

There will be a Quiz on Monday, February 24.



* From the Hitchhikers Guide to the Galaxy – Douglas Adams

EMAC 276

Lecture 14: The Polyolefin Family

Polyethylene – PE

Polypropylene - PP

Poly(1-butene) – Polybutylene – PB

Andy Olah

February 21, 2025

What is a “Olefin” Type Polymer?

Vinyl polymers are the most common type of polymers derived from “vinyl-type” monomers having the general structure:



Where,

polystyrene – $\text{R} = \text{C}_6\text{H}_5$
polyvinyl chloride – $\text{R} = \text{Cl}$
polyvinyl acetate – $\text{R} = \text{O}_2\text{CCH}_3$
polyacrylonitrile – $\text{R} = \text{CN}$

Not to be confused with poly(vinyl chloride) (PVC) materials which have traditionally been identified as “Vinyls”; i.e., vinyl siding, vinyl records, etc.

Olefin polymers are a subgroup of vinyl monomers produced from alkenes having a C_nH_{2n} monomer structure:

polyethylene – $\text{R} = \text{H} \Rightarrow \text{CH}_2 = \text{CH}_2$; ($n = 2$) $\Rightarrow \text{C}_2\text{H}_4$
polypropylene – $\text{R} = \text{CH}_3 \Rightarrow \text{CH}_2 = \text{CH}-\text{CH}_3$; ($n = 3$) $\Rightarrow \text{C}_3\text{H}_6$
polybutylene – $\text{R} = \text{CH}_2-\text{CH}_3 \Rightarrow \text{CH}_2 = \text{CH}-\text{CH}_2-\text{CH}_3$; ($n=4$) $\Rightarrow \text{C}_4\text{H}_8$

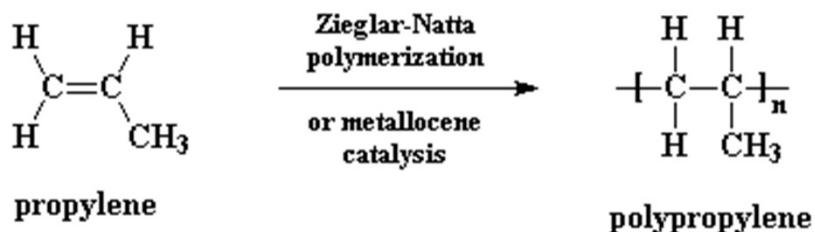
Polypropylene

Phillips Petroleum chemists J. Paul Hogan and Robert Banks first demonstrated the polymerization of propylene in 1951.

Polypropylene was subsequently polymerized by German chemist named Karl Rehn and an Italian chemist named Giulio Natta **to a crystalline isotactic** polymer in 1954. This discovery soon led to a large-scale production of polypropylene starting in 1957 by the Italian firm Montecatini.

Polypropylene is made from polymerization of propylene monomer (an unsaturated organic compound - chemical formula C_3H_6) by:

Ziegler-Natta polymerization or Metallocene catalysis polymerization:

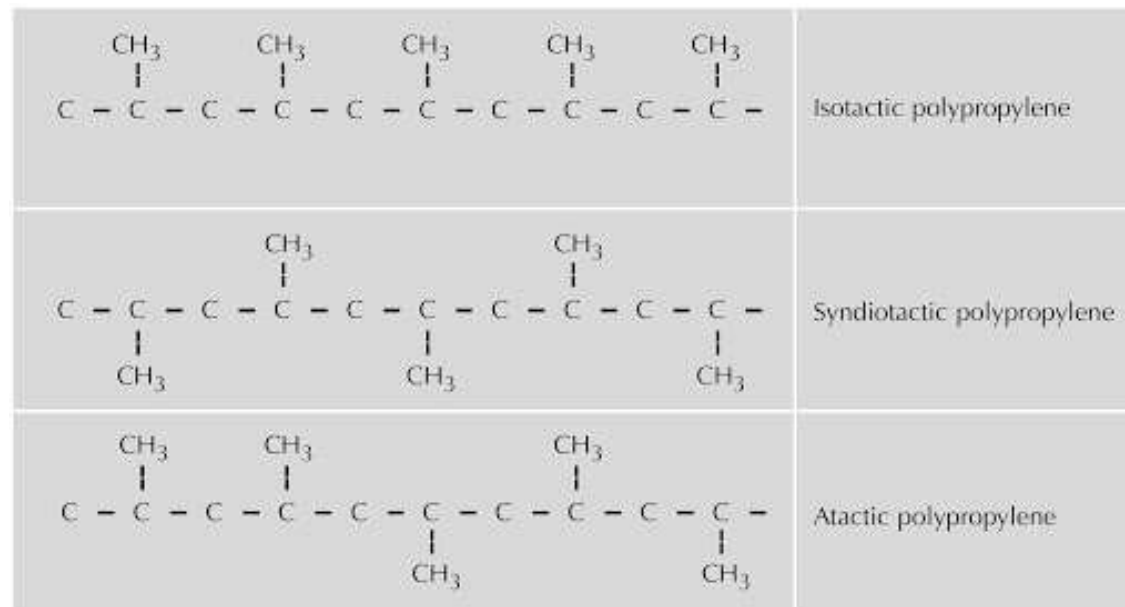


The Four Generations of Polyolefin Catalysis

Catalysts:

- 1st Generation (<1960):** Original Z-N (γ - TiCl_3 + AlCl_3). Al alkyl co-catalyst. 92% isotactic.
- 2nd Generation (1960's):** Modified Z-N. 5x more active than original Z-N catalyst. 96% isotactic.
- 3rd Generation (1970's):** $\text{TiCl}_3/\text{MgCl}_2$. 100x times more active than 1st generation catalyst. 94-96% isotactic.
- 4th Generation (1990's):** Metallocenes (SSC's). 10x more active than 3rd generation catalysts. 94-96% isotactic.

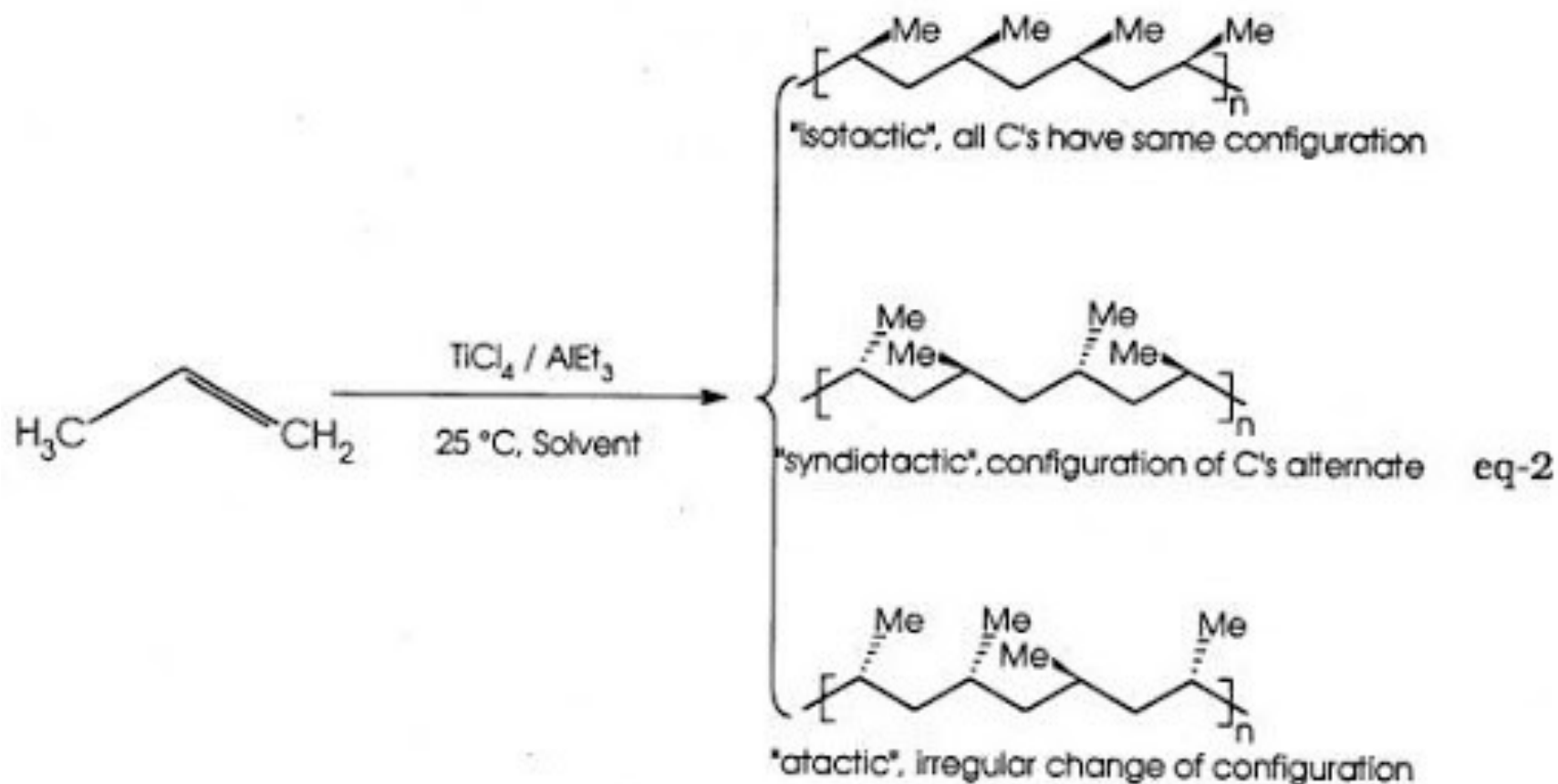
Due to the Asymmetry of the Monomer Three Types of Tacticity for Polypropylene are Possible



