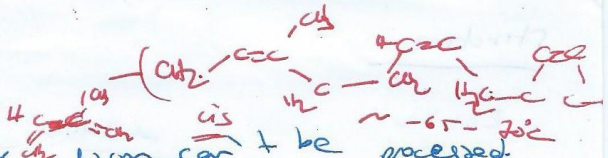
NATURAL RUBBER



1820 → Rubber in latex form can't be processed.

→ hard and stiff in cold water

→ soft and sticky in hot water.

1839 → Goodyear found that rubber which had been heated with sulfur (S_8) retained its elasticity over a wide range of temperature than the raw material and had better resistance to solvents.

sulfur addition is called "vulcanization".

two patent 1843 (British patent), 1844 Good year patent was occured.

1910 → 100000 tons rubber was used in raincoats, footwear, tyre (bicycle and automibe)

Production

latex (from tree) → Rubber in water.

rubber hydrocarbon 35%

non rubber solids (proteins, lipids, inorganic salts 5%
quebrachitol etc)

water 60%

latex diluted by acetic or formic acid → Coagulation

↓

sheet formation on rollers

dry in wood smoke 60°C 4 day

air dry 40°C 7 day

Commonly, field latex is centrifuged to give concentrated latex which has a solid content of about 60%. To preserve such latices over long periods of time, ammonia and other bactericides are added

Structure

Rubber latex → (Toluene, add MeOH) → Rubber spit out,

(consisting of proteins, lipids, quebrachitol (monomethylether of hexahydroxycyclohexane) and inorganic salt

$CH_2=CH-CH=CH_2$ butadiene

$CH_2=C(CH_3)-CH=CH_2$ isoprene (1) (2) (3) (4)

(1) $CH_2=C(Cl)-CH=CH_2$ (2) (3) (4)
Chloroprene

1,2 unit   X = H, CH_3 or Cl   3,4 unit

cis 1,4 unit   trans 1,4 unit

synthetic approach catalyst and temperature play a role.

First time Rubber → ozonolysis

$RHC=CR'R'' \xrightarrow[H_2O]{O_3} RHC=O + R'R''C=O + H_2O$

It was obtained that rubber hydrocarbon consists of isoprene units

$CH_2=C(CH_3)-CH=CH_2$

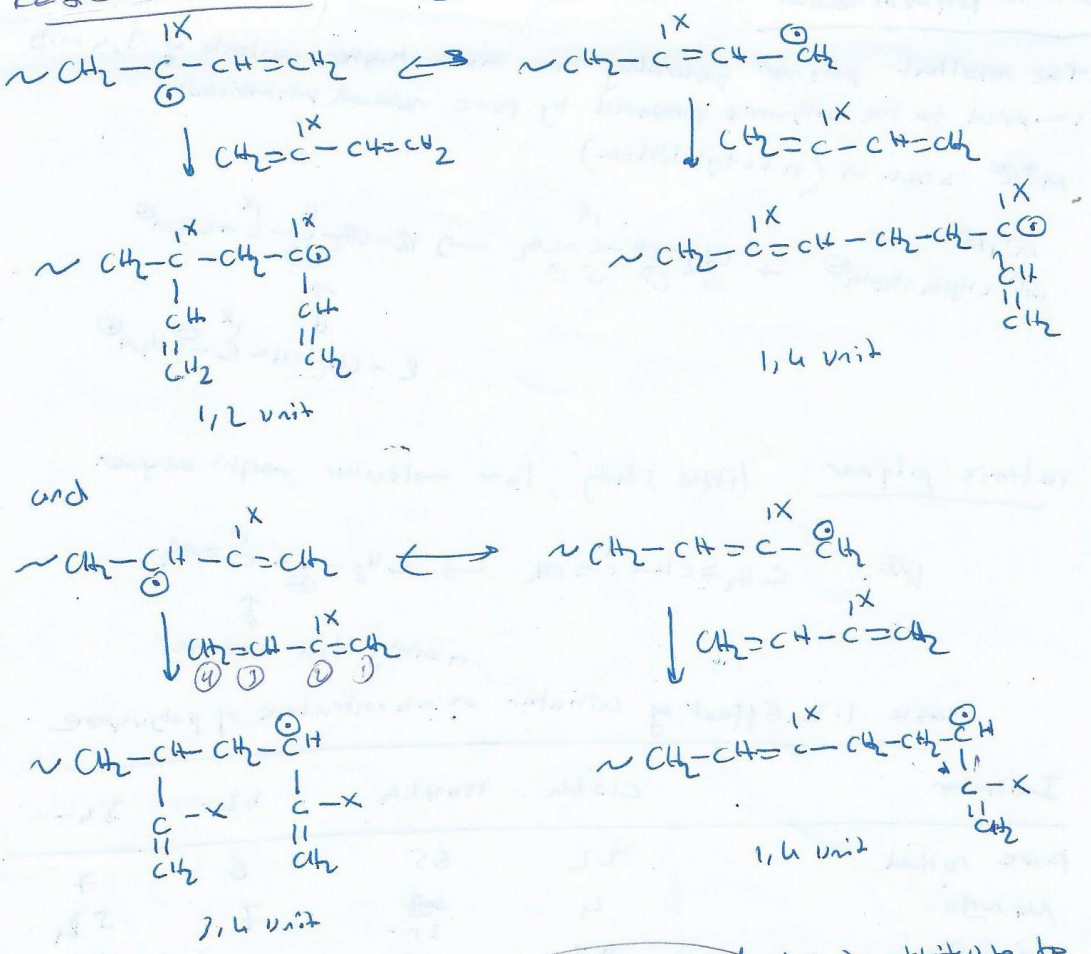
(joined by head to tail by 1,4 links.)

Natural rubber is mainly cis-1,4-polyisoprene.

MWT changes by process because Q can degrade and X-linked can occur. (→ MWT $1,3 \times 10^6$) 1000000

cis, and trans geometric isomers is mainly characterized by X-ray analysis.

Radical polymerization



1,2 unit

1,4 unit

and

1,4 unit

1,4 unit

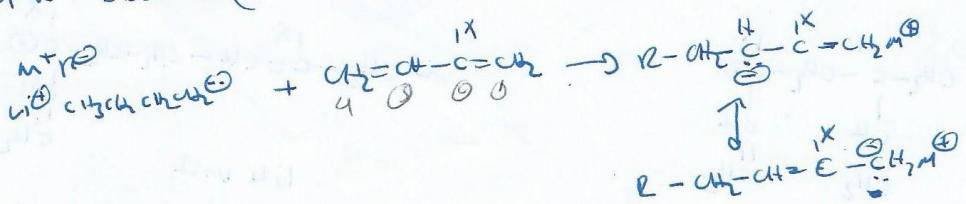
In practice, a preponderance of 1,4 unit is formed; this is attributed to the greater accessibility of the primary radical compared to that of secondary radical. regularity

trans form → more favored than cis form (energetically more favored at low temp.)

