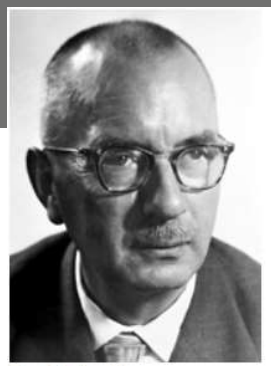
Synthetic methods in chemistry

Elastomers

Content

- Historic aspects, general criteria and properties of elastomeric materials
- Mechanical properties
- Polyisoprene und natural Rubber (IR – isoprene rubber, NR – natural rubber)
- Polybutadien rubber (SBR – styrene butadiene rubber, NBR – nitril butadien rubber)
- Vulcanisation and tire production
- Ethylene-propylene-(diene) rubber (EPM, EPDM)
- Silicones
- Thermoplastic elastomers (TPEs)

History of elastomers



Karl Ziegler

Giulio Natta

1954
EP(D)M
BR

1929
SBR patentiert

1909
Fritz Hofmann „Buna“-Patent

1839
Charles Goodyear ⇨ Vulkanisation

Kautschuk + Schwefel —Erhitzen→ Elastomer

+ wasserdicht	+ wasserdicht
- klebrig	+ nicht mehr klebrig
- Erweichen in der Wärme	+ elastisch
- schnelle Alterung	+ formstabil
	+ alterungsbeständiger

seit 1000 - 700 v. Chr.
Ballspiele der Maya

Kautschuke/ Elastomere: Aspekte/ Kriterien

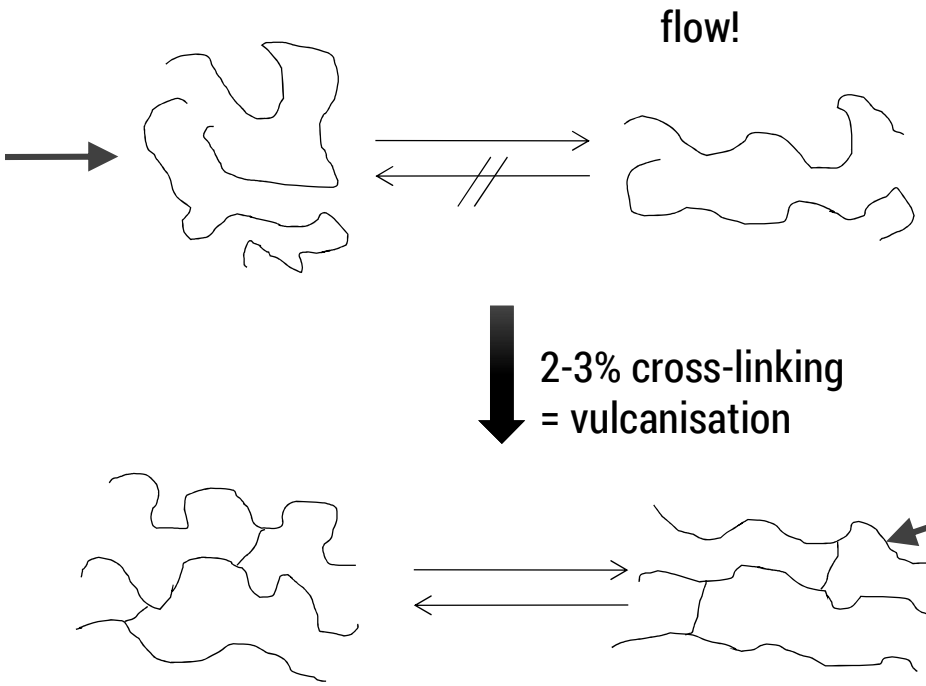
- amorphous or low degree of crystallinity (5-10 % max)
- weakly cross-linked, corss-links can be:

- covalent,
- polar (hydrogen bonds, metal-ligand bonds) or
- physical interactions (bonds) (crystallites, microphases of block copolymers)

- strain > 1000%
- glass transition temperature T_g << 0 °C
- low modulus, soft materials
- mechanical hysteresis
- high viscosities → pressing, kneading, not proceesable from the melt
- classical cross-linking by sulphur vulcanisation

Rubber/ elastomers

rubber: linear polymer with low Tg, which is not or weakly crystalline



elastomer: weakly cross-linked, vulcanized rubber

discovery: C. Goodyear forgtes rubber-sulphur mixture on hot plate and produces vulcanized rubber = elastomer

