



POLYMER TECHNOLOGY (MS41004)

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Materials and civilisation

Stone age (Before 5000 BC)



Copper age (5000 - 3000 BC)



Bronze age (3000 - 800 BC)



Iron age (800 BC - 40 AD)

Plastic age ?

Types of materials



Metal



Ceramic



Polymer

Semiconductors

Composites

Biomaterials

Molecular materials

History of polymers (1500 – present)

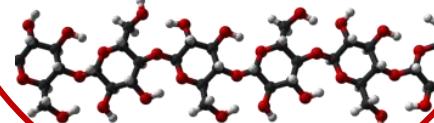
1500's

British explorers discover ancient Mayan civilization in Central America. The Mayans are assumed to be the among The first to find an application of polymers, as their children Were fond of playing with balls made from local rubber tree



1917

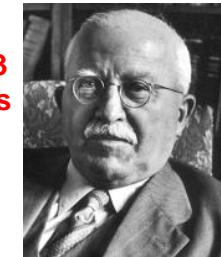
X-ray crystallography is invented as a method of analyzing crystal structure. M. Polanyi discover the chemical structure of cellulose. This establishes the fact that polymer unit cells contain Sections of long chain molecules rather than small molecules



1920

Hermann Staudinger published his classic paper "Uber Polymerization". Demonstrated the existence of macromolecules

Nobel Prize in Chemistry in 1953 for his discoveries in the field of macromolecular chemistry



1839

Charls Godyear discovers **Vulcanisation**. Vulcanised rubber is much more durable than its natural part



1907

The oldest recorded synthetic Plastic is fabricated by Leo Bakeland. Bakelite's hardness and high heat resistance made it an excellent choice as an electrical insulator and many article



1927

Large scale production of PVC resins begins. Widely used today to make plumbing pipe, tiles and bottles.





1930

Polystyrene invented.
Material used in video cassettes ,
toys and other packaging.



1970

Development of liquid
crystalline polymer. Common
application in electronic
devices and Aircraft engines

Xydar® LCP is a glass fiber or mineral-filled
resin that features excellent flow properties.

It can be injection molded into thin-wall
components and has outstanding strength
at extreme temperatures to 300°C. Xydar®
resin is inherently FR, transparent to
microwave radiation, and resistant
to virtually all chemicals.

HBA/TPA/BP

1971

Kevlar developed. High
strength material that can
withstand temp. upto 300 °C.
Used in bullet proof vests, fire proof
garments for fire fighting and
auto racing.



1938

W. Carotheror (DuPont)
Invented Nylon, is a
common material in clothing
and different engineering
products



1941

Polyethylene developed.
Billions of pounds of LDPE
and HDPE is produced today,
everything for packaging
film, piping to toy



1976

The polymer product
industry outstrip steel as
the most widely used material
per unit volume. We now use
more plastic than steel,
aluminum and copper combined

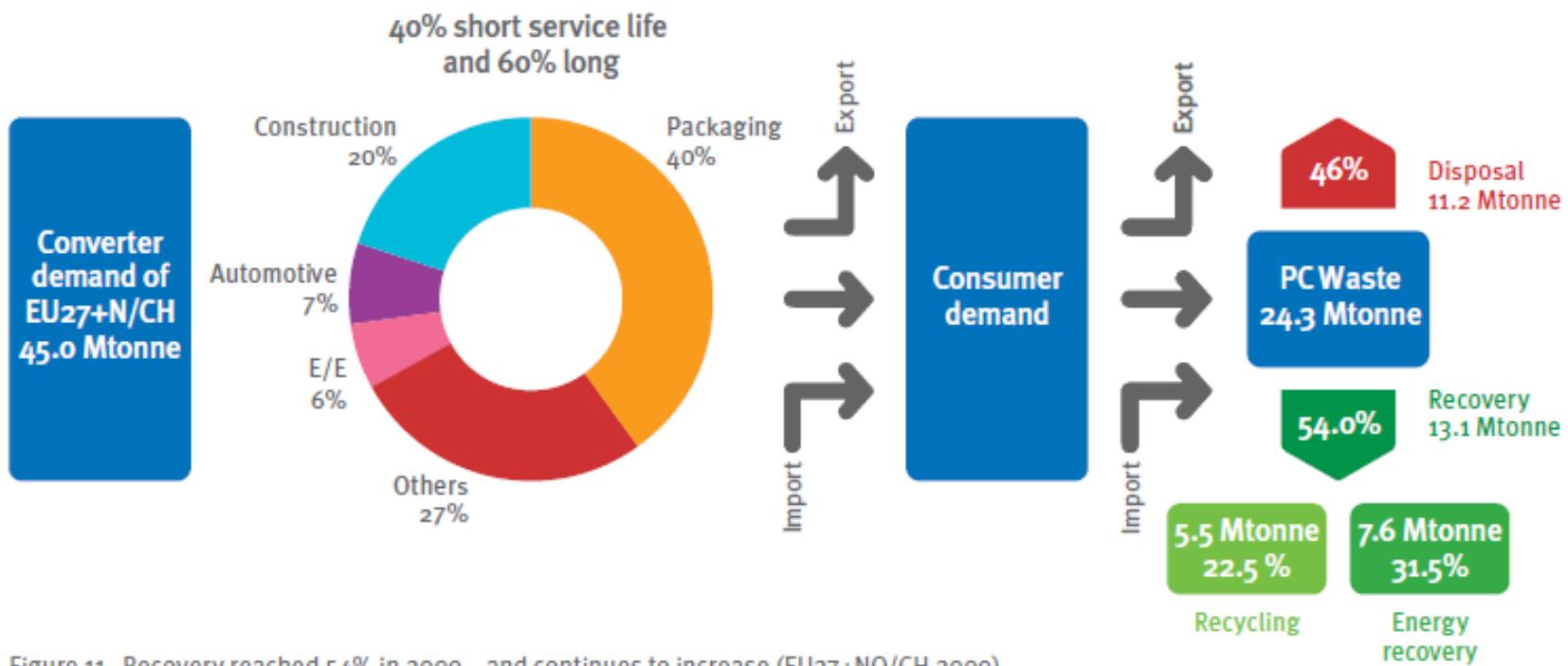


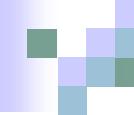
World consumption of polymers

World Consumption – Polymers
(Thousand metric tonnes)

Market sector	2006	2016	2006–2016 CAGR, %	Net trade – 2016 (kmt)
Food	42,025	71,774	5.5%	697
Textiles	32,176	51,630	4.8%	(4,231)
Furniture	13,687	22,993	5.3%	(2,886)
Printing	780	1,220	4.6%	553
Plastic products	43,500	78,361	6.1%	Argentina (1,301)
Fabricated metals	1,519	2,259	4.0%	Other South & Central America (4,412)
Machinery	2,397	3,658	4.3%	Western Europe (406)
Electrical/electronic	13,810	25,499	6.3%	Russia 1,439
Other transportation	9,330	16,181	5.7%	Other Central & Eastern Europe (2,375)
Vehicles & parts	10,746	15,625	3.8%	China (15,588)
Other equipment	3,852	6,334	5.1%	India 1,148
Other manufacturing	21,238	33,569	4.7%	Japan 155
Construction	45,886	72,919	4.7%	South Korea 5,278
Total	240,947	402,022	5.3%	Taiwan 3,679
				Thailand 1,030
				Australia New Zealand (1,302)
				Other Asia Pacific (3,534)
				Middle East 25,251
				Africa (3,125)

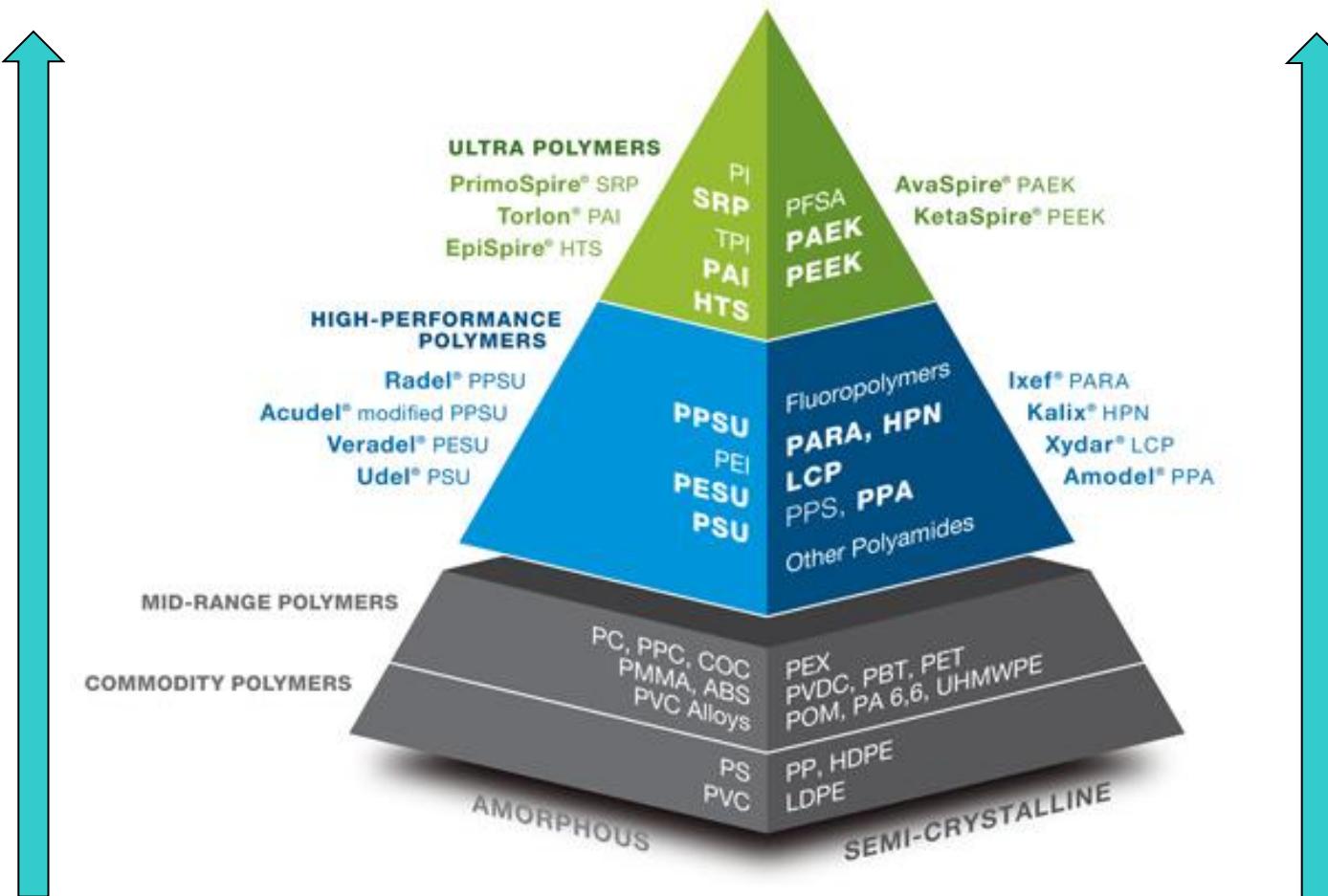
Use of polymers in different sector (European Union)





Cost

Performance



Packaging



Sporting Goods



Consumer products



Aircraft



Automotive



The 100% plastic car – no longer an imaginary concept !!!



Naval Ships



Polymers

- The earliest synthetic polymer was developed in 1906, called Bakelite.
- The development of modern plastics started in 1920s using raw material extracted from coal and petroleum products (Ethylene). Ethylene is called a monomer.
- Polymers are long-chain molecules and are formed by polymerization process, linking and cross linking a particular building block (**monomer**, a unit cell).
- The term polymer means many units repeated many times in a chainlike structure.
- Most monomers are organic materials, atoms are joined in covalent bonds (electron-sharing) with other atoms such as oxygen, nitrogen, hydrogen, sulfur, chlorine,....

Products from Bakelite

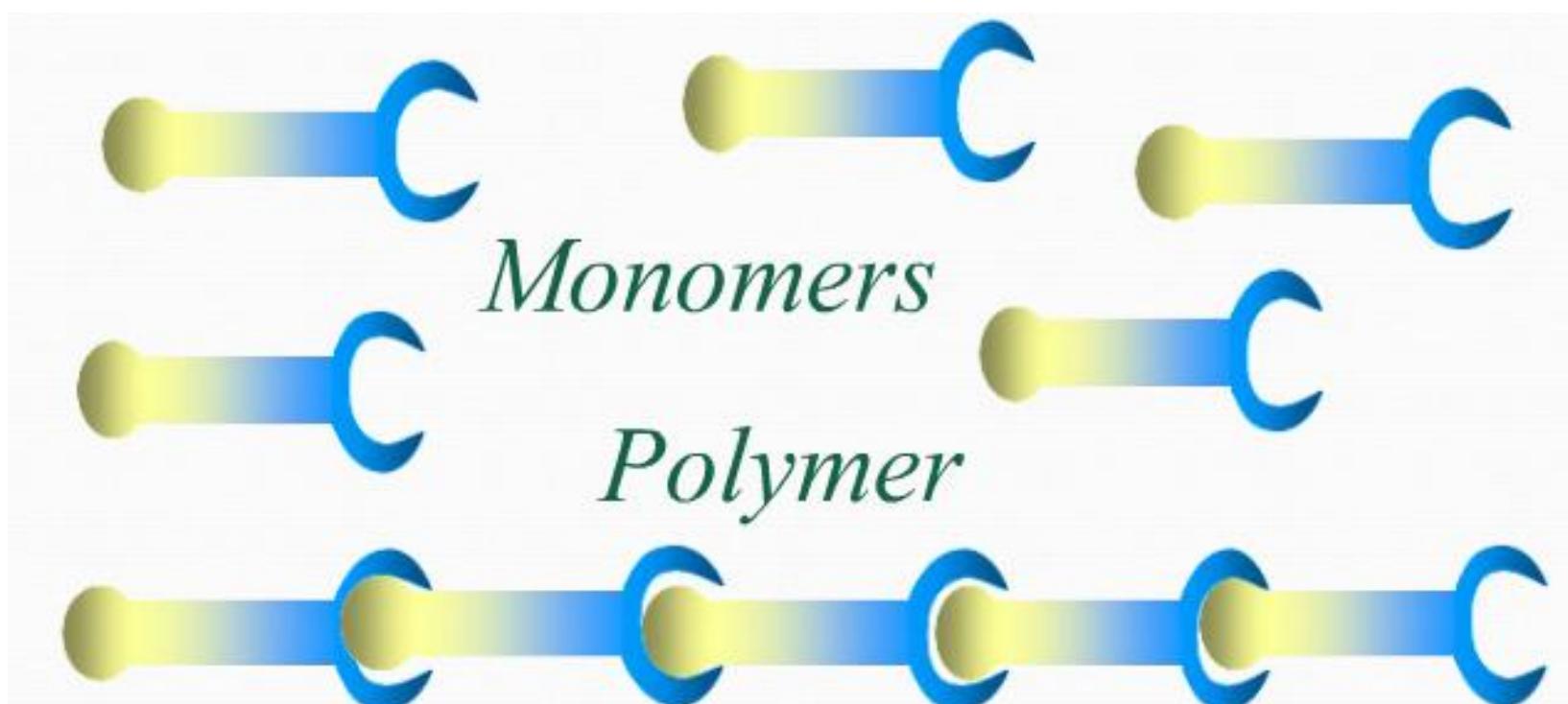
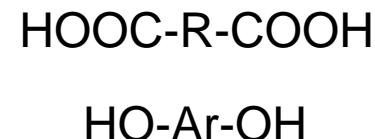




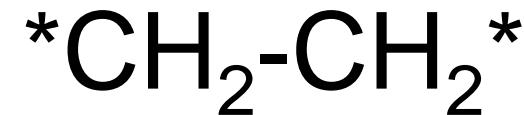
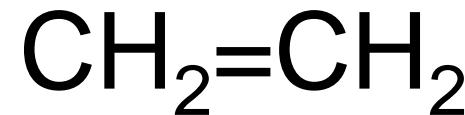
Polymer Building Blocks

- Hydrogen
- Carbon (key)
- Oxygen
- Nitrogen
- Fluorine
- Silicon
- Sulfur
- Chlorine
- Phosphorus

Monomer to Polymer



The word, polymer, implies that polymers are constructed from pieces (monomers) that can be easily connected into long chains (polymer).





Polymer, Monomer; *Structure unit, degree of polymerization*

Poly- means "many" and **-mer** means "part" or "segment". **Mono** means "one".

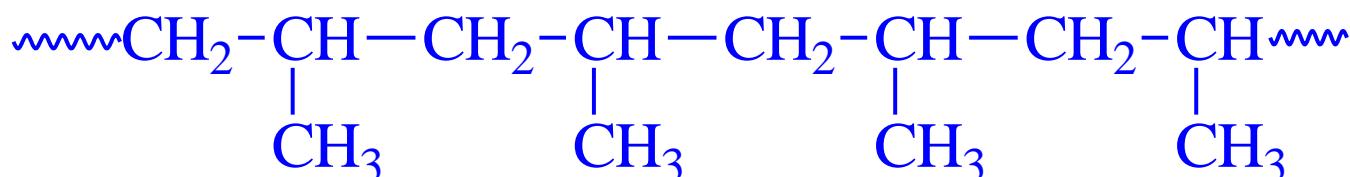
So, monomers are those itty bitty molecules that can join together to make a long polymer chain.

Monomer : material employed in the preparation of the polymer. They are functional & minimum functionality is two.

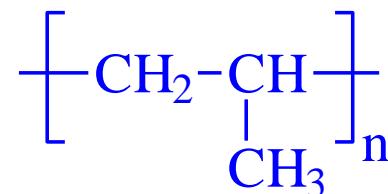
Many many many MONOmers make a POLYmer!

Structure units are connected to one another in the polymer chain, or polymeric structure, by covalent bonds.

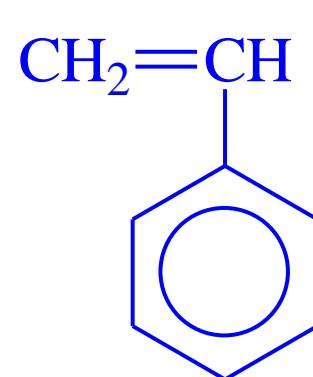
Repeat unit: The atoms that make up the backbone of a polymer chain come in a regular order, and this order repeats itself all along the length of the polymer chain. For example, look at polypropylene :



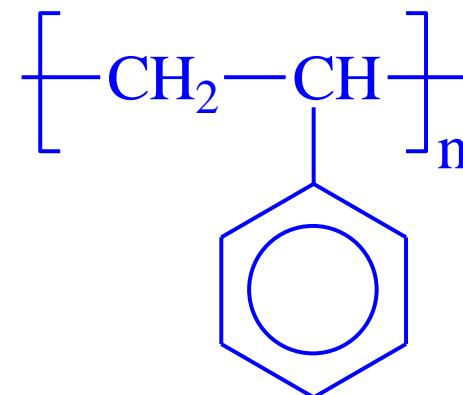
Its backbone chain is made up of just two carbon atoms repeated over and over again. One carbon atom has two hydrogen atoms attached to it, and the other carbon atom has one hydrogen atom and one pendant methyl group (CH_3). This is called the *repeat structure* or the *repeat unit*. To make things simple, we usually only draw one unit of the repeat structure, like this:



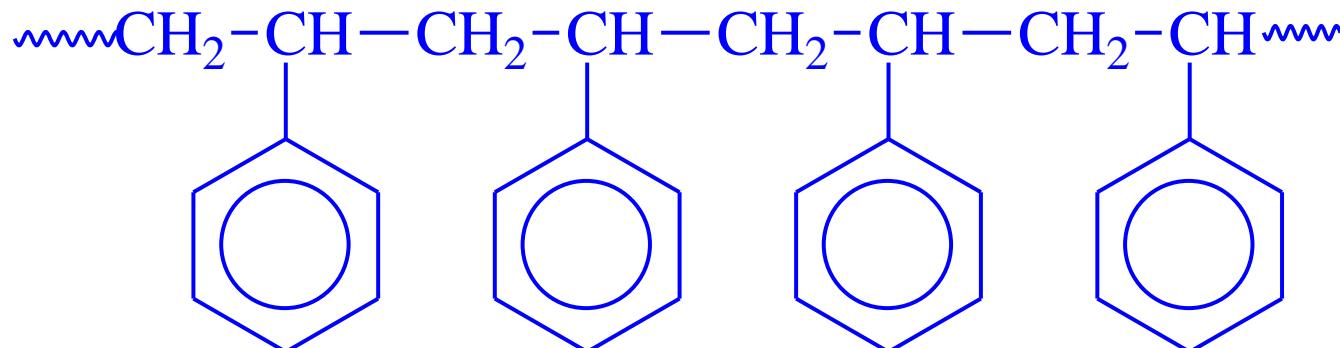
Another example: styrene monomers join together to make polystyrene:



Styrene monomer



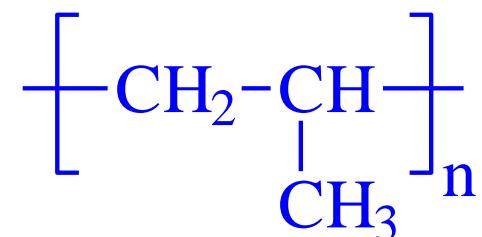
Polystyrene repeat unit



Degree of polymerization: refers to the number average obtained by dividing the total number of structural units by the total number of molecules.

