

EMAC 276

Lecture 16: Polydienes: from Natural Rubber to Synthetic Rubber

Part 2: Polychloroprene, Polybutadiene and Styrene-Butadiene Block Copolymers

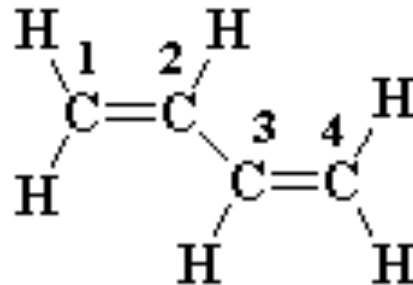
Andy Olah, Ph.D.

February 26, 2025

What is a diene?

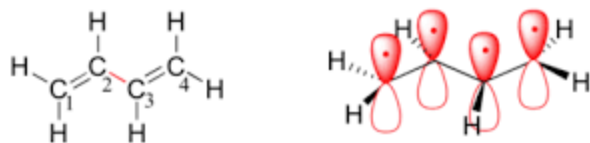
A diene is an unsaturated hydrocarbon containing two double bonds between carbon atoms.

Butadiene is the simplest diene:



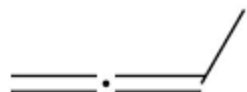
Butadiene has two carbon-carbon double bonds, in the 1 and 3 positions, that is, starting at the carbon atoms numbered 1 and 3.

Dienes and Polydienes can Adopt Numerous Configurations

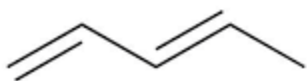


1,3-butadiene

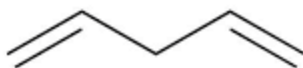
The placement of the double bond.



Cumulated



Conjugated



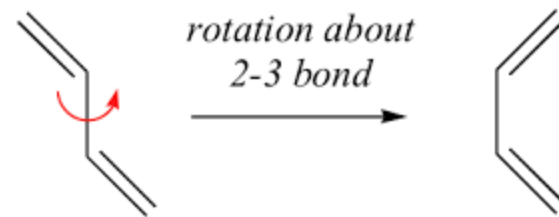
Isolated

Cumulated – pi bonds are adjacent.

Conjugated – pi bonds are separated by exactly ONE single bond.

Isolated – pi bonds are separated by any distance greater than ONE single bond.

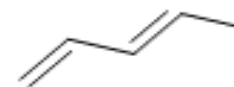
Rotation around the single bond.



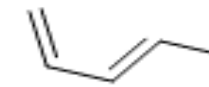
s-trans

s-cis

Isolated



s-trans

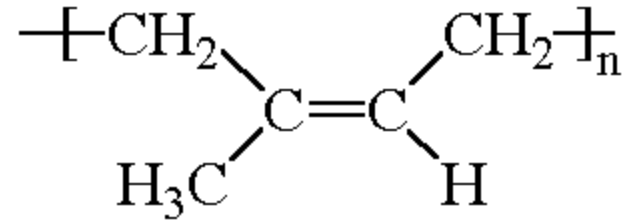


s-cis

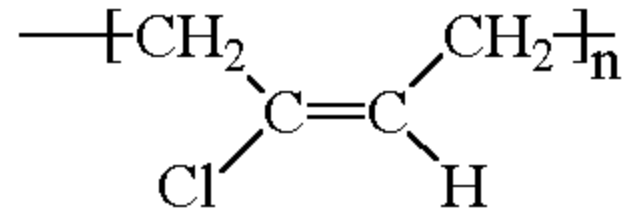
Monomer

Diene Based Polymers that We Will Consider

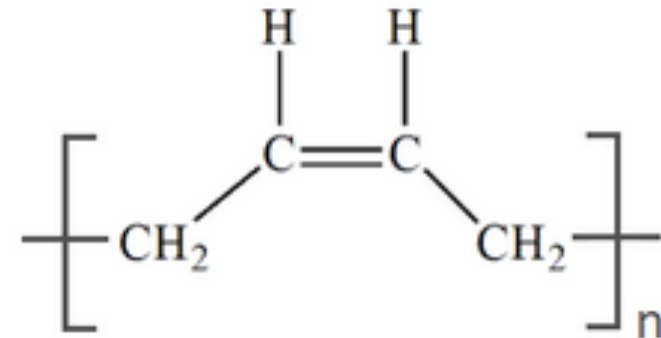
Polyisoprene



Polychloroprene (Neoprene)

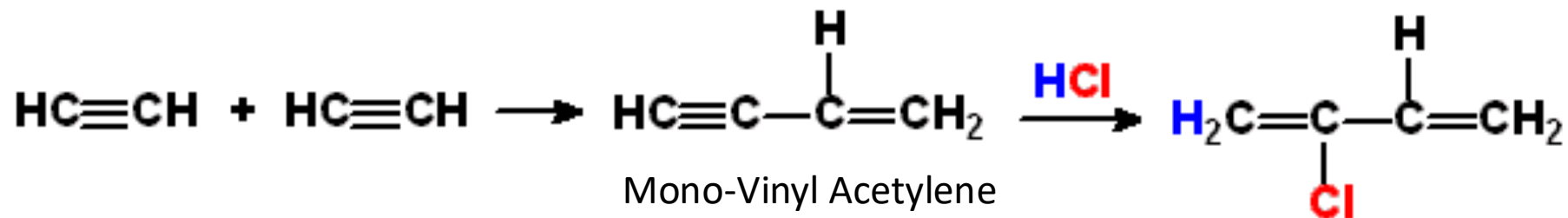
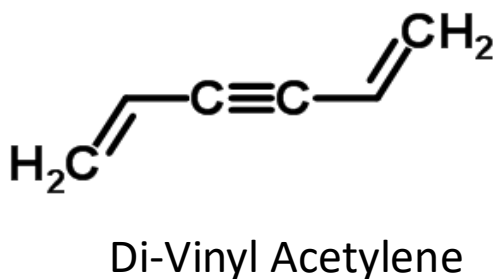


Polybutadiene



Synthesis of Chloroprene Monomer

Neoprene was invented by the DuPont Company on April 17, 1930. The research was **focused on acetylene chemistry** and during the course of this work he **produced divinyl acetylene**, a jelly that forms into an elastic compound similar to rubber when passed over sulfur dichloride. Collins at DuPont focused on **mono-vinyl acetylene and allowed it to react with hydrogen chloride gas, manufacturing chloroprene.**

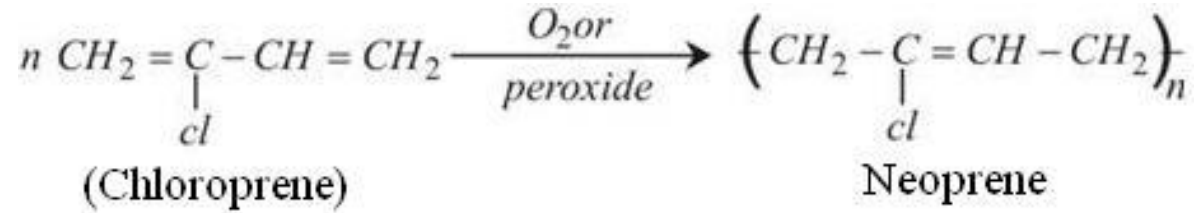


NOTE: Chloroprene commonly refers to the monomer and Neoprene refers to the polymerization of 1,3 chloroprene.

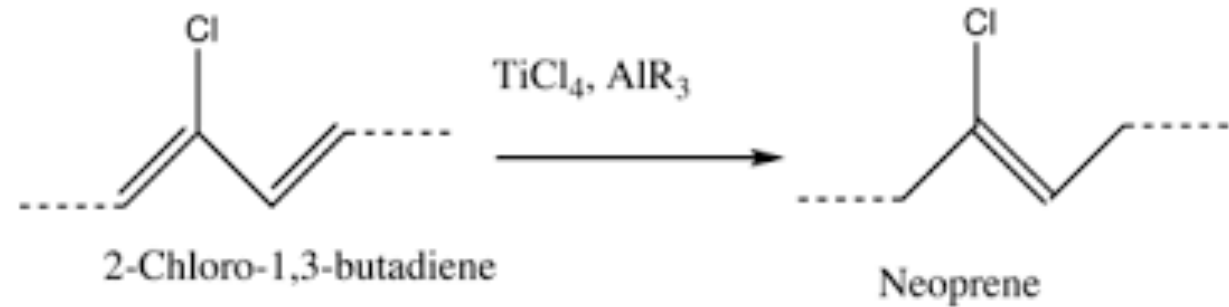
NOTE: The chemical designation of chloroprene monomer is “2-chloro, 1,3-butadiene”.

Synthesis of Neoprene

Neoprene Synthesis



Free Radical



Ziegler-Natta

DuPont first marketed the compound in 1931 under the trade name DuPrene, but its commercial possibilities were **limited by the original manufacturing process, which left the product with a foul odor.**

A **new process** was developed, which **eliminated the odor-causing byproducts and halved production costs.** The trademark was dropped in 1937 and **replaced with a generic name, “neoprene”.**

DuPont then worked extensively to generate demand for its product. By 1939, sales of neoprene were generating profits over \$300,000 for the company (equivalent to \$6,573,000 in 2024).

Commercialization of Neoprene

Neoprene was one of the first synthetic rubbers

Neoprene resists degradation more than natural or synthetic rubber. This relative inertness makes it well suited for applications such as gaskets, hoses, and corrosion-resistant coatings.

It resists burning better than exclusively hydrocarbon based rubbers, resulting in its appearance in weather stripping for fire doors. Because of its tolerance of extreme conditions, neoprene is used to line landfills. Neoprene's combustion occurs around 260 °C (500 °F).

In its native state, neoprene is a very pliable rubber-like material with insulating properties similar to rubber or other solid plastics.

Neoprene foam is used in many applications and is produced in either closed-cell or open-cell form. The closed-cell form is waterproof, less compressible and more expensive. The open-cell form can be breathable. It is manufactured by foaming the rubber with nitrogen gas, where the tiny enclosed and separated gas bubbles can also serve as insulation.