Sulphur and heat is associated with the roman God Vulkan → vulcanization

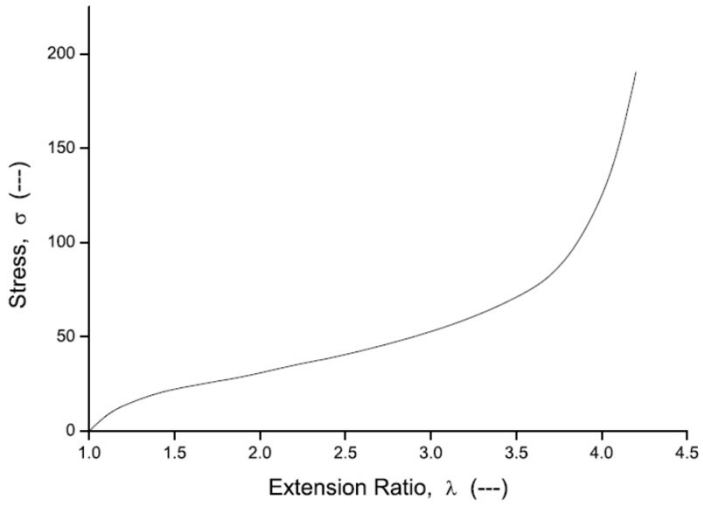
Entropy- and energy elasticity

➢ **elastomers show entropy elasticity!** → coiled, weakly cross-linked chain has many conformations, upon deformation the chain is stretched and the number of conformations is reduced → restoring force: system strives to maximize the number of conformations, → polymer chain behaves as an entropic spring with a spring constant

➢ **energy elastiscity:** deflection of atoms from equilibrium position upon deformation, reversible, restoring force is minimized energy at equilibrium. Classic example are metals. But also deformation of a polymer within the linear regime in a stress-strain curve is energy elastic

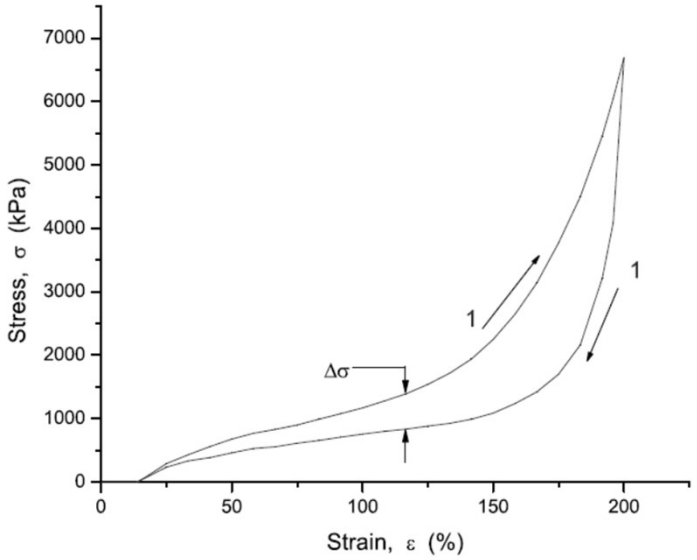
Typical mechanical properties of elastomers

Typical stress-strain curve



- No constant value for the E-modulus!
- Typical „knee“ at lambda 1.0-1.5
- Increase in slope: strain crystallization
- Strain-induced crystallization mostly absent for reinforced elastomers

Hysteresis



- Hysteresis commonyl found with elastomers
- Hysteresis is caused by irreversible or slow molecular processes
- Hysteresis increases for reinforced systems due to filler / polymer chain interactions

Types of rubber

classification (DIN/ISO 1629)

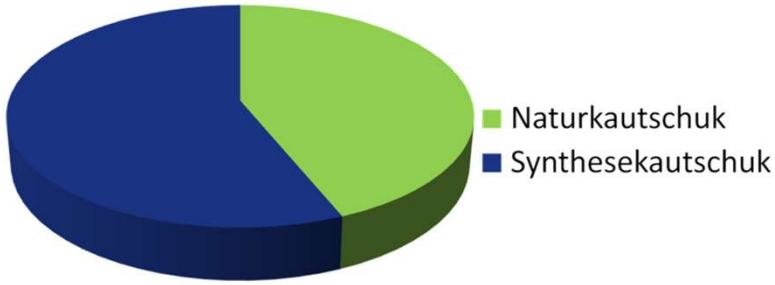
Class	Chemical structure	Examples
R	Rubber with unsaturated hydrocarbons (diene rubber)	NR, SBR, BR, CR, NBR, IR, IIR
M	Rubber with saturated hydrocarbons (polymethylene chains)	EPM, EPDM, CSM, ACM
O	Rubber with C-O-bonds in the main chain	CO
Q	silicon-based rubber	MQ, MVQ
U	Polyurethane rubber	AU, EU
T	Rubber with sulphur in the main chain	Poly sulfide rubber