Polymer molecular weight:

$$M = DP \times M_o$$

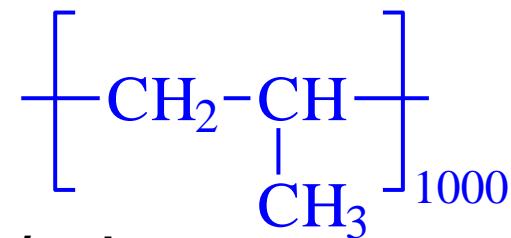


M_o : molecular weight of repeating unit

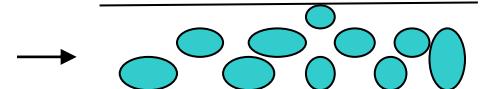
DP: *Degree of polymerization*

As for example look at polypropylene

If $n = 1000$, DP is 1000, This means that propylene unit has repeated 1000 times and M_o for the repeat unit is 42, the molecular weight (M) of the polymer is $42 \times 1000 = 42000 \text{ g/mol}$



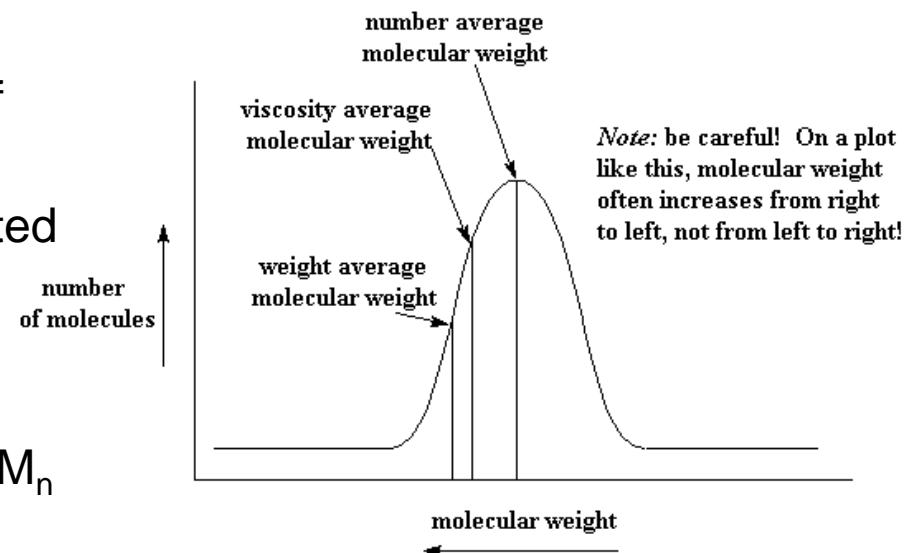
Molecular Weight of Polymers



Unlike small molecules, polymers are typically a mixture of differently sized molecules. Only an average molecular weight can be defined.

- Measuring molecular weight
 - Size exclusion chromatography
 - Viscosity
- Measurements of average molecular weight (M.W.)
 - Number average M.W. (M_n): Total weight of all chains divided by no of chains
 - Weight average M.W. (M_w): Weighted average. Always larger than M_n
 - Viscosity average M.W. (M_v): Average determined by viscosity measurements. Closer to M_w than M_n

Molecular Weight Distribution
 $PDI = M_w/M_n$



Molecular Weight of Polymers

a) Number average molecular weight (M_n)

M_n : This gives you the true average weight

Let's say you had the following polymer sample:

2 chains:	1,000,000 Dalton	2,000,000
5 chains:	700,000 Dalton	3,500,000
10 chains:	400,000 Dalton	4,000,000
4 chains:	100,000 Dalton	400,000
2 chains:	50,000 Dalton	<u>100,000</u>
		10,000,000

$$10,000,000/23 = 435,000 \text{ Dalton}$$

1 Dalton = 1 g/mole

$$M_n = \sum n_i M_i / \sum n_i$$

b) Weight Average Molecular Weight (M_w)

M_w: Since most of the polymer mass is in the heavier fractions, this gives the average molecular weight of the most abundant polymer fraction by mass.

$$\frac{2,000,000}{10,000,000} = 0.20 \times 1,000,000 = 200,000$$

$$\frac{3,500,000}{10,000,000} = 0.35 \times 700,000 = 245,000$$

$$\frac{4,000,000}{10,000,000} = 0.40 \times 400,000 = 160,000$$

$$\frac{400,000}{10,000,000} = 0.04 \times 100,000 = 4,000$$

$$\frac{100,000}{10,000,000} = 0.01 \times 50,000 = 500$$

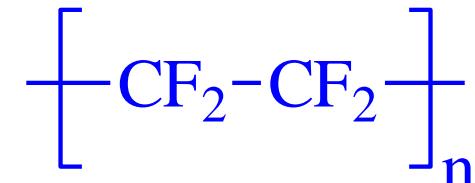
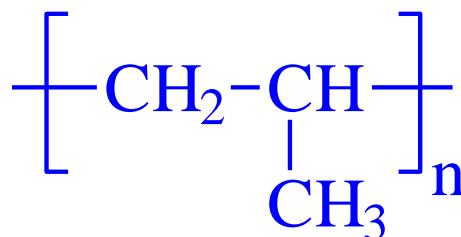
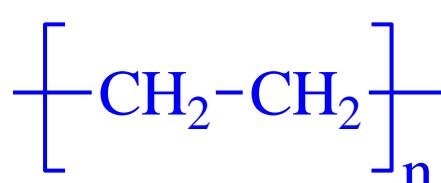
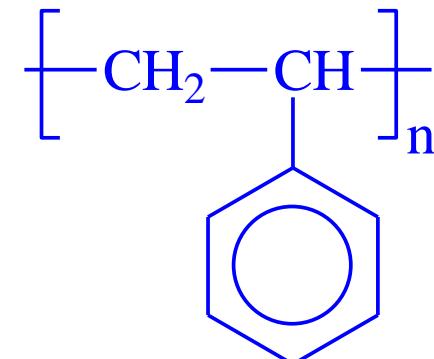
$$\text{Total} = 609,500$$

$$M_w = \sum n_i M_i^2 / \sum n_i M_i$$

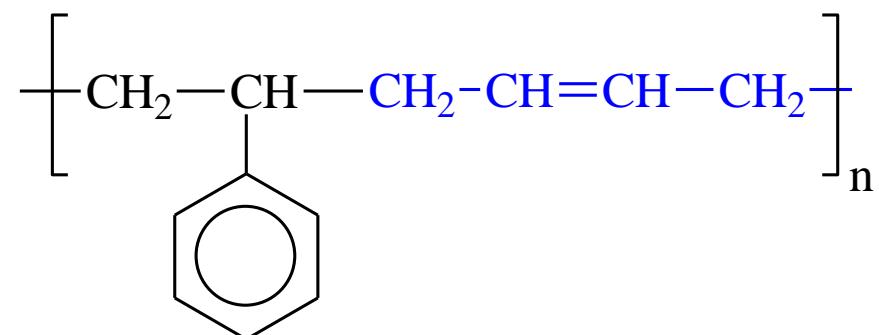
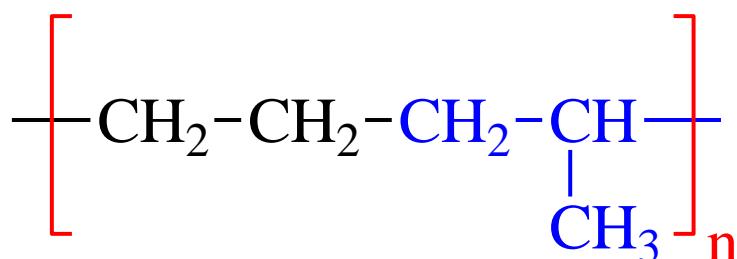
Chemical Structure

Homopolymer- only one monomer
(repeating unit)

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

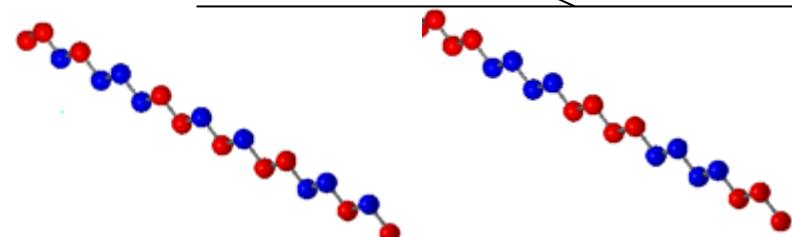
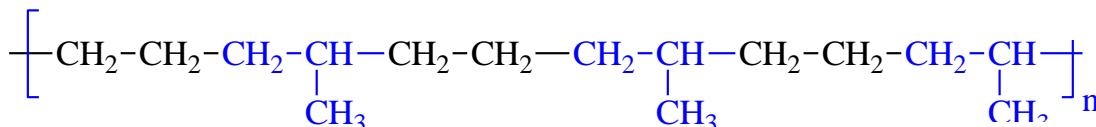


Copolymer – more than one monomer

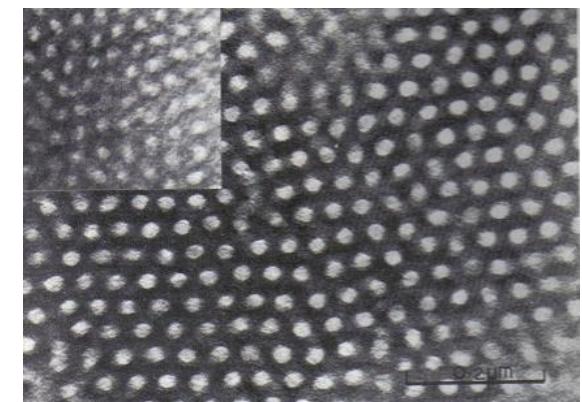
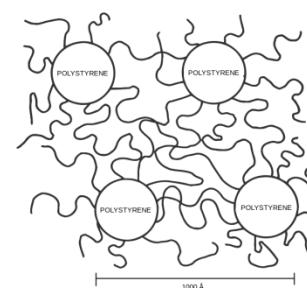
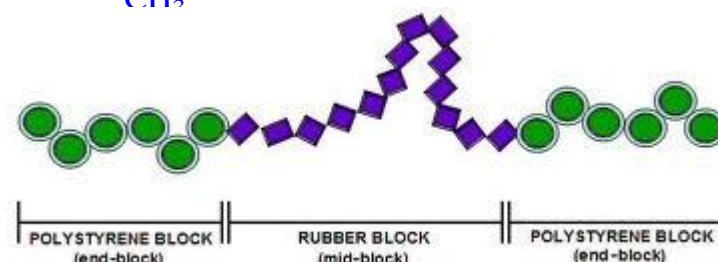
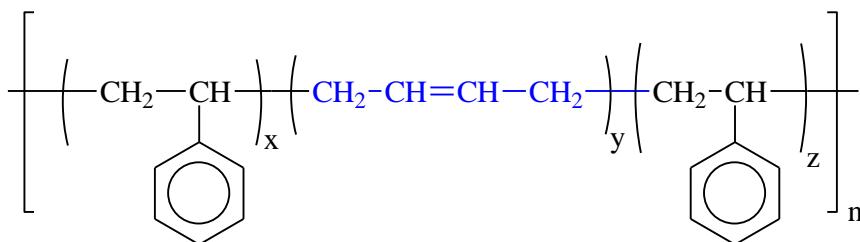


Copolymers

- Alternating and random



Block



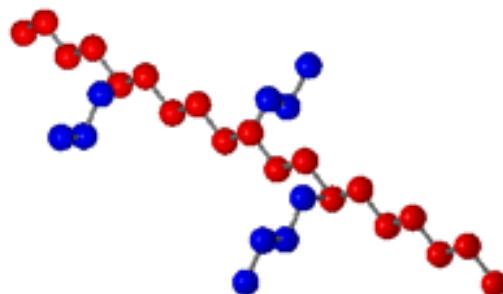
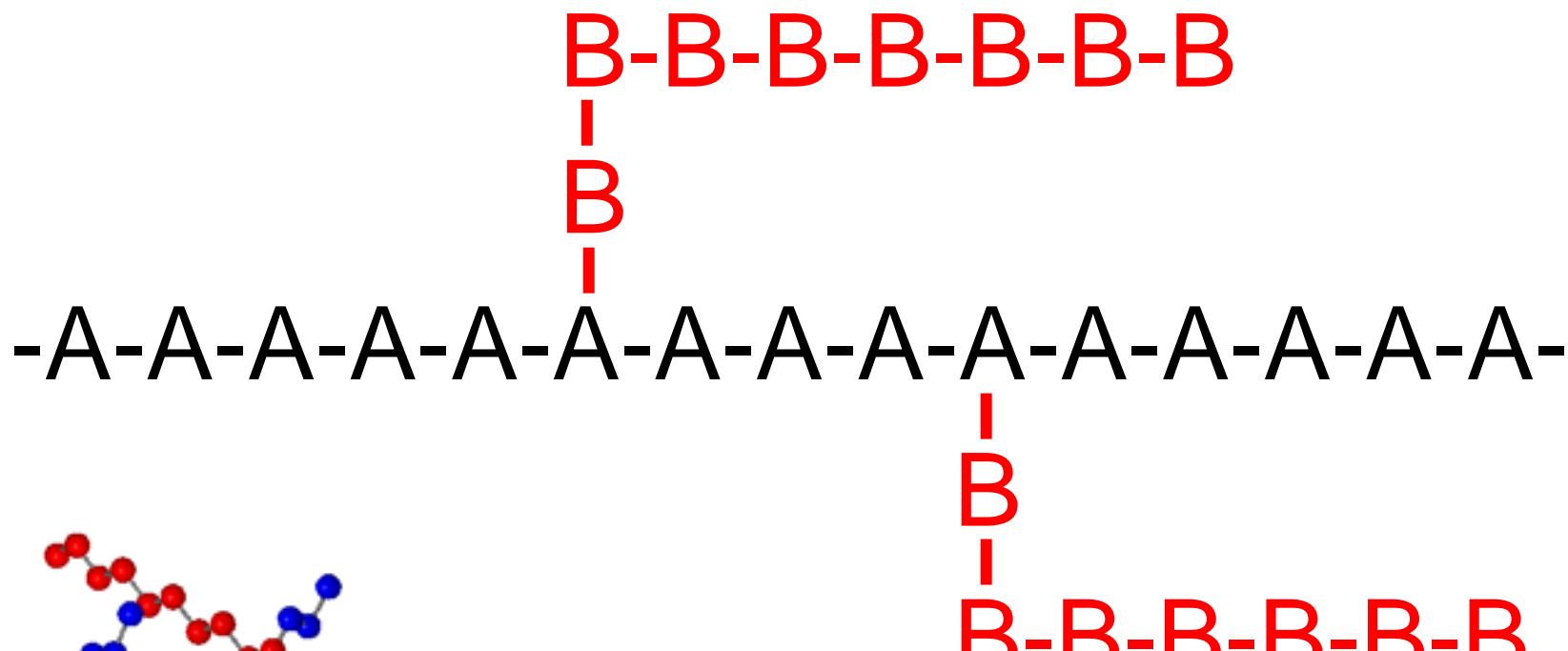
Copolymers can be used to tailor functionality or generate new phases and behaviors.

Copolymers

Polymer Science: Vasant Gowariker, N. V.
Viswanathan, Jayadev Sreedhar

Graft

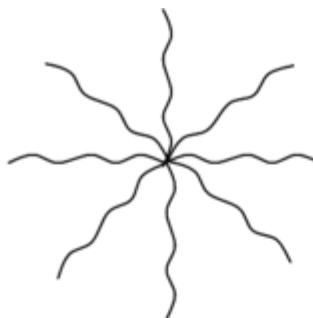
Poly(styrene)-*graft*-poly(butadiene)



Various polymer architectures



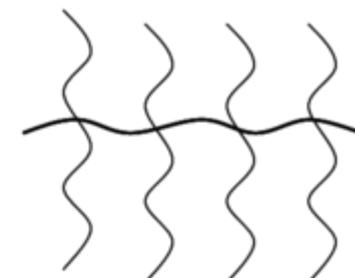
Block copolymer



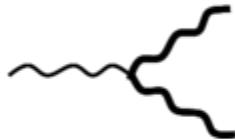
Star polymer



Comb polymer



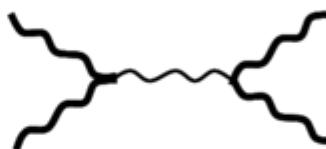
Brush polymer



AB₂ star



Palm-tree AB_n



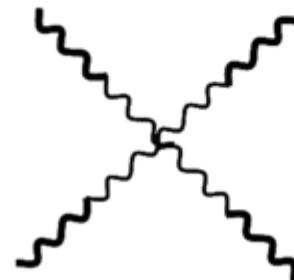
H-shaped B₂AB₂



Dumbbell (pom-pom)



Ring block



Star block AB_n



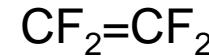
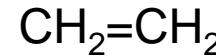
Coil-cycle-coil



Star A_nB_n

- Homopolymers may not always satisfy all the requirements for various practical applications.
- Thus, initially the trend was to develop new polymers from a wide variety of monomers.
- For tailoring or modifying the properties of polymers, copolymerization has been used as an effective technique.
- However, due to the economic and technical uncertainties associated with synthesizing new polymers, recently efforts were focused on multiphase polymeric systems to obtain materials with improved physical and chemical properties and such considerations were the basis of polymer blends.
- Mixing two or more polymers together to produce blends is economically a more attractive way than the copolymerization from the standpoint of commercial applications.
- **BLENDS:** 1. Miscible; 2. Partially miscible; 3. Immiscible (Polymer A & B)

Viton



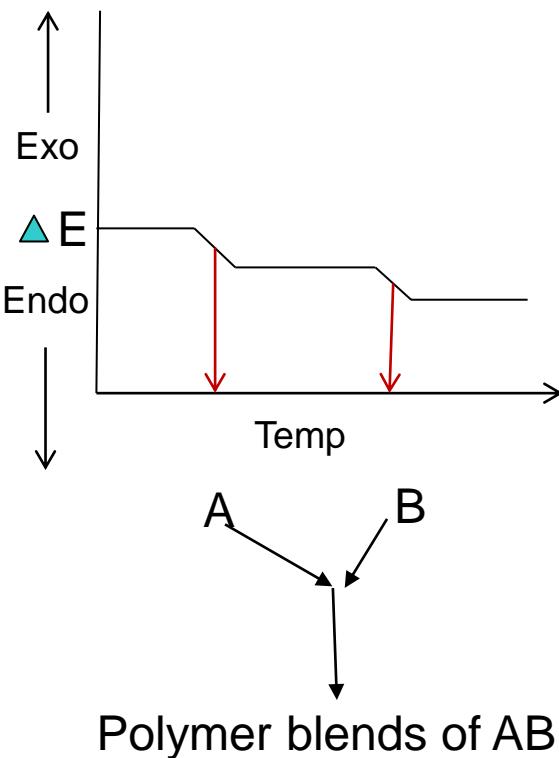
A

B

-(A)x-(B)y-

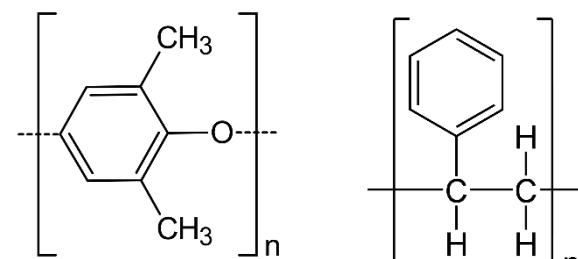
$$1/T_g = W_A/T_{gA} + W_B/T_{gB}$$

A (PPO) = 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100
B (PS) = 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0



2 Homopolymers, 9 copolymers

PPO, $T_g = 210 \text{ }^\circ\text{C}$
PS, $T_g = 100 \text{ }^\circ\text{C}$



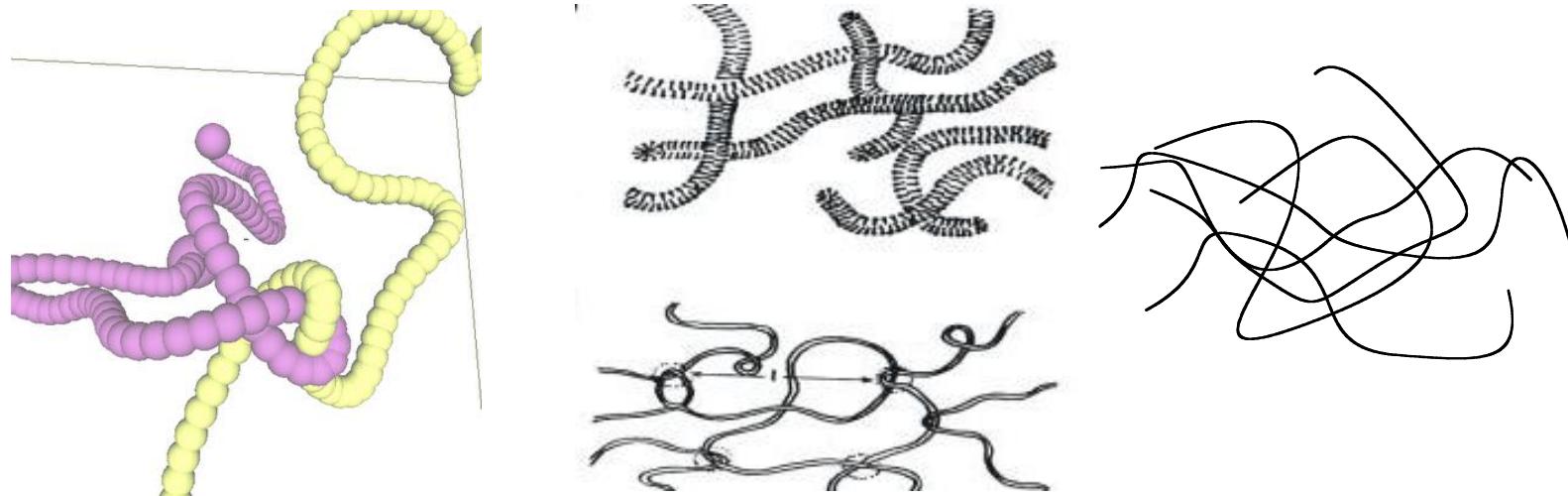
Calculate cohesive energy density by group contribution methods (Bondi)

By measuring the T_g of the blends (DSC)

What makes polymers different

1. Can bend and twist and get all tangled up

- Chain entanglement: Long polymer chains get entangled with each other. The longer a polymer chain is, the more tangled up it can get.
- Since the chains are harder to pull out or separate, that can make things made out of polymers stronger.
- When the polymer is melted (heated), the chains can flow past each other.
- Below the melting point, the chains can move, but only slowly. Thus the plastic is flexible, but cannot be easily stretched.
- Below the glass transition point, the chains become locked and the polymer is rigid