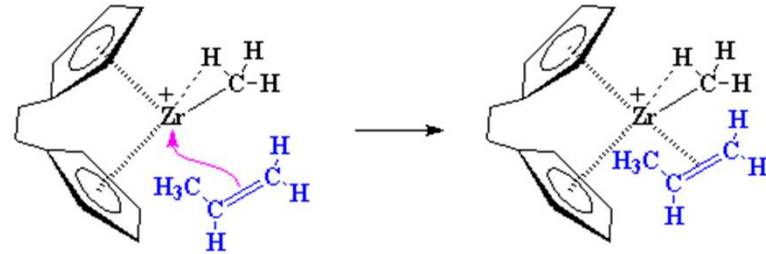
Polypropylene exists in three possible forms:

	<u>Isotactic</u>	<u>Syndiotactic</u>	<u>Atactic</u>
M.P. (°C)	170	135	---
M.W.	~500,000	~300,000	very low
Density (g/cm ³)	0.91	0.88	---
Crystallinity	crystalline	crystalline	amorphous

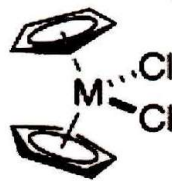
Ziegler – Natta Catalysts can Produce all Three Types of Polypropylene



Metallocene Synthesis can Also Produce All Three Types of Polypropylene Tacticity

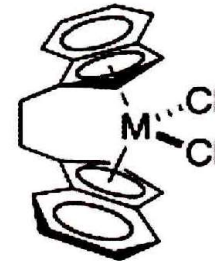


In addition, the use of chiral metallocenes that have bridged cyclopentadienyl rings has made possible highly stereoselective (or stereoregular) polymerization of α -olefins. For example, by using metallocene **1** below for polymerization of propylene, the **atactic** form of polypropylene is obtained, while C2 symmetric metallocene **2** and Cs symmetric metallocene **3** catalyst systems produce the **isotactic** and **syndiotactic** macromolecules, respectively.



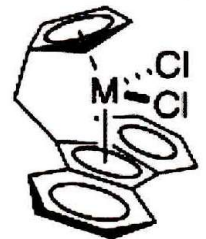
1, M = Zr, Hf

atactic



2, M = Zr, Hf

isotactic

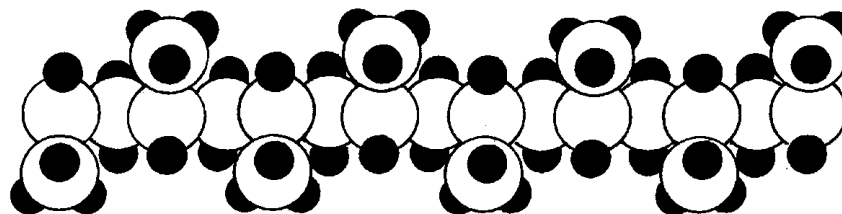


3, M = Zr, Hf

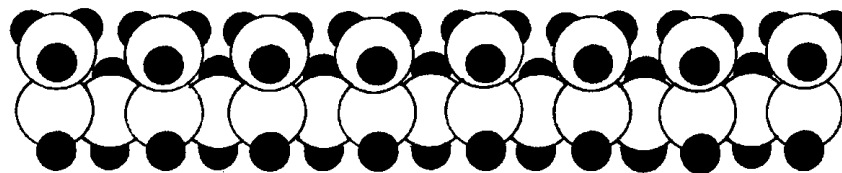
syndiotactic

“Teddy Bear” Chorus Line of Polypropylene Tacticity

Syndiotactic



Isotactic



Atactic

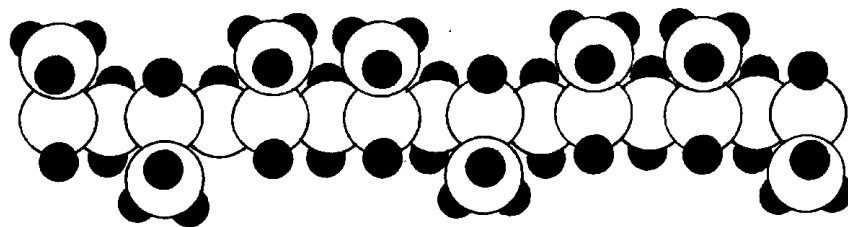
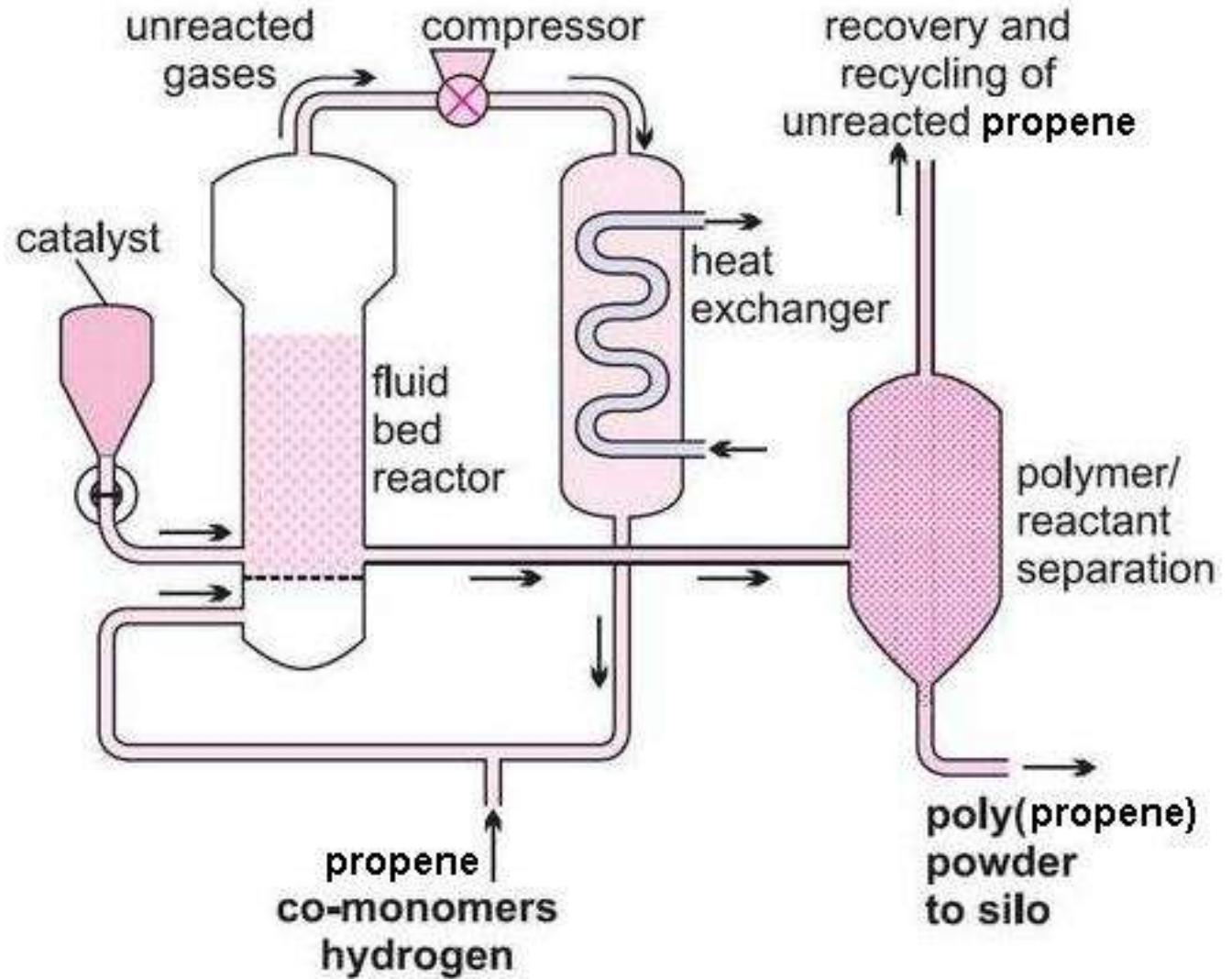
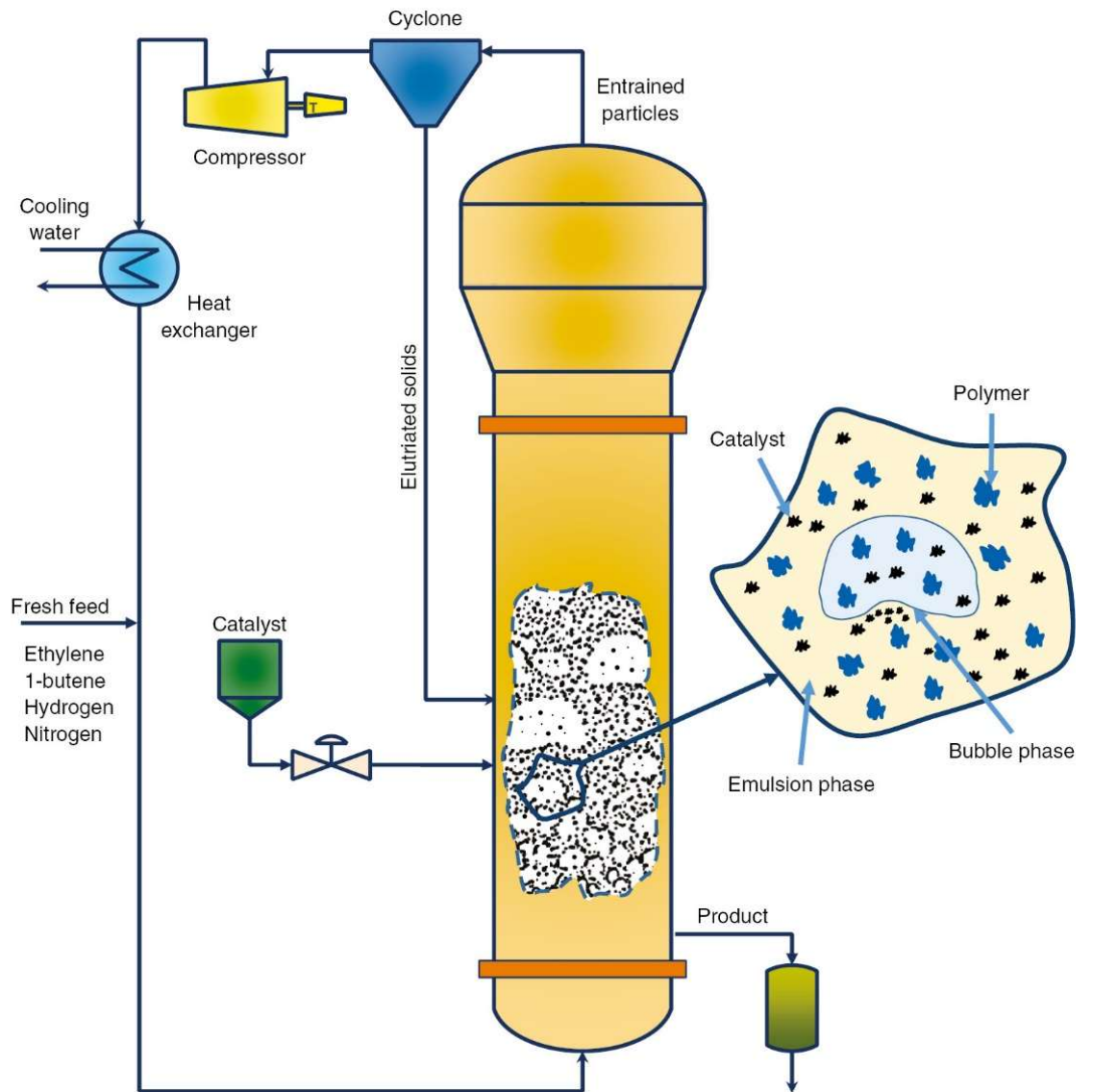
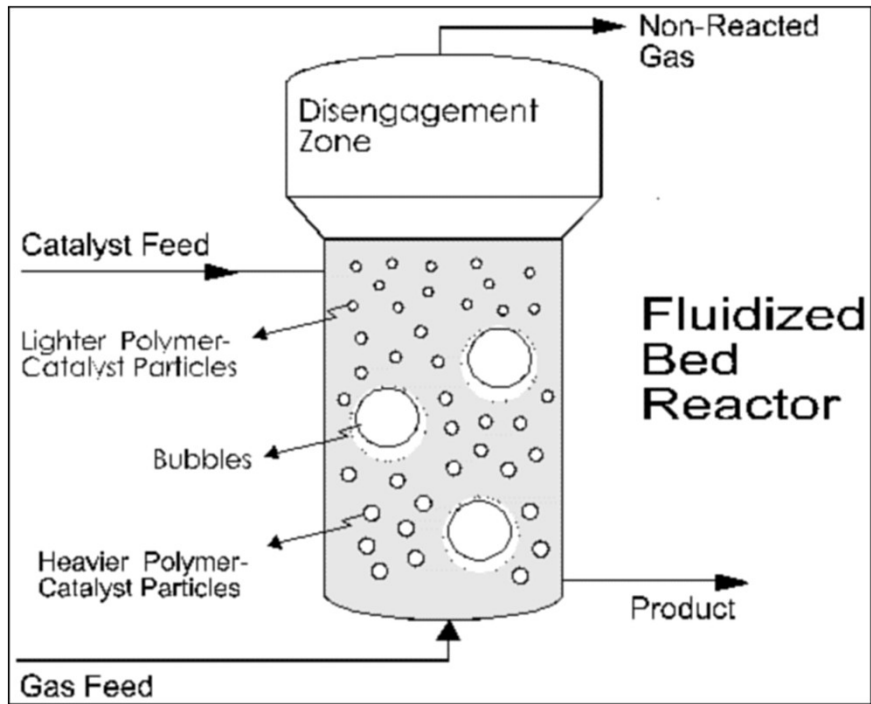