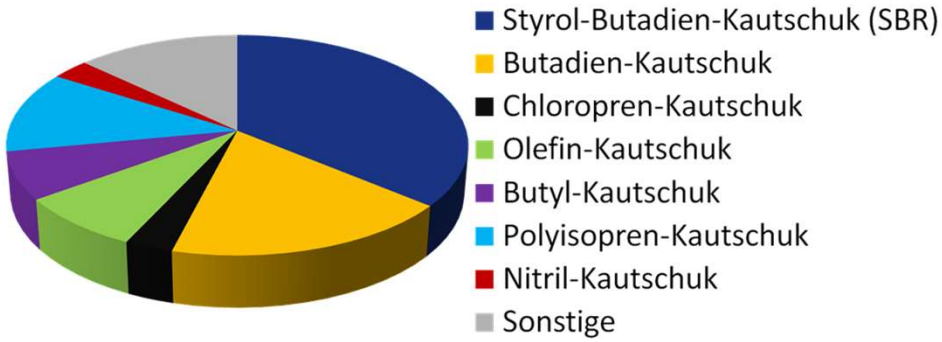
NR = Natur rubber (Naturkautschuk), SBR = Styrol-Butadien-Rubber, BR = Butadien-rubber, CR = Chloropren rubber, NBR = Acrylonitril-butadien-rubber, IR = isopren rubber, IIR = isobutylene isopren rubber, EPM = Ethylen-Propylen-monomer, EPDM = Ethylen-Propylen-Dien-monomer, CSM = Chlorsulfoniertes Polyethylen, ACM = Acrylatkautschuk, CO = Epichlorhydrinkautschuk, MQ = Polydimethylsiloxan, MVQ = Copolymer von Dimethylsiloxan und Vinylmethylsiloxan, AU = Polyester-Urethan-Kautschuk, EU = Polyether-Urethan-Kautschuk

Elastomer demand

rubber: 24,6 mio. tons (2010)

Mayas: **„caao-chu“** („crying tree“) → rubber plant
french: **„caoutchouc“**
german: **„Kautschuk“**

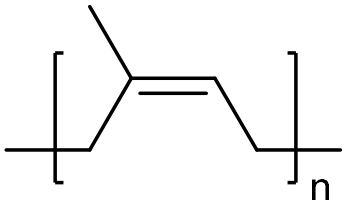




H.-J. Arpe, Industrielle Organische Chemie, Wiley-VCH, 2007

Natural rubber: Poly(cis-1,4-isopren)

- **„Hevea brasiliensis“** – botanical name of the „crying tree“ (rubber plant)
- Origin: Amazonas region
- Most important source of natural rubber: 90 %
- 95 % of natural rubber from south-east asia



Natural rubber vs synthetic polyisoprene

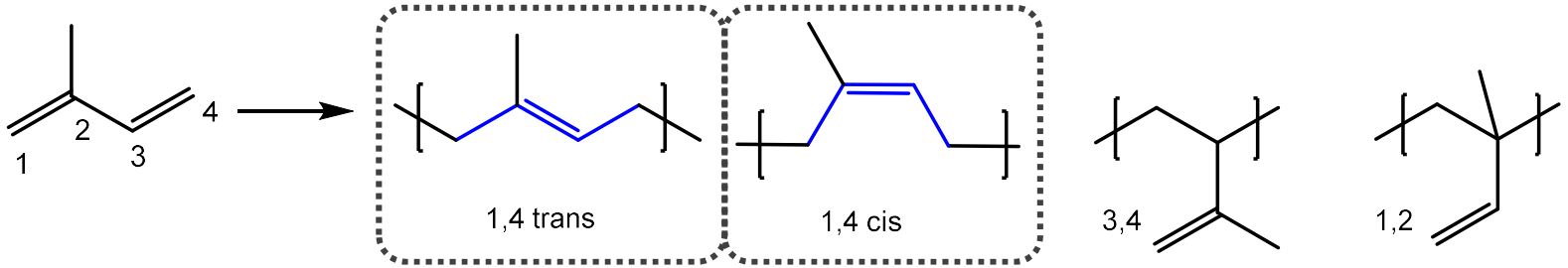
Microstructure of polyisoprene is of utmost importance for elastomeric properties!