Anionic polymerization

The resultant polymer generally have much higher contents of 3,4 units compared to the polymers prepared by free radical polymerization.

M^+R^- such as (n butyl lithium)



Cationic polymer : little study, low molecular weight polymer.

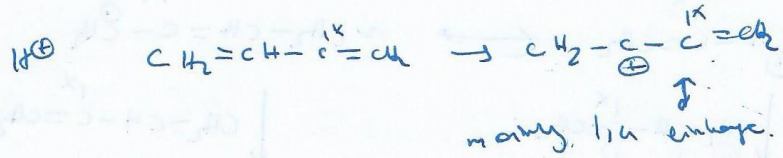


Table 1.2 Effect of initiator on microstructure of polyisoprene

Initiator	cis 1,4	trans 1,4	1,2-	3,4-
Free radical	22	65	6	7
Na NBu	4	~~62~~ 35	~~7~~	54
Li NBu	93	0	0	7
$TiCl_4$-AlEt$_3$ (Ziegler natta)	96	0	0	4
$SnCl_4$	0	89	6	5

vulcanization

vulcanization → x-linked mainly S_8 used

apply a stress

It turns back.

original position.

vulcanizing ingredients (sulfur + accelerators + activators)

↓

Active sulphurating agent

↓ Rubber

Rubber bound intermediate

↓

Initial cross links

↓

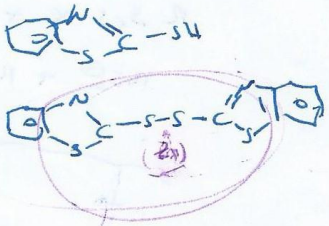
vulcanize networks

↓

Aged vulcanizate network

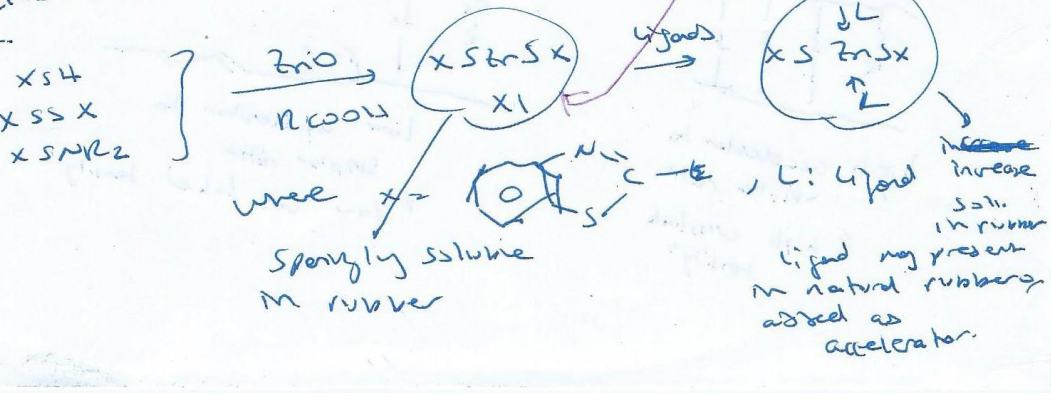
Natural rubber ("sheet form")	100 part
Carbon black	47.5
Sulphur	3.0
mercaptobenzothiazole	0.85 → accelerators
Zinc oxide	5.0
stearic acid	3.0

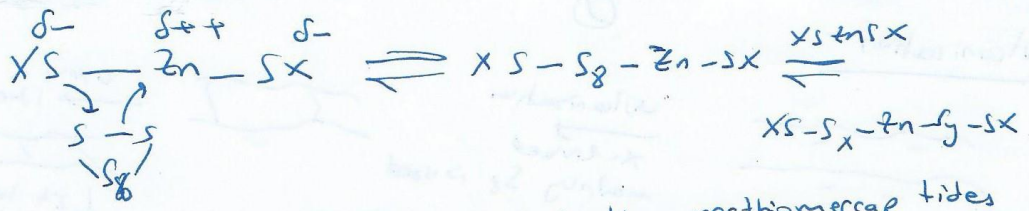
(cure time 30 min at 140°C)



i) formation of the active sulphurating agent

in this step, the accelerators and activators interact to give a species which then reacts with sulphur to form sulphurating agent.

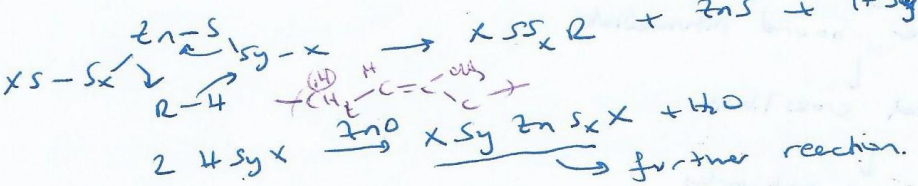




The average values of x and y in the perthiomercaptides will be determined by the relative concentrations of sulphur and the mercaptide complex.

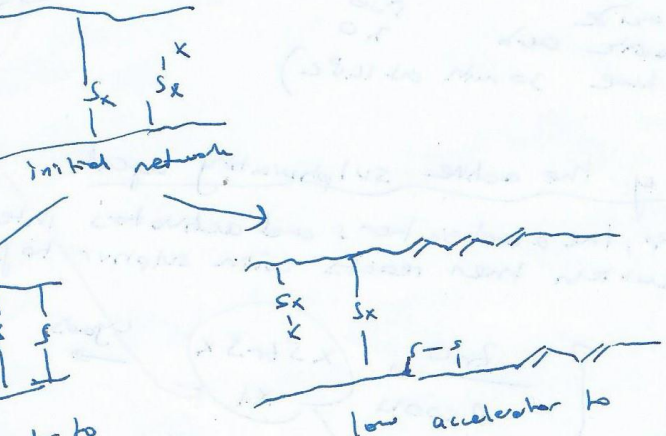
(ii) Formation of the rubber-bound intermediate

the mechanism is not known exactly.



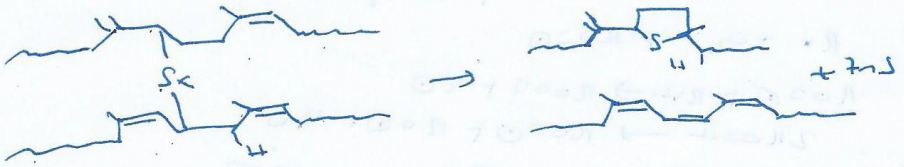
(iii) Formation of initial crosslinks

⇒ involving S–S cleavage



(iv) Formation of vulcanizate network

Degradation and decomposition occur in the reaction condition. i.e thermal condition.