FIGURE 6.5 Space-filling models of syndiotactic (a), isotactic (b), and atactic (c) forms of polypropylene. (My children and now grandchildren believe that the isotactic polypropylene is really a chorus line of dancing teddy bears.)

Fluidized Bed Polymerization is a Common Type of Olefin Reaction Process





Details of a Fluidized Bed Polymerization Process

Both Syndiotactic and Isotactic Polypropylene can Crystallize

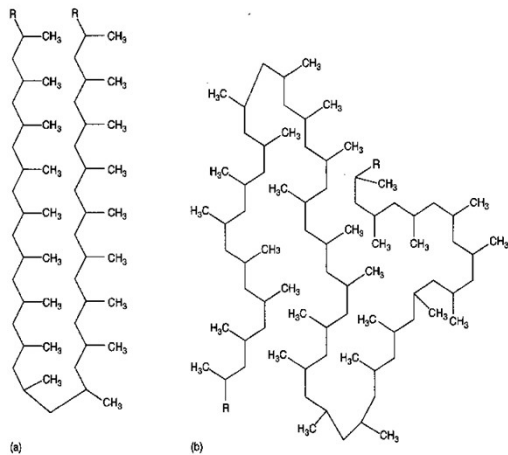
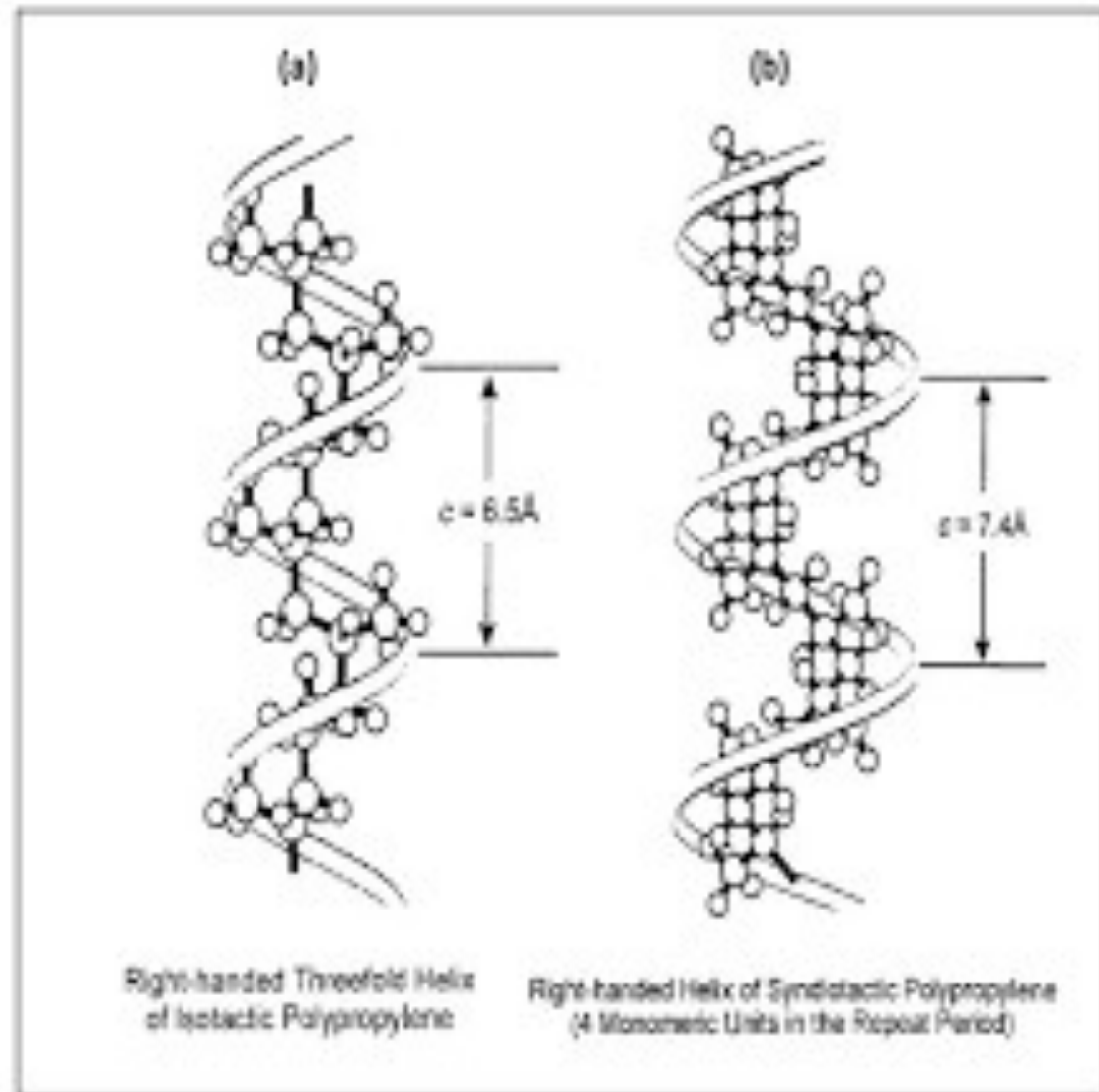


FIGURE 2.8 Representation of a crystalline portion from isotactic polypropylene (a) and an amorphous portion from atactic polypropylene (b).

