Polyethylene

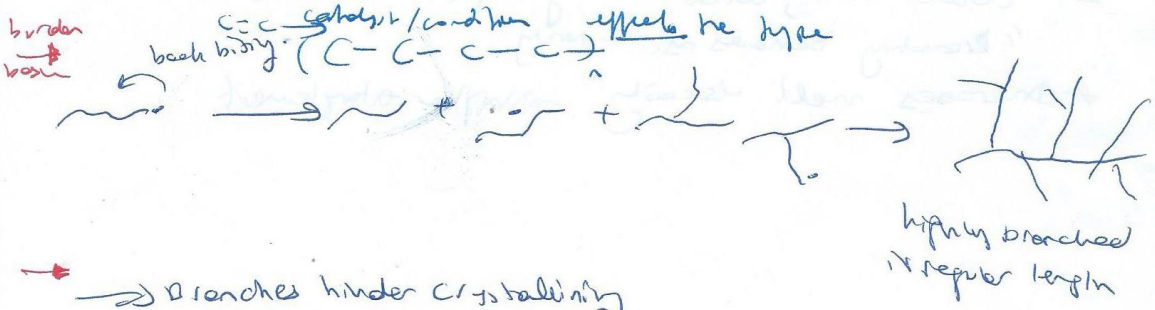
Low density polyethylene (LDPE)

* Formed using traditional free radical polymerization
* It has 40-60% crystallinity
* Its density (ρ) is 0,91 g/cm³
* Melting temperature T_m = 105-115°C
* Glass transition temperature = T_g = -120°C
* soft material, Tensile 1000 psi
* short end more C=C → so, yellowing will be higher (more susceptible)

High density Polyethylene (HDPE)

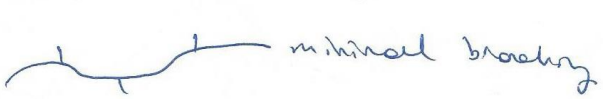
* Formed using a Ziegler Natta catalyst
* Crystallinity is much higher 70-90%
* Its density (ρ) is 0,94 – 0,96 g/cm³.
* T_m > 130°C
* more hard, Tensile 1200 psi

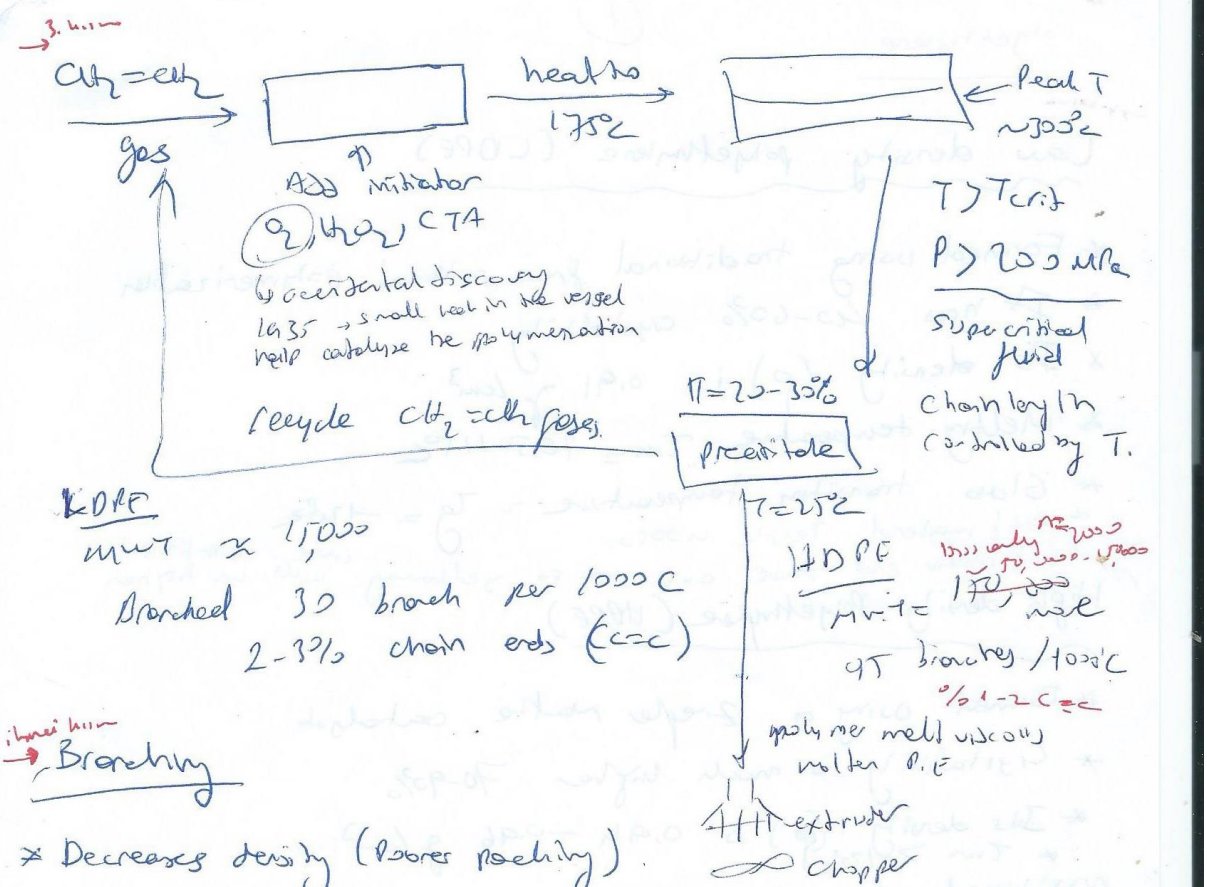
Additionally, the Z-N catalyst can be used to control branching easily to form: Linear Low Density Polyethylene (LLDPE)