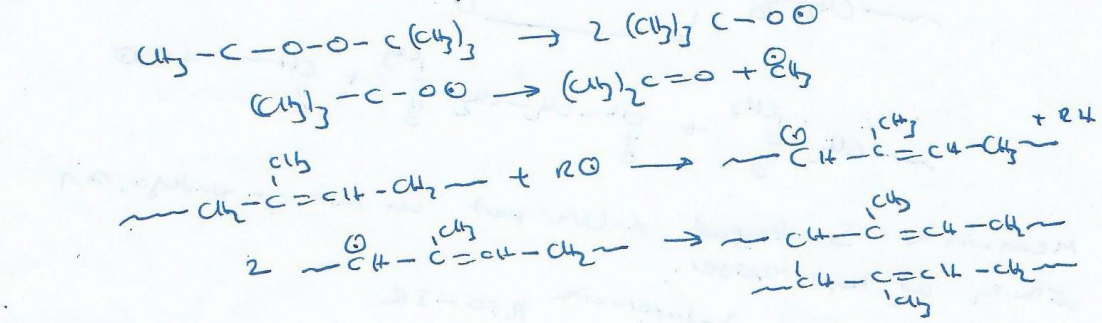
(v) Formation of aged network

x-link and decomposition can continue. Especially polysulphide type (high x-link) unstable and can undergo rxn.

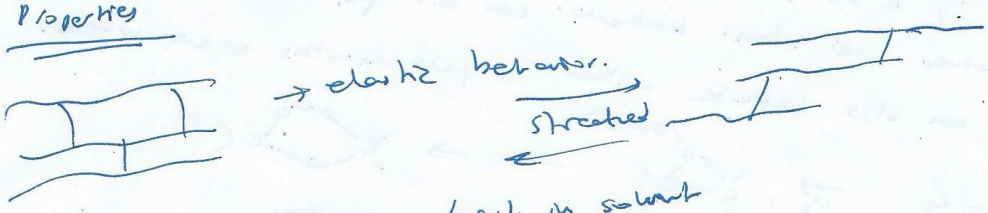
Eg.

Eg 18.2.6.2. Peroxide vulcanization

bi-tert-alkyl peroxide
di-tert-aryl peroxide
} in the most stable vulcanizates of natural rubber.



Properties



→ elastic behaviour.

vulcanizate rubber → not sol. in solvent
→ $KMnO_4$ → degradation.

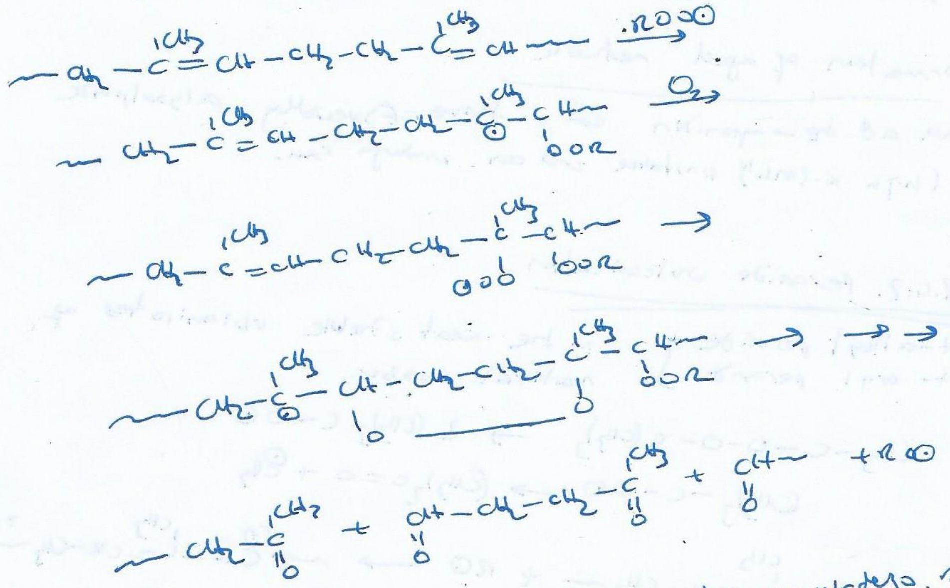
natural rubber $\xrightarrow{O_2}$ aging, physical properties changes.

- Decrease in MWT can observe by time
- loss of useful elastic properties by time (1% by weight O₂ absorption)

$R\bullet + O_2 \rightarrow ROO\bullet$

$ROO\bullet + RH \rightarrow ROOH + R\bullet$

$2ROOH \rightarrow ROO\bullet + RO\bullet + H_2O$



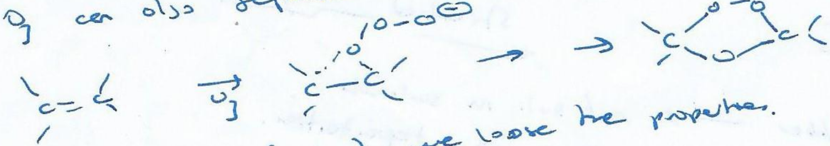
Meanwhile S bonded x-link part can also go undergo rxn with O_2 and hydroperoxides.

$RS-S-R \xrightarrow{\text{hydroperoxide}} RSO-SR$

$2\ RSO-SR \rightarrow RS-SR + RSO_2-SR$

creep and stress behavior can change.

O_3 can also degrade within a few months or even weeks.

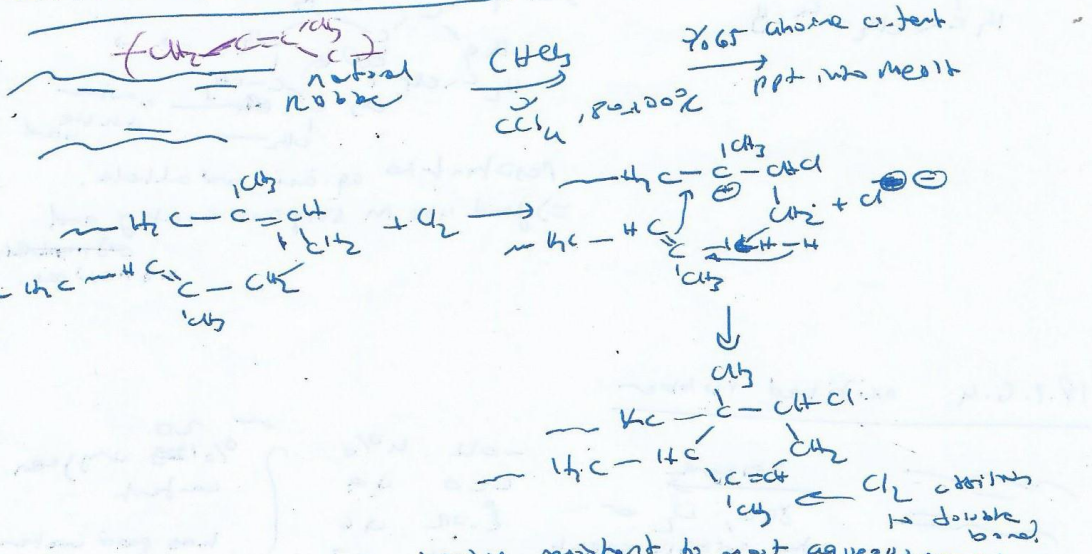


By the time (aging) we loose the properties.