Polypropylene exists in three possible forms:

	Isotactic	Syndiotactic	Atactic
M.P. (°C)	170	135	---
M.W.	~500,000	~300,000	very low
Density (g/cm ³)	0.91	0.88	---
Crystallinity	crystalline	crystalline	amorphous



Polypropylene can Easily Copolymerize with Polyethylene

HOMOPOLYMER

-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-

RANDOM COPOLYMER

-A-A-B-B-A-B-B-B-A-B-B-B-B-A-A-A-B-B-A-B-A-B-

BLOCK COPOLYMER

-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B-B-B-A-A-A-A-A-

A = propylene

B = ethylene

Melting Point of Polypropylene - The melting point of polypropylene occurs at a range.

1. Homopolymer: 160 - 165°C
2. Copolymer: 135 - 159°C

Density of Polypropylene - PP is one of the lightest polymers among all commodity plastics. This feature makes it a suitable option for lightweight\weight saving applications.

1. Homopolymer: 0.904 – 0.908 g/cm³
2. Random Copolymer: 0.904 – 0.908 g/cm³
3. Impact Copolymer: 0.898 – 0.900 g/cm³

Polypropylene can Easily Copolymerize with Polyethylene

Polypropylene Homopolymer is the most widely utilized as a general purpose grade. It contains only propylene monomer in a semi-crystalline solid form. Main applications include packaging, textiles, healthcare, pipes, automotive and electrical applications.

Polypropylene Copolymer family is further divided into random copolymers and block copolymers produced by polymerizing of propene and ethane:

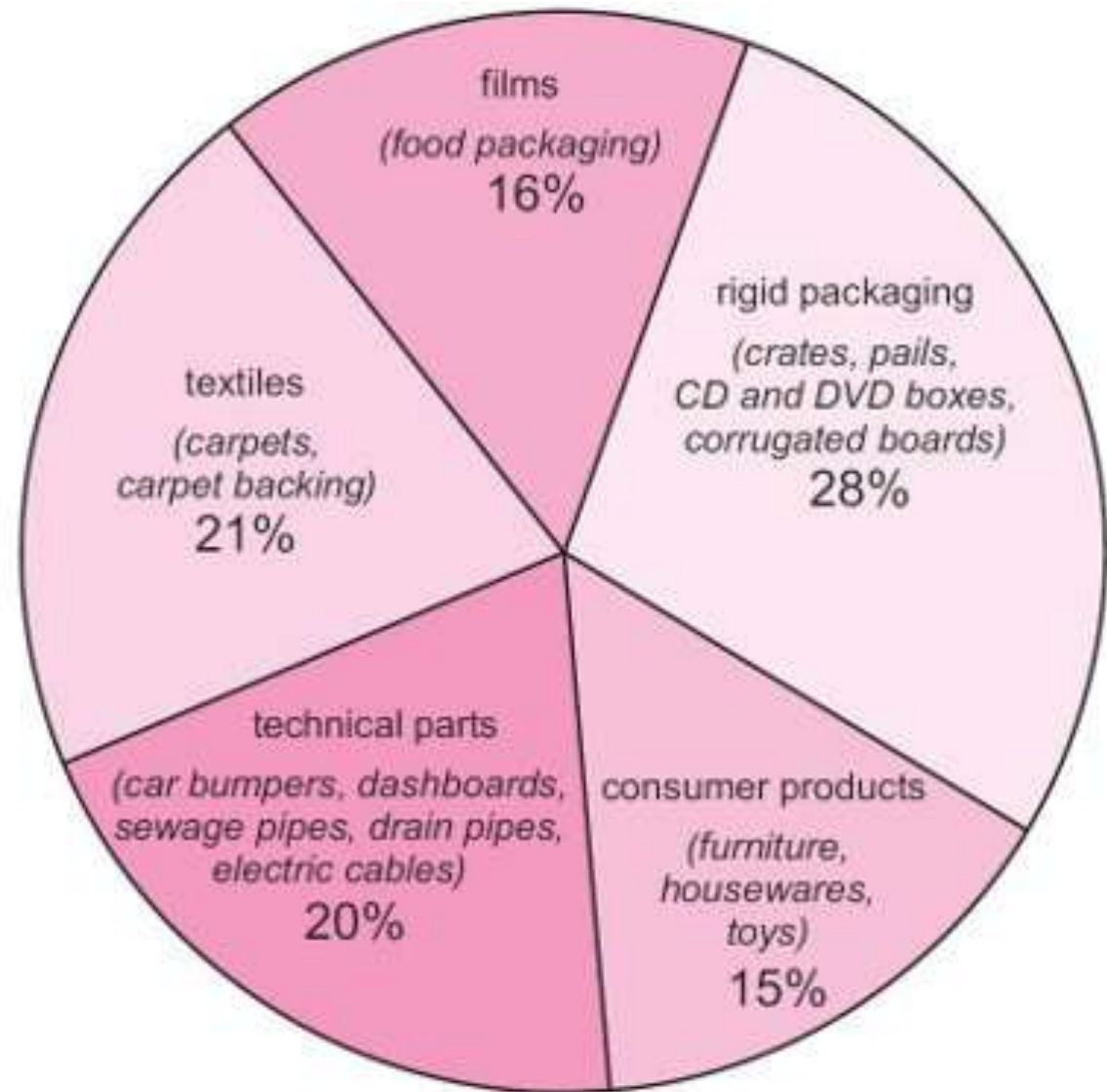
Polypropylene Random Copolymer is produced by polymerizing together ethene and propene. It features ethene units, usually up to 6% by mass, incorporated randomly in the polypropylene chains. These polymers are flexible and optically clear making them suitable of applications requiring transparency and for products requiring an excellent appearance.

While in **Polypropylene Block Copolymer**, ethene content is larger (between 5 and 15%). It has co-monomer units arranged in regular pattern (or blocks). The regular pattern hence makes thermoplastic tougher and less brittle than the random co-polymer. These polymers are suitable for applications requiring high strength, such as industrial usages.

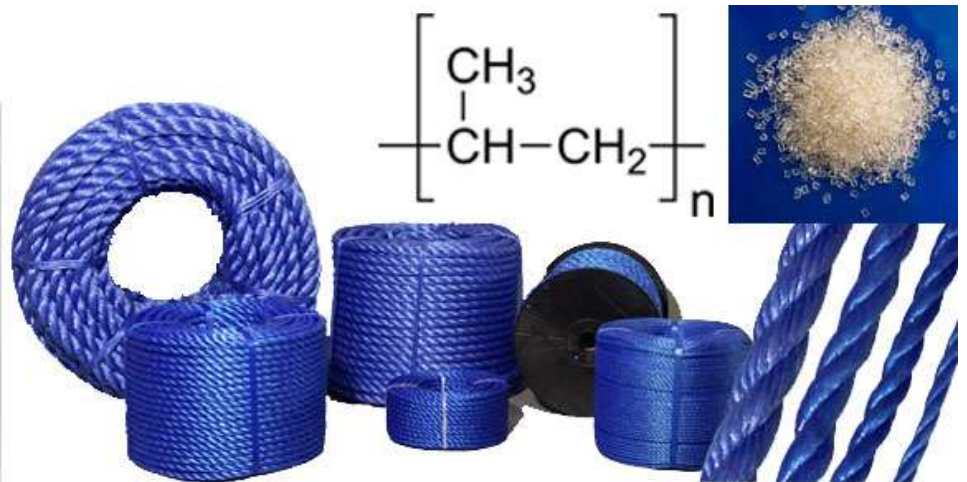
Property Comparison of Polypropylene Homopolymer and Copolymer

Property	Homopolymer			Copolymer	
Melt flow index	3	0.7	0.2	3	0.2
Tensile strength (MPa)	34	30	29	29	25
Elongation at break (%)	350	115	175	40	240
Flexural modulus (MPa)	1310	1170	1100	1290	1030
Brittleness temp. (°C)	+15	0	0	-15	-20
Vicat softening point (°C)	154-150	148	148	148	147
Rockwell hardness (R-scale)	95	90	90	95	88.5
Impact strength (ft Ib)	10	25	34	34	42.5

Applications for Polypropylene



Typical PP Homopolymer Products

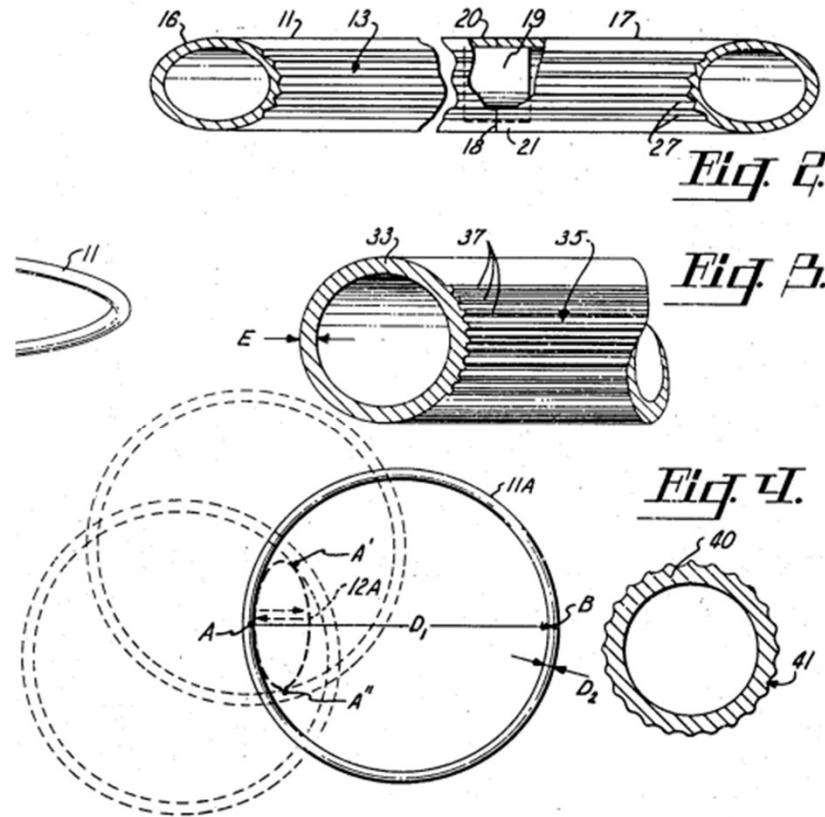


The Product that Saved an Industry

The original polypropylene produced by Phillips Petroleum (Marlex) had very poor properties.