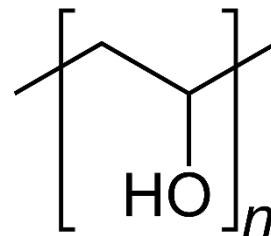


2. Polymer Chains Stick to Other Polymer Chains *(Summation of Intermolecular Forces):*

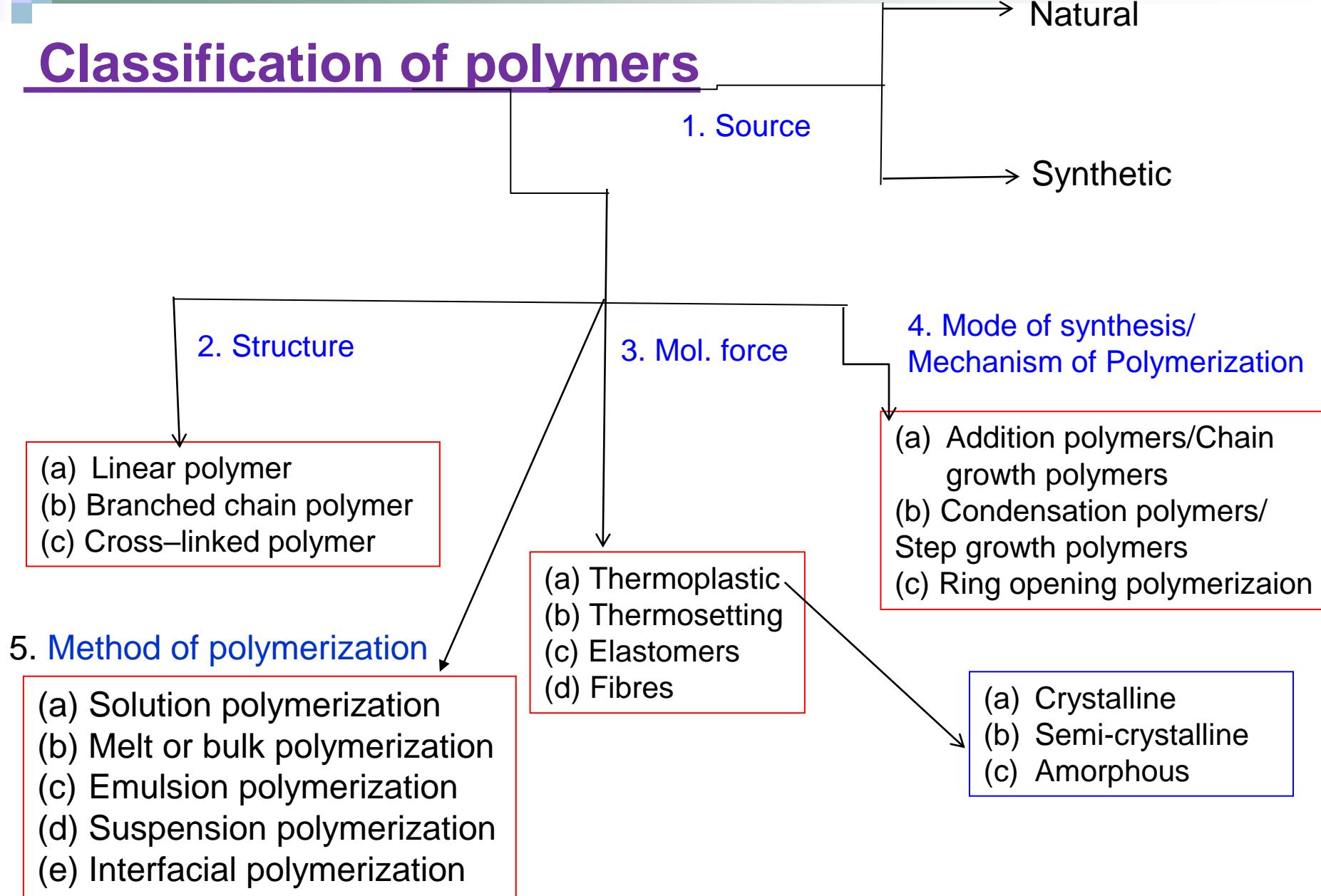
- Think of molecules as being like magnets. Some are like very weak magnets, and some are like strong magnets. So, some can be pulled apart easily, but others take a lot more energy to pull them apart.
- Polymer chains are like this too, but remember that they're much much longer than molecules. When the chains stick together very strongly, it can be really tough to pull them apart.
- If the chains happen to be straight and stiff and all lined up next to each other, it can be REALLY hard to pull them apart. A great example is cellulose in wood. The chains lay next to each other, straight and sticky (like strong magnets). That makes trees (and lots of houses!) strong and tall.

3. Polymer Chains Move Slower than Molecules (Time Scale of Motion)

- We can see what happens when polymers dissolve in a liquid. Those long chains move around so slowly that they make the solution flow much slower. The longer the chains, the slower the flow.
- If we measure how long it takes for a polymer solution to flow through a special tube, we can learn more about how big the polymer chains are.
- By the way, the longer it takes to flow, the more *viscous* (viss-cuss) it is, polymer enhances the viscosity of the medium

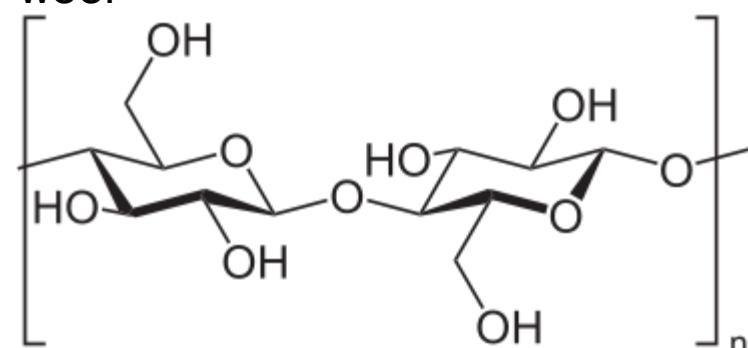
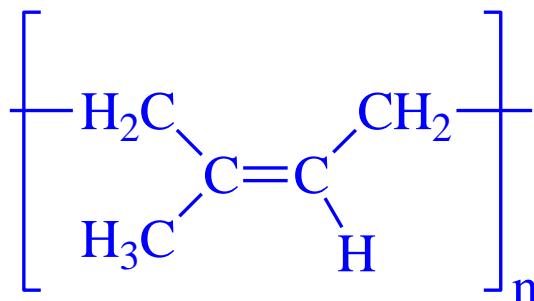


Classification of polymers

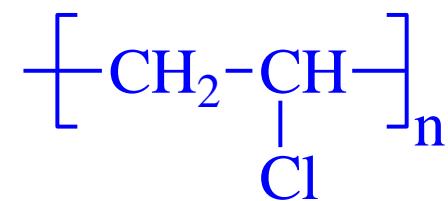
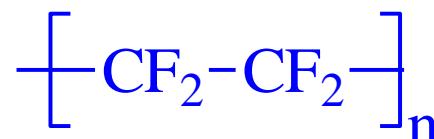
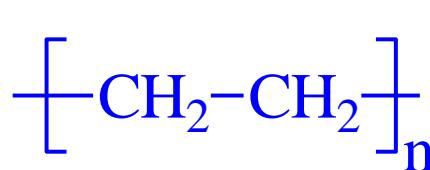


1) Based on the source

- a) Natural polymers: The polymers obtained from nature (plants and animals) are called Natural polymers. Ex. Starch, cellulose, Natural rubbers, proteins, Nucleic acid (DNA, RNA), cotton, silk, wool

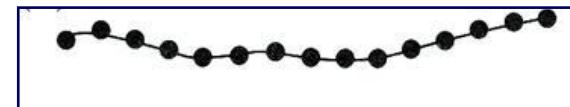
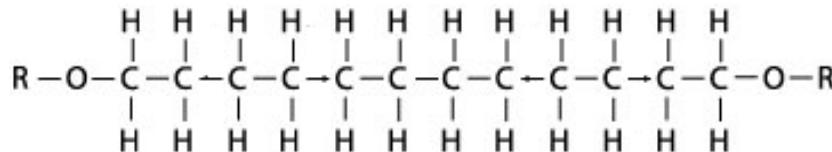


- b) Synthetic polymers: The polymers which are prepared in the laboratories are called synthetic polymers E.g. Polyethylene, polyvinylchloride (pvc), Nylon, Teflon, Bakelite, Terylene etc

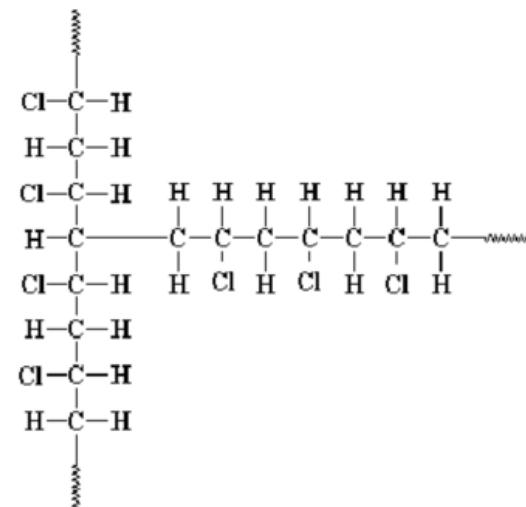
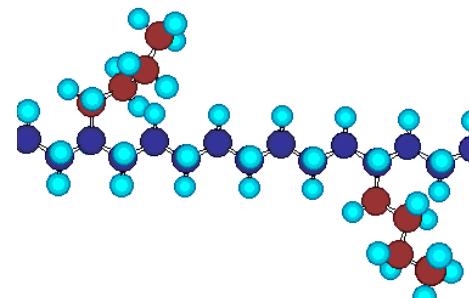
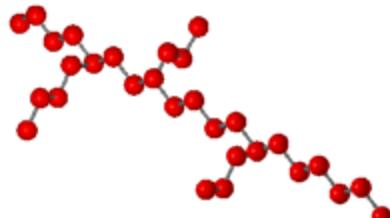


2) Based on the structure

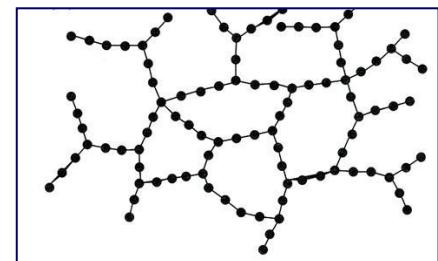
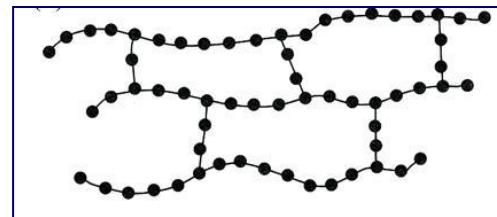
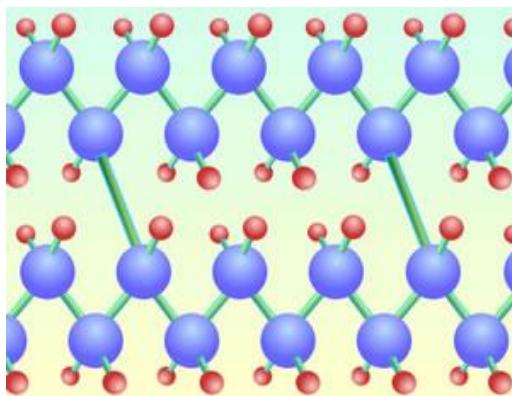
a) Linear polymer : In linear polymer the monomeric units are linked together to form linear chain. E.g. Polyethylene (HDPE), Nylon, polyester etc.



(b) Branched chain polymer : In branched chain polymers the monomeric units are joined to form long chains with side chains (or) Branches of different length. E.g. Glycogen, starch, L.D.P.E. etc



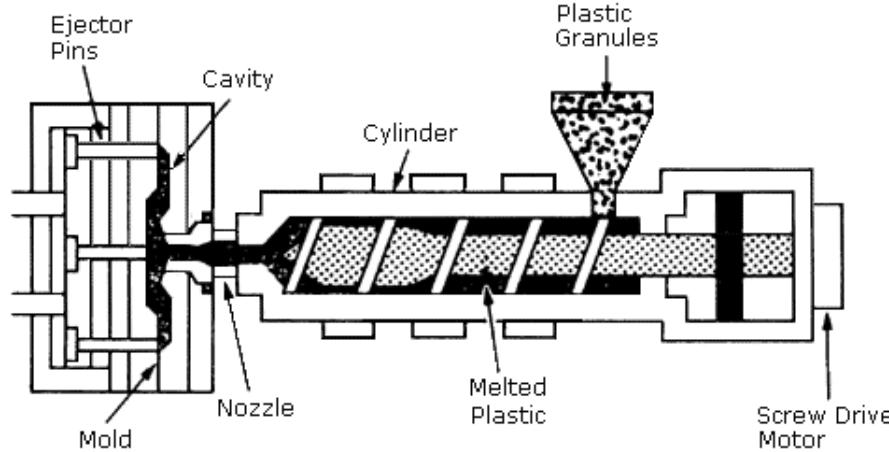
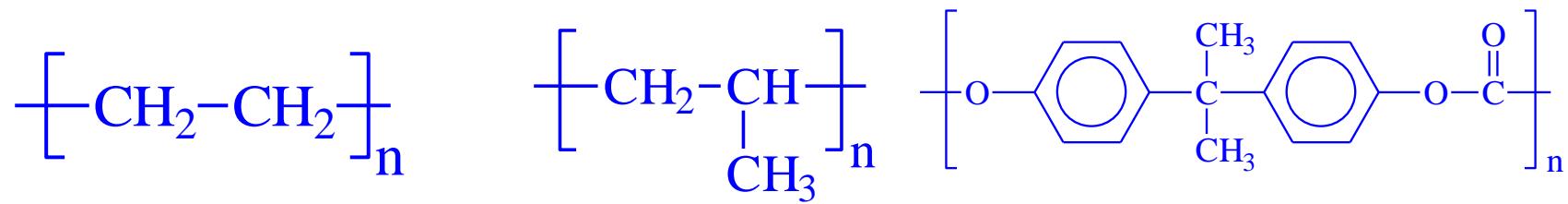
(c) Cross-linked polymer: In cross linked polymers the monomer units are cross linked together to form a three dimensional Network. E.g. Bakelite, melamine-formaldehyde Resin polystyrene-Butadiene.



3) Based on the molecular forces

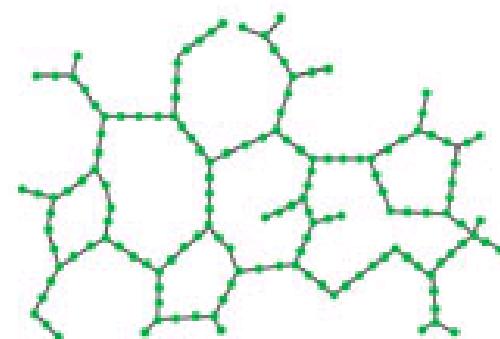
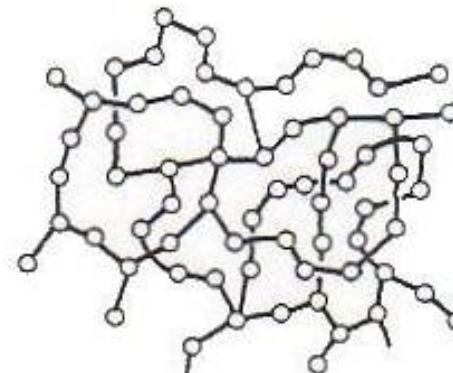
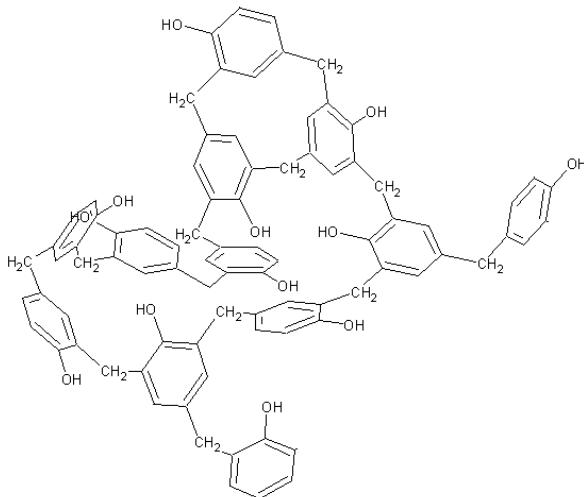
- a) Thermoplastic : Thermoplastics are the polymers which soften on heating and harden on cooling reversibly. E.g. Polyethylene, polystyrene, pvc, Teflon, Nylon, sealing wax.

Linear or branched polymers which can be melted when heat is applied. Can be molded into any shape with processing techniques such as injection molding or extrusion.



b) Thermosetting: Thermosetting plastics are the polymers which undergo permanent change on heating(irreversible) E.g. Bakelite, Polyester, Polysiloxanes.

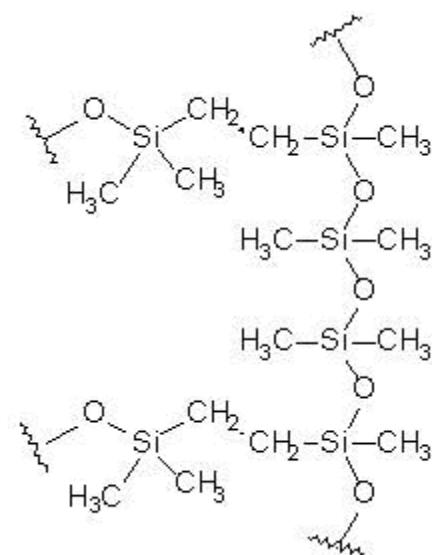
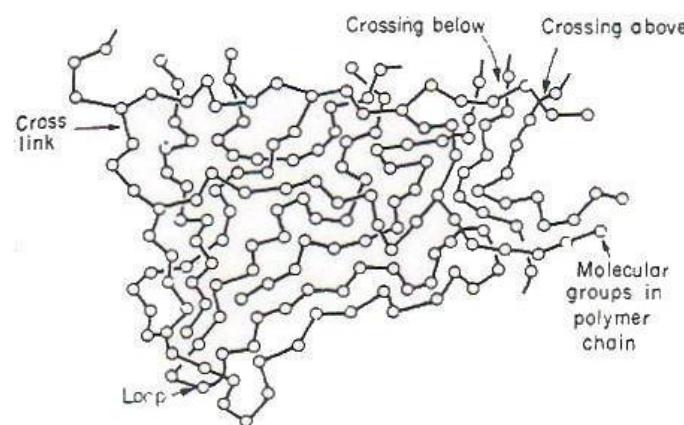
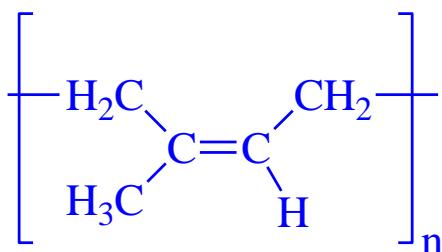
- Normally are rigid materials.
- Network polymers in which chain motion is greatly restricted by a high degree of crosslinking.
- Cannot be reshaped once formed



Crosslinked (Networked) – chains are connected to other chains

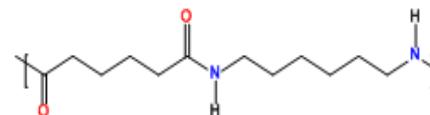
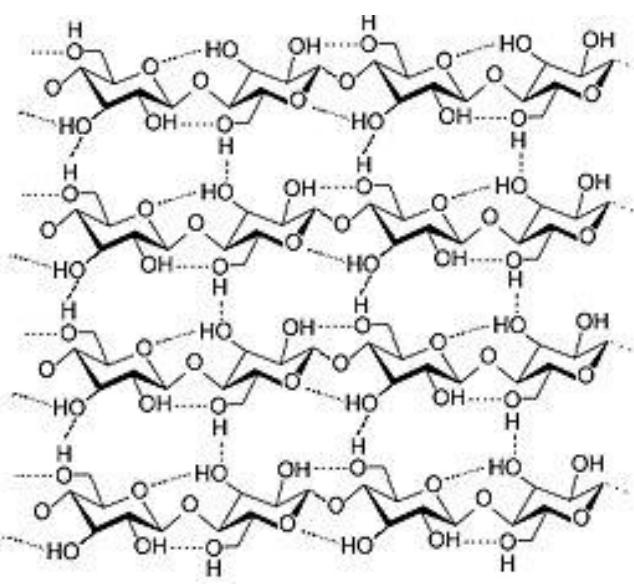
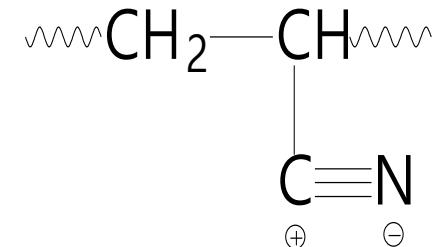
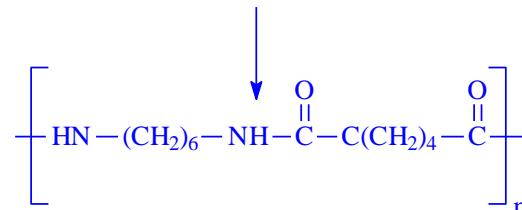
c) Elastomers: Elastomers are the polymers which posses elastic character.
E.g. Natural rubber

- Crosslinked (networked) rubbery polymers that can be stretched easily (3-10x original size)
- Rapidly recover original dimensions when applied stress is released.
- Low degree of crosslinking

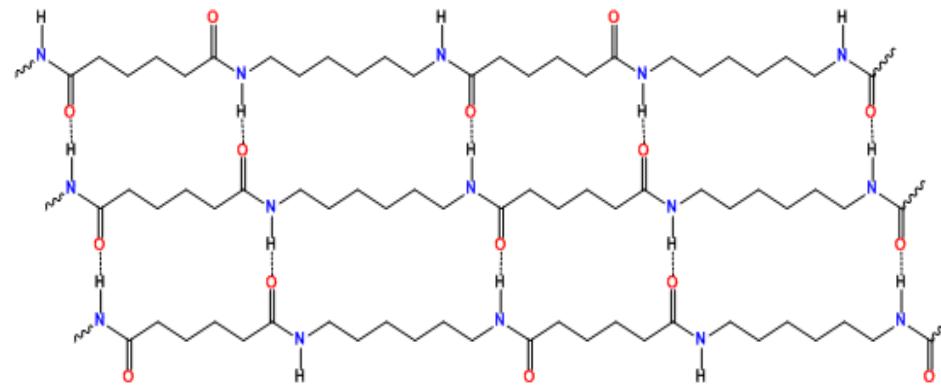


Amorphous Polymer – Lightly Crosslinked

d) Fibres: Fibres are polymers in which the chains are held by intermolecular forces like H–bond, Dipole–dipole interaction. E.g. Nylon, poly Acrylonitrile