18.2.6 Derivatives

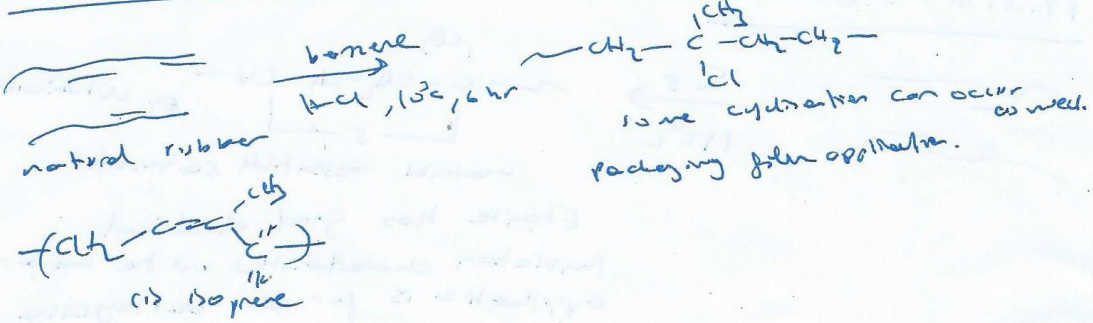
other commercially important rubber is also available in the market.

18.2.6.1. Chlorinated rubber



highly resistant to most aqueous reagent, including mineral acids and alkalis. The main use of the materials is in corrosion resistant coatings.

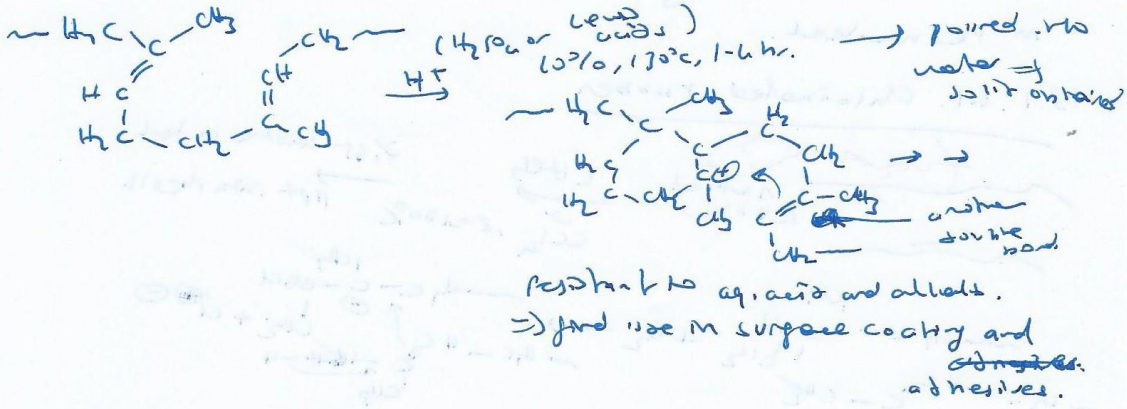
18.2.6.2 Rubber hydrochloride



some cyclisation can occur as well.

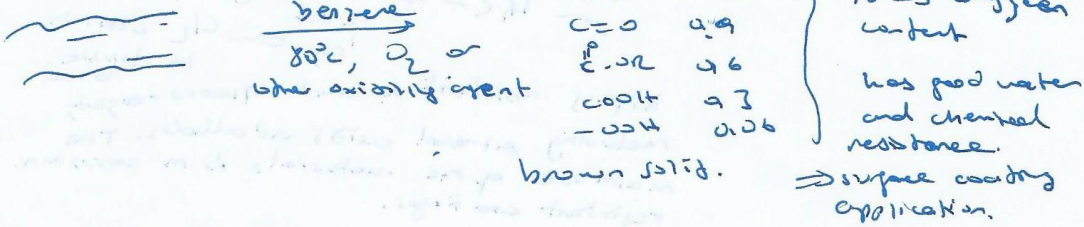
packaging film application.

18.2.6.3. Cyclized rubber



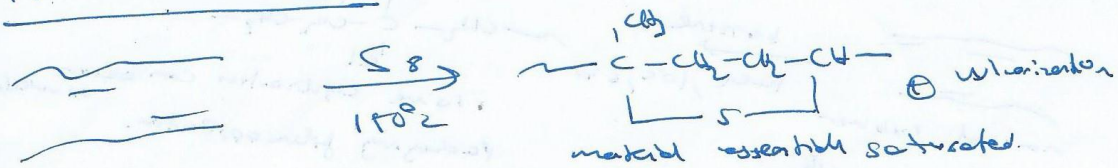
resistant to aq. acid and alkali.
⇒ find use in surface coating and adhesives.

18.2.6.4 oxidized rubber



has good water and chemical resistance.
⇒ surface coating application.

18.2.6.5. Ebonite

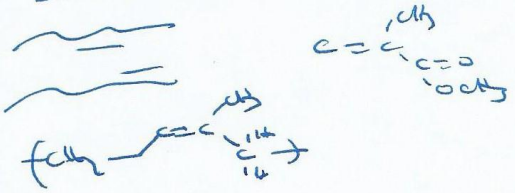


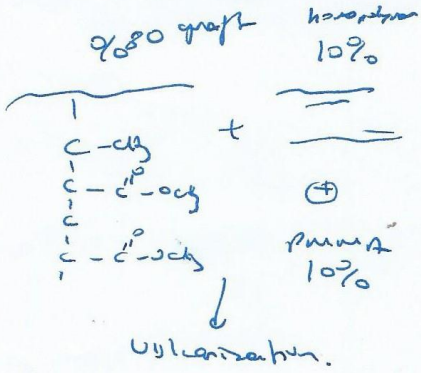
material essentially saturated.

Ebonite has good electrical insulation characteristics and the major application is for car battery cases.

(6)

18.2.6.6. Graft copolymer





Vulcanisation.

Excellent physical properties at high hardness levels and is used to produce hard, rigid mouldings of high impact strength, such as electrical components.