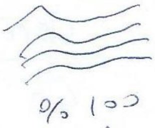
→ Branches hinder crystallinity

Z-N catalyst : reduce transfer

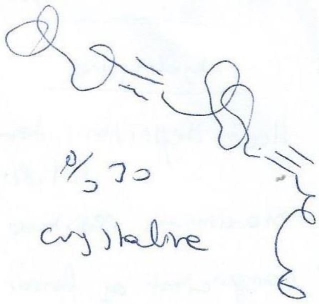



gas
heat to 175°C
Peak T ~300°C
Add initiator
O2, H2O2, CTA
by accidental discovery
1935 → small leak in the vessel
help catalyse the polymerization
T > Tcrit
P > 200 MPa
Supercritical fluid
Chain length controlled by T.
recycle CH2=CH2 gases
π = 20-35%
precipitate
T = 25°C
LDPE
HDPE
Branching
Decreases density (Poorer packing)
Decreases % crystallinity
Decrease in tensile properties
Lower Tm, wider melting range
"Branchy behaves as impurity"
Increases melt viscosity ⇒ higher entanglement
extruder
chopper

%100 amorphous
Soft, low tensile strength
ductile



%100
crystaline
hard,
high tensile
brittle, fragile
kırılgan
narin,



%70
crystaline

High pressure polyethylene had 80% crystalinity
(not good)

Thermoplastic polymer should be saturated

Including unsaturation is terible C=C → undesirable
O_2 → give yellowing, brittle problem

But polyethylene containing a lot of C=C so early PE contain antioxidant.

High pressure Polyethylene Process contain 1-2% C=C

$-(CH_2)-$ UV transparent

Seralarda polyethylene kullanılıyor. Cam geçirir görünüyor ama UV'yi geçirmiyor. UV bitki için gerekli.

General Physical Properties of Selected PE

Polyethylene	LDPE	HDPE	UHMWPE
Heat deflection temperature (1,820 kPa, °C)	40	50	85
maximum resistance to continuous heat	40	80	80
coefficient of linear expansion (cm/cm °C, 10^{-5})	10	12	12
compressive strength (kPa)	—	2×10^{4}	—
Impact strength (Izod, cmN/cm notch)	no break	30	no break
Tensile " (kPa)	5×10^{3}	3×10^{4}	6×10^{4}
Density (g/mL)	0,91	0,96	0,93

There are many types PE in the market. Sometimes it is problem to identify.

HDPE → produced by using Zigler-Natta or philips catalyst. Low molecular weight (chain lengths in hundreds) HDPE is "wax" while typical HDPE is a tough plastic. chain length rarely is longer than 2000 ethylene unit.

bottles, food containers, toys, pipes

LLDPE → It is actually a copolymer of ethylene with about 8-10% of an α-olefin such as 1-butene, 1-pentene, 1-hexene or 1-octene. property is between LDPE and HDPE. Low branches than LDPE. It is used in film application as packaging for cables, toys, pipes and containers.

pipe and cable insulators, bottles, films

VLDPE → density 0,88 - 0,915 g/mL. It is structurally similar to LLDPE except the α-olefins are generally longer (1-butene, 1-hexene 1-octene is used) resulting is a lower density.

