UNIVERSITY OF ZAGREB

FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

POLYMER SCIENCE AND TECHNOLOGY

Lecturer: Ljerka Kratofil Krehula

krehula@fkit.hr

Production of rubber

Vulcanization

Elastomers

Materials that withstand significant deformation under the action of force without fracturing; the material fully returns to its original shape once the force is removed.

Their fundamental property is elasticity, which implies complete recovery of the material after deformation.

Deformation

When a body is subjected to external stress or pressure, a change in shape or volume occurs. Mechanical testing of rubber involves applying force to a sample and measuring the resulting deformation, or applying a specific deformation and measuring the required force. Results are expressed as stress and strain, making them independent of the sample's geometric shape.

Stress – force per unit of cross-sectional area (unit: N/m^2 or Pa)

Strain – deformation per unit of length (dimensionless)

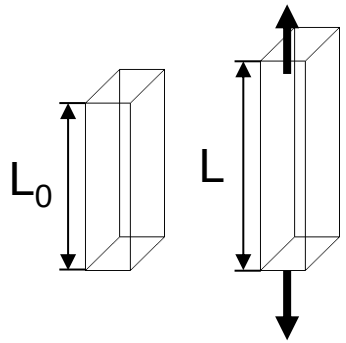
The ratio of stress to strain – modulus.

Uniaxial stretching

- A rubber band with an initial length L_0 is stretched uniaxially to a length L. **ΔL = L – Lo, λ = L/Lo**

- Elongation **ε**

$$\varepsilon = \frac{\Delta L}{L_o} = \frac{L - L_o}{L_o} = \lambda - 1$$



Uniaxial stress – stress where the tensile force required to stretch a material of length L_0 and cross-sectional area A_0 to a length L is measured, and which is defined by the equation:

$$\sigma = \frac{f}{A_o}$$

- f is the tensile force,
- A_0 is the cross-sectional area of the undeformed specimen

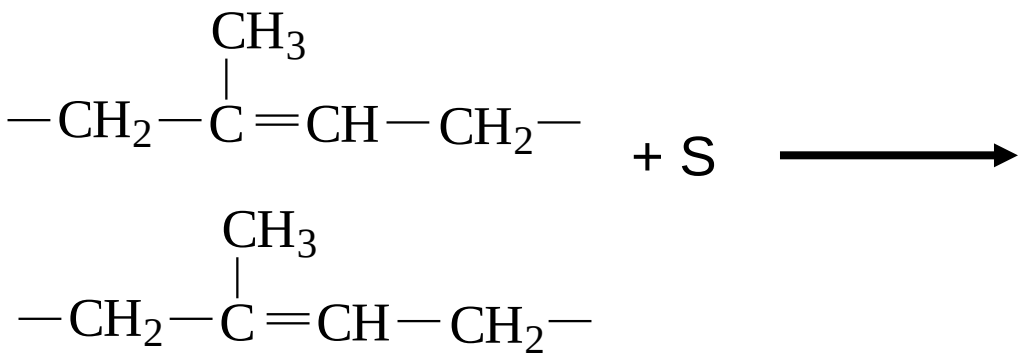
Chemistry and technology of vulcanization

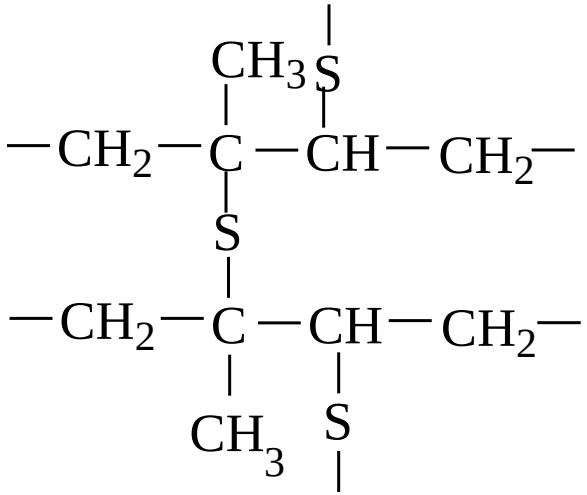
Charles Goodyear was first who vulcanized rubber just unexpectedly, in 1839 he heated natural caoutchouc cis-1,4-polyisoprene with small quantity of sulphur.