18.2.7. Gutta percha and balata

Gutta percha
latex from Malaysia and Indonesia trees →

10% resinous substance
↓
extract with petroleum ether

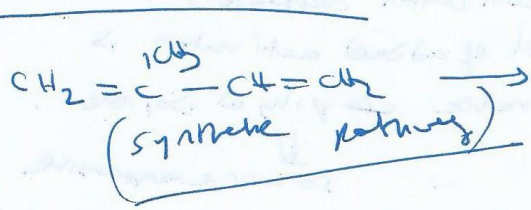
trans 1,4 polyisoprene
30,000 MWT.
non-elastic and crystalline material.
applied as thermoplastic material not as vulcanisation process.

more susceptible to penetration of water is low

Gutta percha has a lower water absorption than natural rubber and is a good dielectric.
They are used in underwater cable insulation and golf ball covers.

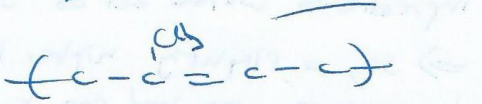
Balata is obtained from trees mainly in central America.
high trans 1,4- polyisoprene + resin, but this not important any more

18.3 Polyisoprenes (4)



(synthetic pathway)

↙ refer Table 1.2 page 2



trans or cis 1,4 polyisoprene depends on using different catalyst.

Commercial importance are those with a high cis 1,4 content (although a small amount of high trans 1,4-polyisoprene is produced as a replacement for gutta percha.)

isoprene → Ziegler Natta catalyst, 50°C, n-pentane

~80-90 conversion is restricted since chain scission appears to occur at higher conversions, resulting in material of low molecular weight.

↓ add MeOH

two layer occur. / Pentane MeOH, H2O catalyst removed.

↓

add H2O to org. phase evaporate solvent the polymer is collected, washed and dried.

properties: The properties of synthetic cis 1,4 polyisoprene are very similar to those of natural rubber.

The raw synthetic rubber is softer than raw natural rubber. (due to the a reduced tendency for stress-induced crystallization) and is therefore more difficult to mill, the band tends to fall apart and compounding ingredients tend to remain in aggregates. (synthetic rubber is also more flows, so it is advantageous in injection molding.

Natural rubber contains small amount of non rubber ingredients which act as vulcanization activators.

⇒ So, a slightly higher level of added activator is therefore required for synthetic cis-poly cis isoprene.

↓
so more expensive

18.4. Polybutadienes

is a gas, b.p. -4°C.

$CH_2=CH-CH=CH_2$ — 1926 in Germany polymer is obtained

or — 1927

$CH_2=C-C=CH_2$ (with CH_3 CH_3 on the two middle carbons) — 1911 Bayer produced high amount

called "metyl rubber".

$CH_2=CH-CH=CH_2$ —(coordination catalyst and alkyllithium catalyst)→ $-(CH_2-C=C-CH_2)-$; some amount $-C-C-$ (with $C=C$ side group)

thermal cracking naphta —(distillation)→ $CH_2=CH-CH=CH_2$

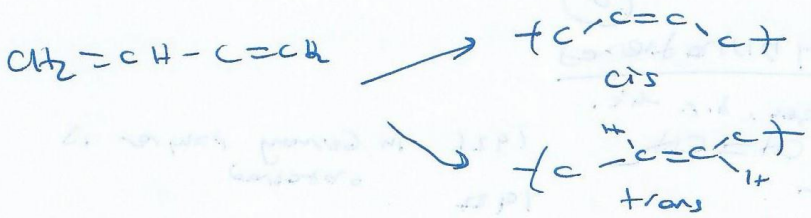
or

$CH_2-CH_2-CH=CH_2$ —(catalytic dehydrogeation)→ $H_2C=CH-CH=CH_2+H_2$

cracking petroleum fraction

table 18.3. Effect of initiator on microstructure of polybutadiene

Initiator	structural units % cis 1,4	trans 1,4	1,2-
Free radical	19	60	21
Na	10	25	65
Li	35	52	13
LinBu	33	55	12
$TiI_4-AltBu_3$	95	2	3
$CoCl_2-AlEt_2Cl$-pyridine	98	1	1
UCl_3-AlEt_3	0	99	1



High cis 1,4 polybutadien crystalizes on streatching. whereas 1,4-polybutadiens with between 25-80% cis content show no tendency to crystalize.

thus high cis 1,4-polybutadiene has higher tensile strength but poorer low temperature properties.

Butadiene rubber → processed and vulcanized as however compound operation is more difficult, suitable instrument should be used.

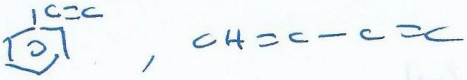
polybutadiene tyres have relatively poor road adhesion in wet conditions.

polybutadiene vulcanizates have lower tensile strength and tear resistance. (yırtılmaya dayanıksız)

Butadiene rubbers are generally used in blends with natural or styrene-butadiene rubbers; such blend usually contain less than 50% polybutadiene.

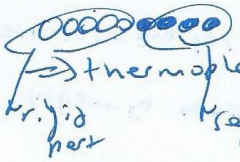
(9)

Styrene - butadiene copolymers



1942 studied to produce GRS 400,000 tons/year.

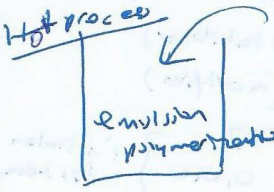
1965 block type copolymer produced – rubber like properties



may be processed at elevated temperature

preparation → Cold process
→ hot process

Hot process



Butadiene 75 parts by weight
Styrene 25
water 180
Rosin acid soap 5.0 (emulsifier)
n-dodecyl mercaptan 0.5 (modifier)
potassium persulfate 0.30 (initiator)

↓ 50°C, 12 hr.

Conversion 72%. Add hydroquinone to prevent crosslinking.

remove unreacted monomers and add antioxidant to protect the rubber during drying and subsequent storage (N-phenyl-2-naphtylamine)

↓

Coagulate by addn weak sulphuric acid soln.

↓

wash with hot water and finally dried for about 2 hr at 80°C.

$S_2O_8^{=}$ + C_2H_2SH → $C_{12}H_{25}SH^{\oplus}$ + $HSO_4^{\ominus}$ + $SO_4^{\ominus}$

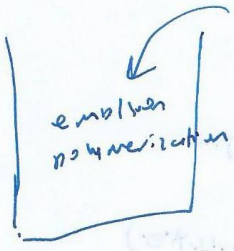
$+C-C=C-C=C-CH_2+_n$

Mwt ≈ 100,000 g/mol

cis 1,4- ; trans 1,4- and 1,2 butadiene units

18 : 65 : 17

cold process : a large proportion of styrene-butadiene made.