It was extremely brittle restricting any large volume sales. Phillips had a large stockpile of polypropylene which they could not move from inventory.

UNTIL: A new revolutionary product came along which utilized all of the overstock that Phillips had



March 5, 1963

A. K. MELIN

HOOP TOY

Filed May 13, 1959

3,079,728

Development of Wham-O and the Hula Hoop

In 1948, friends Arthur Melin and Richard Knerr founded a company in California to sell a slingshot they created to shoot meat up to falcons they used for hunting. The company's name, Wham-O, came from the sound the slingshots supposedly made.

Wham-O eventually branched out from slingshots, selling boomerangs and other sporting goods. Its first hit toy, a flying plastic disc known as the **Frisbee**, debuted in 1957. The Frisbee was originally marketed under a different name, the **Pluto Platter**, in an effort to capitalize on America's fascination with UFOs.

Melin and Knerr were inspired to develop the Hula Hoop after they saw a wooden hoop that Australian children twirled around their waists during gym class. Wham-O began producing a plastic version of the hoop, dubbed "Hula" after the hip-yrating Hawaiian dance of the same name, and demonstrating it on Southern California playgrounds. Hula Hoop mania took off from there.

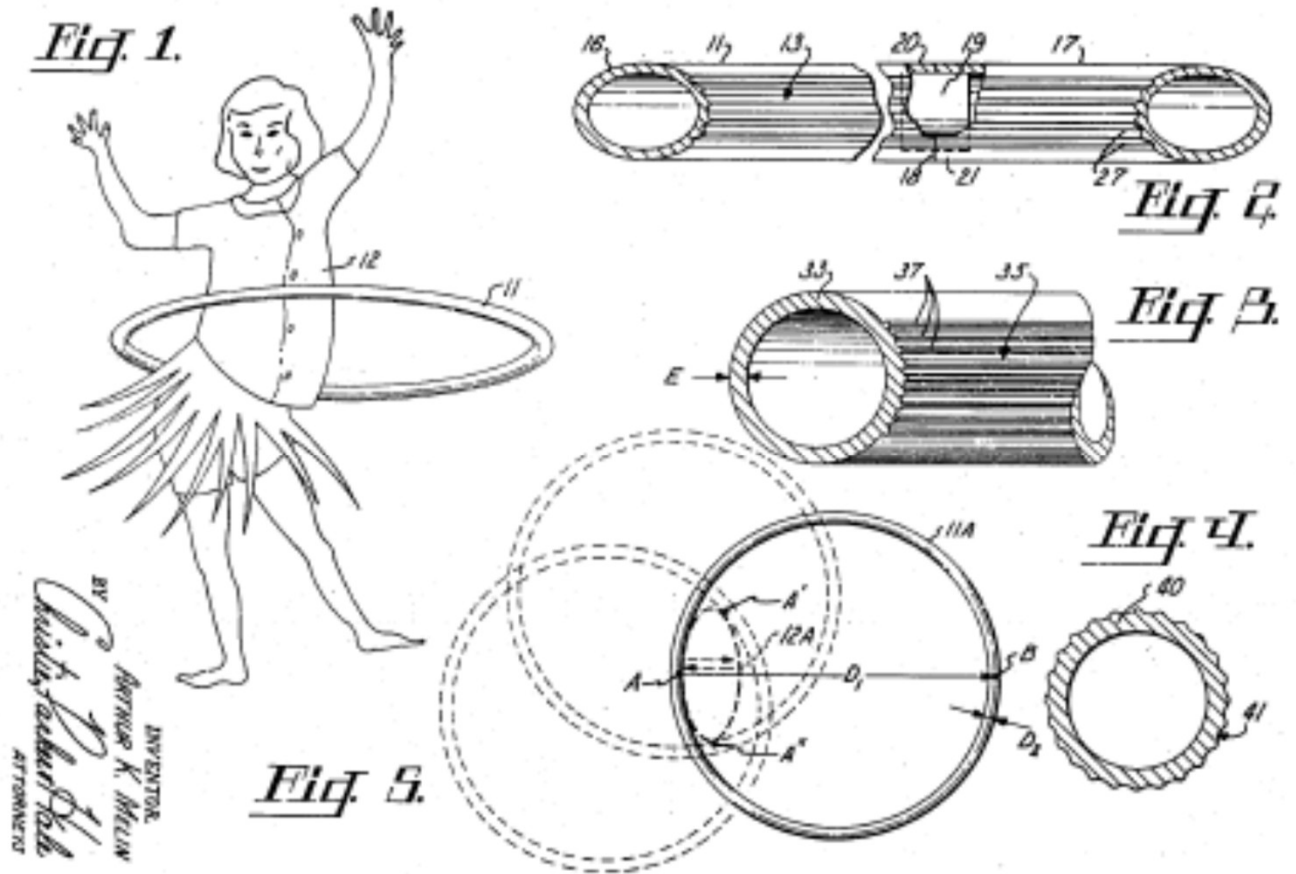
An Original Use for a New Polymer - Polypropylene

US Patent - 3,079,728

HOOP TOY

Arthur K. Melin, Pasadena, Calif.

Filed May 13, 1959 Ser. No. 813,030



March 5, 1963

A. K. MELIN
HOOP TOY

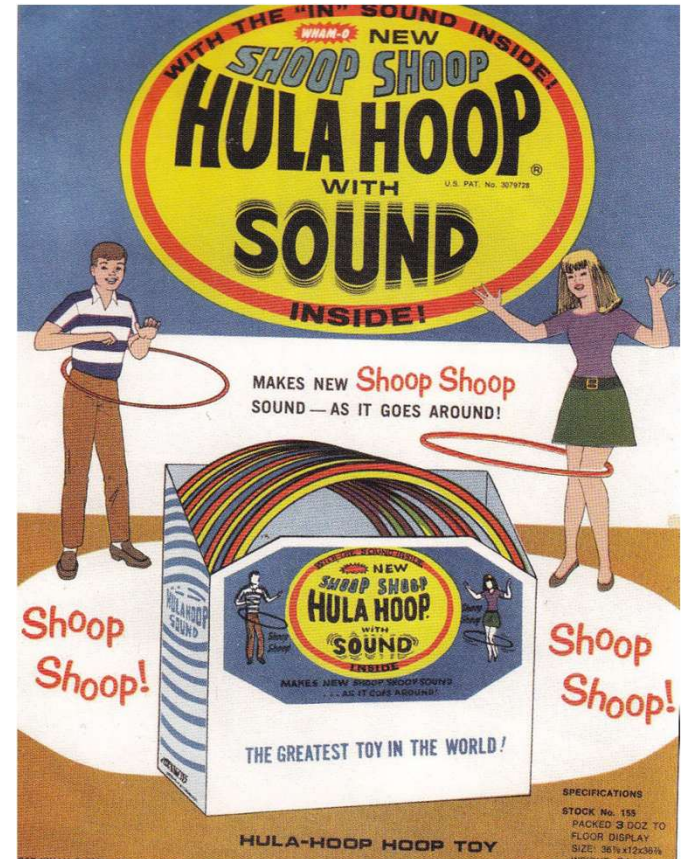
3,079,728

Filed May 13, 1959

The Hula Hoop Saved the Polypropylene Industry

Wham-O's nationwide daily production ultimately peaked at about 20,000 per day. **There soon was not enough Grex and Phillips Petroleum's once ignored miracle polypropylene, Marlex, was suddenly very much in demand.**

Plastic Hula-Hoop plants sprang up in Chicago, Newark and Toronto, Canada. **The completely unanticipated demand for Marlex gave Phillips the time necessary to resolve initial production problems and position itself as a prime source of plastic resins.**