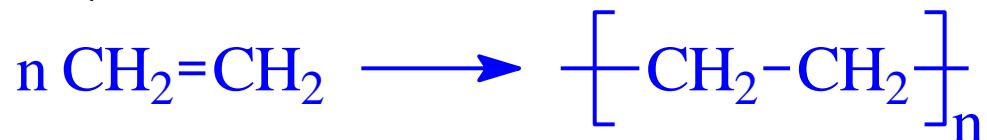


Repeating Unit
Nylon 6,6

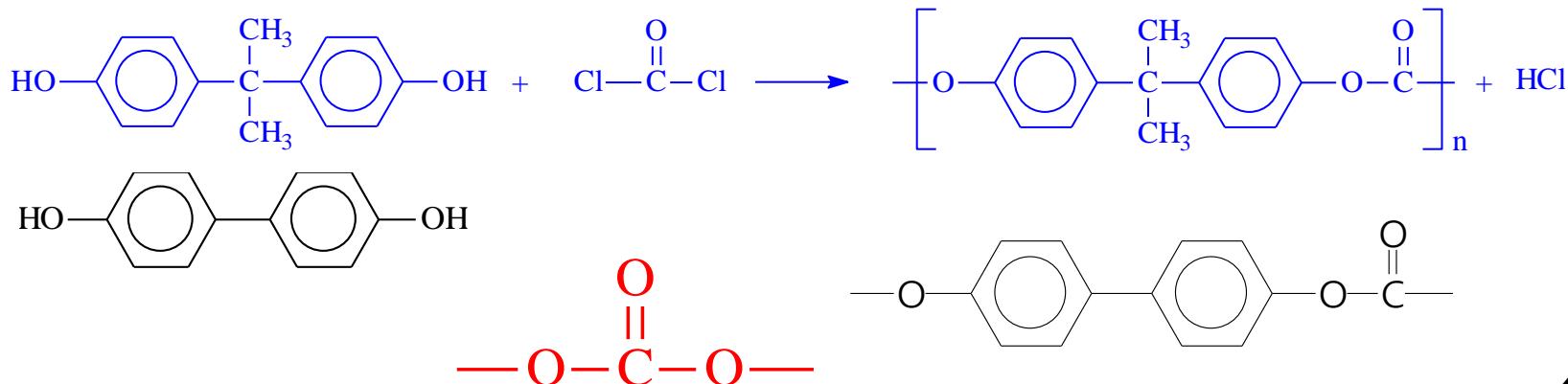


4) Based on the mode of synthesis (mechanism of formation)

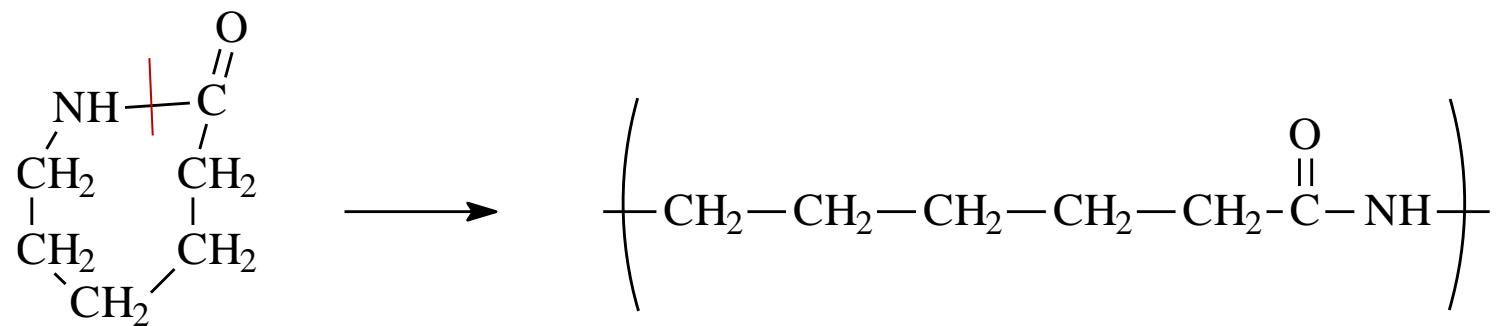
a) Addition polymers : A polymer formed by direct addition of repeated monomer without the elimination of by product molecules are called Addition polymer. E.g. Polyethylene, polypropylene, pvc, Teflon, orlun, Neoprene, pvp (polyvinyl pyrrolidone)



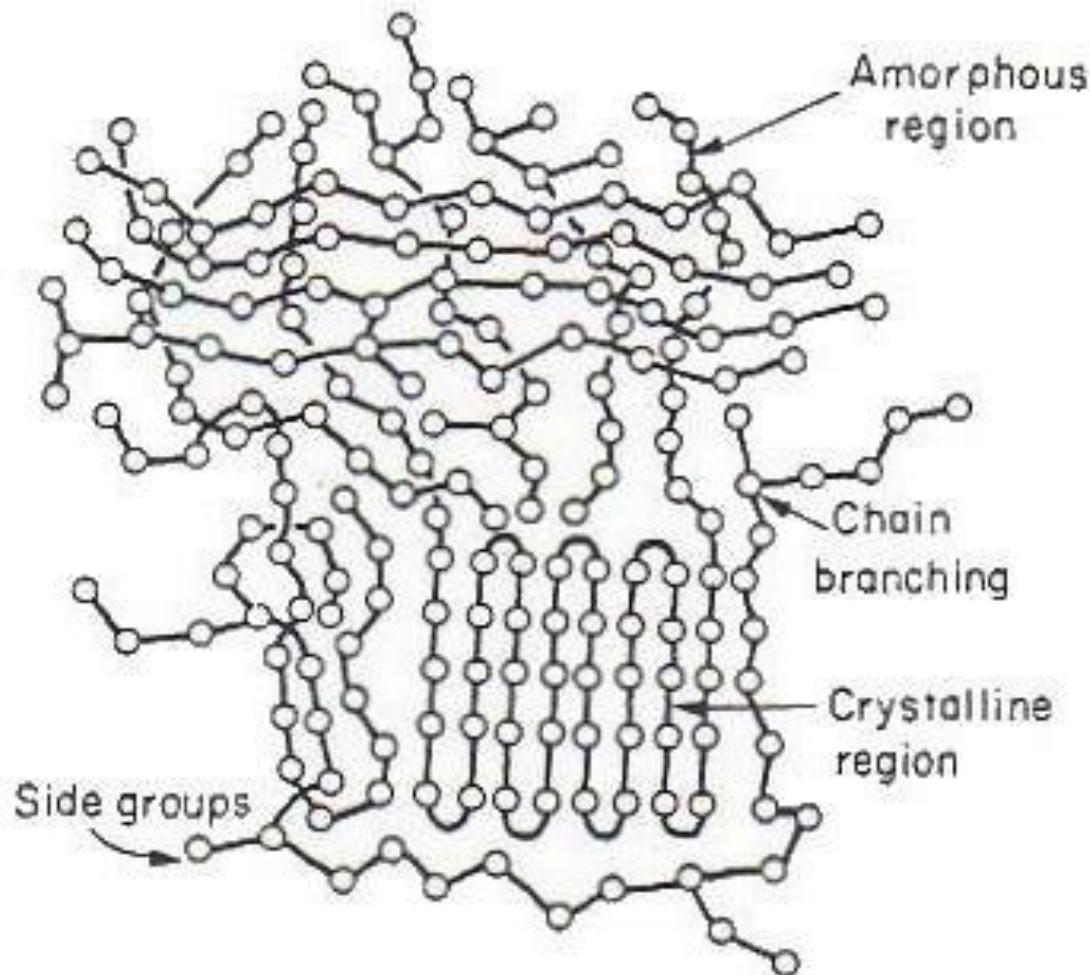
b) Condensation polymers: A polymer formed by the condensation of two (or) more monomers with the elimination of simple molecule like H_2O , NH_3 , HCl , alcohol etc. are called condensation polymer. E.g. Polyester, Nylon 6,6, Bakelite, Polycarbonate



ROP

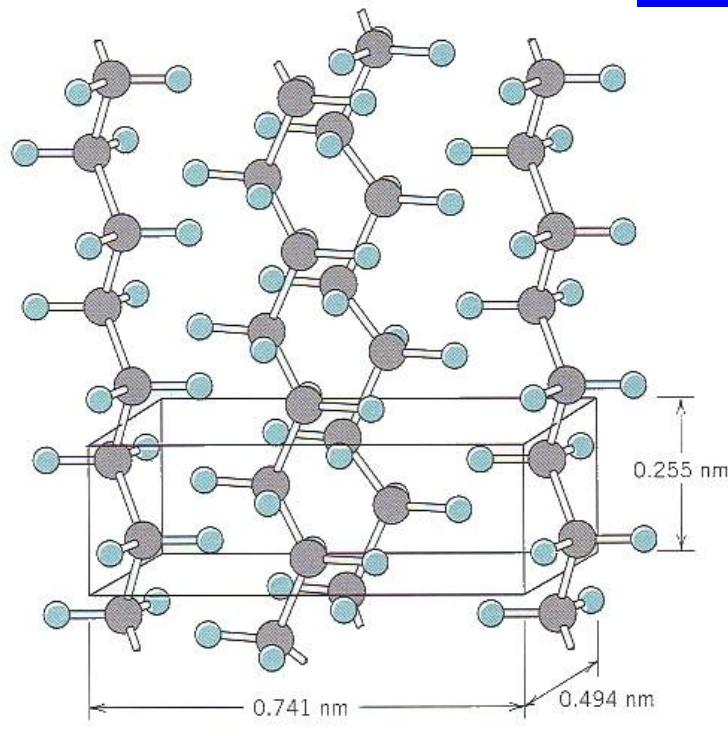
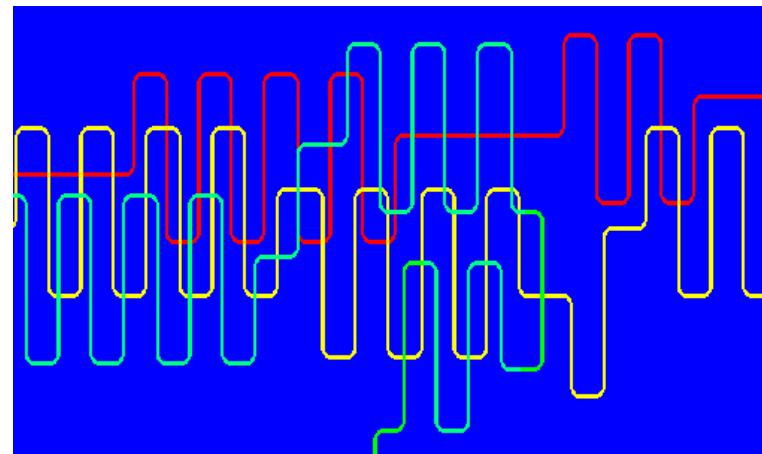


Semicrystalline Thermoplastic

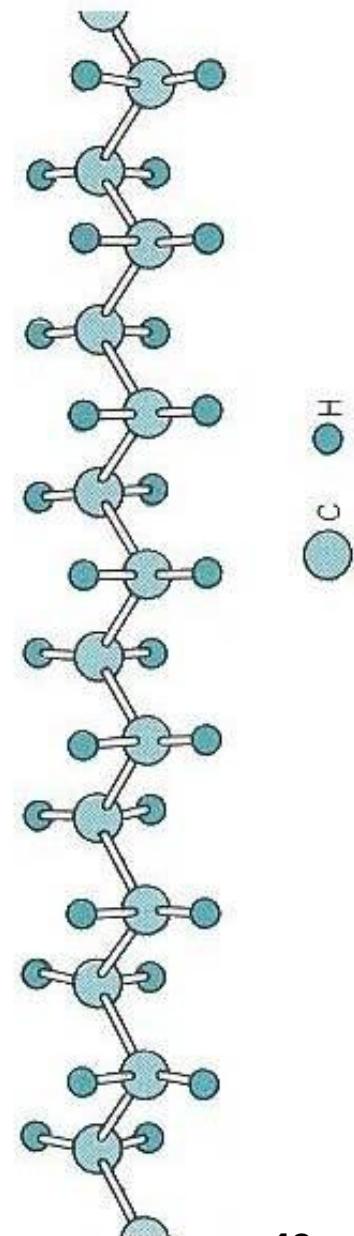


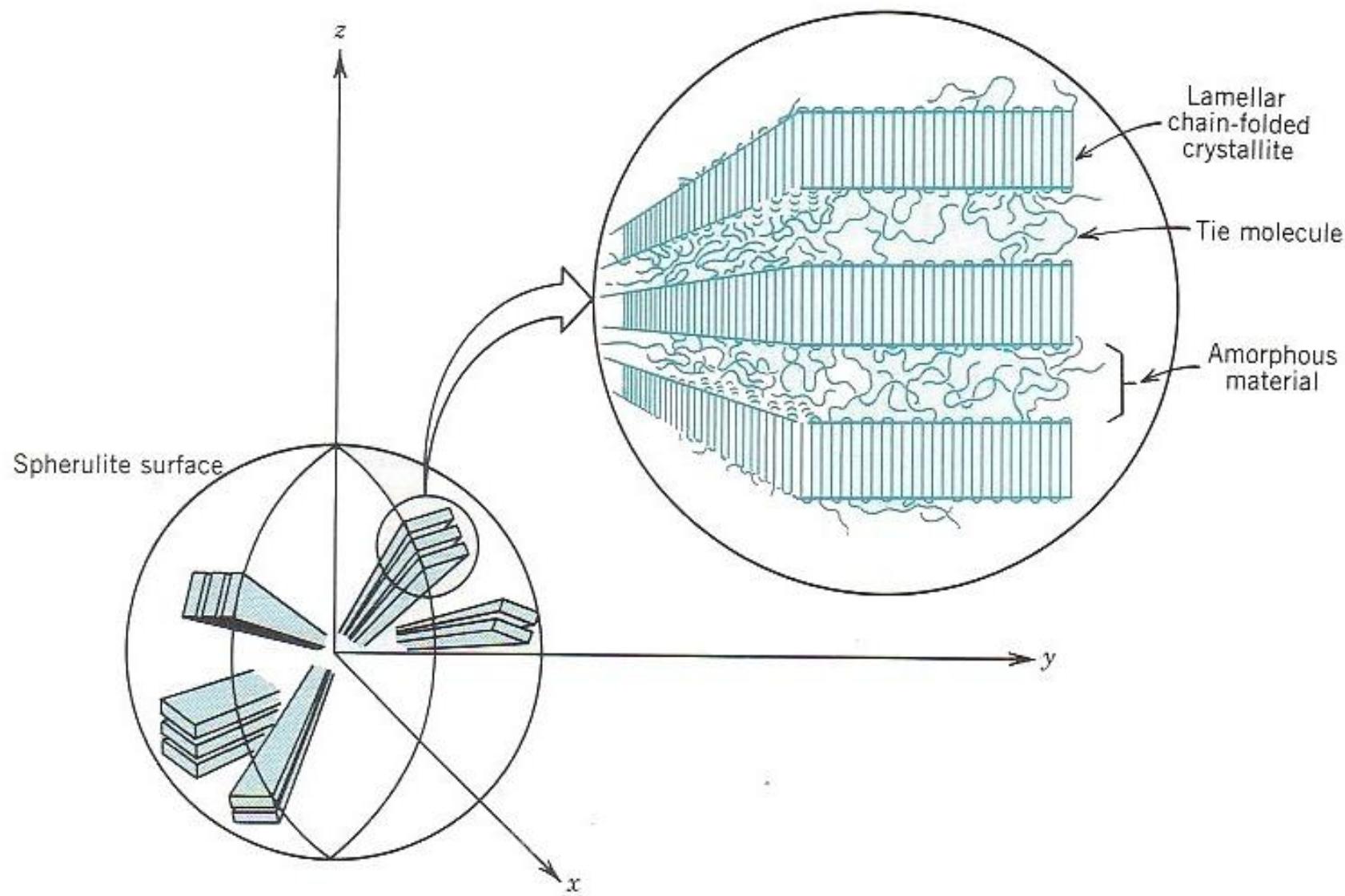
Crystalline

Example: Polyethylene



● C ● H

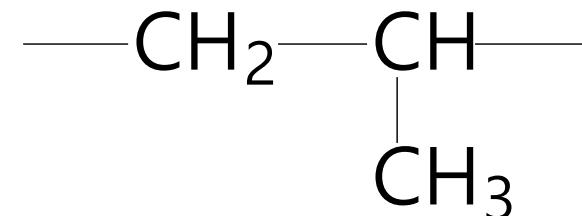
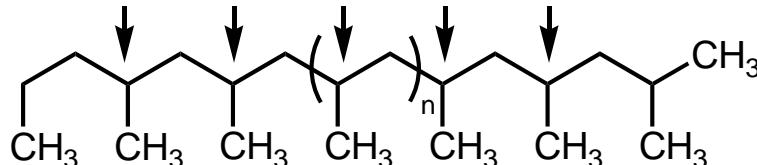




Polymer Microstructure

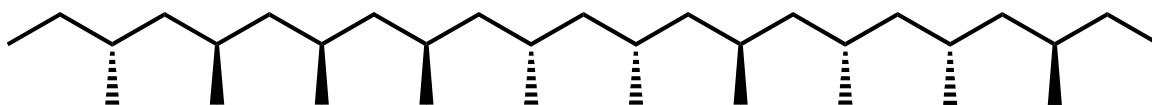


Polyolefins with side chains have stereocenters on every other carbon



With so many stereocenters, the stereochemistry can be complex. There are three main stereochemical classifications for polymers.

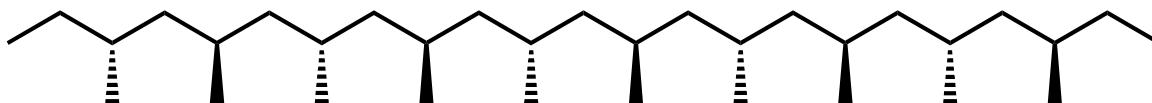
Atactic: random orientation

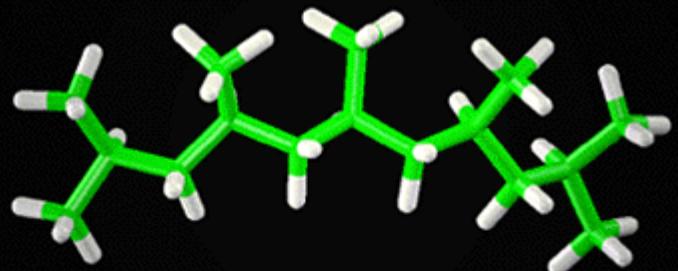
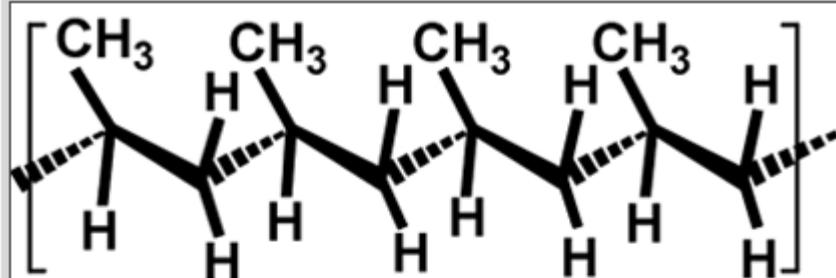


Isotactic: All stereocenters have same orientation

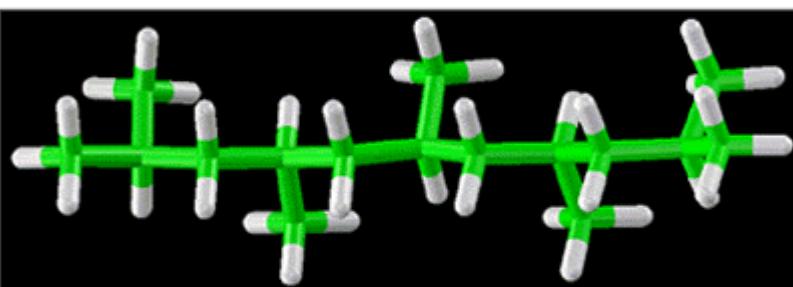
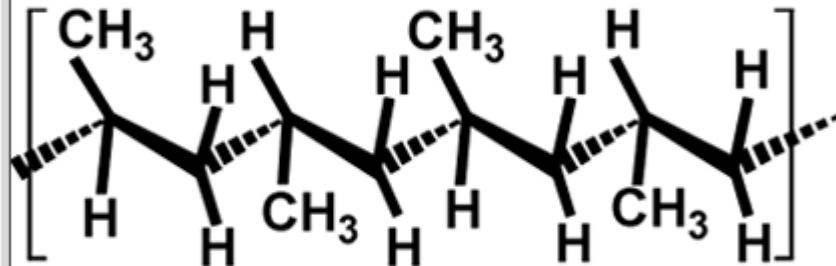


Syndiotactic: Alternating stereochemistry

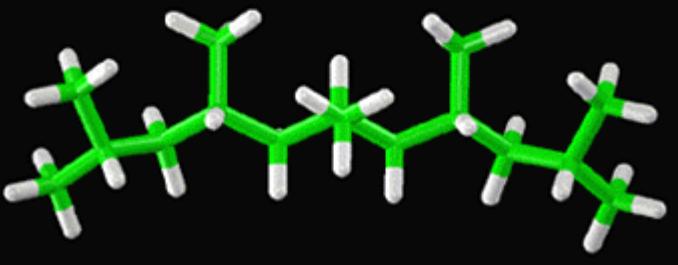
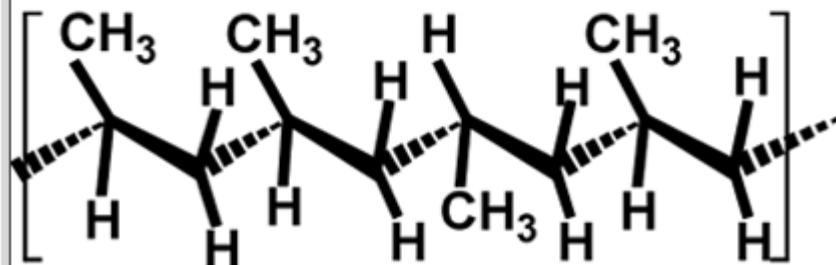




isotactic



syndiotactic



atactic

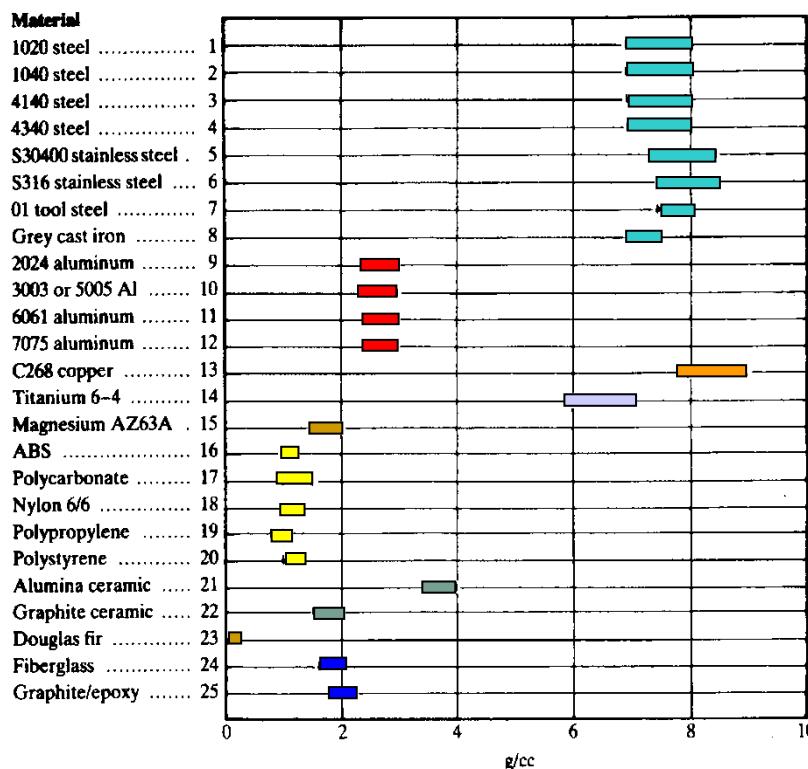


Why is this important?