Butadiene	72 parts by weight
Styrene	28
water	180
Fatty acid soap	4.5 (emulsifier)
Auxiliary surfactant	0.3 (stabilizer)
Potassium chloride	0.3 (stabilizer)
t-dodecyl mercaptan	0.2 (modifier)
p-menthane hydroperoxide	0.063
Ferrous sulphate ($FeSO_4.7H_2O$)	0.010
Ethylene diamine tetraacetic acid Sodium salt	0.050
Sodium formaldehyde sulphoxylate	0.050

} initiator system

↓ 5°C, 12hr

60% conversion. Then stop by addition of N,N-dimethyldithiocarbamate

↓

then usual work up as hot process

$R COOH + Fe^{++} \rightarrow RO^{\bullet} + Fe^{3\oplus} + OH^{\ominus}$

cold process → less branching with respect to hot process
→ higher trans/cis content
→ a narrower molecular weight distribution.
→ give tyres with improved abrasion and cut-growth resistance
→ on the other hand, "hot" rubbers are somewhat easier to process.

properties
styrene-butadiene rubber → vulcanization → S, peroxide → chains irregular → little tendency to crystallize on stretching (in contrast to natural rubber)

so black color
↓
as filler"

→ reinforcement with carbon black leads to vulcanizates which resemble those of natural rubber.

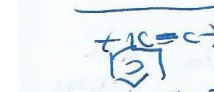
thus → natural rubber and styrene butadiene rubber are interchangeable in most application.

The styrene-butadiene vulcanizates show a high heat build-up on flexing (resistance) which makes them unsatisfactory for the carcasses of large tyres.

chemical oxidation (radical, O_2) → greater stability. (low C=C content) with respect to the natural rubber.

most application in car tyres
paper making to improve strength.
carpet manufacturing as a binder.
the preparation of foam sponge rubber.

high-styrene resin



85% styrene in the backbone → "high-styrene" resin.

↳ vulcanizates to give hard products

⇓

used in the reinforcement of natural and styrene-butadiene rubber

⇓

A typical use of these composition is in the production of shoe soles with good abrasion and (textbook) flex resistance.
"esneh"

Block copolymers

S-S-S-B-B-B-B-S-S-S-S

(50 styrene unit) (100 butadiene unit)

~ 30% styrene content and mwt ≈ 85,000 g/mol

anionic type polymerization

n-butyllithium
styrene
benzene

→ then add $CH_2=CH-CH=CH_2$ → then add styrene → put by adding ethanol

Two different blocks aggregate into separate domains leading to a dispersion of polystyrene domain in a continuous matrix of polybutadiene.

polystyrene domains are styled and immobilize the ends of the polybutadiene segments ⇒ serving both as crosslink and filler particles.

⇒ So the system has the strength of a filler-reinforced vulcanizates amorphous elastomer.

At temperatures above T_g of polystyrene (≈100°C), the polystyrene domains are readily disrupted and the material may be melt processed.

⇒ max. service temperature fabricated from the copolymer is 60°C.

⇒ Application is toys, sports-goods, elastic bands, kauçuklar, çocuk oyun alanları etc.

18.6. Acrylonitrile-butadiene copolymers

$CH_2=CH-C\equiv N$ + $CH_2=CH-CH=CH_2$ → polymer ⇓ oil resistant rubber.

1979 production in US.

Synthesis → cold / not } the same ingredients

emulsion polymerization

poly acrylonitrile-butadiene copolymer %25, %70 - %40 by weight of acrylonitrile commonly produced.

repeat unit butadiene composition (for %28)

⇒ cis 1,4 (12.5 %)
trans 1,4 (77,5 %)
1,2 unit (10%)

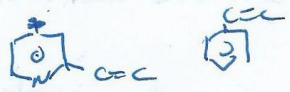
poly acrylonitrile-butadiene → S / peroxide ⇒ vulcanization.

vulcanizates and reinforcement with carbon black leads to tensile strength approaching that obtained with natural rubber

⇒ resistance to wear and non polar solvents such as petrol and oils.

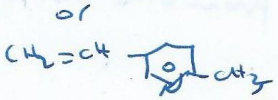
⇒ oil tank sealing gaskets used.

18-7 Vinyl pyridine rubbers



$CH_2=C-CH=CH_2$ 1940 USA

or



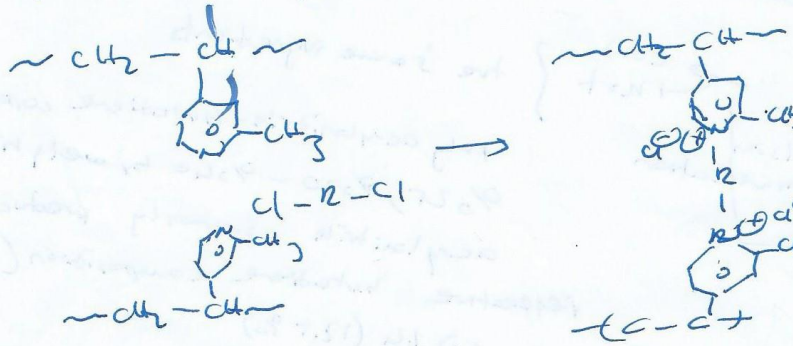
20 : 80 by mole → commercially available

→ vulcanizates ⇒ similar properties as styrene–butadiene copolymer

⇓

The vinylpyridine rubbers show improved low temperature flexibility, abrasion resistance and oil resistance.

Improved oil resistance may be obtained by including active organic halides (e.g. p-xylene hexachloride, benzotrichloride and tetrachloro quinone) in the formulation.

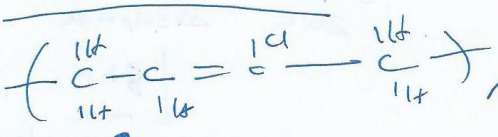


⇒ Become polar and acquire good swell resistance toward petrol, oil and many other solvents.

⇒ vinylpyridine rubbers in latex form for the treatment of textile fibres to improve rubber to textile adhesion in tyres.

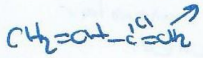
→ it - bonds? textile cord

Polychloroprenes



Du Pont 1930.

