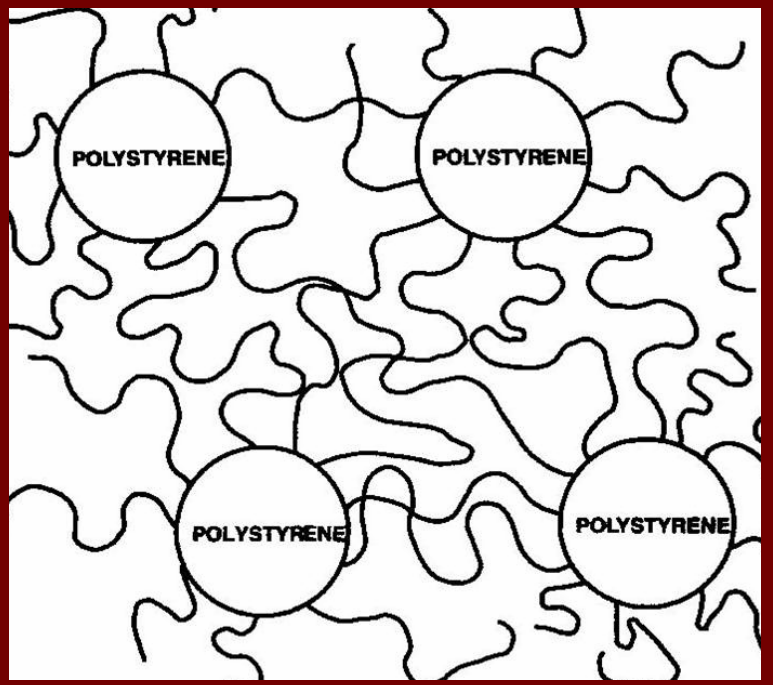
- Copolymer of 98% isobutene
  - 2% isoprene or butadiene
  - Cationic polymerization
  - Air impermeable
  - Inner tubes for tires



Thermoplastic Elastomers

- Rubbers which can be melt processed after "crosslinking"
- Immiscible block copolymers
  - Form matrix of rubbery polymer with spheres of hard segments
  - Most common: Styrene-Butadiene-Styrene (SBS)





Pictures: http://en.wikipedia.org/wiki/Copolymer

Requirements to make a Rubber

- High Molecular Weight
  - Rubber elasticity is due to the coiling/uncoiling of chains
- Use temperature must be above Tg
  - To allow for molecular motion
- Amorphous in its unstretched state
  - Crystals would hinder coiling/uncoiling
- Chains tied together to prevent flow
  - Traditionally through crosslinking
  - Hard/Soft Domains
  - Entanglements
    - All polymers above Tg act as rubbers due to entanglements
    - However, when the entanglements break, the polymer will begin to flow

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References

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From Curiosity to Product (1820-1840)

- T. Hancock
  - Pickling Machine – produce homogeneous rubber 'dough'
  - Spreader – the standard coating machine used today
- M. Faraday
  - Established empirical formula of natural rubber (C_5H_8)

Natural Rubber Production

- Wild Production
  - Amazon River and its tributaries
  - Africa
- 1876 - H. Wickham
  - Sent 70,000 Hevea seeds to Britain
  - 2397 germinated
  - Plants sent to Singapore, India, Malaysia
  - Foundation of the eastern rubber plantations (1895)
- 1913-1914 - Plantation rubber exceeds wild