Commercialization of Neoprene

Chloroprene is used primarily for gaskets, cable jackets, tubing, seals, O-rings, tire-sidewalls, gasoline hoses and weather-resistant products such as wet suits and orthopedic braces. It is also used as a base resin in adhesives, electrical insulations and coatings.



Polybutadiene - History

1910 - The Russian chemist Sergei Vasilyevich Lebedev was the first to polymerize butadiene.

1926 - Lebedev invented a process for manufacturing butadiene from ethanol, and in 1928, developed a method for producing polybutadiene using sodium as a catalyst.

1936 - The Soviet Union built the world's first polybutadiene plant in which the butadiene was obtained from petroleum. By 1940, the Soviet Union was by far the largest producer of polybutadiene with 50,000 tons per year.

1930 – 1940 - Other industrialized countries such as Germany and the United States developed polybutadiene and SBR as an alternative to natural rubber.

Polybutadiene - History

1940 – 1950 - Although the Goodrich Corporation had successfully developed a process for producing polybutadiene in 1939, the government of the United States opted for the use of Buna-S to develop its synthetic rubber industry after its entry into the World War II, using patents of IG Farben obtained via Standard Oil.

1950- 1960 - After the war, the production of synthetic rubber was in decline due to the decrease in demand when natural rubber was available again. However, interest was renewed in the mid-1950s after the discovery of the Ziegler–Natta catalyst. The following year, Firestone Tire and Rubber Company was first to produce low *cis* polybutadiene using butyllithium as a catalyst.

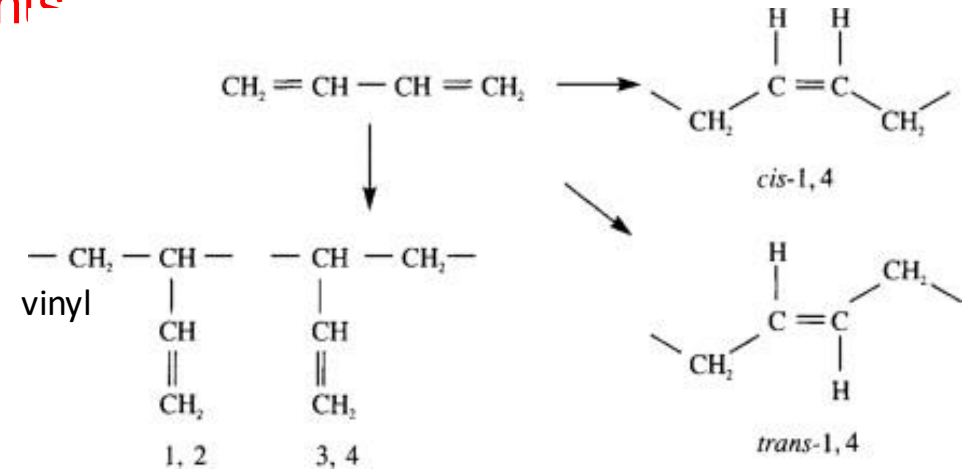


Polybutadiene

The monomer 1,3-butadiene is an organic compound that is a simple conjugated diene hydrocarbon (dienes have two carbon-carbon double bonds).

Polybutadiene forms by linking many 1,3-butadiene monomers to make a much longer polymer chain molecule. In terms of the connectivity of the polymer chain, butadiene can polymerize in three different ways, called *cis*, *trans* and *vinyl*. The *cis* and *trans* forms arise by connecting the butadiene molecules end-to-end, so-called 1,4-polymerisation.

The properties of the resulting isomeric forms of polybutadiene differ. For example, **"high cis"-polybutadiene has a high elasticity and is very popular,** whereas the so-called "high *trans*" is a plastic crystal with few useful applications. The vinyl content of polybutadiene is typically no more than a few percent. In addition to these three kinds of connectivity, polybutadienes differ in terms of their branching and molecular weight⁶

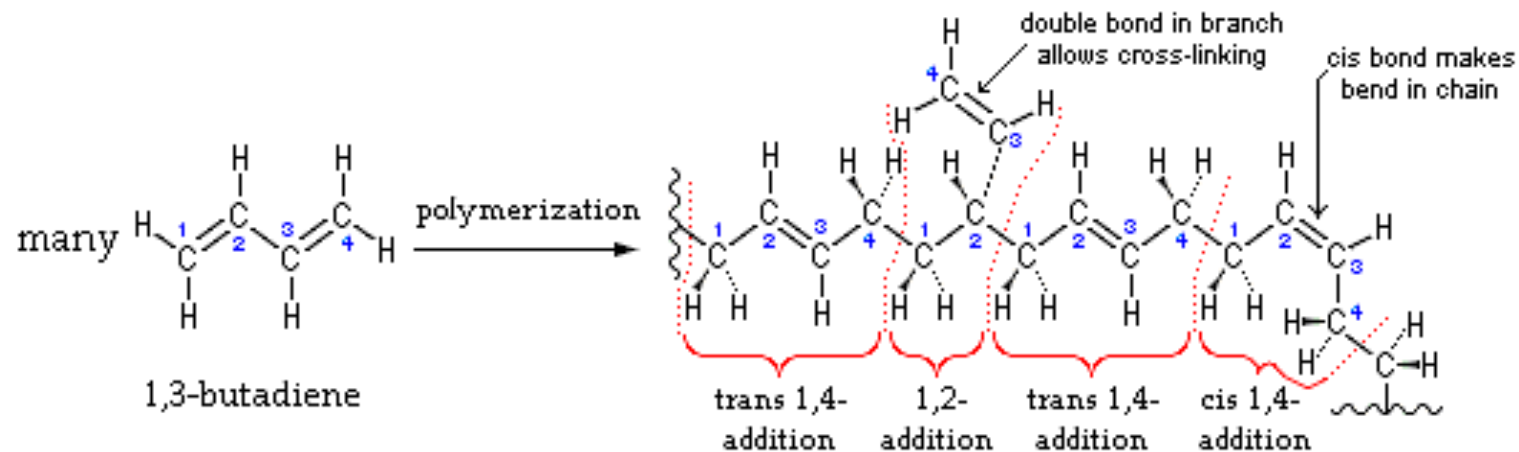


Polymerization of Butadiene

The *trans* double bonds formed during polymerization allow the polymer chain to stay rather straight, allowing sections of polymer chains to align to form microcrystalline regions in the material.

The *cis* double bonds cause a bend in the polymer chain, preventing polymer chains from aligning to form crystalline regions, which results in larger regions of amorphous polymer. It has been found that a substantial percentage of *cis* double bond configurations in the polymer will result in a material with flexible elastomeric (rubber-like) qualities.

In free radical polymerization, both *cis* and *trans* double bonds will form in percentages that depend on temperature. The polymerization catalysts influence the *cis* vs *trans* ratio.



Commercialization of Polybutadiene

Polybutadiene is largely used in various parts of automobile tires; the manufacture of tires consumes about 70% of the world production of polybutadiene, with a majority of it being high *cis*.

The polybutadiene is used primarily in the sidewall of truck tires, this helps to improve fatigue to failure life due to the continuous flexing. It is also used in the tread portion of giant truck tires to improve the abrasion, i.e. less wearing.

Its main competitors in this application are styrene-butadiene rubber (SBR) and natural rubber. Polybutadiene has the advantage compared to SBR in its lower glass transition temperature, which gives it a high resistance to wear and a low rolling resistance. This gives the tires a long life and low fuel consumption.

However, the lower transition temperature also lowers the friction on wet surfaces, which is why polybutadiene almost always is used in combination with any of the other two elastomers.

About 1 kg of polybutadiene is used per tire in automobiles, and 3.3 kg in utility vehicles.