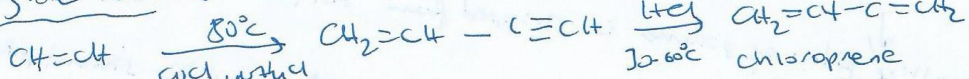
Commercial production in 1932.



many types of polymer and copolymer ⇒ Neoprene

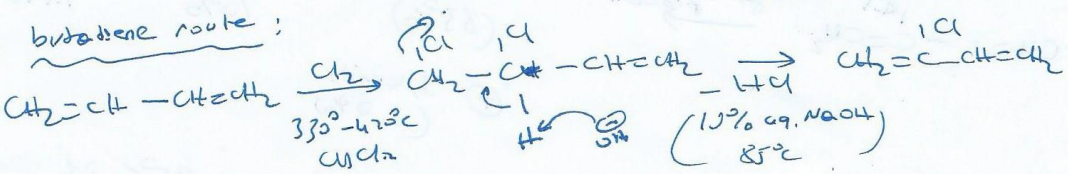
Preparation of monomer

acetylene route:

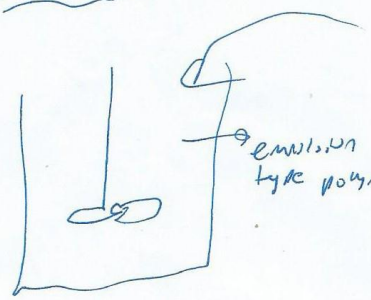


chloroprene
b.p. 59°C,
distilled (purified) in the presence of polymerization inhibitor.

butadiene route:

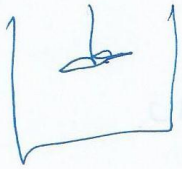


preparation



emulsion type polymerization

Chloroprene	100	parts by weight
water	150	
Rosin	4	} stabilizer
NaOH	0.8	
Methylene bis (naphtalene sulphonic acid) sodium salt	0.3	emulsifier
Sulphur	0.6	modifier
Potassium persulphate	0.2–1.0	initiator



$\xrightarrow{40^\circ C}$ 90% conversion $\xrightarrow{\text{cooled to } 20^\circ C}$ add tetraethylthiuram disulphide $(C_2H_5)_2N-\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-N(C_2H_5)_2$

↓ 8 hr mix

until the desired molecular weight is reached.

← acidify by acetic acid ← cool $-5^\circ C$

Coagulation

↓ pour (increase)

rotating drum

↓

resulting film of polymer is stripped from roll

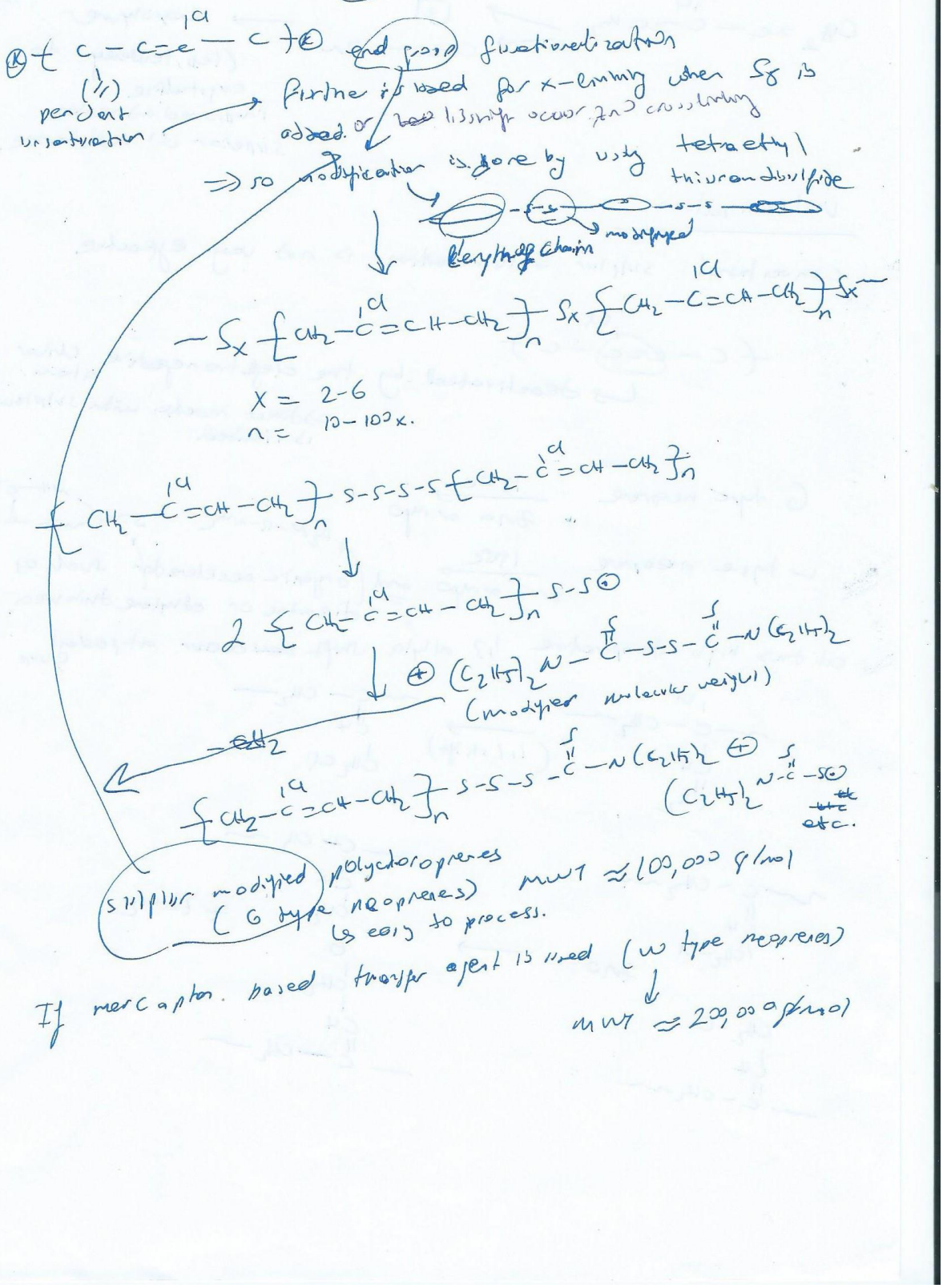
↓

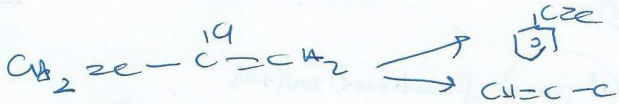
washed → dried in air at $120^\circ C$ → cut into small pieces.

$CH_2=\underset{Cl}{C}-CH=CH_2$ $\xrightarrow{\text{free radical process}}$ trans 1,4 units (85%) ⊕ cis 1,4 units 10% ⊕ 1,2 1.5%

⊕ 3,4 units (1.0%)

trans unit can be increased to 95% if polymerization temperature $-40^\circ C$.


end point fluorination
pendant unsaturation
Further is used for x-linking when Sg is added or less sulfur occur and cross linking
⇒ so modification is done by using tetraethyl thiuram disulfide
Elastomer chain
modified
X = 2-6
n = 10-100 x.
(modified molecular weight)
sulphur modified polychloroprenes
(G type neoprenes) MWT ≈ 100,000 g/mol
is easy to process.
If mercapton based transfer agent is used (W type neoprenes)
MWT ≈ 200,000 g/mol

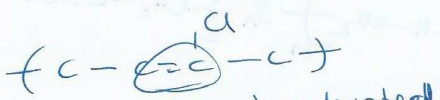


→ copolymer

(less tendency to crystallize
improved adhesion
superior oil resistance.