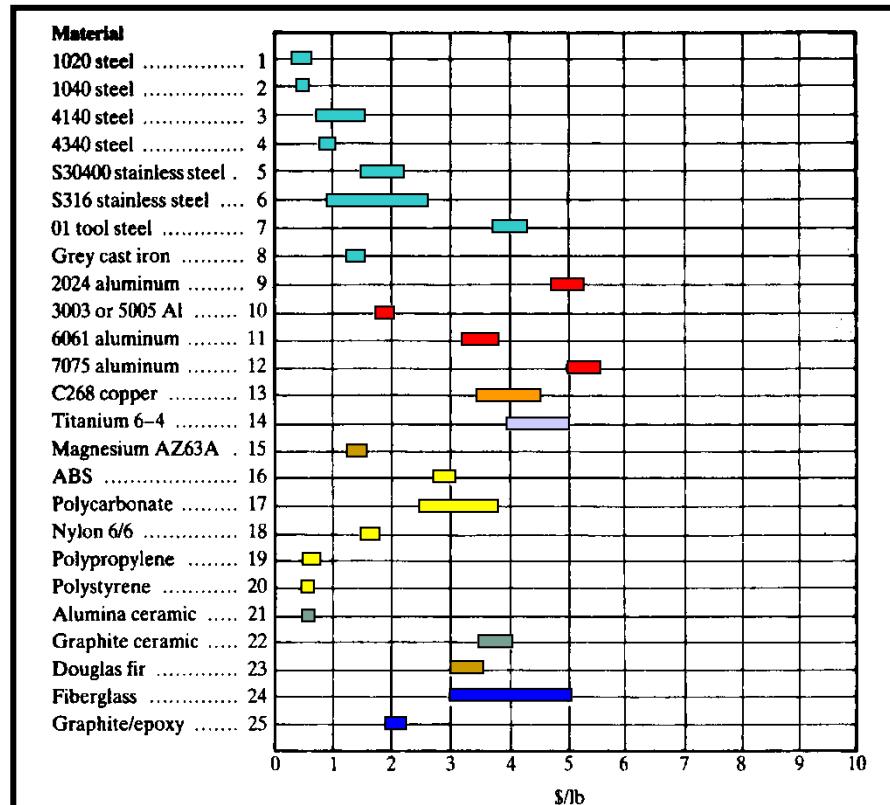
- Tacticity affects the physical properties
 - Atactic polymers will generally be amorphous, soft, flexible materials
 - Isotactic and syndiotactic polymers will be more crystalline, thus harder and less flexible
- Polypropylene (PP) is a good example
 - Atactic PP is a low T_g , gooey material
 - Isoatactic PP is high melting (176°), crystalline, tough material that is industrially useful
 - Syndiotactic PP has similar properties, but is very clear. It is harder to synthesize

Why Design with Polymers?

- Light weight, high strength to weight ratio, particularly when reinforced
- Relatively low cost compared to metals and composites



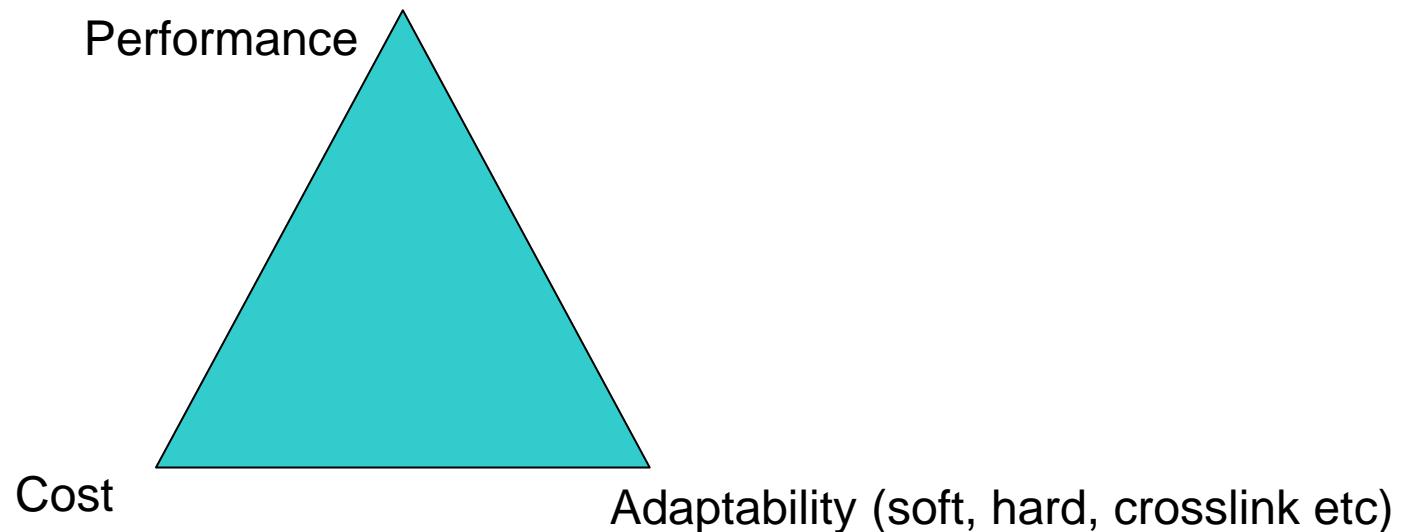
Density



Cost

Why Design with Polymers?

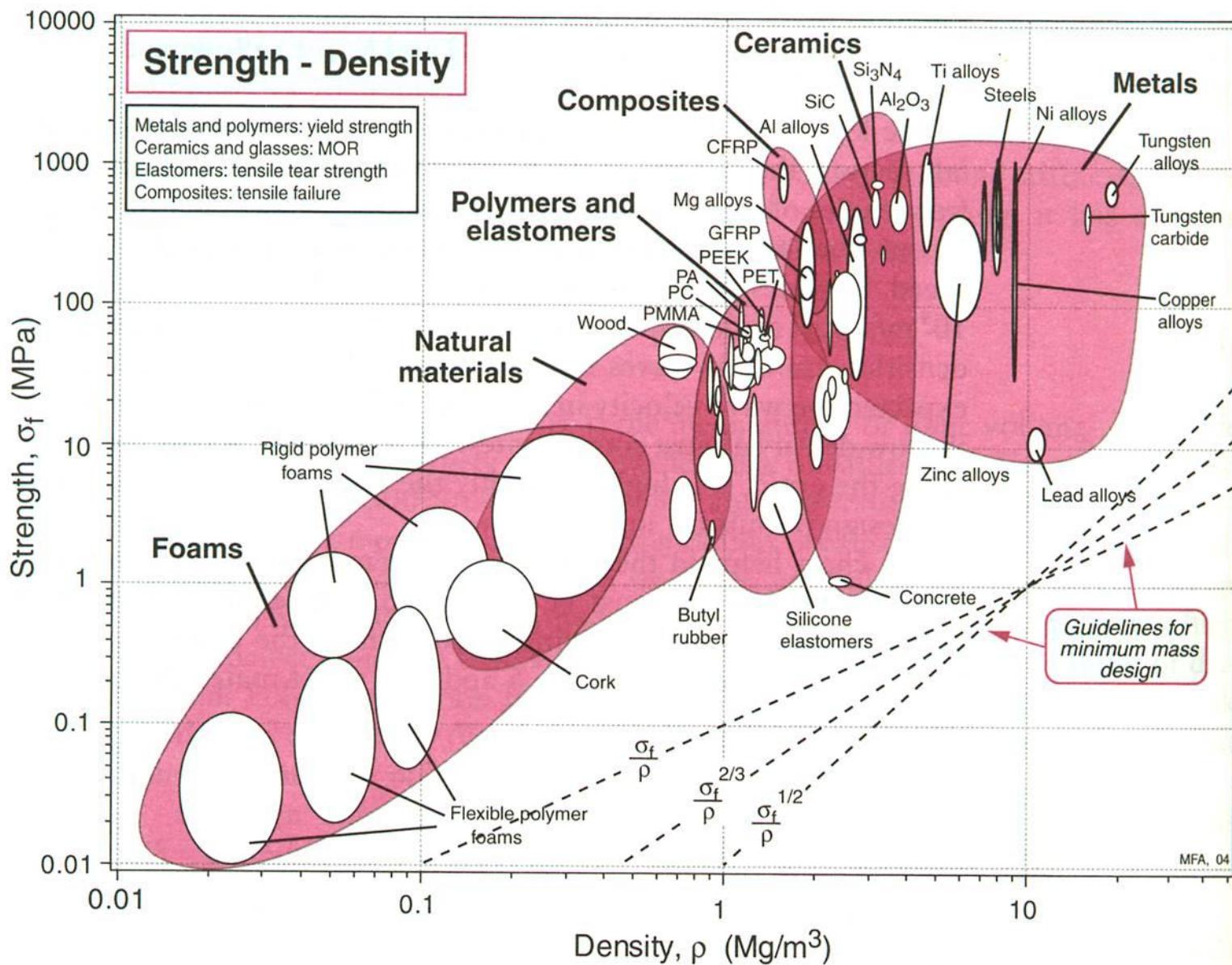
- Corrosion resistance
- Low electrical and thermal conductivity, insulator
- Easily formed into complex shapes, can be formed, casted and joined.
- Wide choice of appearance, colors and transparencies





Disadvantages of using Polymers

- Low strength
- Low useful temperature range (up to 600 °F)
- Less dimensional stability over period of time (creep effect)
- Aging effect, hardens and become brittle over time
- Sensitive to environment, moisture and chemicals
- Poor machinability



Mechanical Properties of Various Plastics

Material	UTS (MPa)	E (GPa)	Elongation (%)	Poisson's ratio (ν)
ABS	28–55	1.4–2.8	75–5	—
ABS, reinforced	100	7.5	—	0.35
Acetal	55–70	1.4–3.5	75–25	—
Acetal, reinforced	135	10	—	0.35–0.40
Acrylic	40–75	1.4–3.5	50–5	—
Cellulosic	10–48	0.4–1.4	100–5	—
Epoxy	35–140	3.5–17	10–1	—
Epoxy, reinforced	70–1400	21–52	4–2	—
Fluorocarbon	7–48	0.7–2	300–100	0.46–0.48
Nylon	55–83	1.4–2.8	200–60	0.32–0.40
Nylon, reinforced	70–210	2–10	10–1	—
Phenolic	28–70	2.8–21	2–0	—
Polycarbonate	55–70	2.5–3	125–10	0.38
Polycarbonate, reinforced	110	6	6–4	—
Polyester	55	2	300–5	0.38
Polyester, reinforced	110–160	8.3–12	3–1	—
Polyethylene	7–40	0.1–1.4	1000–15	0.46
Polypropylene	20–35	0.7–1.2	500–10	—
Polypropylene, reinforced	40–100	3.5–6	4–2	—
Polystyrene	14–83	1.4–4	60–1	0.35
Polyvinyl chloride	7–55	0.014–4	450–40	—

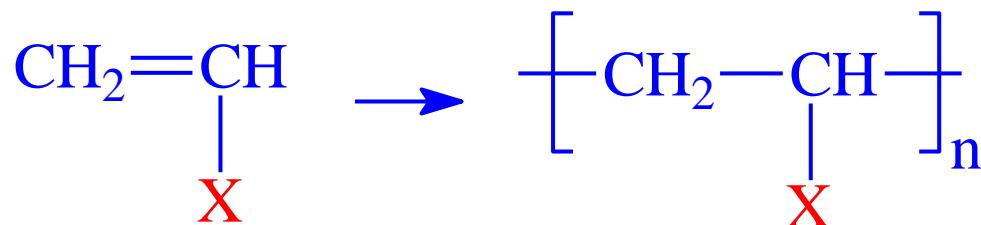
Steel: 350 to 1900 MPa Brass: 200 to 850 MPa Aluminum: 100 to 550 MPa

Polymer Synthesis

- There are two major classes of polymer formation mechanisms
 - Addition polymerization: The polymer grows by sequential addition of monomers to a reactive site
 - Chain growth is linear
 - Maximum molecular weight is obtained early in the reaction
 - Step-Growth polymerization: Monomers react together to make small oligomers. Small oligomers make bigger ones, and big oligomers react to give polymers.
 - Chain growth is exponential
 - Maximum molecular weight is obtained late in the reaction

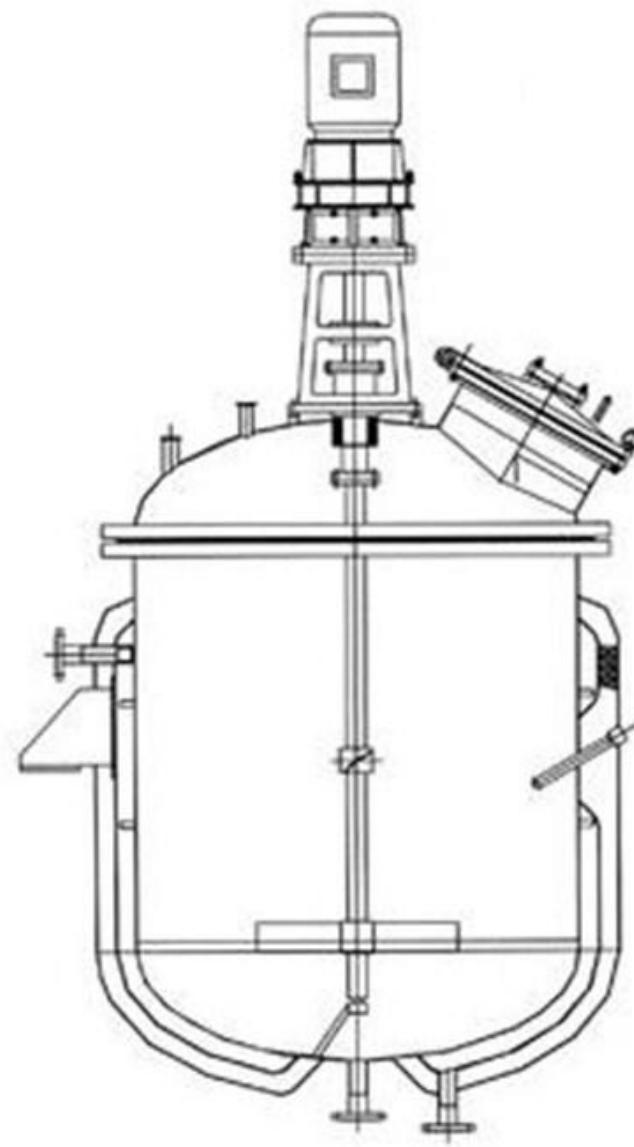
Polyaddition

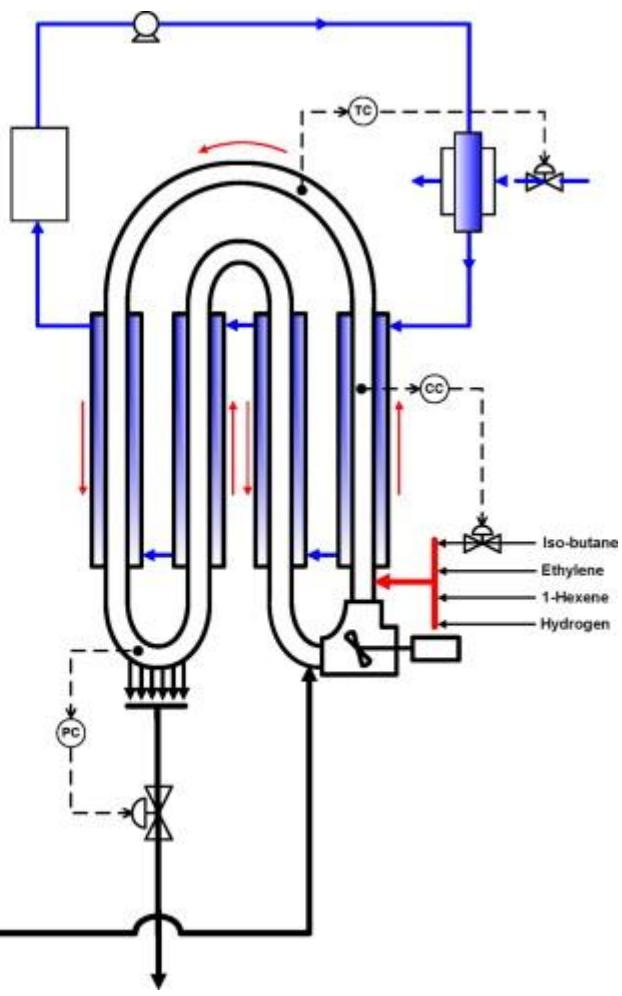
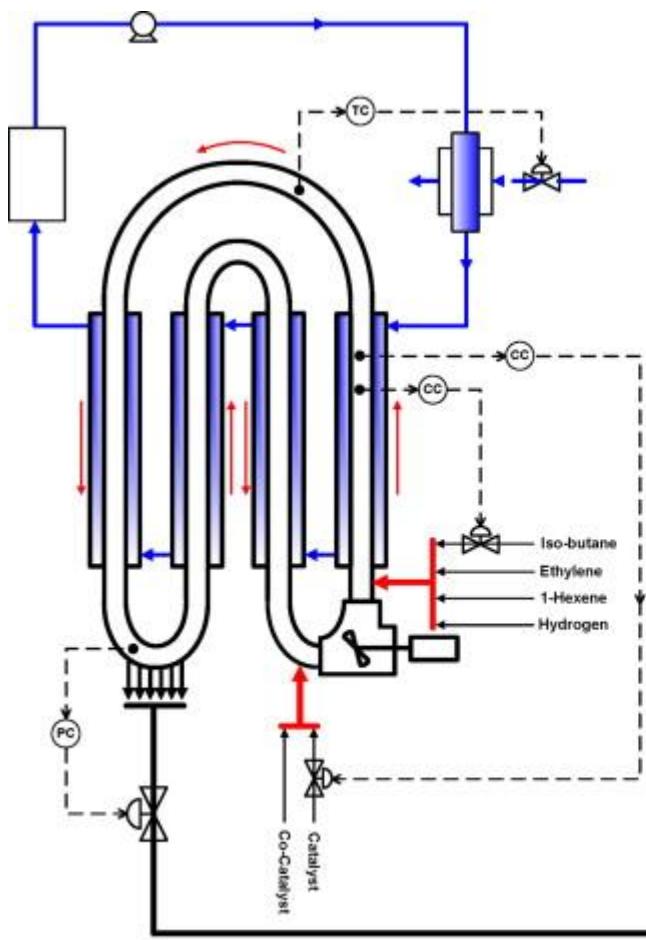
- Reactions in which monomers combine without the elimination of a small molecule.



$\text{X} = \text{H}, \text{CH}_3, \text{Cl}, \text{CN}, \text{Ph}, \text{COOCH}_3, \text{COOH}$

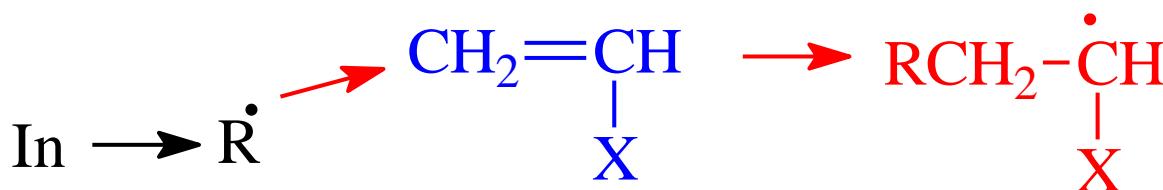
- Usually involves the breaking of a double bond.



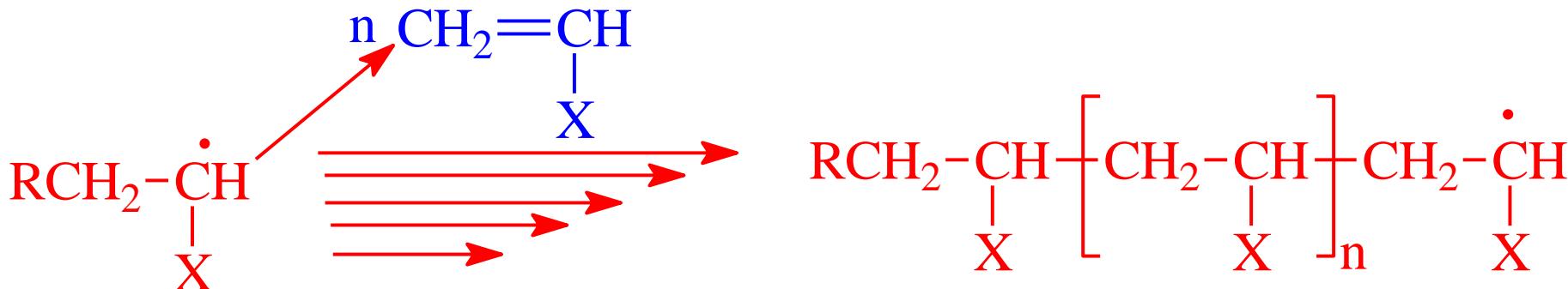


Polyaddition with Radicals

- Initiation – Creation of an active site (free radical).

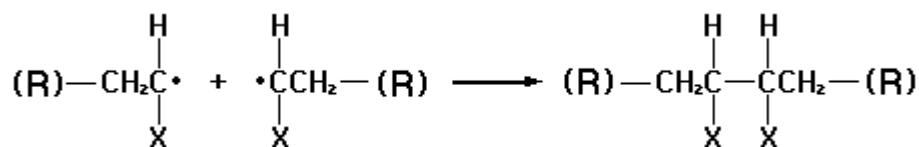


- Propagation – Growth of polymer chain by addition of a monomer to an active site and the creation of a new active site.