→ High content of cis 1,4 needed for elastomeric behaviour

→ Anionic polymerization: only limited amount of cis 1,4 (BuLi)

→ Arrival of Ziegler Natta catalysts led to an increase in cis-1,4 ($TiCl_4$/ AlR_3)

→ Synthetic IR has higher purity and better batch-to-batch reproducibility than NR



Guttapercha NR

	NR	Ziegler-Natta-IR	anionic-IR
Microstructure/ %			
Cis 1,4	100	98,5	90
Trans 1,4	0	1	5
3,4	0	0.5	5
1,2	0	0	0
Purity/ rubber content/ %	94	> 99,5	> 99,5

Alternative sources for NR

- Car tyre mixture must contain a certain fraction of NR (ca. 15-40 %) to yield optimum mechanical properties
- Mono cultures in sub-tropical countries have known drawbacks
- Alternatives: **Guayule-bush** (deserts in Mexico → Bridgestone) or russian der **russischer dandelion** (*Taraxacum koksaghyz*)→ grows anywhere
- Latex milk from dandelion roots
- Car tyres with same properties compared to NR → Continental

http://www.zeit.de/mobilitaet/2015-10/reifen-kautschuk-alternativen-loewenzahn

https://www.fraunhofer.de/de/presse/presseinformationen/2015/Juni/naturkautschuk-aus-loewenzahn.html

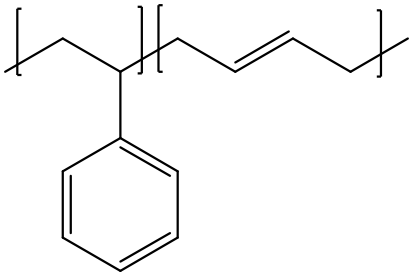
Polybutadiene rubber (BR)

- PB rubber is a common term for all homopolymers from 1,3 butadiene
- Largest fraction goes into car tyre production
- free radical polymerisation (emulsion), anionic (BuLi is initiator) or coordinative
- As for PI, microstructure is of utmost importance for elastomeric properties
- Coordinative polymerization: many possibilities for microstructure tuning
- OH radical-initiated FRP of B: bis-hydroxy-terminated PB-Polyol for elastomeric PUs
- Use of B with other monomers: styrene→ SBR („Buna-S“, acrylonitrile → NBR („Buna-N“)
- Copolymer architecture: statistic, block, graft copolymers

metal	polymerization	cis 1,4	trans 1,4	1,2
Neodym	Coordinative	98	1	1
Cobalt	Coordinative	97	1	2
Cobalt	Coordinative	3	0	97
Nickel	Coordinative	97	2	1
Titanium	coordinative	93	3	4
Lithium	Anionic	36-38	52-53	10-12
--	Free radical	~40	~40	~20

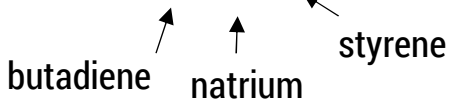
Synthesis of SBR (Styrene/Butadiene rubber)

- SBR: family of S/B copolymers (not to be mixed up with TPE SBS triblockcopolymer)
- First synthetic rubber, also most important rubber (2012: 5.4 Mt)
- First synthesis by 1927 W. Bock and E. Tschunkur (I.G. Farben) via emulsion polymerisation
- Typical composition 25% S, 75% B, more S makes SBR less rubbery and vice versa, e.g. winter tires contain less S
- SBR more abrasion resistant than natural rubber and ages slower



Solution polymerisation

- (anionic, „BuNa-S“)