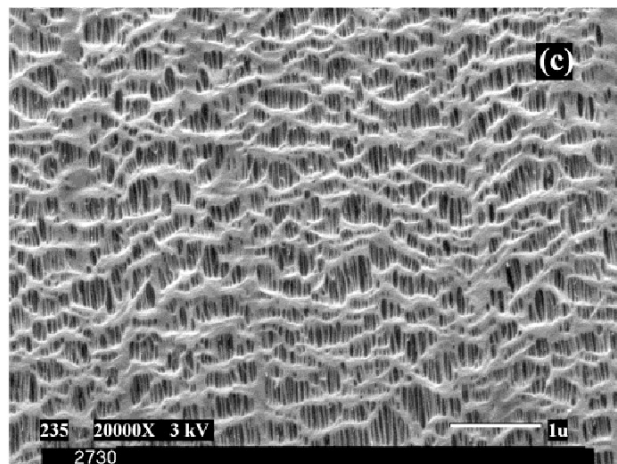
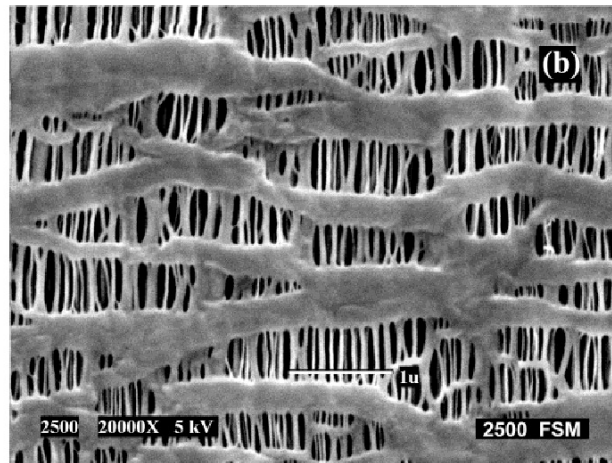
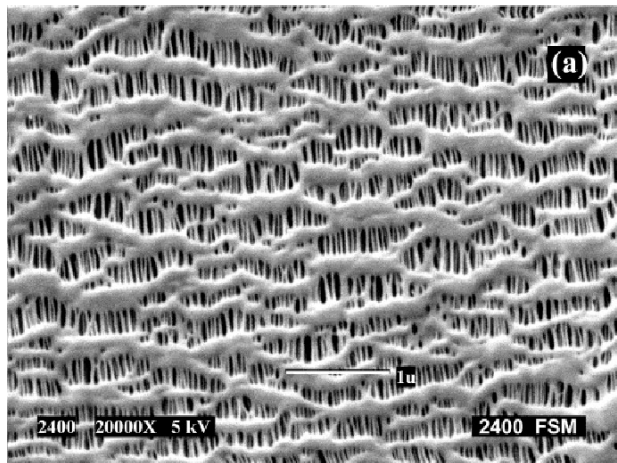


The **Shoop Shoop Hula Hoop** was nutty. Literally. Originally, Wham-O experimented with **walnut shells inside** the hoops to **make sound**. The shells were later replaced by **ball bearings**, which did the trick.

Advantages and Disadvantages of Polypropylene

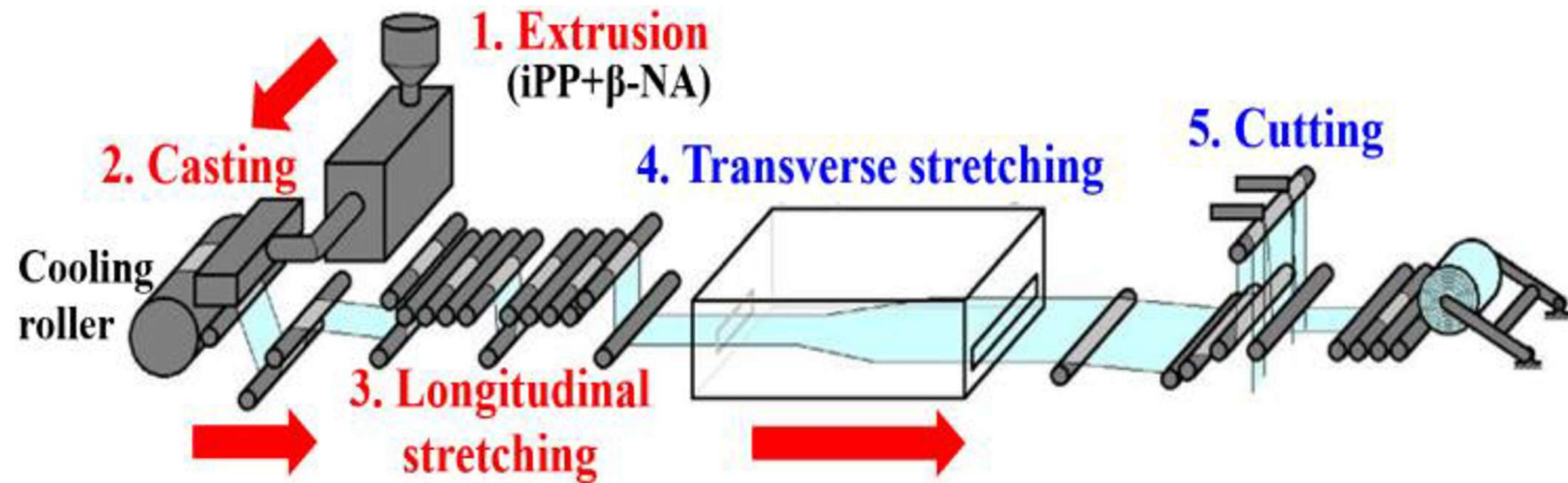
Advantages of PP		Disadvantages of PP
Homo-polymer	Copolymer	Degraded by UV (Ultraviolet)
Process ability, Good	Process ability, High	Flammable, but retarded grades available
Impact resistance, Good	Impact resistance, High	Attacked by chlorinated solvents and aromatics
Stiffness, Good	Stiffness, High	Difficult to bond
Food contact, Acceptable	Food contact, Not preferable	Several metals accelerate oxidative degrading
		Low temperature impact strength is poor

Polypropylene is the Basic Material in Celgard



The **Celgard** membrane is **made of** PP, which is a low-cost and quite inert polymer. It is resistant to extreme pH conditions and is insoluble in most solvents at room temperature. It swells in polar solvents such as carbon tetrachloride. No solvent is required for the preparation of the membrane.

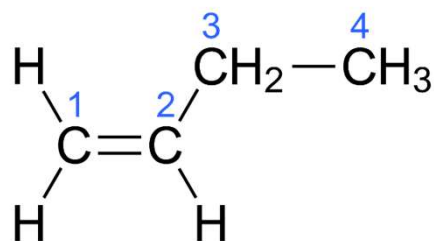
How is Celgard Made?



Importance of Celgard in Lithium Ion Batteries

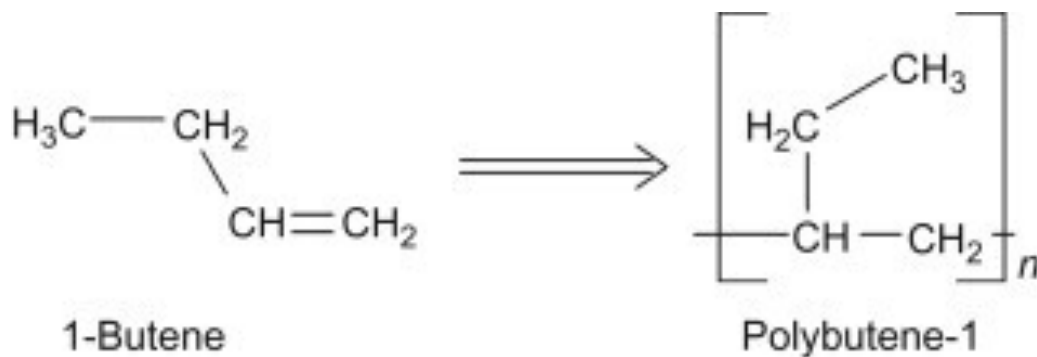
MARKET	EDV		
	Battery Electric Vehicles (BEV)	Plug-In Hybrid Electric Vehicles (PHEV)	Hybrid Electric Vehicles (HEV)
CELGARD PRODUCT SOLUTIONS	Trilayer PP/PE/PP H-Series (High Porosity Trilayer) Q-Series (Ceramic Coated)	Trilayer PP/PE/PP H-Series (High Porosity Trilayer)	H-Series (High Porosity Trilayer) Monolayer PP
MARKET NEEDS	<ul style="list-style-type: none"> • Vehicle Range • Long Battery Life • Safety 	<ul style="list-style-type: none"> • High Power for Acceleration • Long Battery Life • Consistent Energy Output over an Extended Period of Time 	<ul style="list-style-type: none"> • High Power for Acceleration • Ability to Withstand Frequent Charges and Discharges over the Life of the Battery
FEATURES	<ul style="list-style-type: none"> • Low Ionic Resistance and High Porosity • PP Outer Layers Provide High Temperature Melt Integrity (HTMI) and Oxidative Resistance • PE Inner Layer Provides High-Speed Shutdown During a Thermal Event 	<ul style="list-style-type: none"> • Excellent Electrolyte Absorption for Fast Ion Transfer • Sustained Separator Mechanical Integrity over the Life of the Battery 	<ul style="list-style-type: none"> • High Cycle Life • Unparalleled Tolerance or Resistance to Electrochemical Oxidation at Elevated Temperatures and Voltages
APPLICATION/ BATTERY BENEFIT	<ul style="list-style-type: none"> • Increased Battery Energy Density for Longer Driving Ranges • Increased Battery Longevity and Strength • Increased Battery Safety 	<ul style="list-style-type: none"> • High Battery Discharge Rate for Vehicle Acceleration • Ability to Withstand Deep Battery Discharges • Increased Battery Longevity and Strength 	<ul style="list-style-type: none"> • Fast Charge and Discharge Rates over the Life of the Battery • Increased Battery Longevity and Strength

Poly(butene-1) or Polybutylene



1 – Butene Monomer

Polybutylene is produced by polymerisation of 1-butene using supported Ziegler–Natta catalysts. PB-1 is a high molecular weight, linear, isotactic, and semi-crystalline polymer. PB-1 combines typical characteristics of conventional polyolefins with certain properties of technical polymers.