Vulcanization

conventional sulphur vulcanization is not very effective

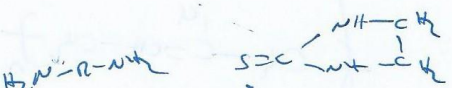


↳ deactivated by the electronegative chlorine atom.

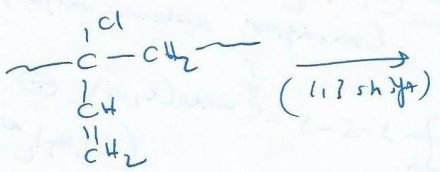
→ direct reaction with sulphur is limited.

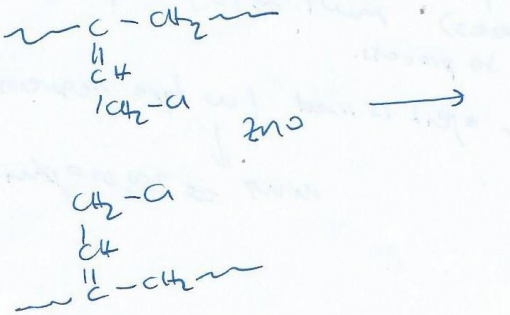
G type neoprene $\xrightarrow[\text{ZnO and MgO}]{150^\circ C}$

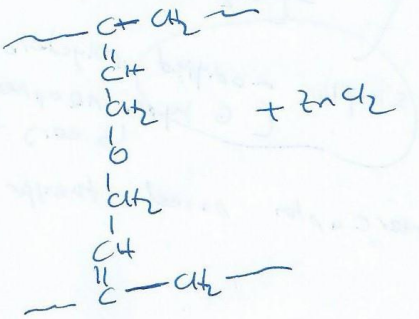
W type neoprene $\xrightarrow[\text{ZnO and MgO}]{150^\circ C}$ and ($H_2N-R-NH_2$ organic accelerator such as diamine or ethylene thiourea



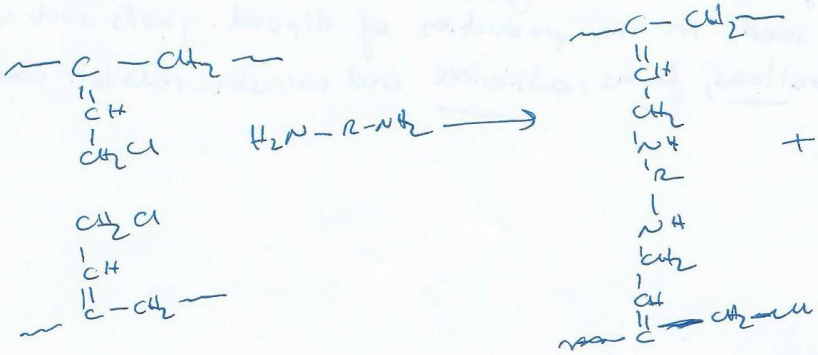
at this high temperature 1,3 allylic shift can occur at pendant group



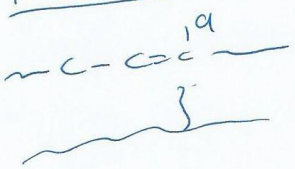




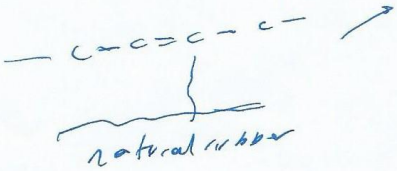
when diamines are included in the vulcanization system, a similar cross linking reaction can occur.



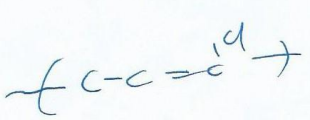
Properties



→ physical strength and elasticity similar. → however better heat resistance at about 170°C in air. (physical properties reasonable well.)



natural rubber



highly regular structure (high trans content) readily crystallizes and become stiff when cooled below −10°C. (think butter and oil)

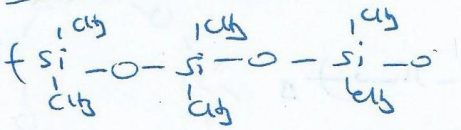
polychloroprene vulcanizates → have a high order of oil and solvent resistance (less resistance than nitrile rubber)

→  good resistance to most chemicals, oxygen and ozone

→ high chlorine content result in products which are generally self-extinguishing.

Polychloroprene rubbers find use in such applications as cable-sheaths (kelly), hose and weather strips (Jeerit). Latices are used in the production of dipped goods such as gloves (pencere bandi) and balloons, foams, adhesives and corrosion-resistant coatings.

Polysiloxanes



Silicon makes up 27% of the earth's crust by mass and it is second in abundance in the world (after oxygen).

Silicon has semi-metallic properties. ⇒ used in semiconductor industry

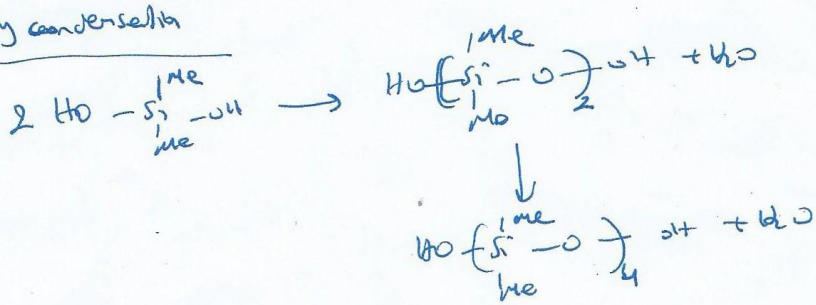
Si–O–Si is more stable than {Si–Si}
↳ this bond slightly weaker than the C–C bond as we

⇓

they have also low lying d orbitals, both promote nucleophilic attack. (so, reactivity is higher than carbon)

Siloxane synthesis → step-growth polymerization
→ ring-opening copolymerization

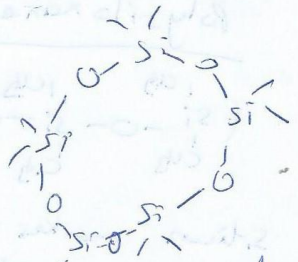
Polycondensation



Homo condensation

* ring-opening pathway

(AB) catalyst → A (Si–Si–O) B



Decamethylcyclopentasiloxane

—Flexible
— low surface energy
— low Tg
— permeability to gases (much higher than any other polymers)

The higher flexibility, the lower Tg.

* medical applications: prostheses, artificial organs, catheters, contact lenses, drug delivery

* non medical applications: membranes, electrical insulators, water repellent mold release agent, adhesive.