- Expensive, fast
- Continuous or batch

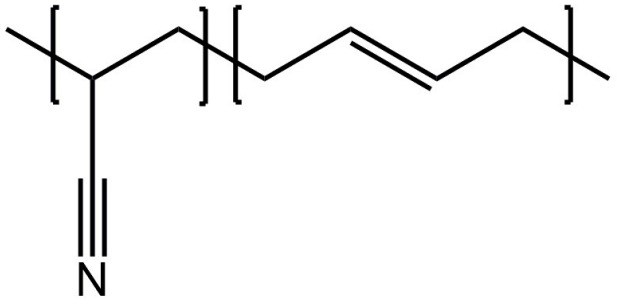
Emulsion polymerization

Water, monomers, peroxo-sulfates, SDS, Fe-salts

- Cheap, slower
- continuous

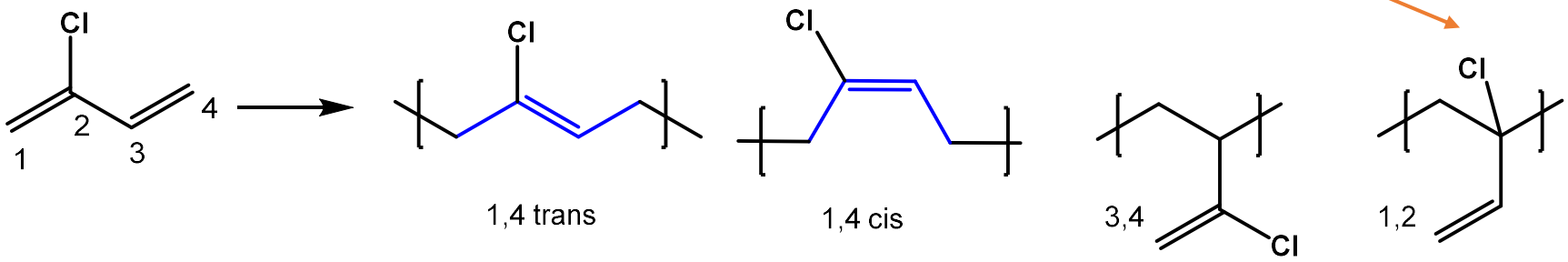
Nitrile-butadiene rubber (AB or NBR, formerly „Buna-N“)

- Patented 1934 by E. Konrad and E. Tschunkur (I. G. Farben)
- FRP (emulsion) of acrylonitrile (A) and butadiene (B), A content 18-50 %
- Vulcanisation leads to NBR with good resistance to aliphatic compounds (mineral oils, A increases hydrophilicity!), low friction, good elasticity at low temperatures
- Higher A content: increased stiffness, better resistance to aliphatics, lower elasticity at low temperatures
- Applications: sealings, O-rings, nitril-gloves
- Hydrogenated version: HNBR: increased oxidative stability



Chloroprene-rubber (CR)

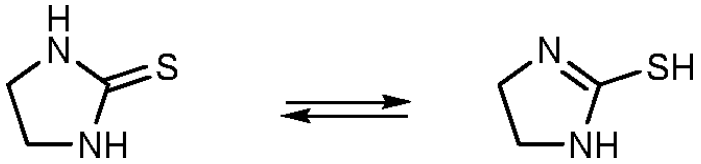
- Also: polychloroprene or chlorobutadiene-rubber
- Trade name Neopren (DuPont), Baypren (Lanxess)
- Monomer: 2-Chlor-1,3-butadiene



trans:cis = 9:1

[3,4 und 1,2 im Bereich von 1%]

- Emulsion polymerisation
- High content trans-isomer facilitates crystallization → hardening of material
- Chlorines not very reactive except 1,2 isomer → cross-linking with metal oxides such as ZnO, MgO, PbO and ethylene thiourea harnstoff (ETU = ethylene thiourea) as source of sulphur



Chloroprene-rubber (CR)

properties

- Slow-burning
- Good chemical resistance, good resistance against ageing, weathering and ozone
- Good swelling resistance in water, grease, low molar mass aliphatic hydrocarbons
- Strongly swelling in aromatic compounds (benzene, toluene), chlorinated hydrocarbons, esters, ether and ketones