History of Polybutylene

1974 - Invented by Witco Chemical

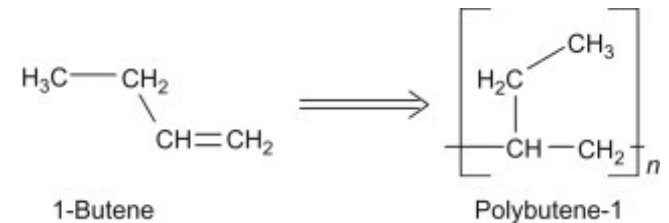
Ethyl side groups in a linear backbone structure

Linear isotactic material upon cooling the crystallinity is 30%

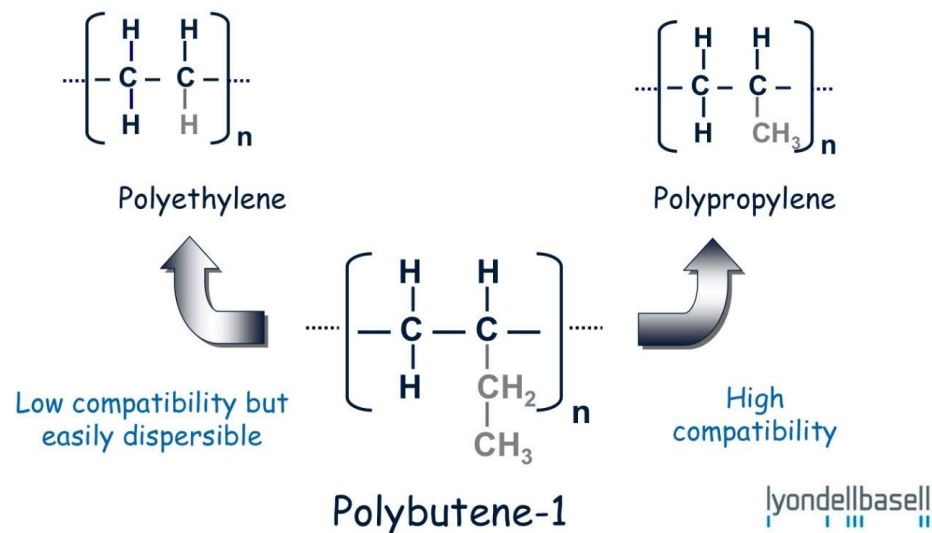
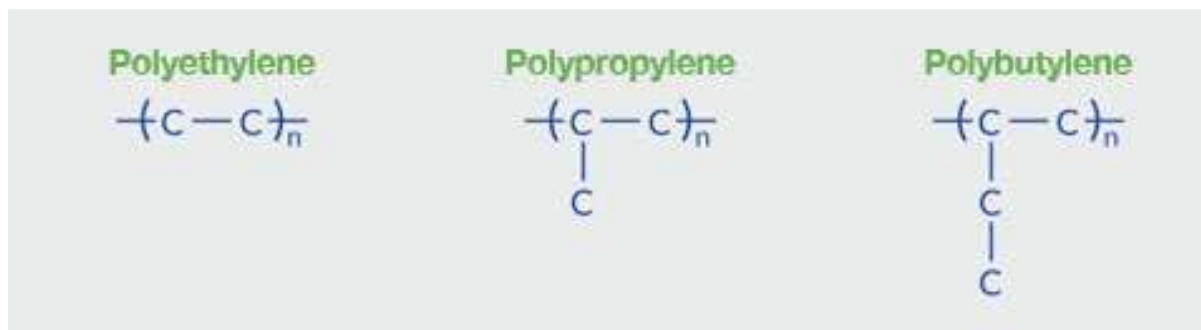
Post-forming can increase crystallinity to 55%

Processed by conventional thermoplastic techniques

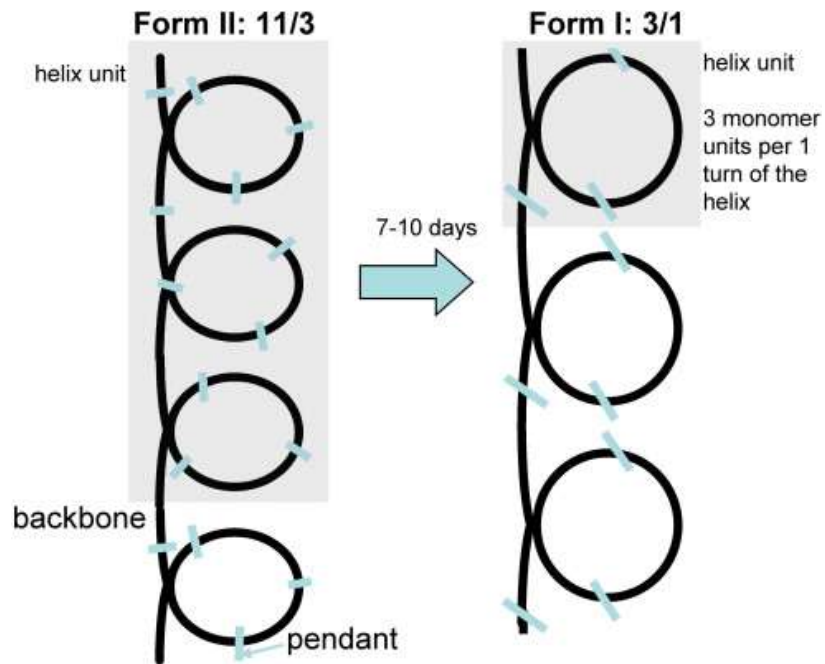
Applications primarily in pipe and film; also, tank liners, hot melt adhesives, coextruded as a moisture barrier and heat sealable packaging



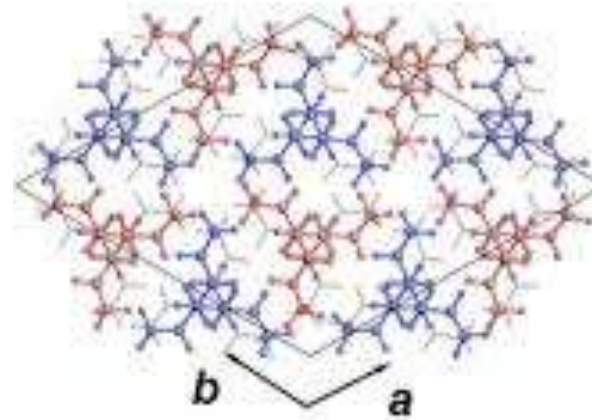
Polybutylene Comparison to Polyethylene and Polypropylene



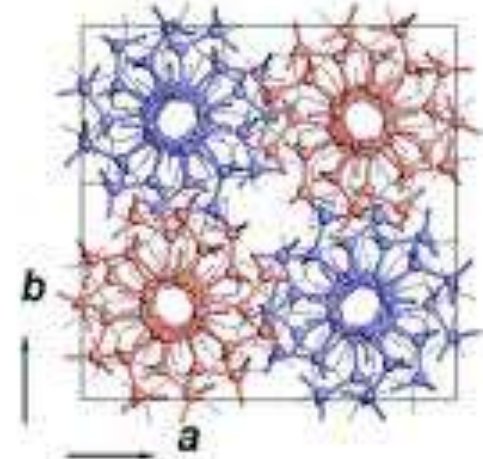
Two Crystal Forms Exist for Polybutylene



isotactic Polybutene-1
Crystal Form I



Crystal Form II



Each Form of Polybutylene Crystal has a Specific Melting Point and Density

Polymorph	Structure	How Obtained	Density (g/cm ³)	Melting point (°C)
Form I	Hexagonal (twined)	Stable form produced by transition from other forms	0.95	125-136
Form I'	Hexagonal (untwined)	Directly from solution	-	90-100
Form II	Tetragonal	Directly from the melt, and directly from solution at room temperature	0.88-0.90	118-126
Form III	Orthorhombic	Directly from solution	-	90-103