Vulcanization – a process by which uncrosslinked material (caoutchouc) becomes crosslinked (rubber).

Crosslinked material (rubber) can not be dissolved or melted.

polyisoprene caoutchouc





crosslinked polyisoprene (polyisoprene rubber)

RUBBER PRODUCTION

Caoutchouc must be subjected to many processes in order to obtain a product of relatively high elasticity - rubber.

Different additives are added to the rubber and the mixture is subjected to heat treatment: vulcanization.

The following stages are present in the rubber production process:

1. mastication

2. preparation of the mixture of caoutchouc and additives

3. shaping of products and vulcanization



1. Mastication

Mastication is a process that increases the plasticity of raw rubber, thereby facilitating greater homogeneity when incorporating various additives and fillers.

Natural and synthetic rubber are delivered to factories in large bales or blocks; before further processing, these must be reduced in size using specialized machines equipped with cutting blades.

Mastication involves intensive mechanical processing accompanied by heating. During this process, the rubber (a high-molecular-weight polymer) undergoes degradation: it is a favourable degradation.

The goal of mastication is to bring the material to the consistency required to accept the additive mixture and ensure good blending. Mastication results in a reduction of polymer chain size.

Long-chain molecules are broken, and the molecular mass decreases. Catalysts (chemical plasticizing agents) are required to facilitate this process; they accelerate mastication in the presence of oxygen (typically sulfur compounds, most commonly thiophenols).

Two basic types of mixers are in use:

1. A Banbury-type mixer with rotors that rotate at different speeds, creating a kneading action similar to that used in handling bread dough. A shearing action also occurs between the rotors and the mixer walls..



https://www.youtube.com/watch?app=desktop&v=1_W_v2R_P1s

2. Shaw Intermix-type mixer uses rotors that rotate at the same speed; the mixing action resembles that of a mill.







https://www.isaacsmachinery.com/machine/shaw-intermix-k4-mk5-mixer-body-and-hopper/

2. Preparation of the mixture of caoutchouc and additives

The quality of the rubber product depends on:

- the composition
- the homogeneity of the mixture before the vulcanization.

The primary ingredient of any compound destined for processing into rubber is **raw rubber** (unvulcanized polymer, caoutchouc).
However, the mixture for vulcanization must also contain **a vulcanizing agent** (most commonly sulfur) as well as a **vulcanization accelerator** and an **accelerator activator**.
In addition to the main ingredients, the compound contains various **additives** designed to facilitate processing, reduce the cost of the finished product, and achieve the desired properties of the final product.
The relative composition of the compound is not expressed in percentages; instead, the amount of raw rubber, as the main ingredientis designated as 100, while the quantities of other components are expressed relative to that amount of rubber using the unit "phr" (parts per hundred).

For reaction of vulcanization the components are:

1. uncrosslinked material (caoutchouc)
2. agents for vulcanization (sulphur or other)
3. accelerators (merkaptanes)
4. ZnO – activator of accelerator
5. stearic acid
6. different types of additives

The mixture for vulcanization can be prepared using the same mixers used for mastication.

Sometimes these are not separate operations; instead, the rubber is masticated while the necessary components are simultaneously added and mixed in.

The rubber is loaded into the mixer first and mixed briefly, followed by the addition of fillers, plasticizers, and additives designed to enhance the rubber's properties.

As the temperature of the compound rises rapidly, the rotors are intensively cooled with water.

Due to the risk of premature vulcanization, the vulcanizing agent, accelerator, and activator are rarely added simultaneously.

3. shaping of products and vulcanization

The thoroughly mixed rubber compound must be shaped or formed into objects or into the material from which final rubber products will be created after vulcanization:

- tires
- electrical conductor insulation
- rubber surfaces (e.g. mats, floor coverings)
- rubber pipes and hoses
- gaskets/seals
- various rubber products (stoppers, pads/tiles)

Vulcanization takes place in a large plants and factories for production of tires and other products.

1. Vulcanization in autoclaves
2. Continuous vulcanization
3. Vulcanization by pressing

1. Vulcanization in autoclaves

- the type of vulcanization with water vapour, which is carried out in cylindrical autoclaves, which can be vertical or horizontal, it is possible to use hot air vulcanization.