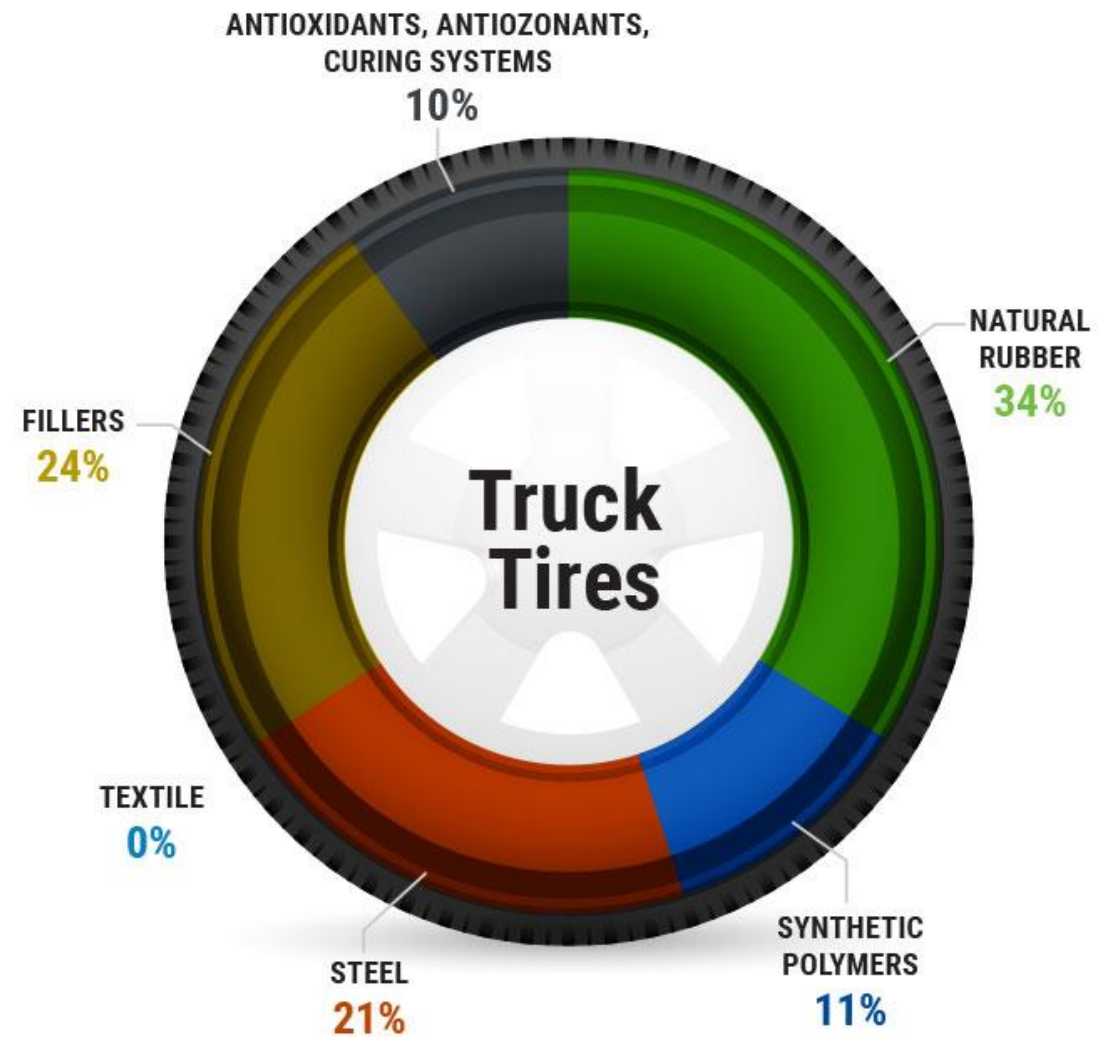
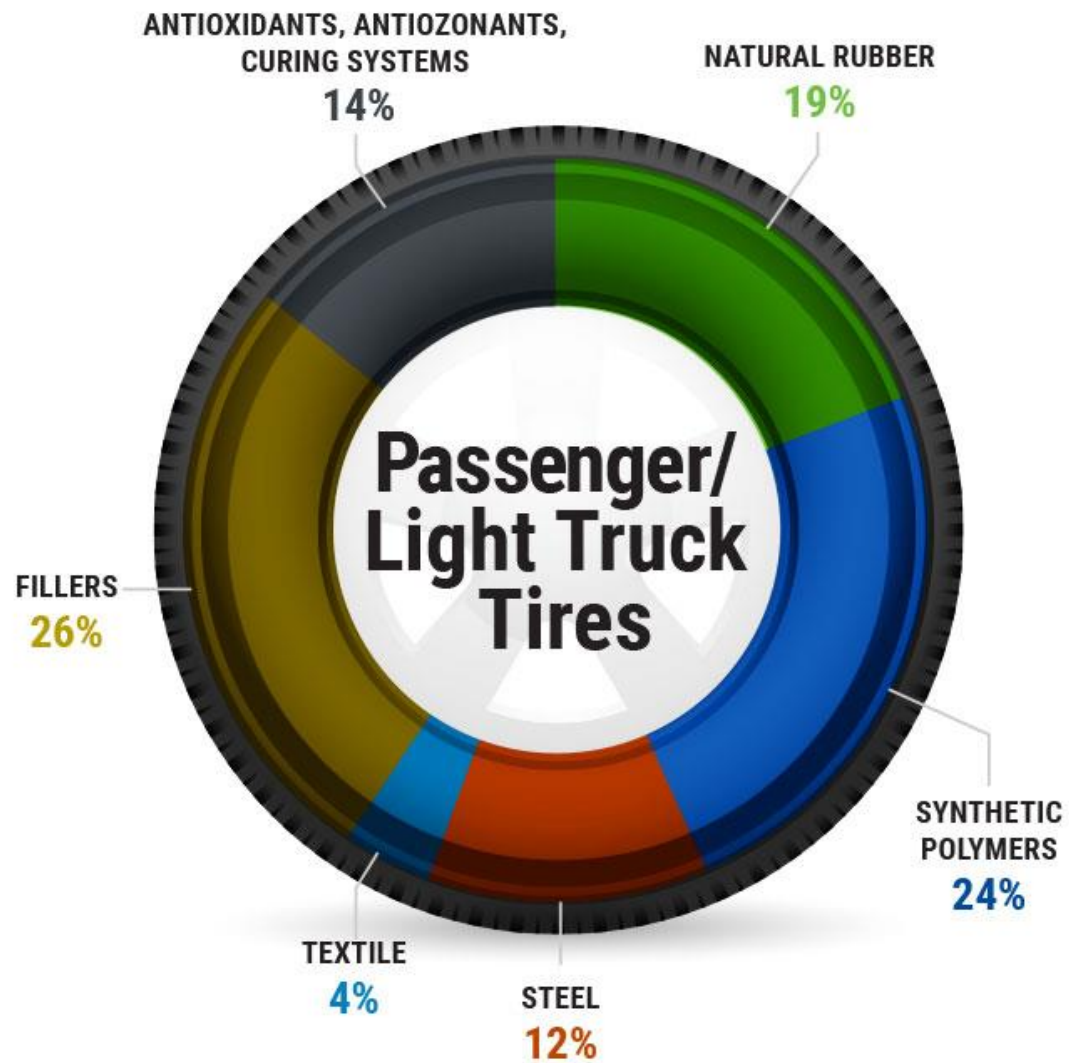
Commercialization of Polybutadiene

About 25% of the produced polybutadiene is used to improve the mechanical properties of plastics, in particular of high-impact polystyrene (HIPS) and to a lesser extent acrylonitrile-butadiene-styrene (ABS). The addition of between 4 and 12% polybutadiene to polystyrene transforms it from a fragile and delicate material to a ductile and resistant one.

The quality of the process is more important in the use in plastics than in tires, especially when it comes to color and content of gels which have to be as low as possible. In addition, the products need to meet a list of health requirements due to its use in the food industry



Material Composition of Tires



Composition & Source



Carbon black and silica are the basic tire fillers, providing the necessary "structure" to the compound



Other chemicals have various functions, like oils, zinc oxide or anti-degradants to protect the compound



Synthetic rubber is added to natural rubber to achieve the desired elasticity

2/5/2013



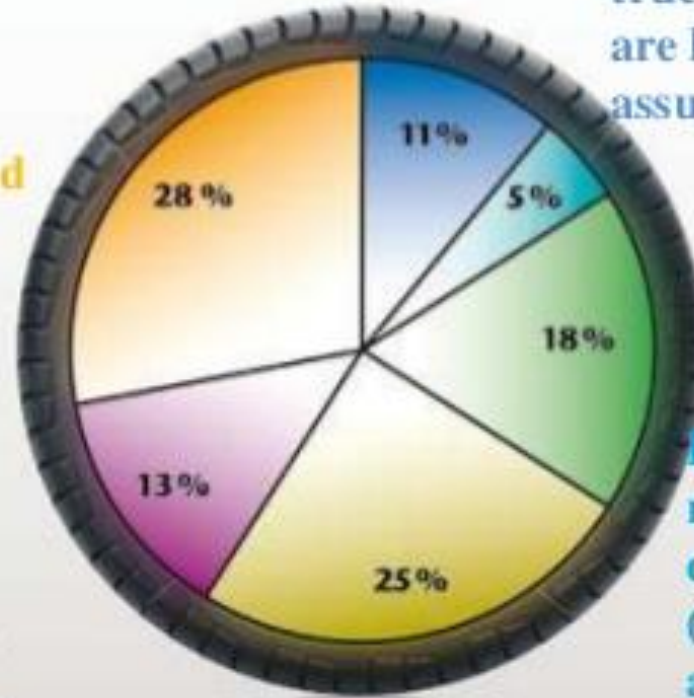
High-strength steel cords are applied under the tread of passenger car tires (and in the carcass of truck tires) while other steel wires are located near the bead to assure adherence to the rim



Passenger car tires feature rayon or polyester cords radially disposed along the carcass ("radial tires"), while nylon cords are placed under the tread or near the bead area



Natural rubber has unique elastic properties and is an essential element of a tire. Truck tires have an even higher natural rubber content than passenger car tires



Material Composition of Tires

Polybutadiene is Used in Solid Fuel Rockets

HTPB - Hydroxyl-terminated polybutadiene is a telechelic polymer with more than two terminal hydroxyl groups according to its functionality mainly used for manufacturing adhesives and coatings from one side and as a binder for composite rocket propellant on the other side.

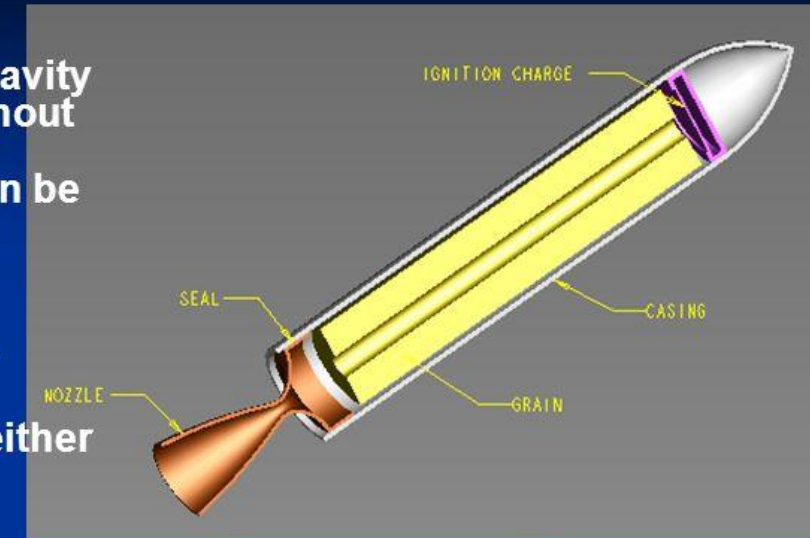
PBAN - Polybutadiene acrylonitrile copolymer, also noted as polybutadiene—acrylic acid—acrylonitrile terpolymer is a copolymer compound used most frequently as a rocket propellant fuel mixed with ammonium perchlorate oxidizer.