Properties of Polybutylene

Mechanical Properties of Polybutylene

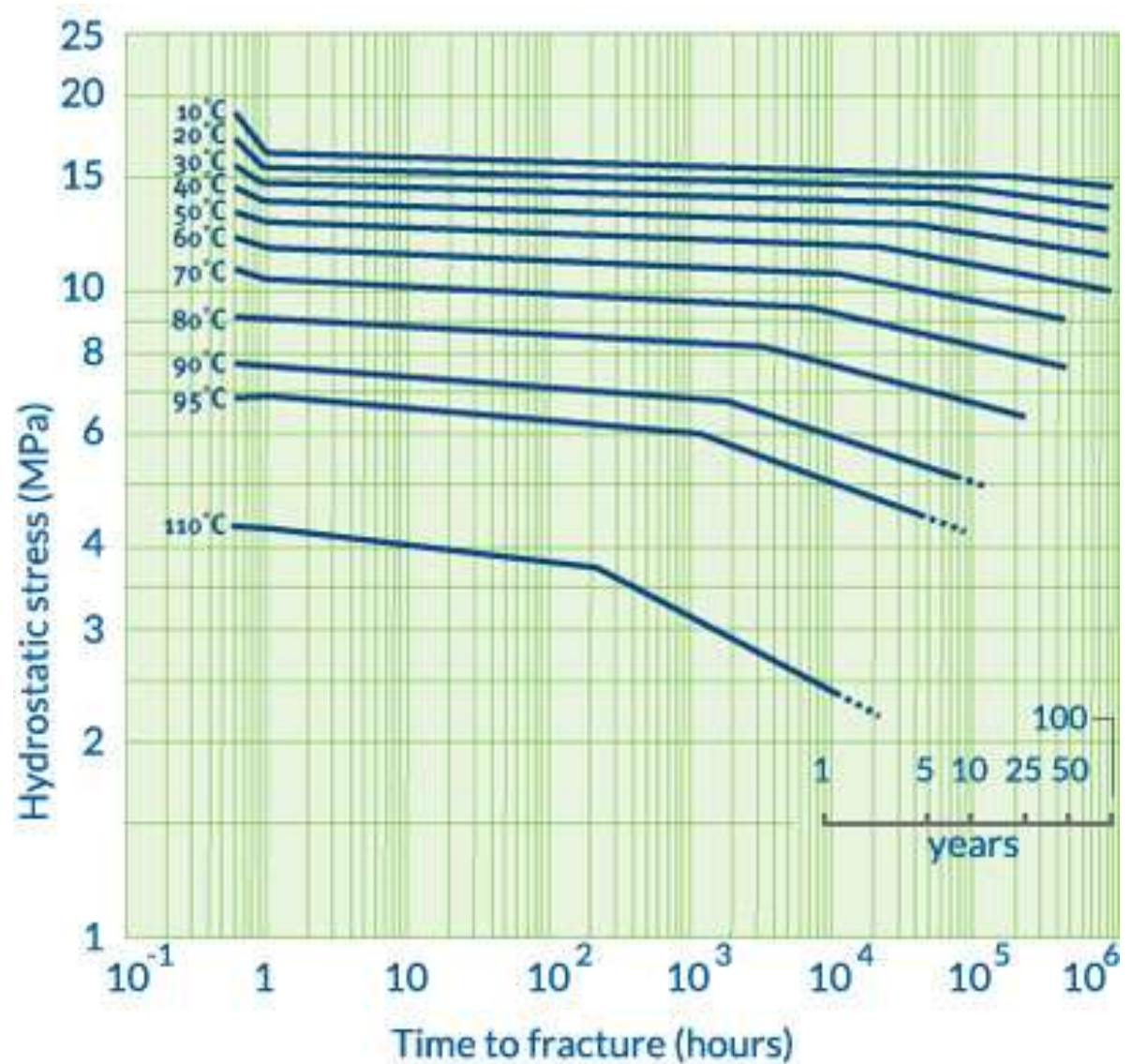
	Polybutylene	Polypropylene	LDPE (For Comparison)	HDPE (For Comparison)
Density	0.908 - .917	0.90	0.91- 0.925	0.959-0.965
Crystallinity	30% to 50%	30% to 50%	30% to 50%	80% to 91%
Tensile Strength, psi	4,000	4,500 – 5,500	600 - 2,300	5,000 – 6,000
Tensile Modulus, psi	10K – 40K	165K – 225K	25K – 41K	150K – 158 K
Tensile Elongation, %	300% - 400%	100% - 600%	100% - 650%	10% - 1300%
Impact Strength ft-lb /in	No break	0.4 – 1.2	No break	0.4 – 4.0
Hardness	Shore D55 – D65	R80 - 102	D44 – D50	D66 – D73

Additional Properties of Polybutylene

Some properties:

•Elastic modulus	290–295 MPa
•Tensile strength	36.5 MPa
•Molecular weight	725,000 (g/mol)
•Crystallinity	48–55%
•Water absorption	<0.03%
•Glass transition temperature	–25 to –17 °C
•Thermal conductivity	0.22 W/(m*K)

Long Term Stress
Rupture
Performance
Indicated that
Polybutylene could
be a Good Hot- and
Cold-Water Piping
Material



Polybutylene Plumbing was Popular in North America between 1978 and 1997

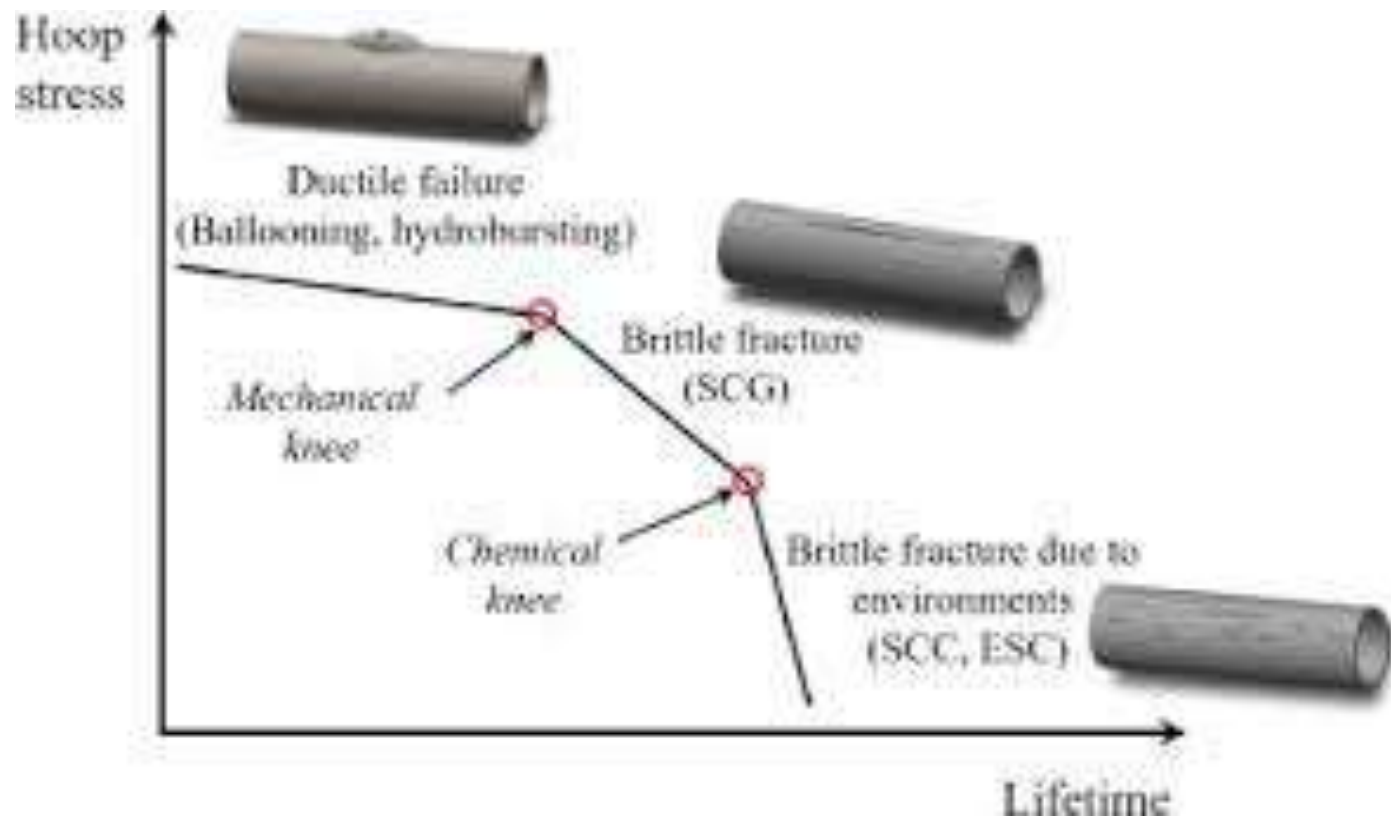


Polybutylene in Hot Water Piping Systems

The main use of PB-1 is in flexible pressure piping systems for hot and cold drinking water distribution, pre-insulated district heating networks and surface heating and cooling systems. ISO 15876 defines the performance requirements of PB-1 piping systems. The most striking features are weldability, temperature resistance, flexibility and high hydrostatic pressure resistance. The material can be classified PB 125 with a minimum required strength (MRS) of 12.5 MPa. Other features include low noise transmission, low linear thermal expansion, no corrosion and calcification.

PB-1 piping systems are no longer being sold in North America. The overall market share in Europe and Asia is rather small but PB-1 piping systems have shown a steady growth in recent years. In certain domestic markets, e.g. Kuwait, the United Kingdom, Korea and Spain, PB-1 piping systems have a strong position.

Illustration of the Environmental Degradation Failure on a Hoop Stress vs Failure Time Plot



Polybutylene Water Pipes Began Leaking



Removal of Polybutylene Piping in North America

Polybutylene plumbing was used in several million homes built in the United States from around 1978 to 1997. Problems with leaks and broken pipes led to a class action lawsuit, Cox v. Shell Oil, that was settled for \$1 billion. The leaks were associated with degradation of polybutylene exposed to chlorinated water.

Polybutylene water pipes are no longer accepted by United States building codes and have been the subject of class action lawsuits in both Canada and the U.S. The National Plumbing Code of Canada 1995 listed polybutylene piping as acceptable for use with the exception of recirculation plumbing. The piping was removed from the acceptable for use list in the 2005 issue of the standard.

1

There is evidence to suggest that the presence of chlorine and chloramine compounds in municipal water (often deliberately added to retard bacterial growth) will cause deterioration of the internal chemical structure of polybutylene piping and the associated acetal fittings. The reaction with chlorinated water appears to be greatly accelerated by tensile stress, and is most often observed in material under highest mechanical stress such as at fittings, sharp bends, and kinks.

Lesson 14: Polypropylene PP Poly(1-butene) – Polybutylene - PB

Questions?



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

"I don't always go the extra mile, but when I do it's because I missed my exit."