Advantage: uniform heating because there are no parts of cold surfaces.

Disadvantage: rubber is easily oxidized in the air, therefore, vulcanization is often carried out in autoclaves with steam.

Vulcanization in autoclaves





2. Continuous vulcanization

This process is usually connected to the extrusion or calendering (production of pipes, profiles, rubber insulated wires and cables).

a) Vulcanization in a tunnel with hot air – it is rarely performed because of low heat transfer and the possible deformation of extruded profiles and the product.

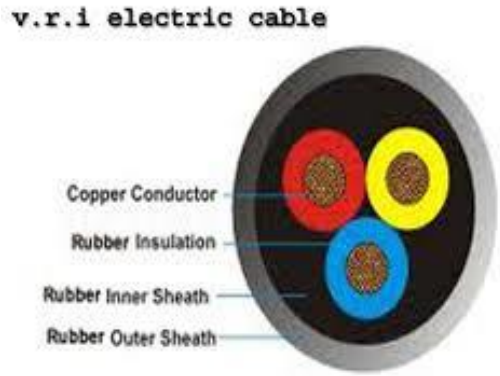
b) Vulcanization in the tunnels of hot steam – continuous vulcanization of cables and wires for insulation

c) Vulcanization in a bath of ethylene glycol - a simple procedure but with disadvantage because of the evaporation of the ethylene glycol from the bath and a product after vulcanization must be washed.

d) Vulcanization in the bath with the molten metal - not a suitable procedure for vulcanizing - the frequent deformation of products and harmful phenomena which metals cause to the surface of the product.

e) Fluid bed vulcanization - procedures in which the products pass through a heated bath stuffed with small glass pearls of diameter of ~ 0.2 mm; from the bottom of the bath the air, nitrogen or steam blows and the beads (pearls) behave as a liquid media.
Advantage: fast vulcanization → heat transfer in a media is higher than in gas and deformations are minimized.





3. Vulcanization by pressing

-molding product is molded by pressing while warming up, the procedure is carried out in strong hydraulic presses

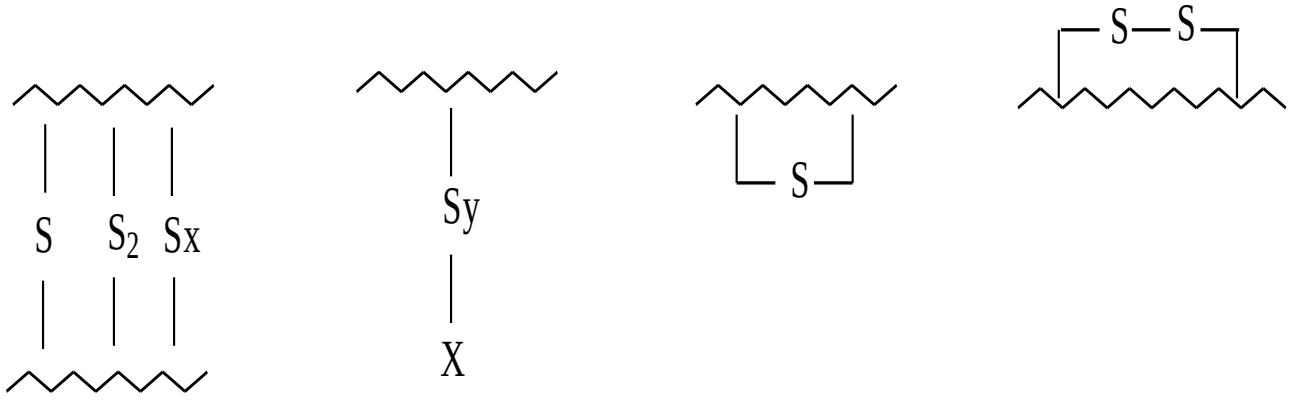
-moulds in presses are heated with steam or by electricity for vulcanizing at higher temperatures