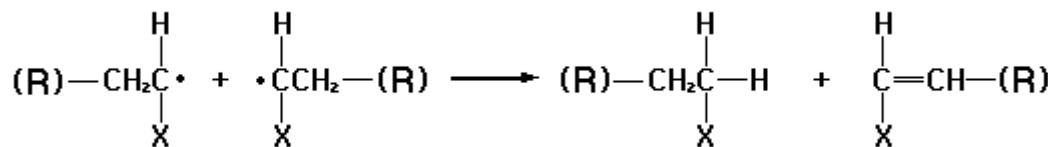


Polyaddition with Radicals

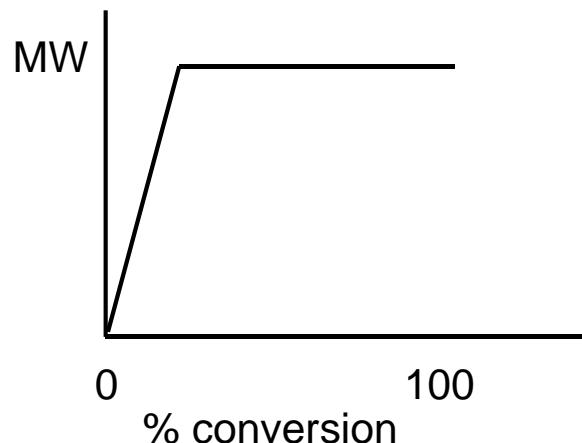
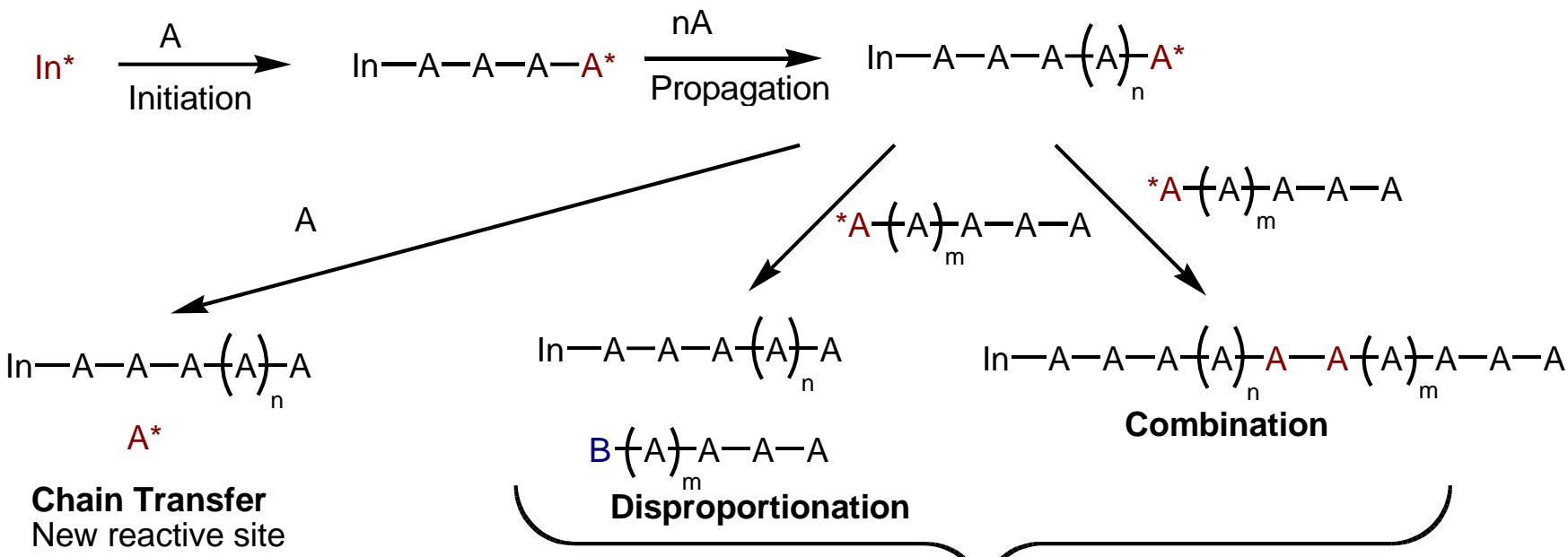
- Termination – Growth of chain stops.
 - Combination – Two growing chains collide.



- Disproportionation – A hydrogen atom is added to the end of a growing chain.



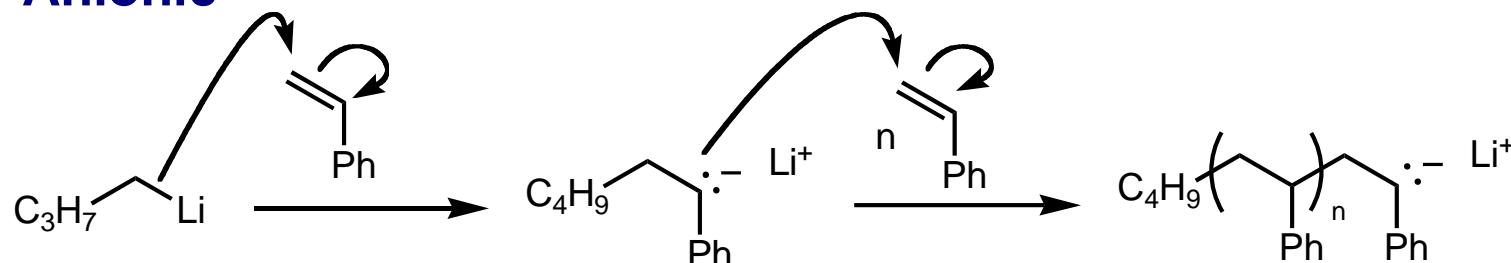
Addition Polymerization



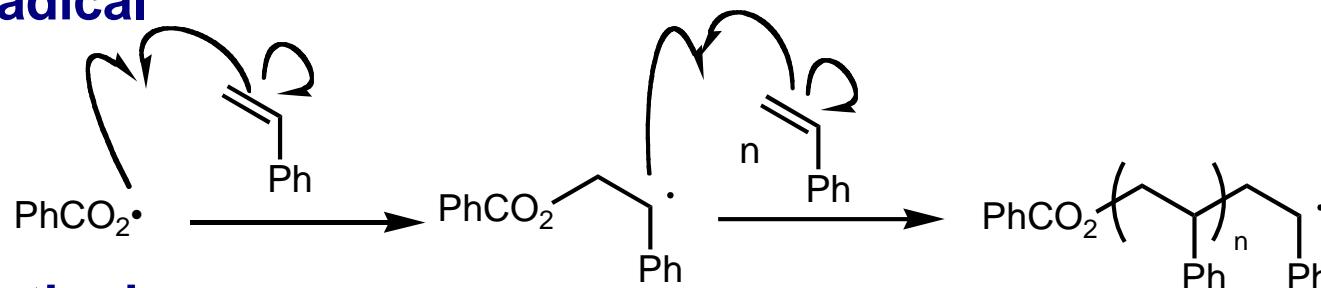
$$MW \propto \frac{k_{\text{propagation}}}{k_{\text{termination}}}$$

Types of Addition Polymerizations

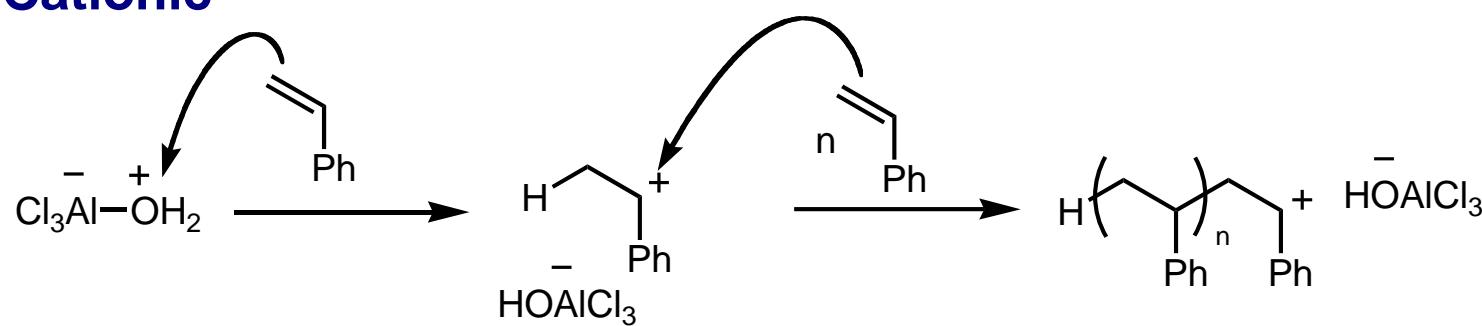
Anionic



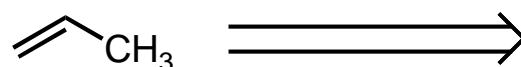
Radical



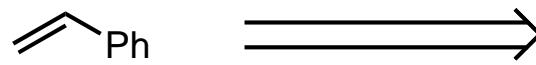
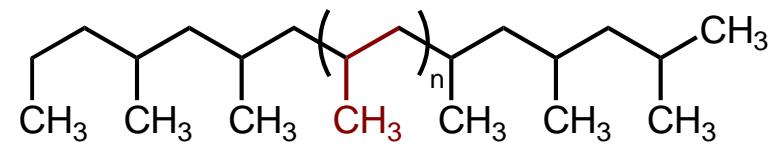
Cationic



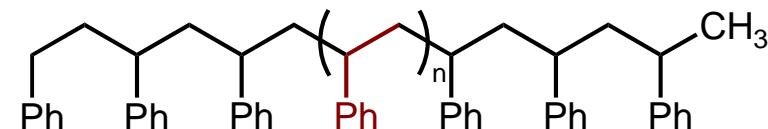
Common Polyolefins



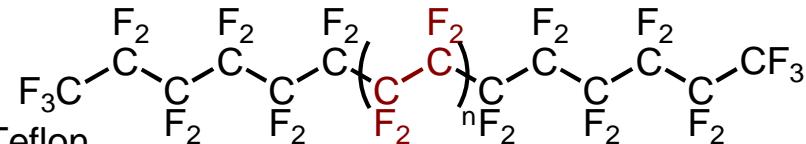
Propylene



Styrene

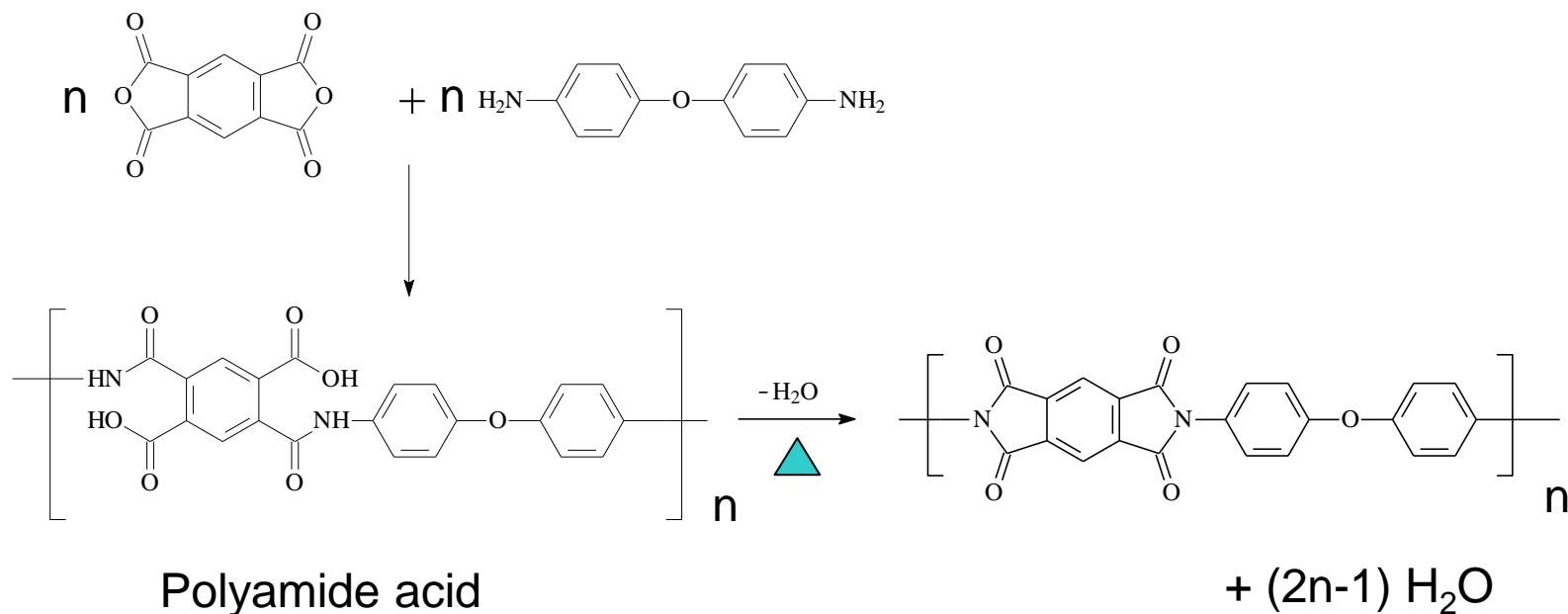


Tetrafluoroethylene



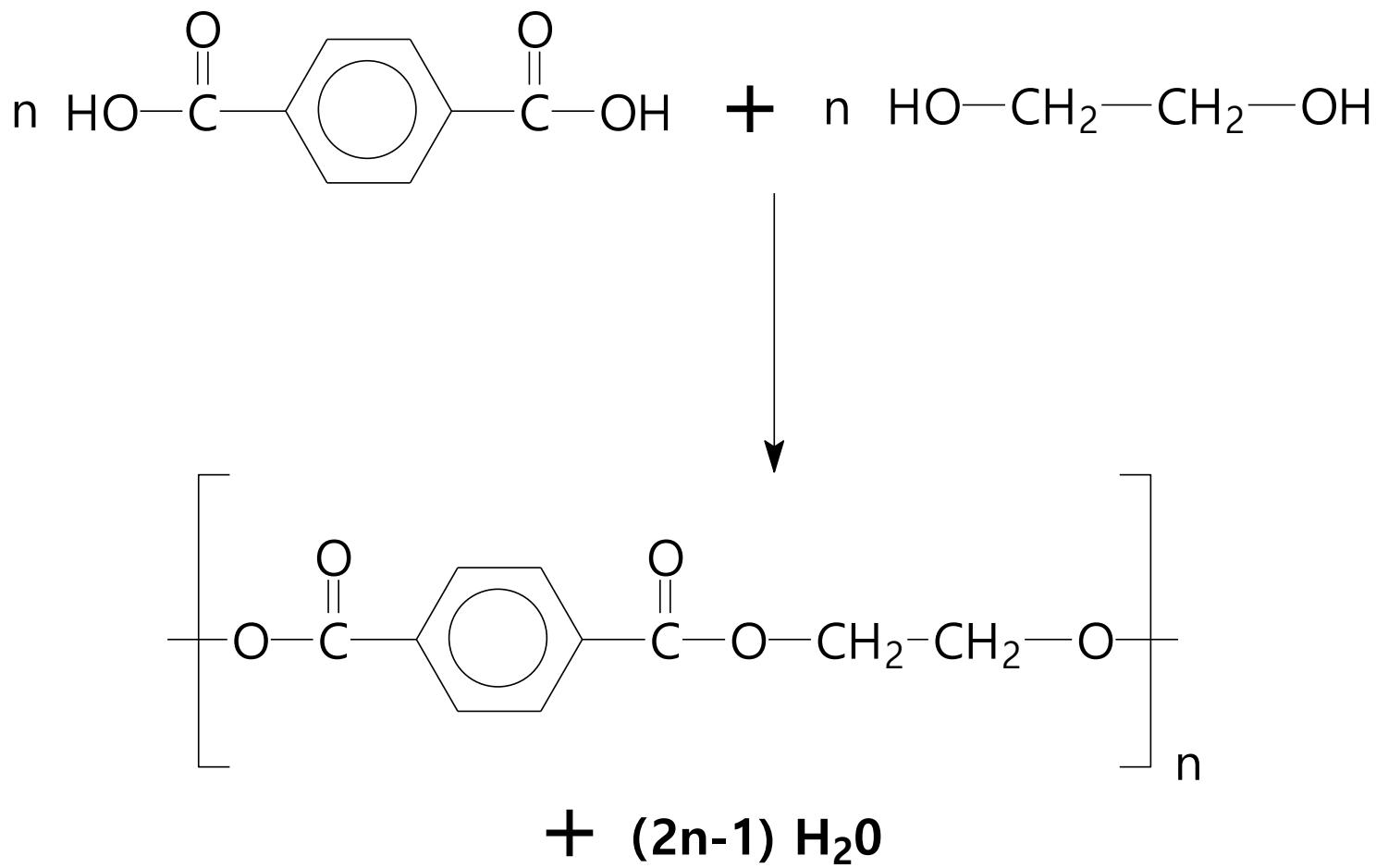
Polycondensation

- Reactions in which small molecules (H_2O , HCl) are eliminated when the monomers combine.

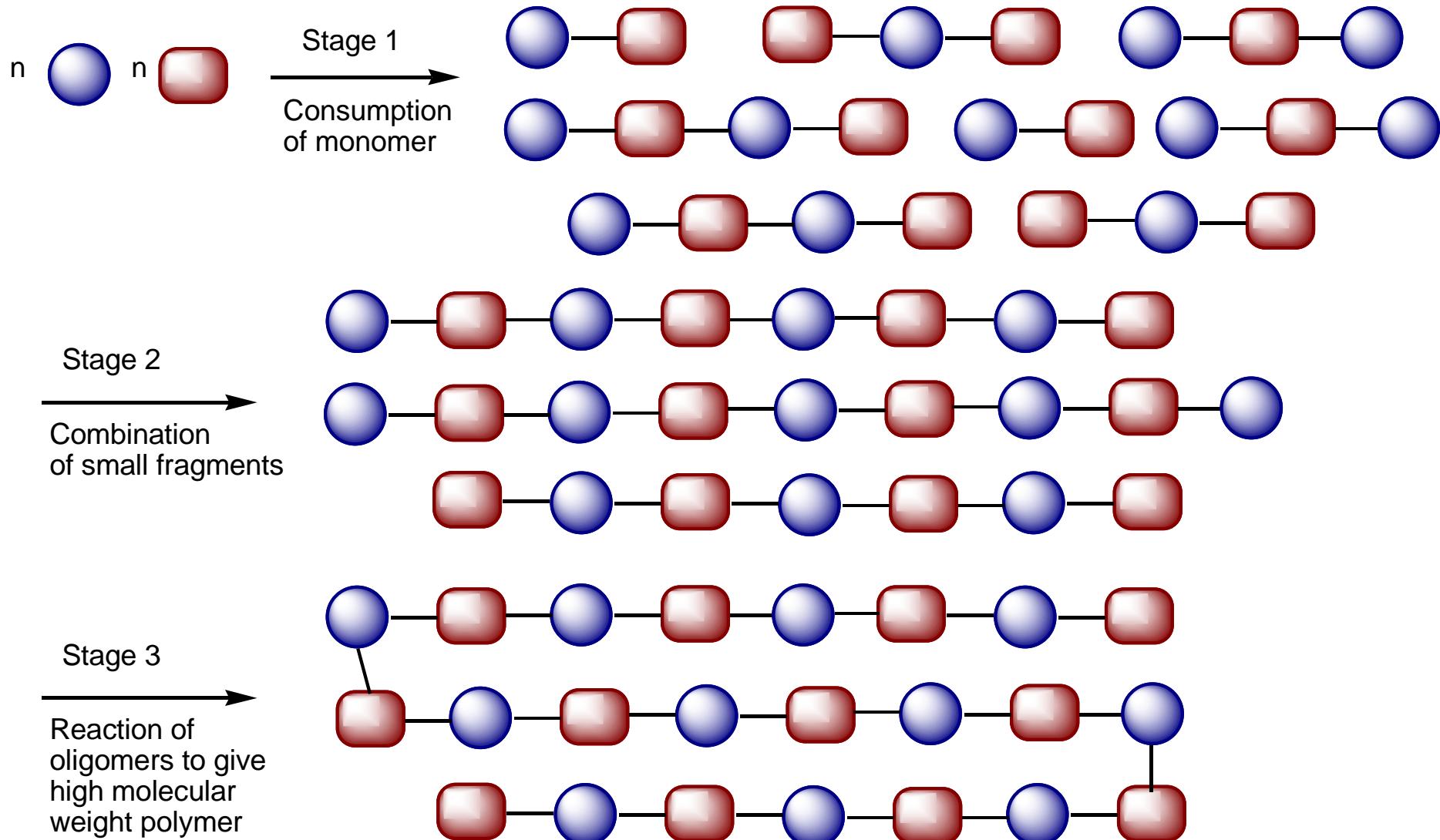


Principles of polymerization

Textbook by George G. Odian



Step-Growth Polymerization



Step-Growth Polymerization

- Because high polymer does not form until the end of the reaction, high molecular weight polymer is not obtained unless high conversion of monomer is achieved.