Solid Propellants

The cast fuel has a central cavity to allow burning throughout the length of the rocket motor, in shapes that can be anything from a simple cylinder to a star

Solid rocket fuel is typically identified by the type of chemical binder used - either HTPB or PBAN

Hydroxyl-terminated polybutadiene, or HTPB, is a rubber-like binder that is stronger, more flexible, and faster-curing than PBAN, but suffers from a slightly lower I_{sp} , and uses fast-curing, toxic isocyanates



Polybutadiene Core for Golf Balls

Polybutadiene is preferred to other elastomers due to its high resilience.

The core of the balls are formed by compression molding with chemical reactions.

First, polybutadiene is mixed with additives, then extruded, pressed using a calendar and cut into pieces which are placed in a mold. **The mold is subjected to high pressure and high temperature for about 30 minutes, enough time to vulcanize the material.**

The golf ball production consumes about **20,000 tons of polybutadiene per year.**



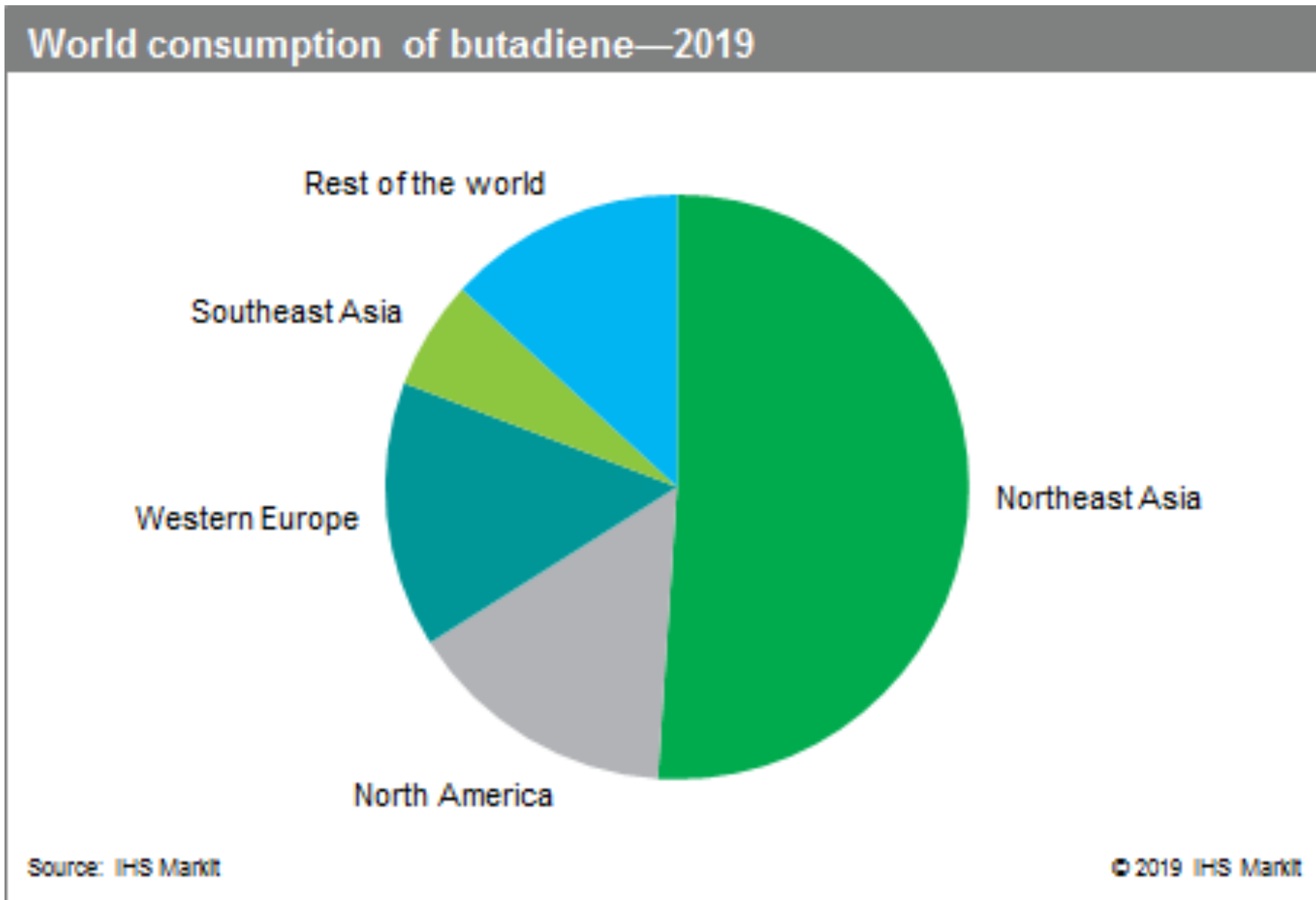
Commercial Uses of Polybutadiene

➤ APPLICATIONS AND USES

- Tire production (SBS)
- Conveyor belt
- Water hoses
- Gaskets
- Golf ball & super ball
- Engine belt
- As fuel in space shuttle for boosting rockets



World Consumption of Polybutadiene



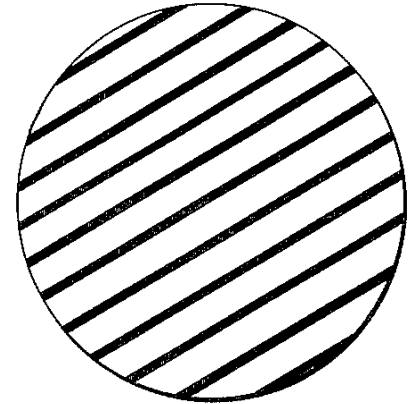
March 22, 1966

N. H. STINGLEY

3,241,834

HIGHLY RESILIENT POLYBUTADIENE BALL

Filed Aug. 25, 1965



BALL MATERIAL:

SPECIFIC GRAVITY	-	1-1.3
POLYBUTADIENE	-	ABOUT 100 PARTS
SULFUR VULCAN. AGENT	-	0.5 to 15 PARTS
HYDRATED SILICA	or	} - 5 to 15 PARTS
CARBON BLACK	or	
LITHIUM OXIDE		

This compound is vulcanized with sulfur at a temperature of 165 °C (329 °F) and formed at a pressure of 3,500 psi (24 MPa).

Stingley sought uses for his polybutadiene synthetic rubber, as well as someone to manufacture it. He first offered his invention to the Bettis Rubber Company, for whom he worked at the time, but they turned it down because the material was not very durable.

Polybutadiene Brought Us the “SuperBall”

So Stingley took it to toy company Wham-O; they worked on developing a more durable version which they still manufacture today.

A **SuperBall** is a bouncy ball based on a type of synthetic rubber invented in 1964 by chemist Norman Stingley.



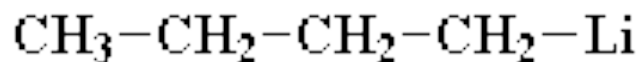
"It took us nearly two years to iron the kinks out of Super Ball before we produced it," said Richard Knerr, President of Wham-O in 1966. "It always had that marvelous springiness.... But it had a tendency to fly apart. We've licked that with a very high-pressure technique for forming it.

Synthesis of S-B-S Rubber via Anionic Polymerization

Anionic polymerization is a type of vinyl polymerization.

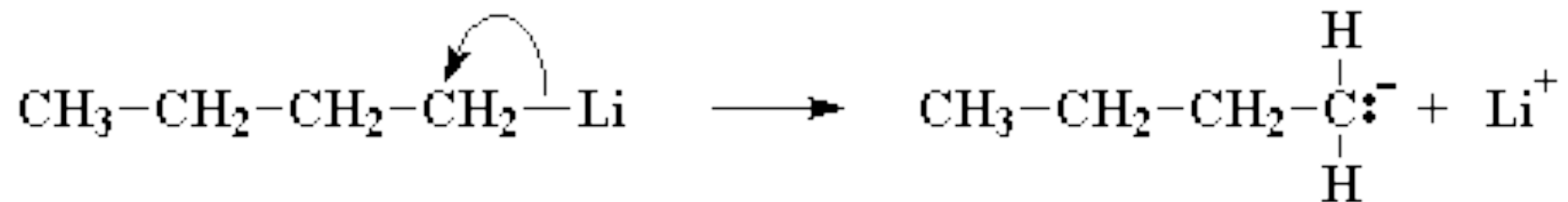
The initiator is an anion having a negative electrical charge.

The most common anionic initiator is n-butyl lithium:



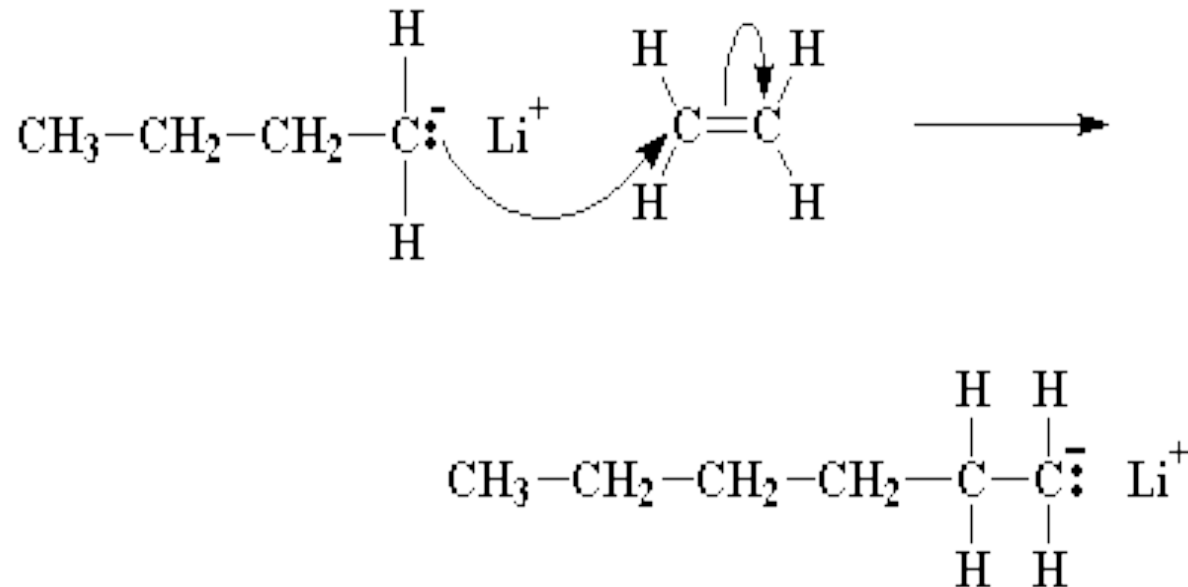
butyl lithium

The n-butyl lithium disassociates to a positive lithium cation and a negative anion with the negative charge on the terminal carbon (i.e., carbanion).