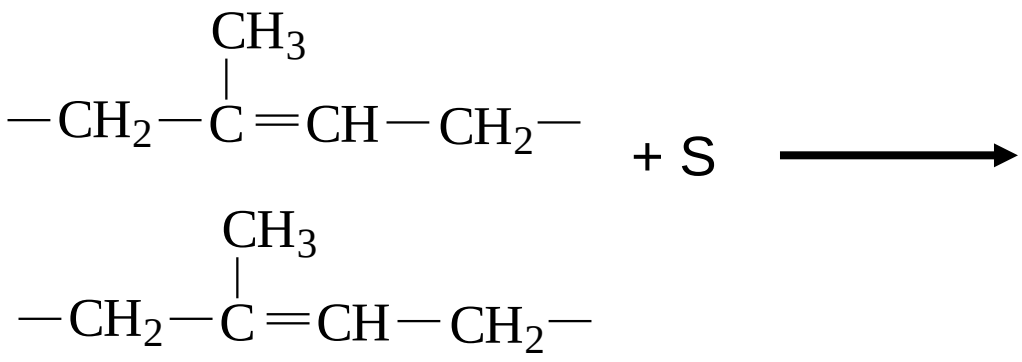
a) sulphur vulcanization

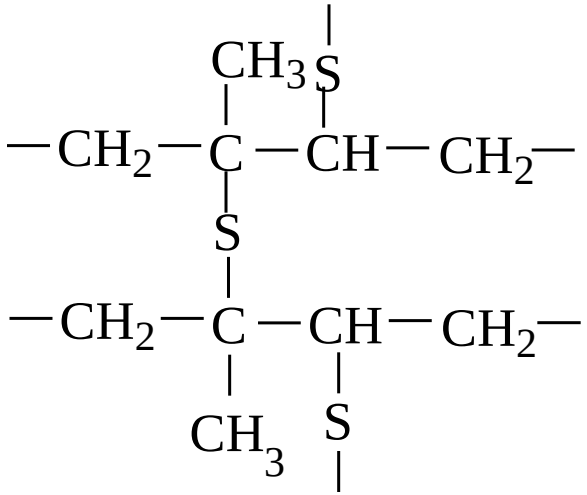
Sulphur is usually present in quantities of
2,5-3,0 phr (phr – parts per hundred)

Sulphur in vulcanization process may be present as:
monosulphide, disulphide, polysulphide
or cyclic monosulphide and cyclic disulphide:



polyisoprene caoutchouc

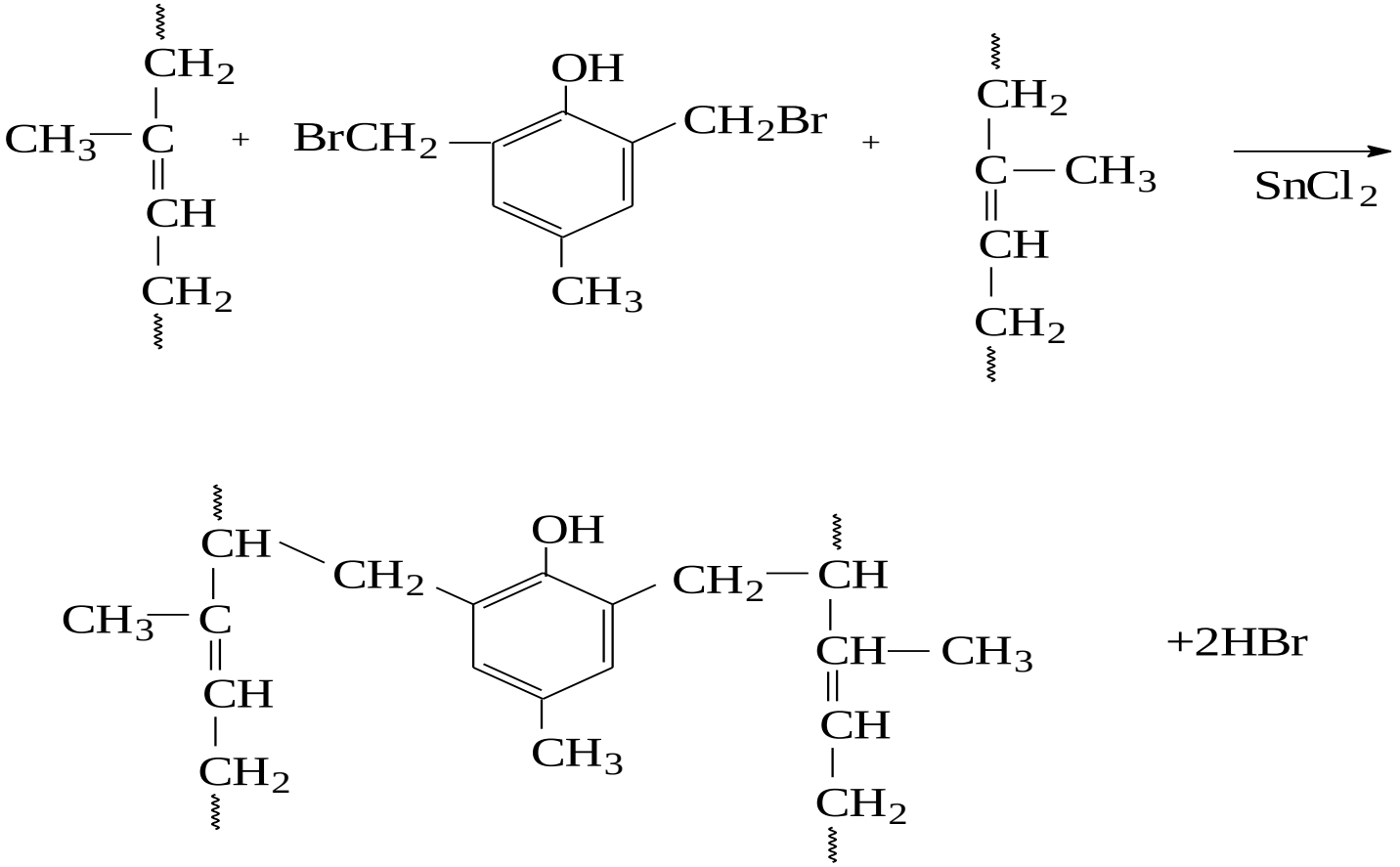




crosslinked polyisoprene (polyisoprene rubber)

b) vulcanization with phenol formaldehyde resins

- For vulcanization of olefinic rubber with accelerator $SnCl_2$, usually halogen resin is used:



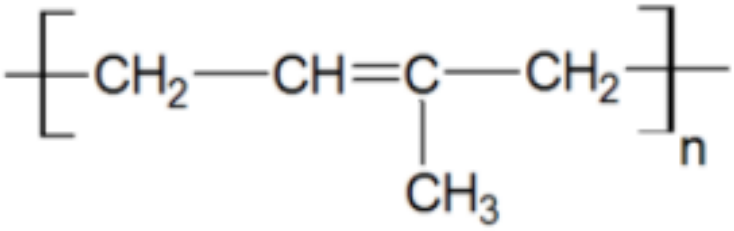
Chemical Name	Abbreviation		Trade Name
	ASTM D1418	ISO/DIN 1629	
M-class (rubbers having a saturated chain of the polymethylene type)			
Polyacrylate Rubber	ACM	ACM	-
Ethylene Acrylate	AEM	-	Vamac®
Chlorosulfonated Polyethylene Rubber	CSM	CSM	-
Ethylene Propylene Diene Rubber	EPDM	EPDM	-
Ethylene Propylene Rubber	EPM	EPDM	-
Fluorocarbon Rubber	FKM	FPM	Viton®
Tetrafluorethylene Propylene Copolymer	FEPM	FEPM	-
Perfluorinated Elastomer	FFKM	-	Kalrez®
O-class (rubbers having oxygen in the polymer chain)			
Epichlorohydrin Rubber	CO	CO	-
Epichlorohydrin Copolymer Rubber	ECO	ECO	-
R-class (unsaturated hydrogen carbon chain)			
Butadiene Rubber	BR	BR	-
Chloroprene Rubber	CR	CR	Neoprene
Isobutene Isoprene Rubber (Butyl Rubber)	IIR	IIR	-
Isoprene Rubber / Natural Rubber	IR	IR	-
Nitrile Butadiene Rubber (BUNA-N)	NBR	NBR	-
Styrene Butadiene Rubber (BUNA-S)	SBR	SBR	-
Hydrogenated Nitrile	HNBR	-	-
Q-class (with Silicone in the main chain)			
Fluorosilicone Rubber	FVMQ	FMQ	-
Methyl Vinyl Silicone Rubber	VMQ	VMQ	-
U-class (with carbon, oxygen and nitrogen in the main chain)			
Polyester Urethane	AU	AU	-
Polyether Urethane	EU	EU	-

https://practicalmaintenance.net/wp-content/uploads/Information-on-Elastomers.pdf

Structure-properties relationship

R rubber

- **IR** – cis-1,4-polyisoprene



- good mechanical properties
- good resistance to abrasion
- use in the temperature field: from -50 to 100 °C
- low resistance to oxidation and to atmospheric conditions due to the presence of double bonds (some of double bonds will react during vulcanization but some of them will not)

There is a need to stabilize this rubber against that influences.