LDPE → packaging products, bags, industrial sheeting, and piping and tubing, drum liners, bottles, films (tiner kutusu)

Ultrahigh molecular weight Polyethylene (UHMWPE) is a high density polyethylene with chain lengths over 100,000 ethylene units. Because of the great length of the chains, they "inter-tangle" causing physical cross links, increasing the tensile strength and related properties of these materials.

* resistance to corrosion and environmental stress cracking
* outstanding abrasion resistance and impact toughness
* good resistance to cyclical fatique and radiation failure
* low surface friction

battery seperators, automobile parts, truck liners, wear shoes, can and bottle handling machines, neutron shields

Ultra linear polyethylene (ULPE) - high chain length with a narrower molecular weight spread along with a decreased amount of short chained alkyl branching.

Extremely strong and resistant to punctures and even cutting by scissors

"Spectra" → 70,000 units long ; It is used → bullet-resistant vest
— surgical gloves
(so, cutting itself by sharp equipment prevented)

"Spectra" → 10 times stronger than steel on a weight basis
%35 stronger than Kevlar.

VLDPE (plastomers) is a type of copolymer that have a little crystalinity, but are largely amorphous. They are more elastic than LLDPE but less stiff (Sect). They are used in frozen food and ice bags, food packaging, stretch wrap.

Polypropylene

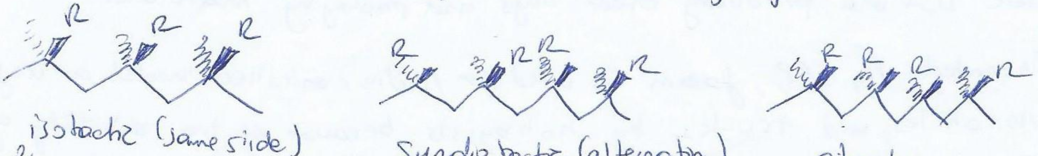
(after PE, world production is second)

$-(CH_2-\overset{CH_3}{\underset{H}{C}})-$

Atactic PP: $T_g \sim -70°C$
fully non crystalline
liquid like, paste

Isotactic PP: $T_m = 170°C$
highly crystalline
amorphous region: $T_g \sim -50°C - -60°C$
insoluble

Syndiotactic PP: very crystalline $T_m \sim 130°C$



isotactic (same side)
%99 isotacticity can be obtained.

syndiotactic (alternating)

atactic
"no sequence, random"

Coordination catalyst = usually metal / metal halide or oxide complex
→ promote stereospecific + controlled addition of monomer

Ziegler and Natta Nobel Prize, 1963
"Germany" "Italy"

$Cl-\overset{Cl}{\underset{|}{Ti}}-Cl$ + $\overset{Cl}{Al}-CH_2-CH_3$ (CH₂-CH₃) (or beta

~ G
group metal$^+$ $RHC=CH_2$ ⟶ $H-\underset{R}{\overset{H}{C}}-\overset{H_2}{C}-G$

escort for insertion of new monomer

1 gram catalyst produce 1 kg PP

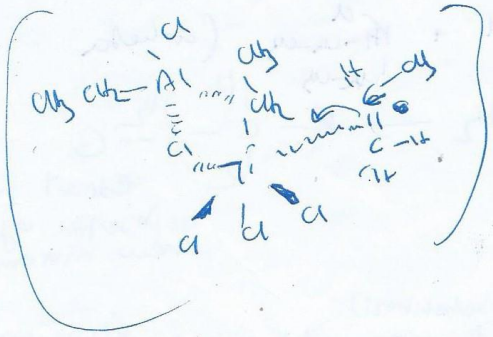
Application: film in disposable diapers and hospital gowns (bebek bezi) (elbise-geceliği) to geotextile liners (astar); plastic applications as disposable food containers and automotive components; and fiber applications such as in carpets, furniture fabrics, and twine (sicim, ip)

aPP → amorphous
iPP rsPP → crystaline } Being crystaline causes the polymer to be stronger, denser, less porous to small molecules like water and oxygen, and to have a higher melting point.

Stretching a film tends to orientate the polymer chains, Biaxially stretched or oriented PP, BOPP is strong and clear, resulting in its wide use and producing clear bags and packaging materials.

Expanded PP, EPP, foam is used for radio controlled model aircraft, automobiles, and trucks by hobbyists because of the ability of the foam to absorb impacts and its low density.

1970's market used to establish 100 million dollar (today ~ 1 billion dollar) catalyst so important many company discussed and fight each other "we have best product and catalyst", first application is used for frizbie than after baby potter and detergent bottle.



mechanism Ziegler-natta