Synthesis of S-B-S Rubber via Anionic Polymerization

A pair of electrons from the butyl anion will be donated to one of the double bond carbon atoms of the monomer. This forms a new carbanion, with the negative charge resting on the new terminal carbon. The process in which the butyl lithium falls apart, and the butyl anion reacts with a monomer molecule is called *initiation*.



Synthesis of S-B-S Rubber via Anionic Polymerization

Definition of a Living Polymer

This propagation step continues until the monomers in the reactor have been incorporated into the propagating chains.

If more monomers are introduced into the reactor the polymerization will continue.

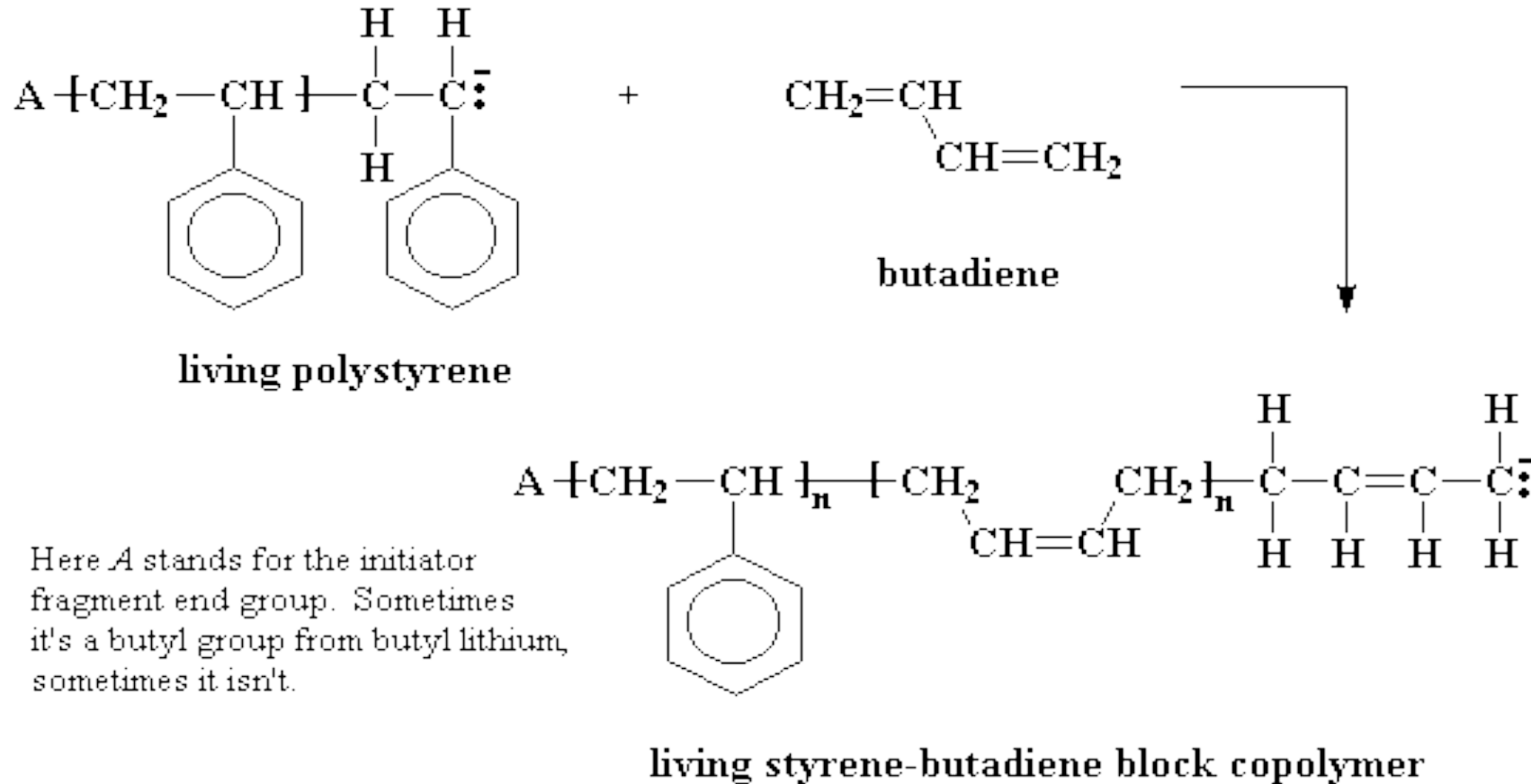
Only when a chemical terminator such as water is introduced will polymerization stop.

Hence the name: living anionic polymerization.

If after depletion of the styrene monomer in the reactor butadiene monomer is introduced a polymer is produced comprising a block of styrene followed by a block of butadiene.

Synthesis of S-B-S Rubber via Anionic Polymerization

After depletion of the styrene monomer in the reactor butadiene is introduced a polymer is produced comprising a block of styrene monomers and a block of butadiene monomers.



Also, described as: **S-S-S-S-S-S-S-S-S-B-B-B-B-B-B-B-B-B**

Synthesis of S-B-S Rubber via Anionic Polymerization

Three methods exist to produce a styrene-butadiene-styrene triblock polymer:

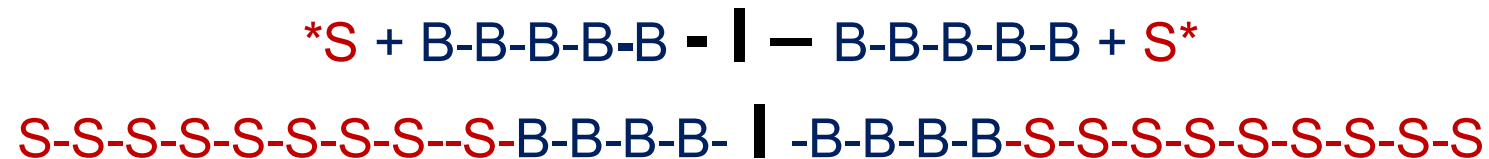
- 1) Linear anionic polymerization of styrene monomer followed by butadiene monomer followed by styrene monomer:



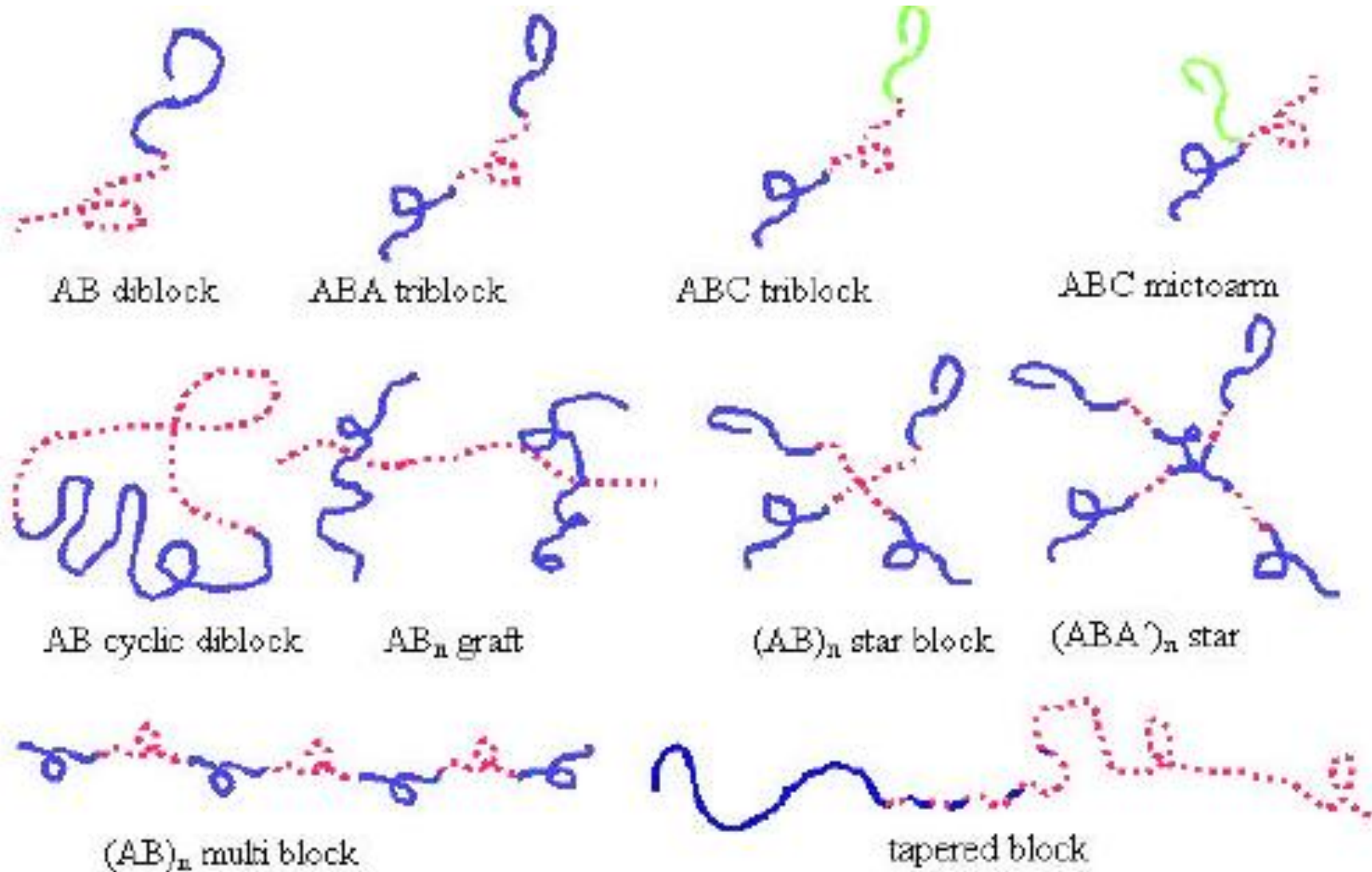
- 1) Reacting two styrene butadiene di-block polymers at the internal butadiene:



- 1) Employing a di-functional initiator and polymerizing butadiene then styrene:



Various Molecular Architectures can be Produced by Anionic Polymerization



Domain Formation by Block Copolymers

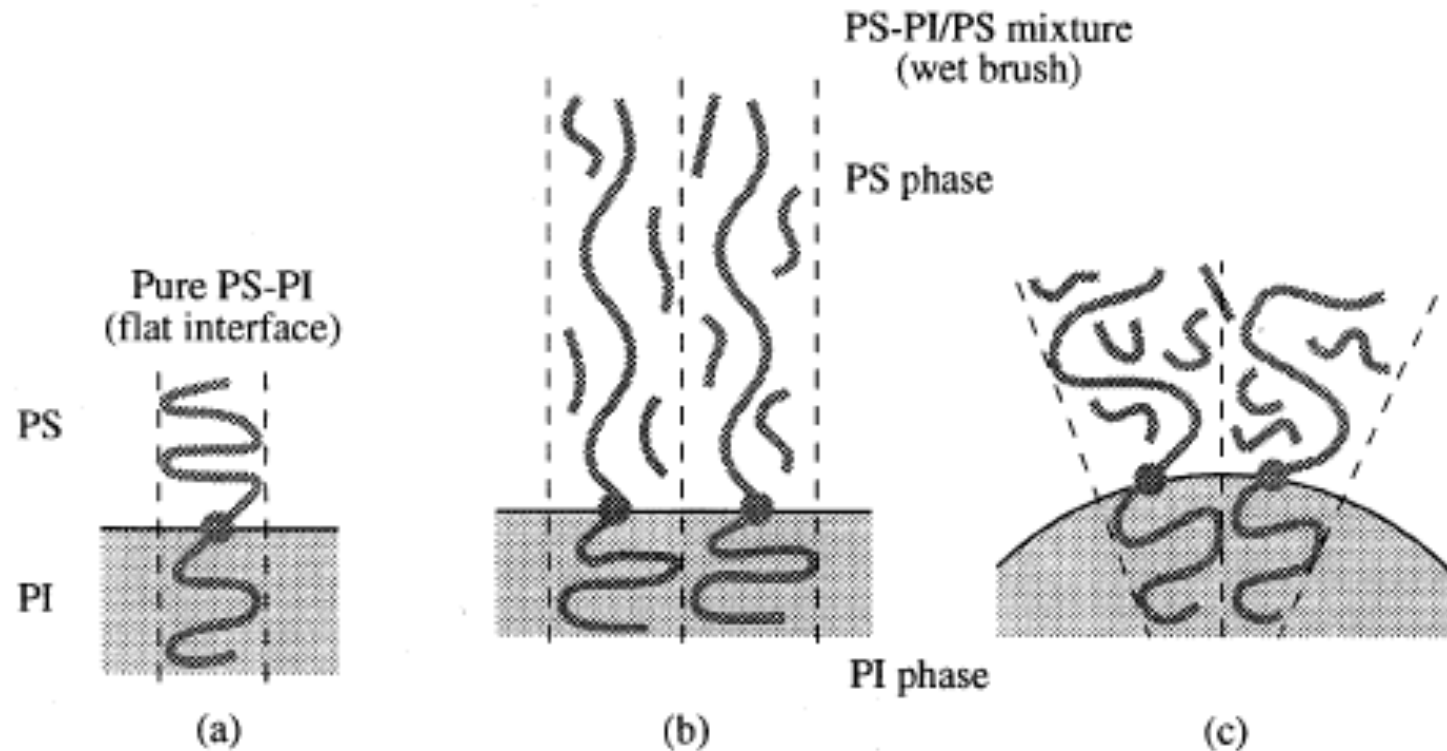
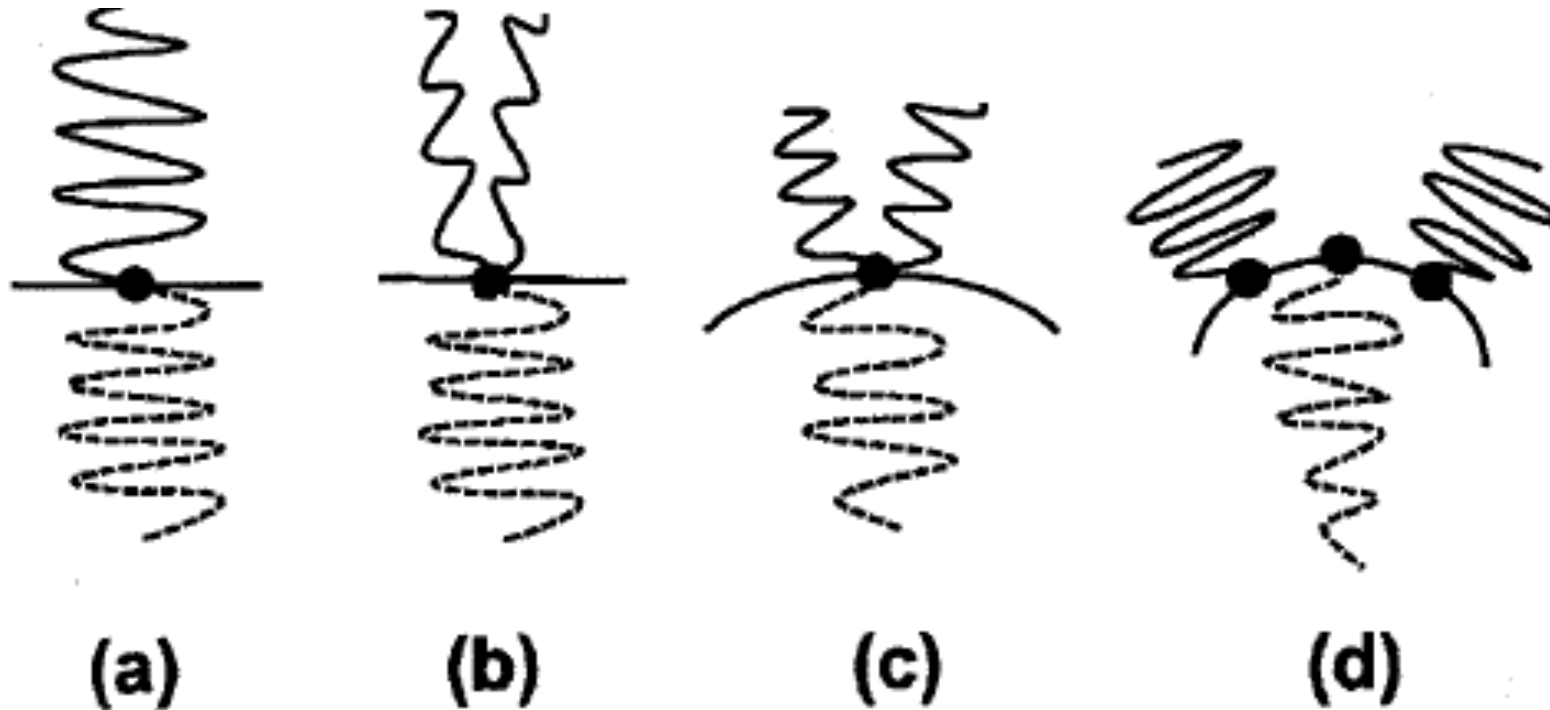