R rubber

- **SBR** – copolymer of butadiene and styrene

  - good mechanical properties

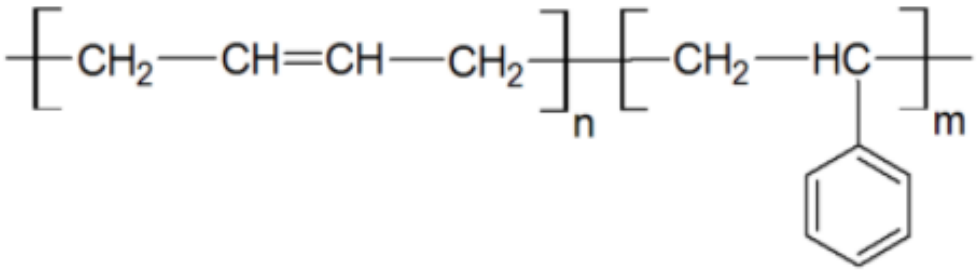
  - good resistance to abrasion

  - use in the temperature field: from -25 to 100 °C

  - low resistance to oxidation and to atmospheric conditions due to the presence of double bonds (some of double bonds will react during vulcanization but some of them will not)

  There is a need to stabilize this rubber against that influences.

.



M rubber

- **FKM** – fluoroelastomers

– one type: copolymer of hexafluoropropylene and vinylidene-fluoride

- **good resistance to thermal and chemical influences as well as to the oxidation, ozonization: due to the saturated structure (without double bond) and due to the presence of fluor**

- it has a high price: it is used only for special applications

- use in the temperature field: from -20 to 250 °C (even to 300 °C)

$CH_2=CF_2$
vinilidene-fluoride

$CF_2=CF-CF_3$
hexafluoropropylene

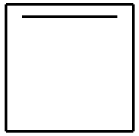
Ring-opening polymerization

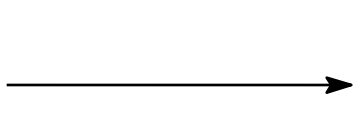
Monomers - cyclic monomers:

cyclobutene, cyclopentene, norbornene,

cyclobutene

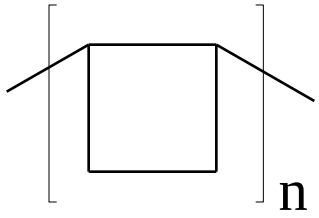
cyclobutene





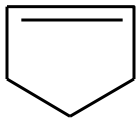
- cis and trans isomers

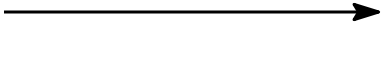
breaking of the double bond

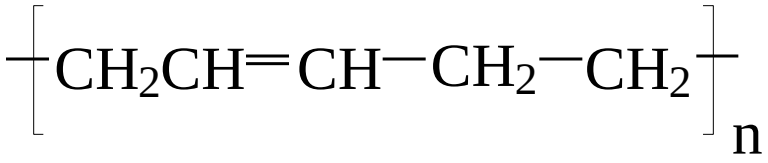


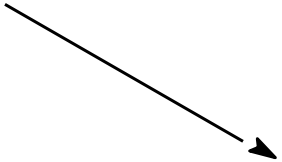
Cyclopentene

Cyclopentene

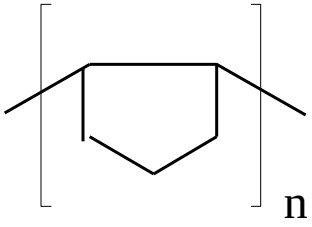








breaking of the double bond



caprolactone: polymerization to polycaprolactone (PCL)