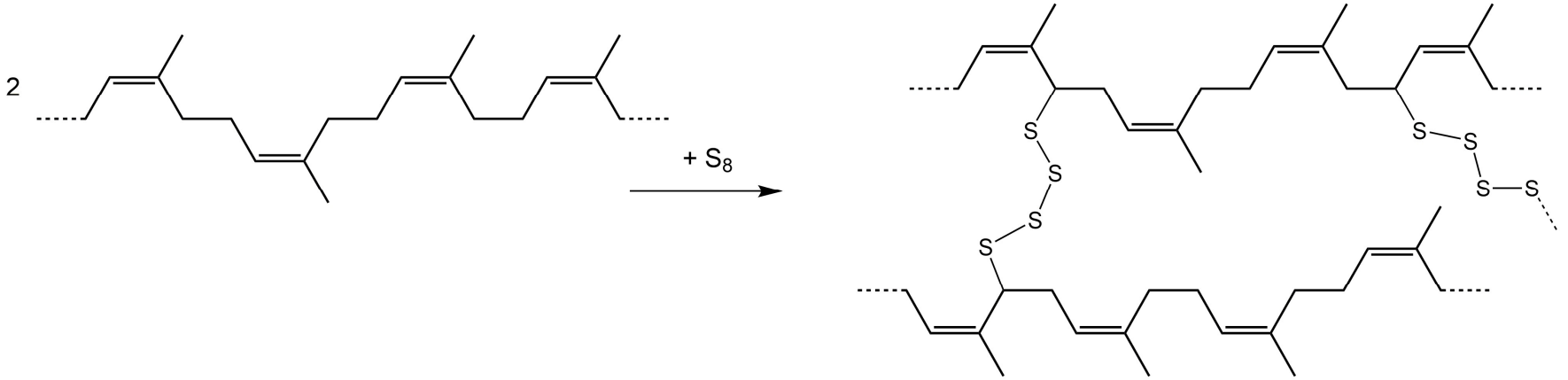
usage

- Adhesives
- Sealings, tubings
- diving suits

Bildnachweis: www.wikipedia.de

Vulcanisation

- The term „vulcanisation“ is generally used in the elastomer area



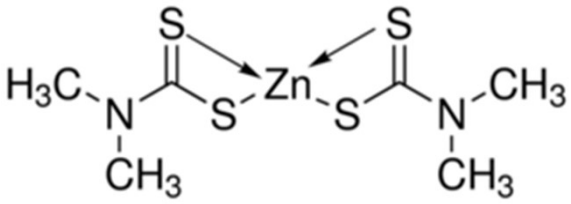
- Hot vulcanization (120-160 °C): S_8 hot vulcanisation is slow and requires accelerators such as dithiocarbamates
- Cold vulcanization: S_2Cl_2
- Reactive sites: allylic C-H bonds! (Compare reaction of propylene and isobutylene with radical initiators)
- X-links: S_x with X= 1-8
- Shorter S links have better temperature stability

- also: peroxides (EPM), metal oxides (polyc hloropren)

Recipe for car tyre

100 g SBR
3 g sulphur
40 g carbon black (→ filler, reinforment, UV stabilizer)
10 g mineral oil (→ plasticizer)
0,3 g accelerator zinc dimethyldithiocarbamate
1 g antioxidant (phenylnaphthylamine)

Com-
pression molding
10 min, 120-160°C



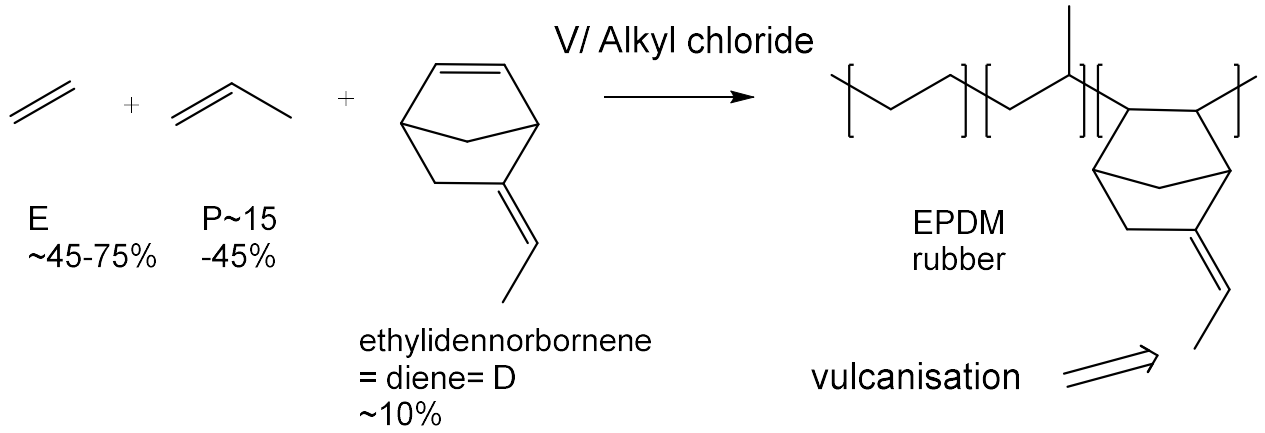
Walzwerk

Reifenpresse

Walzwerk mit Stockblender im Gummiversuchsbetrieb des Kautschukzentrallabors. Bild aus dem Jahr 1959, aufgenommen im Gebäude K 10 des Leverkusener Chemparks, dem heutigen Sitz des Spezialchemie- Konzerns LANXESS AG.