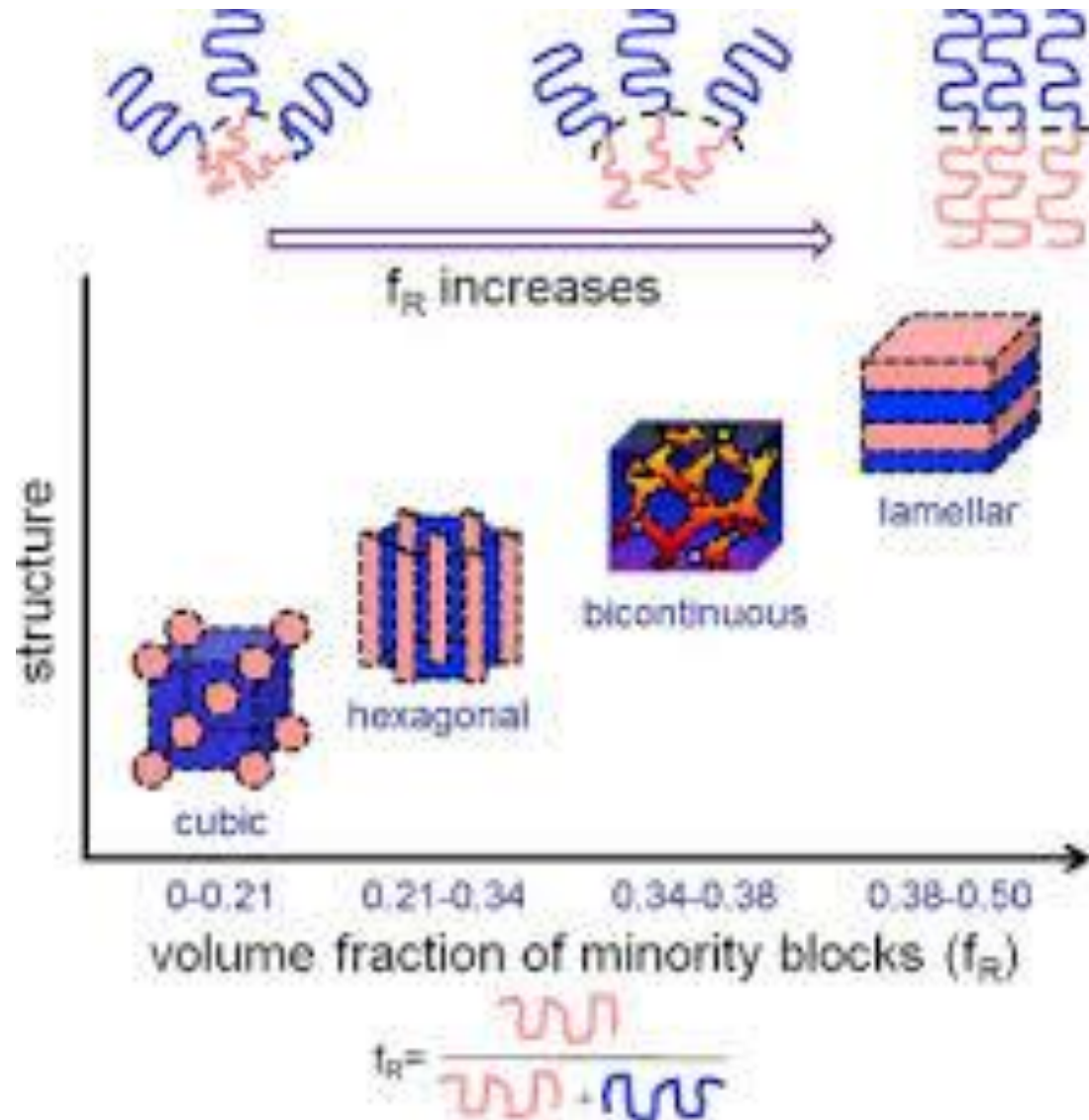
Figure 2.11: Schematic illustration of chain packing: a) pure SI diblock copolymer chain with symmetrical volume fraction forming a flat interface, b) swelling of PS lamellae by uniform solubilization of hPS molecules causes stretching of PS-block chains and/or compression of PI-block chains resulting in a decrease in conformational entropy, c) alternatively a curved interface is formed to gain entropy [76].

Domain Formation by Block Copolymers



2.6: Schematic of A-B junction points on an interface for a) $(2A)B$ linear diblock copolymers, b) A_2B block copolymers with a trifunctional branch point at a flat interface, c) A_2B single graft block copolymer with a trifunctional branch point at a curved interface and d) A_2B block copolymers with approximation of equal spacing between the grafted A blocks. The curvature of the interface represents the shifts of the OOT lines towards higher B volume fractions on the morphology diagrams [30,32].

Domain Formation by Block Copolymers



Curvature of the interface is based upon the ratio between the styrene and the butadiene segments and is critical in determining the morphology of the domains.

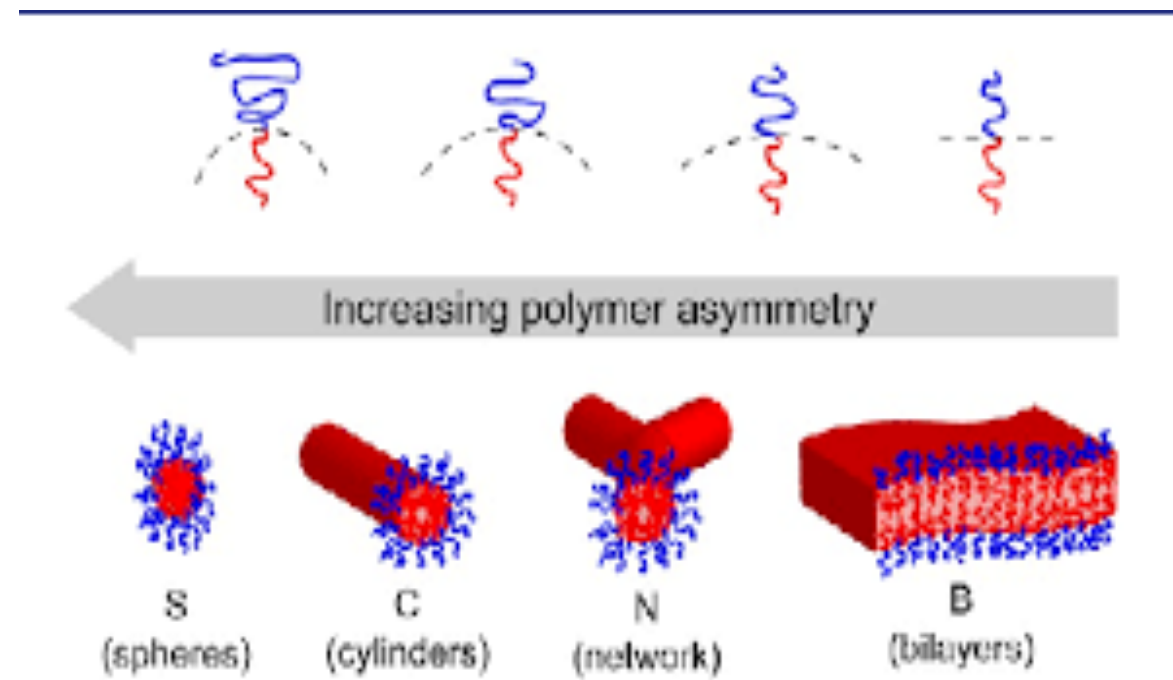


Figure 2. Morphological transitions of block copolymers.