$$DP = (1+r)/(1+r-2rp)$$

$$\text{Where } r = N_A/N_B$$

If there is no stoichiometric

Imbalance; $N_A = N_B$

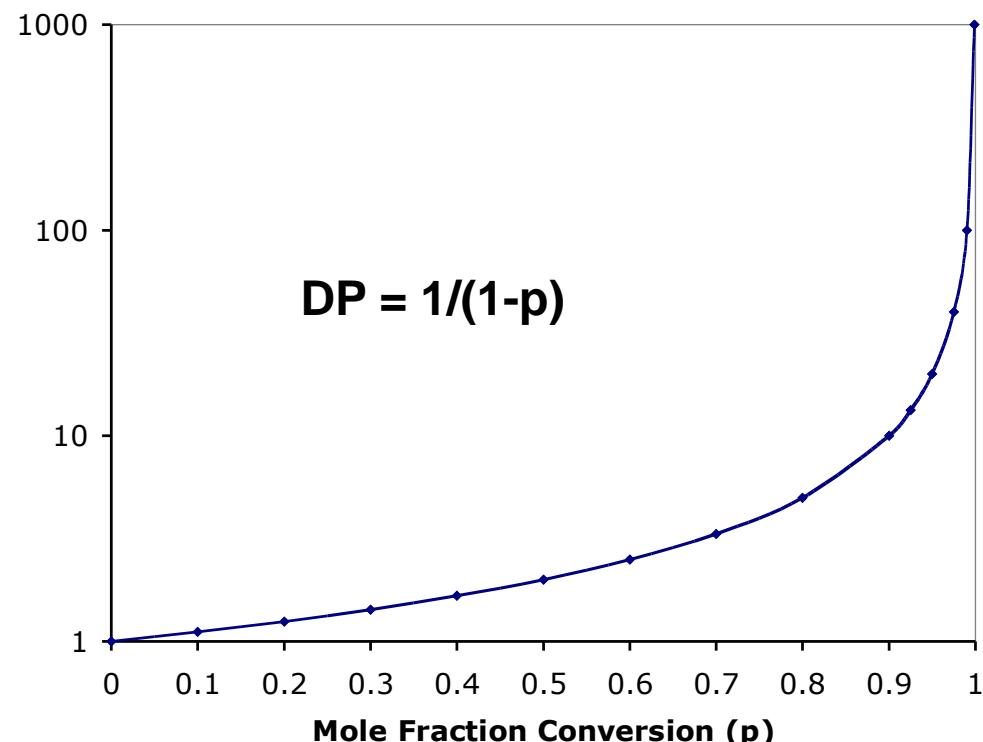
$$DP = 1/(1-p)$$

$$p = 1$$

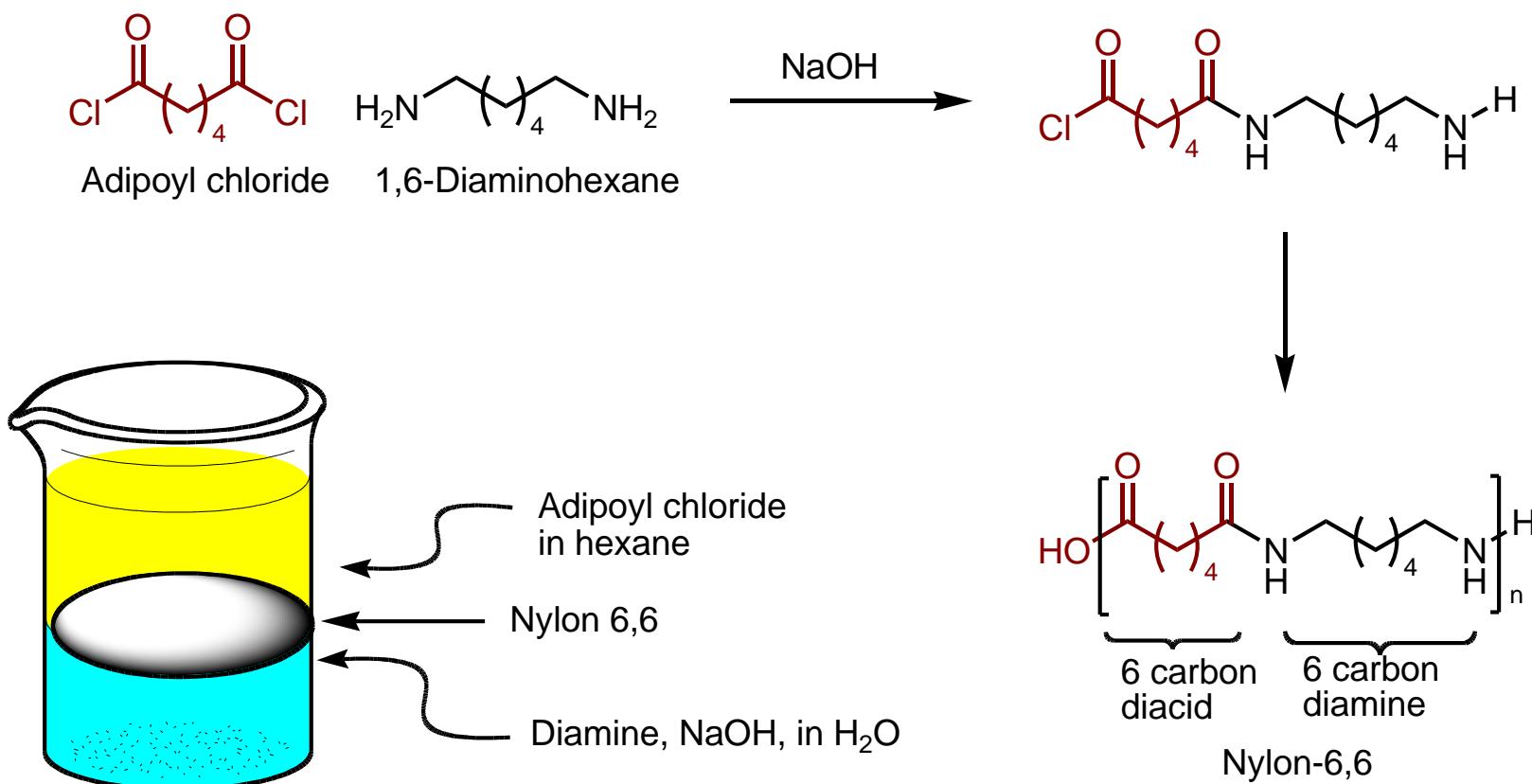
$$DP = (1+r)/(1-r)$$

DP = Degree of polymerization

p = mole fraction monomer conversion

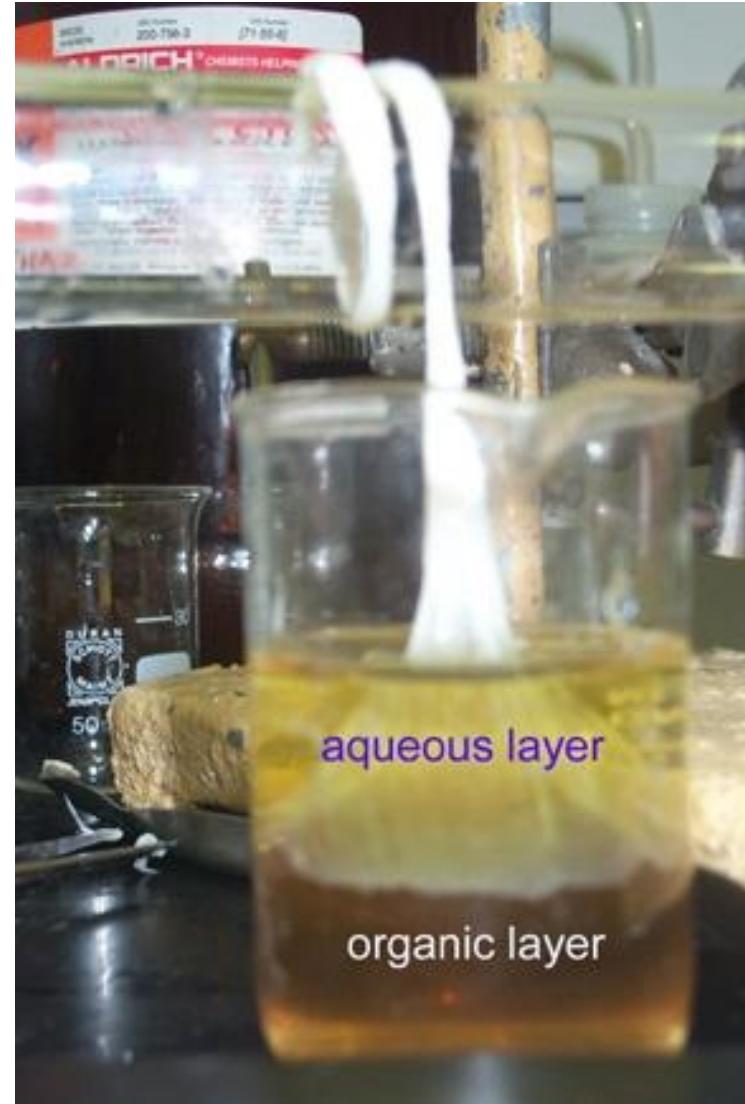
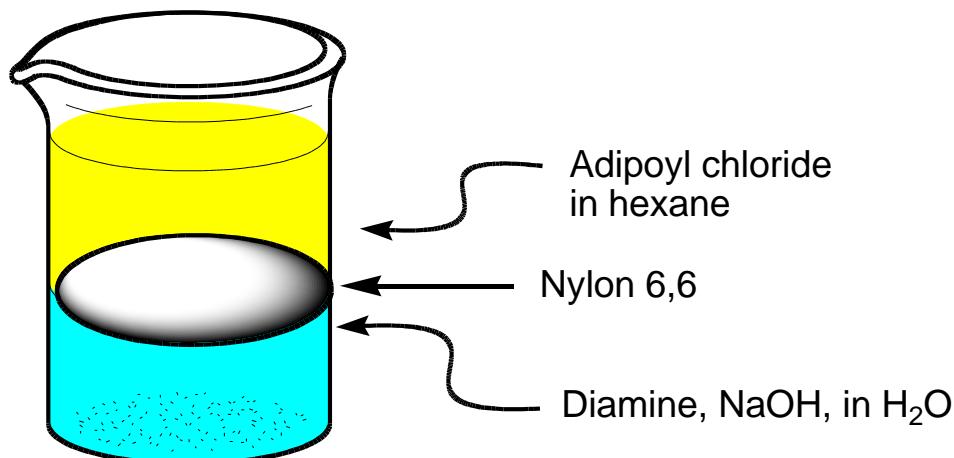


Nylon-6,6



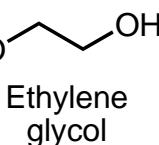
Nylon-6,6

Since the reactants are in different phases, they can only react at the phase boundary. Once a layer of polymer forms, no more reaction occurs. Removing the polymer allows more reaction to occur.



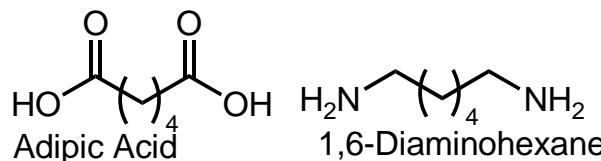
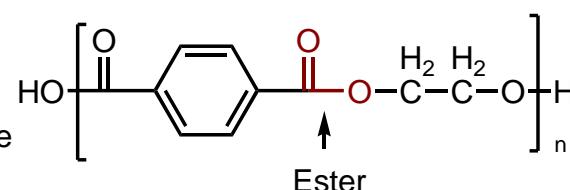
Polyesters, Amides, and Urethanes

Monomer

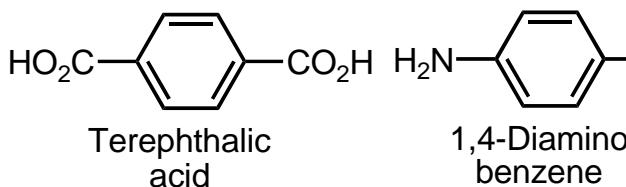
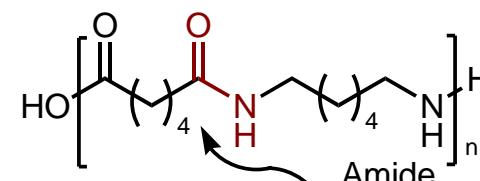


$\xrightarrow{\hspace{1cm}}$
Poly(ethylene terephthalate)

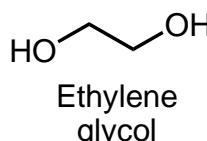
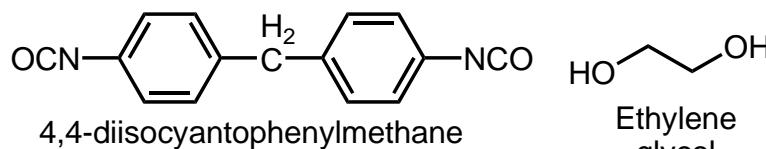
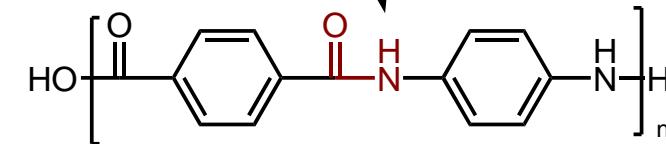
Polymer



$\xrightarrow{\hspace{1cm}}$
Nylon 6,6



$\xrightarrow{\hspace{1cm}}$
Kevlar

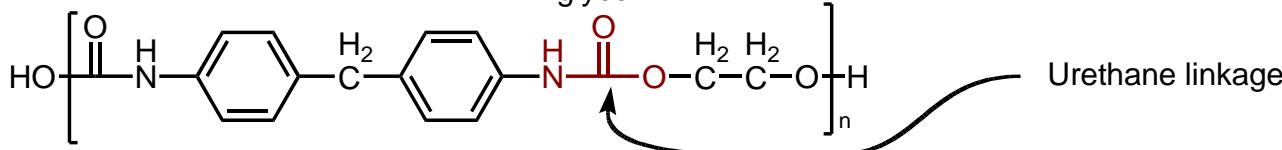


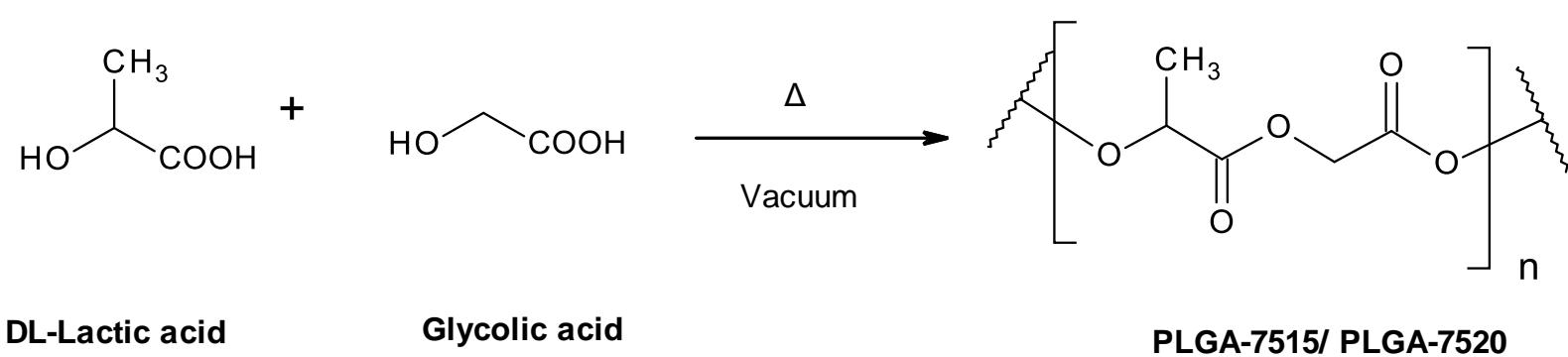
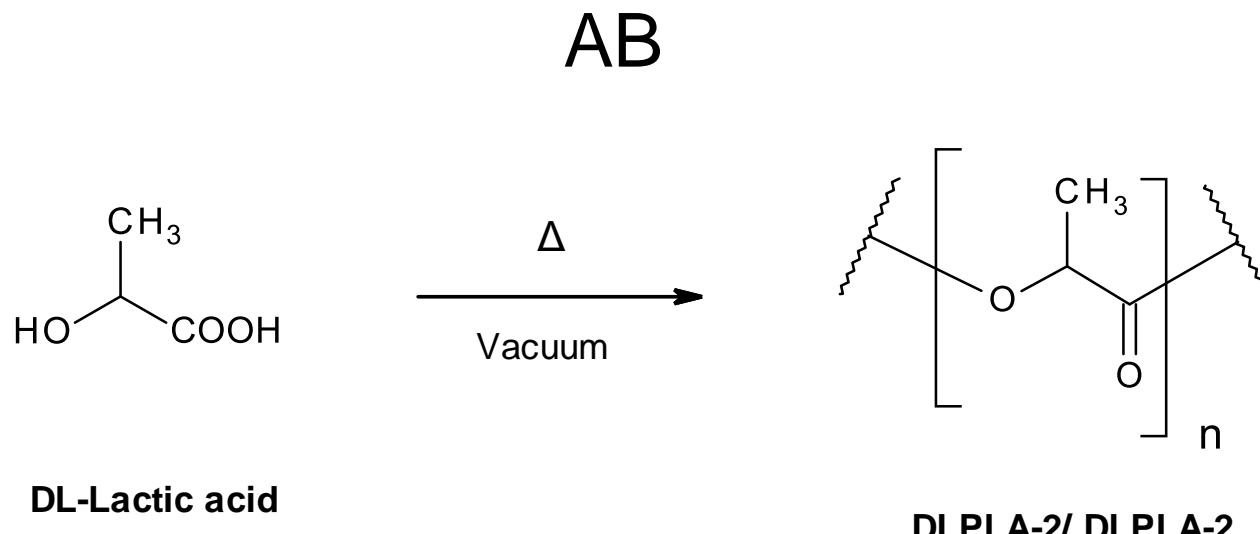
$\xrightarrow{\hspace{1cm}}$
Spandex

A2 or B2

AB

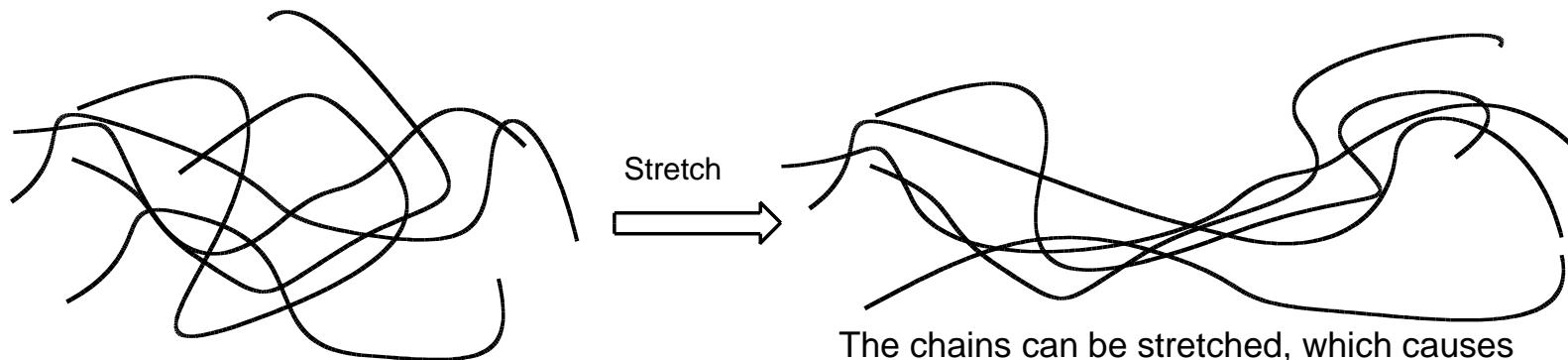
HO-R-COOH





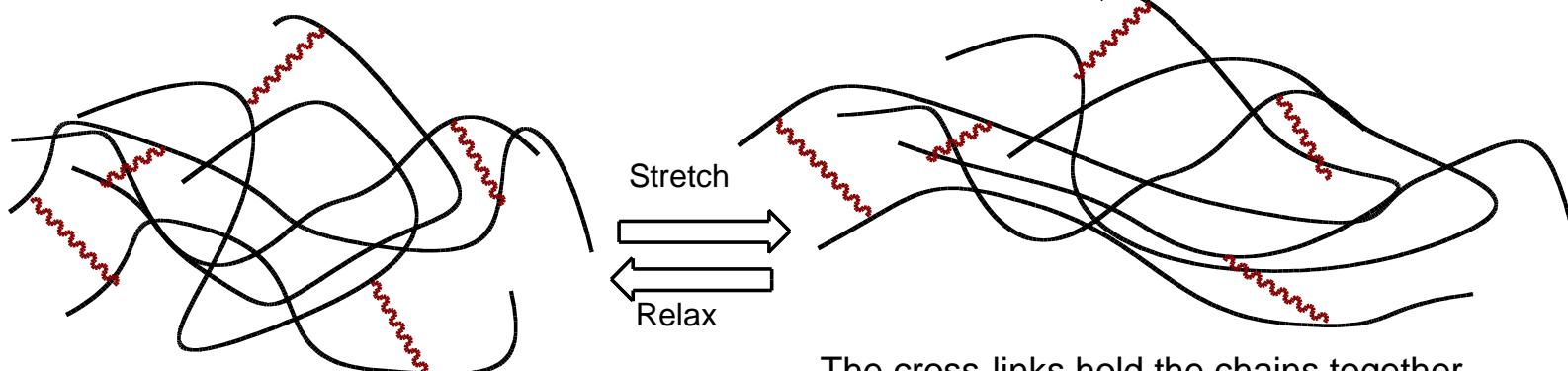
Physical Properties

Linear Polymer



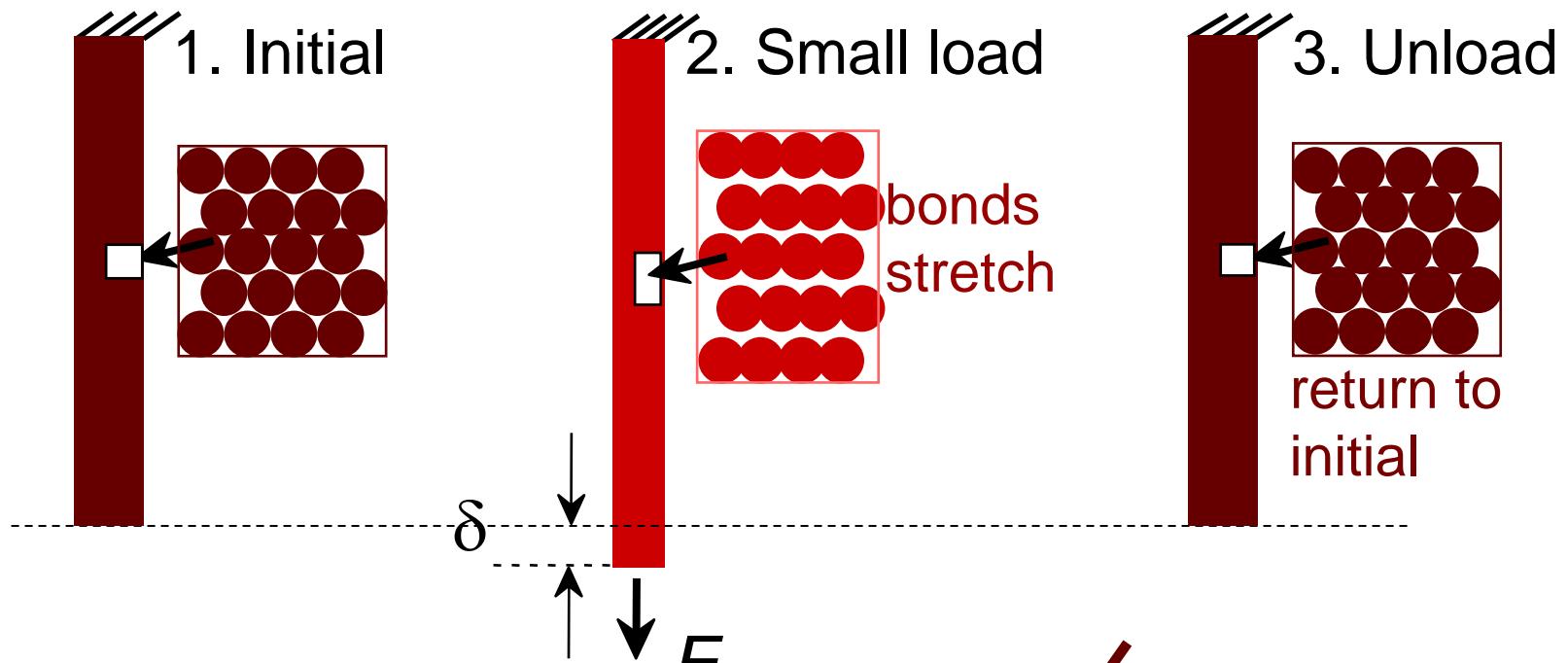
The chains can be stretched, which causes them to flow past each other. When released, the polymer will not return to its original form.