http://live2.mail.lanxess.com/de/100-years-photos/historie/98/

EPDM elastomers

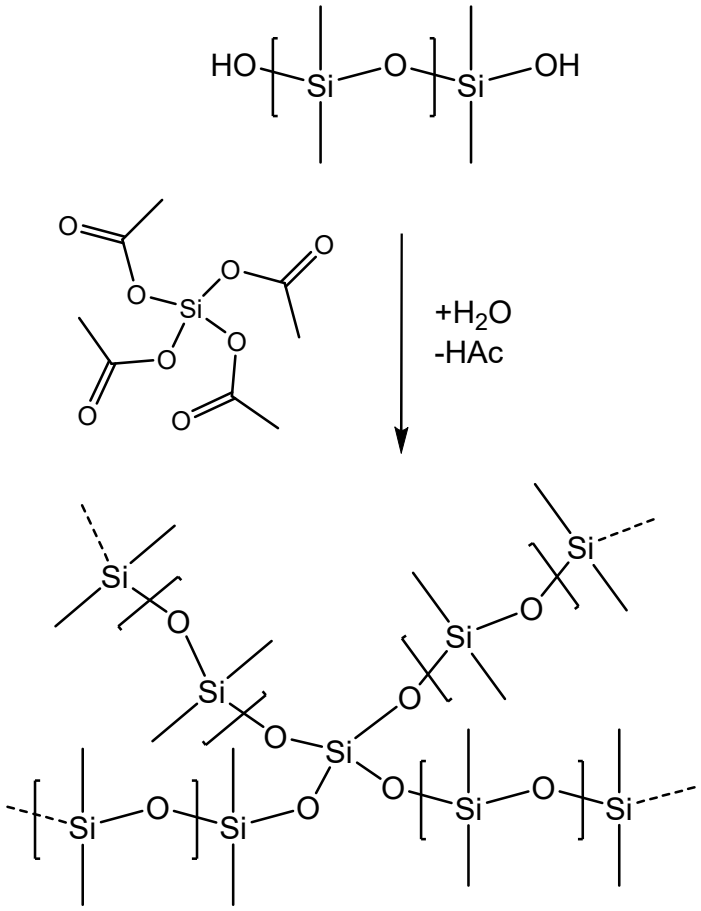


- Copolymers from ehylene and propylene 45-75% ethylene (why does that yield an elastomer?)
- Up to 55% ethylene: amorphous, 55% bis 65% semicrystalline, > 65% large crystalline domains (thermoplastic elastomers)
- Main chain saturated compared to PI or PB→ diene comonomer required for vulcanisation with sulphur (up to 12% ethylidene norbornene, dicyclopentadiene, 1,4-hexadiene) = EPDM
  OR vulcanisation with peroxides or beta/ gamma-rays
- polymerisation with Ziegler-Natta-catalysts in solution, suspension or gas phase
- Good resistance to weathering, UV-light, oxidation, heat, good flexibility at low temperatures, high electrical resistance → applications as sealings: O-rings, flat sealings, sealings for rooftops
- Low tensile strength, tear propagation resistance (compared to diene rubber , low resistance to mineral oils