Domain Morphology of Block Copolymers

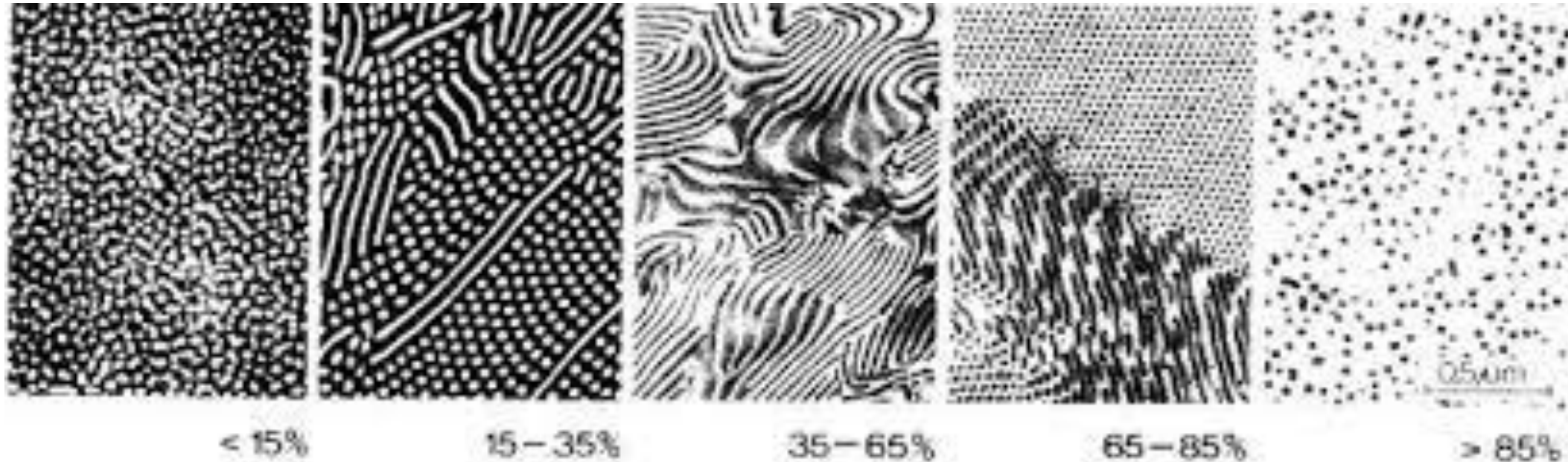
Spheres

Cylinders

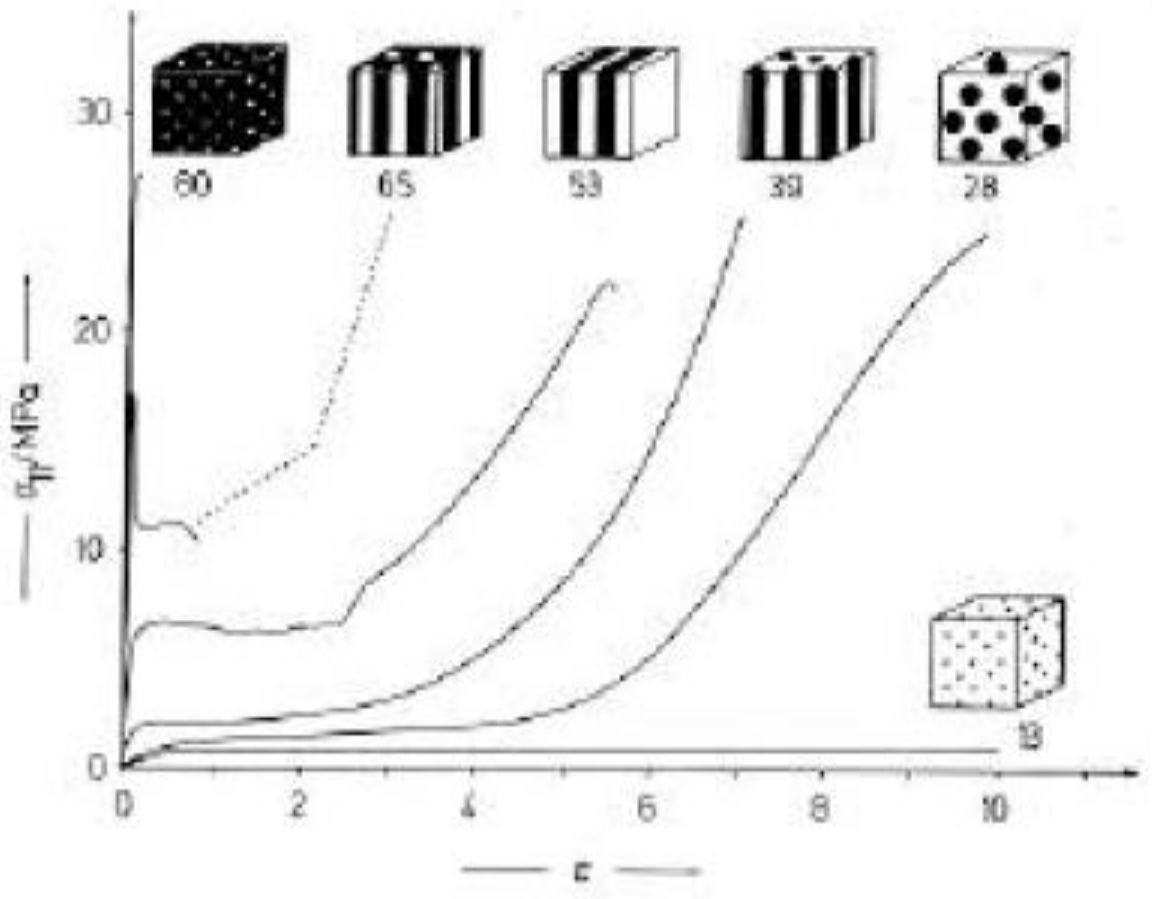
Lamella

Cylinders

Spheres



Phase Dependent Mechanical Properties

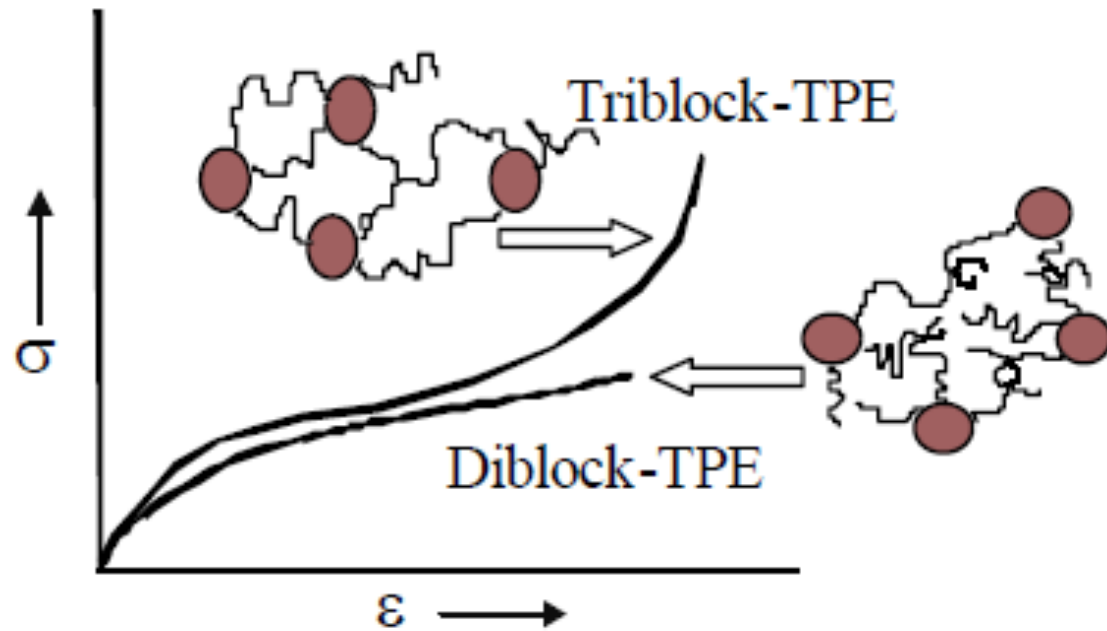


Phase Dependent Mechanical Properties

Styrene – Black Domain – Hard Phase

Butadiene – White Domain – Soft (Rubber) Phase

Elastomers are Derived from a Tri-block Copolymer



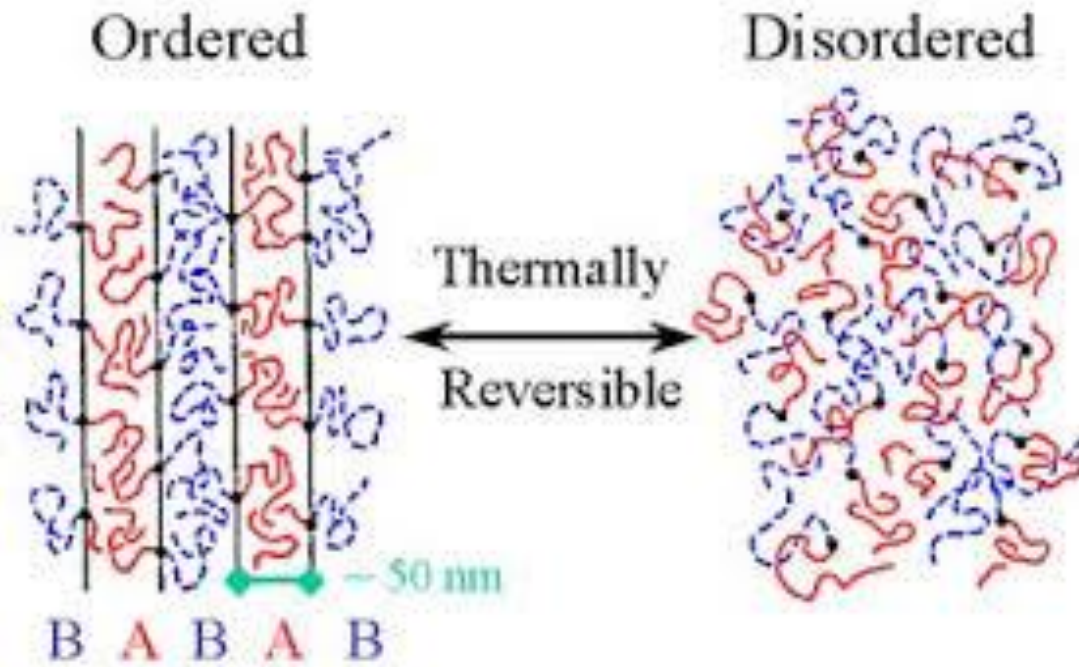
A styrene-butadiene-styrene copolymer defines the morphology of a thermoplastic elastomer.

The styrene segments are the minor component of the S-B-S copolymer and the butadiene segments are the major components.

The styrene components form the rigid spherical domains acting like crosslinks.

The butadiene segments form the elastomeric network.

What defines a Thermoplastic Elastomer?



When the temperature is raised above the glass transition temperature of styrene (i.e., 100C) the styrene domains melt allowing the material to Become disordered and flow.

Once this melt is formed into the final form or geometry the material is cooled and the styrene domains are formed imparting the elastomeric properties.

Examples of S-B-S Thermoplastic Elastomer Products



Comparative Mechanical Properties of Elastomers

	Durometer hardness range	Tensile strength at room temp, psi	Elongation at room temp, %	Temp. range of service °C	Weather resis- tance
Natural rubber	20–100	1,000–4,000	100–700	–55–80	Fair
Styrene-butadiene rubber (SBR)	40–100	1,000–3,500	100–700	–55–110	Fair
Polybutadiene	30–100	1,000–3,000	100–700	–60–100	Fair
Polyisoprene	20–100	1,000–4,000	100–750	–55–80	Fair
Polychloroprene	20–90	1,000–4,000	100–700	–55–100	Very good
Polyurethane	62–95 A 40–80 D	1,000–8,000	100–700	–70–120	Excellent
Polyisobutylene	30–100	1,000–3,000	100–700	–55–100	Very good

Table 1 Selected properties of some elastomers.

Comparative Properties of Elastomers

ISOPRENE BASED RUBBERS

NATURAL (ISOPRENE) RUBBER AND POLYISOPRENE

ADVANTAGES:

NATURAL RUBBER exhibits high resilience, good tensile strength, and tear resistance. In addition to excellent wear resistance, NATURAL RUBBER also offers low permanent set characteristics plus good flexing qualities at low temperatures.

DISADVANTAGES:

NATURAL RUBBER does not perform well when exposed to chemicals and petroleum derivatives, including petrochemicals. It is not recommended for outdoor applications where maximum resistance to sunlight, ozone, oxygen or heat aging is major factors.

TYPICAL APPLICATIONS: Boots, belts, bumpers, tubing.

Comparative Properties of Elastomers

BUTADIENE BASED RUBBERS

SBR (STYRENE BUTADIENE RUBBER) RUBBER AND POLYBUTADIENE

ADVANTAGES:

SBR provides good abrasion, wear, and tensile qualities. SBR can be readily substituted for NATURAL RUBBER in many applications with significant cost savings. Resilience is about the same as NATURAL RUBBER.

DISADVANTAGES:

Like its natural counterpart, SBR offers little resistance to oils and chemicals. SBR must be specially compounded to provide resistance to ozone, sunlight, and heat.

TYPICAL APPLICATIONS:

Washers, gaskets, grommets.

Comparative Properties of Elastomers

NEOPRENE® (POLYCHLOROPRENE) RUBBER

ADVANTAGES:

NEOPRENE® is resistant to ozone, sunlight, oxidation and many petroleum derivatives. Added advantages include good resistance to water, many chemicals, good resilience characteristics and high tensile strength properties.

DISADVANTAGES:

NEOPRENE® has few practical limitations. While NEOPRENE® is slightly higher in price than general purpose synthetic rubbers, its resistance to ozone, oil and chemicals make it cost effective in many applications. It is generally attacked by strong oxidizing acids, esters, ketones, chlorinated, aromatic and nitro hydrocarbons.

TYPICAL APPLICATIONS:

Plumbing fixtures; gaskets; hose; mechanical seals; mechanical belts; solid rocket propellant; garden hose; inner tubes; laboratory tubing.

Lesson 15: Polydienes – From Natural Rubber to Synthetic Rubber Part 2: Polychloroprene, Polybutadiene and Styrene-Butadiene Block Copolymers

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

“There are three signs of “old age”. The first is memory loss and . . . I forget the other two.”