Silicon elastomers

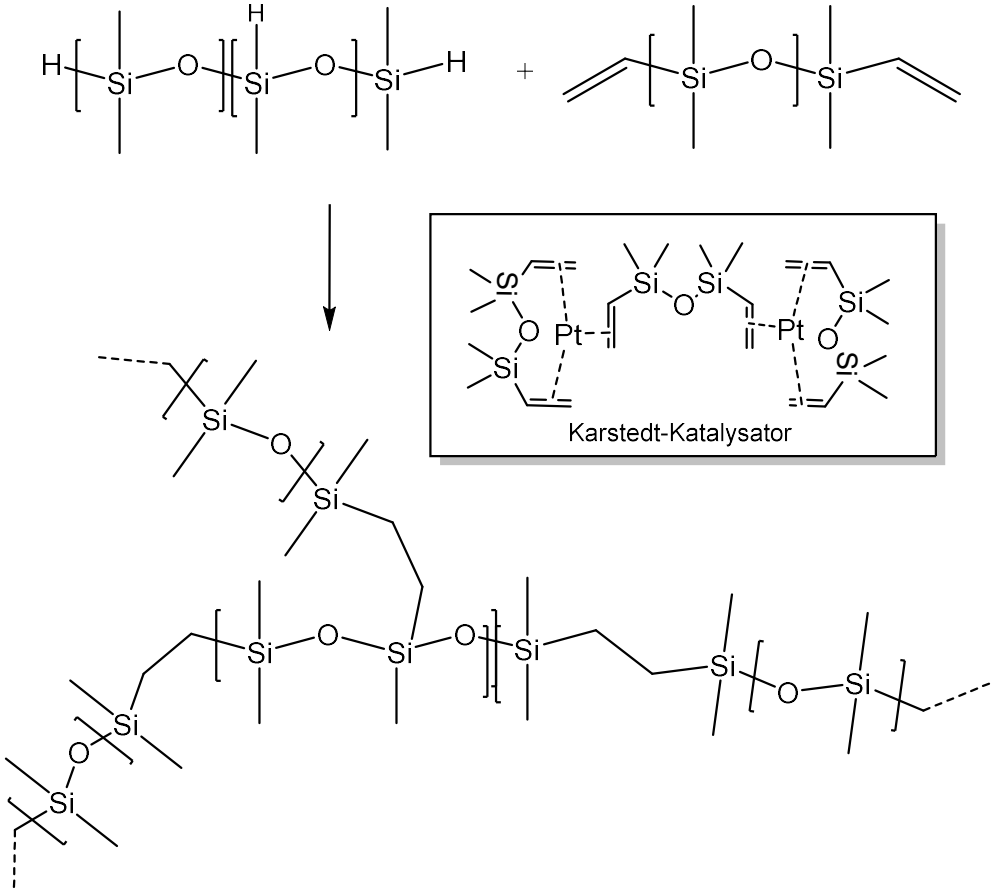
Polycondensation of HO-terminated PDMS

- at RT, needs moisture



Polyaddition (Pt.-cat. Hydrosilylation)

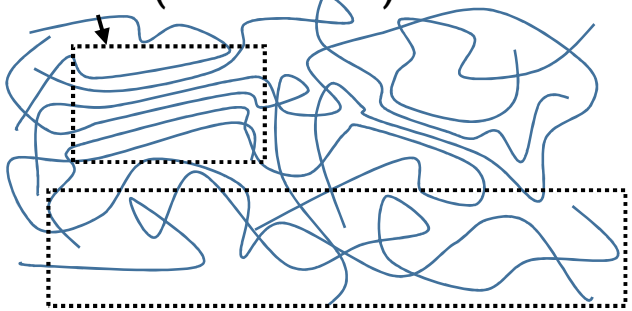
- PDMS with Si-H bonds (more than two per chain!)
- α,ω-vinylterminated PDMS



Thermoplastic elastomers (TPEs)

➢ thermoreversible Vernetzung durch Kristallite oder Mikrophasen→ bei RT Elastomer, durch Schmelzen der Kristallite oder Erreichen von T_{ODT} (bei BCP) thermoplastische Verarbeitung

kristallin (max. 5-10%)



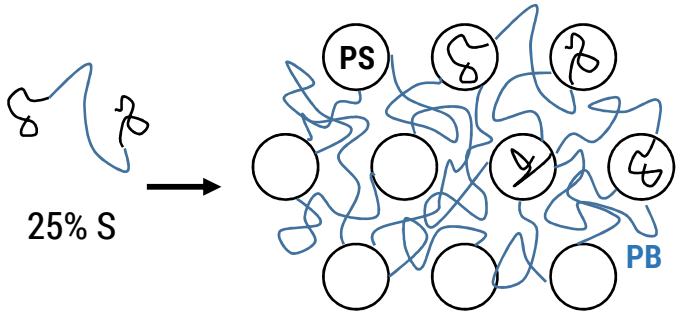
amorph

$T > T_m$

$T < T_c$

melt

Bsp. SEBS, PUR, etc.

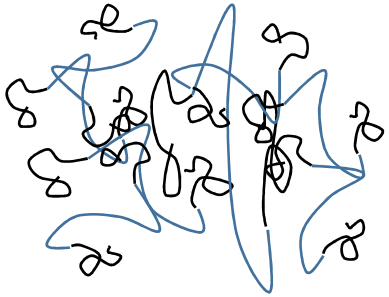


25% S

µ-Phasensep.:
Harte PS Kugel in weicher PB Matrix

$T > T_{ODT}$

$T < T_{ODT}$



homogeneous melt

Bsp. SBS Triblock (Kraton®)