Cross-Linked Polymer

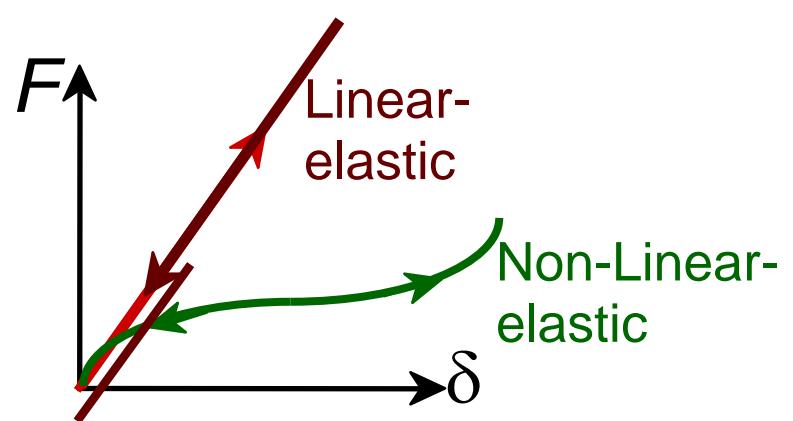


The cross-links hold the chains together. When released, the polymer will return to its original form.

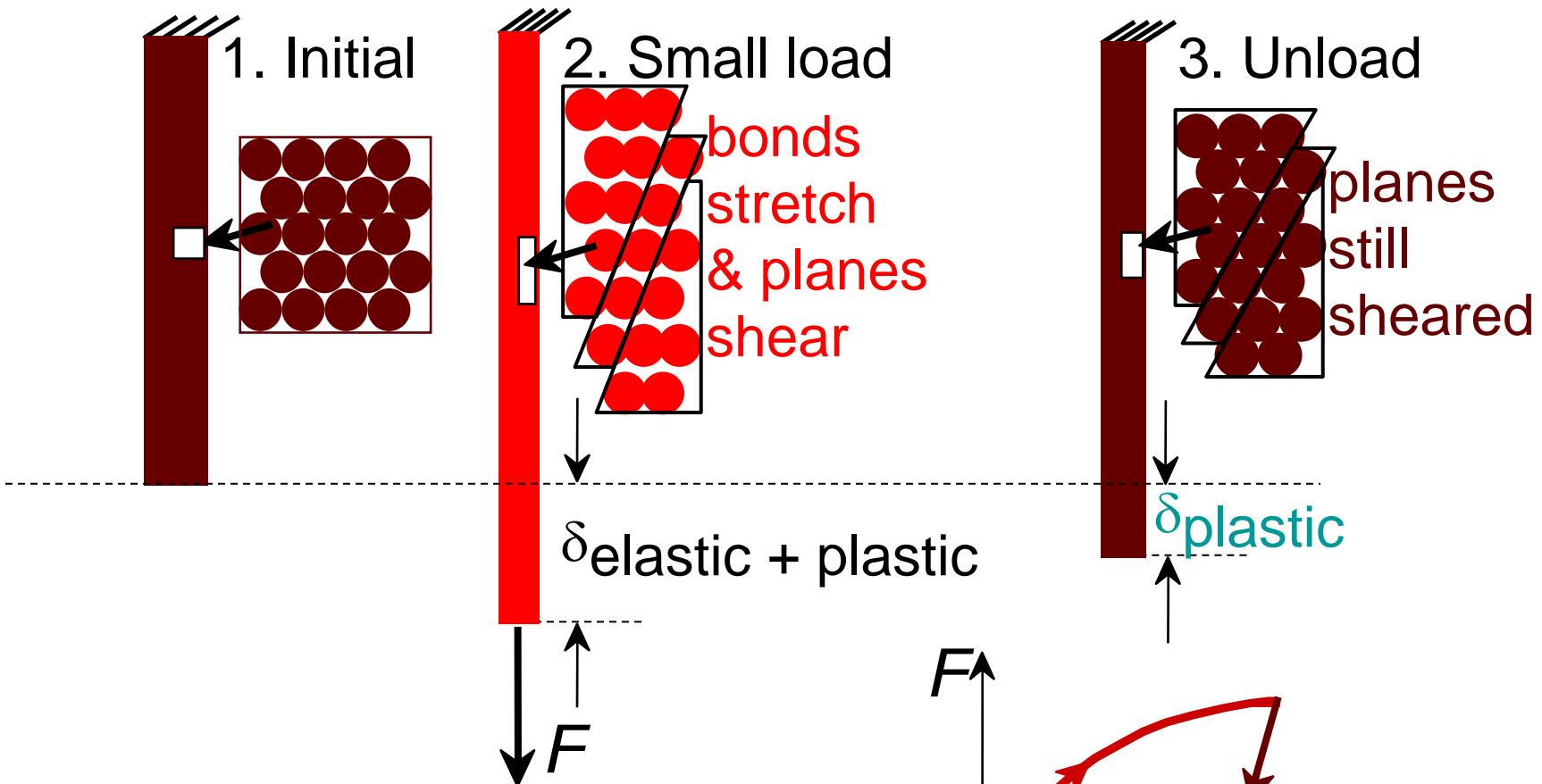
Elastic Deformation



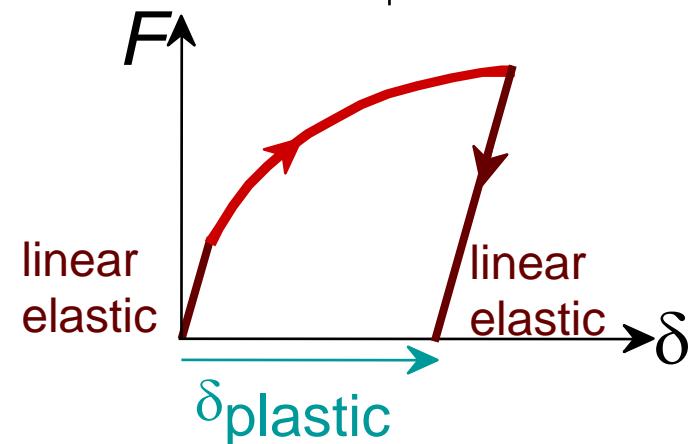
Elastic means **reversible!**



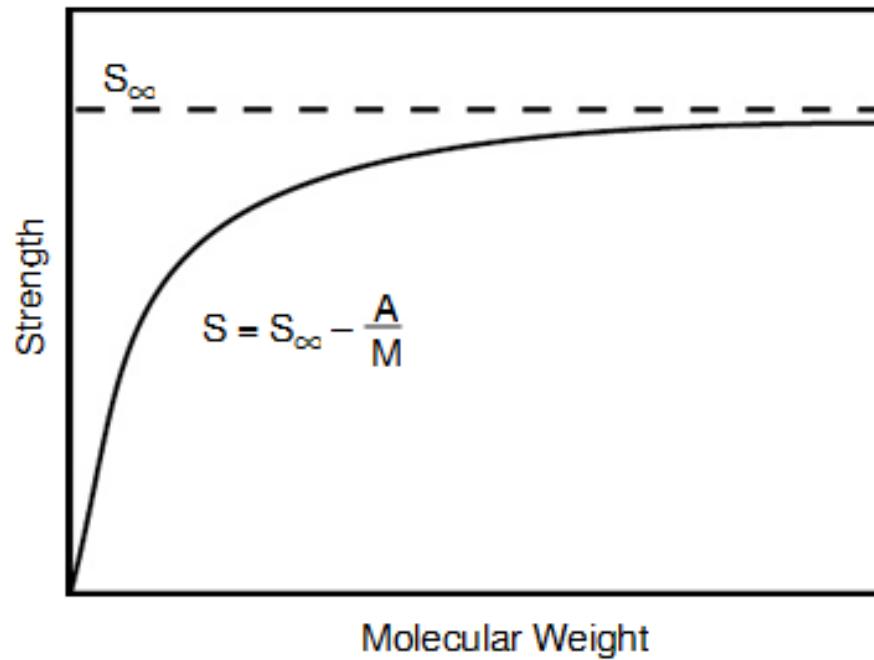
Plastic Deformation (Metals)



Plastic means permanent!



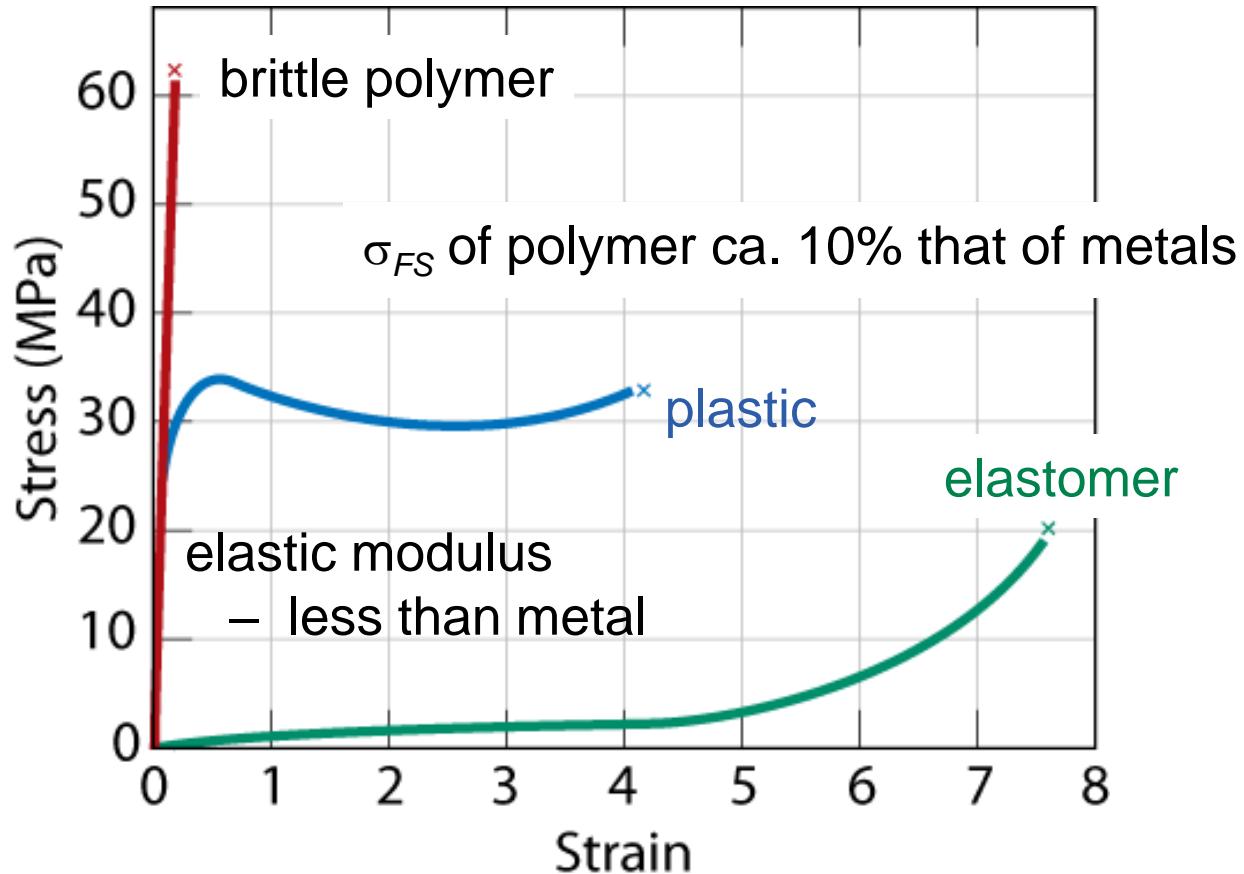
Tensile strength function of Mol. Wt. of the polymer



Strength as a function of molecular weight. At low molecular weight, the strength is too low for the polymer material to be useful. At high molecular weight, the strength increases eventually saturating to the infinite molecular weight result of S_∞ .

Mechanical Properties

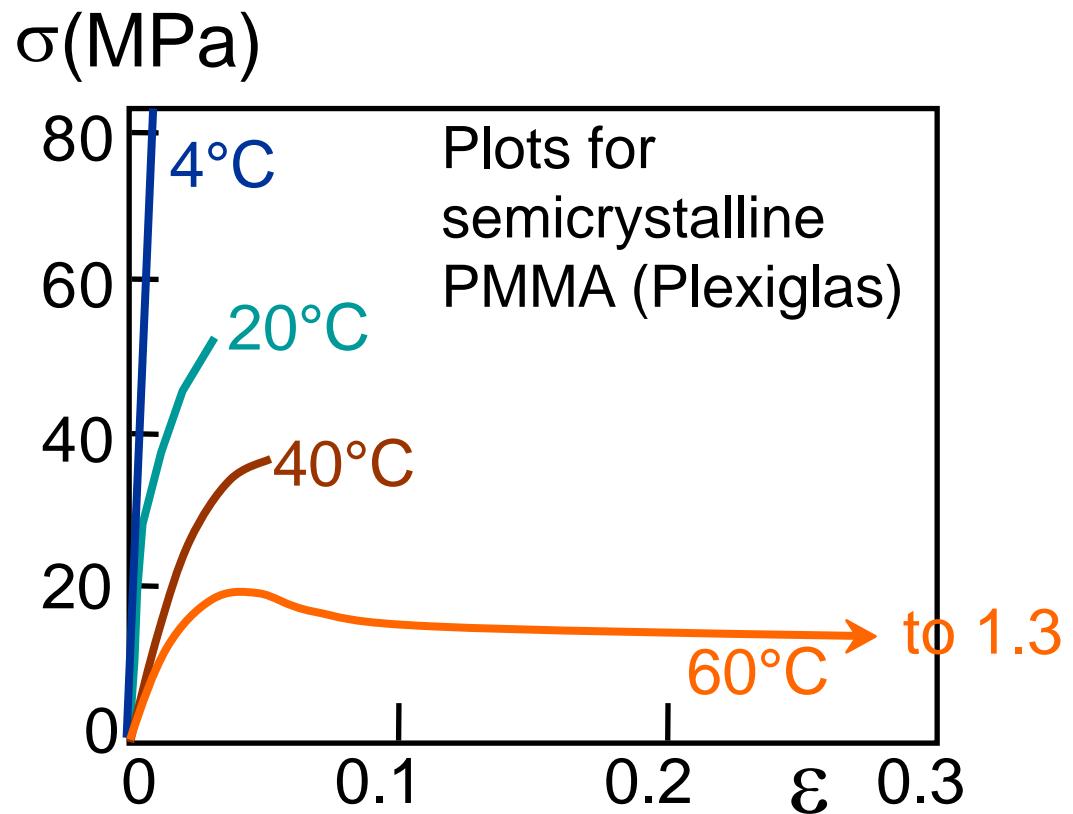
- i.e. stress-strain behavior of polymers



Strains – deformations > 1000% possible
(for metals, maximum strain ca. 10% or less)

Influence of T and Strain Rate on Thermoplastics

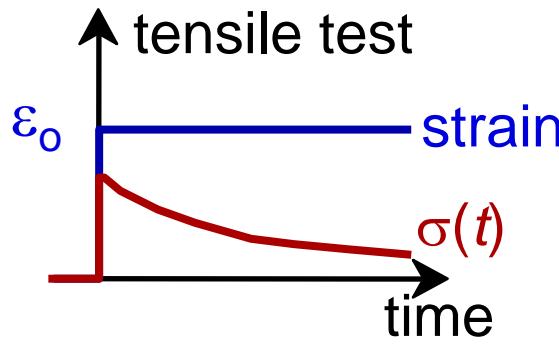
- Decreasing T ...
 - increases E
 - increases TS
 - decreases $\%EL$
- Increasing strain rate...
 - same effects as decreasing T .



Adapted from Fig. 7.24, Callister & Rethwisch 3e. (Fig. 7.24 is from T.S. Carswell and J.K. Nason, 'Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics', *Symposium on Plastics*, American Society for Testing and Materials, Philadelphia, PA, 1944.)

Time-Dependent Deformation

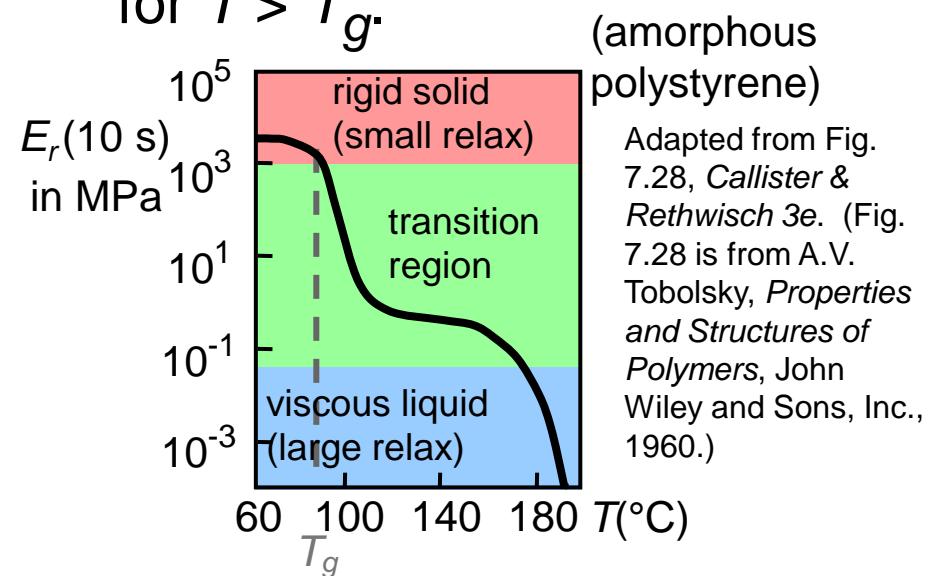
- Stress relaxation test:
 - strain in tension to ε_0 and hold.
 - observe decrease in stress with time.



- Relaxation modulus:

$$E_r(t) = \frac{\sigma(t)}{\varepsilon_0}$$

- There is a large decrease in E_r for $T > T_g$.



Adapted from Fig. 7.28, Callister & Rethwisch 3e. (Fig. 7.28 is from A.V. Tobolsky, *Properties and Structures of Polymers*, John Wiley and Sons, Inc., 1960.)

- Representative T_g values (°C):

PE (low density)	- 110
PE (high density)	- 90
PVC	+ 87
PS	+ 100
PC	+ 150

Selected values from Table 11.3, Callister & Rethwisch 3e.

Melting and Glass Transition Temperature

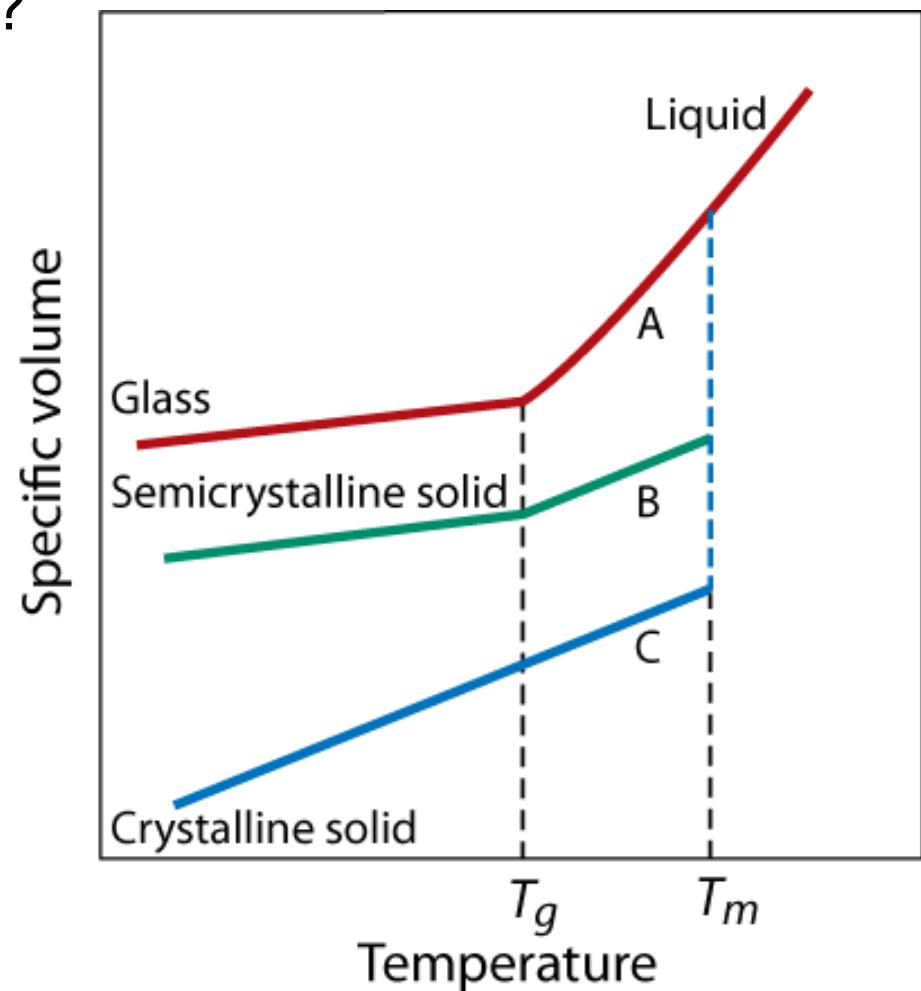
- Melting of a crystalline polymer
 - transforming solid with an ordered structure to a viscous liquid with a highly random structure
- Amorphous glass transitions
 - transformation from a rigid material to one that has rubberlike characteristics
 - temperature has large effect on chain flexibility
- Below glass transition temperature, T_g , polymers are usually brittle and glass-like in mechanical behavior.
- Above glass transition, T_g , polymers are usually more elastic.
Why is That?

Bond rotations are “freezing” which means chains can’t slip past each other so polymer becomes brittle, (no plastic deformation)

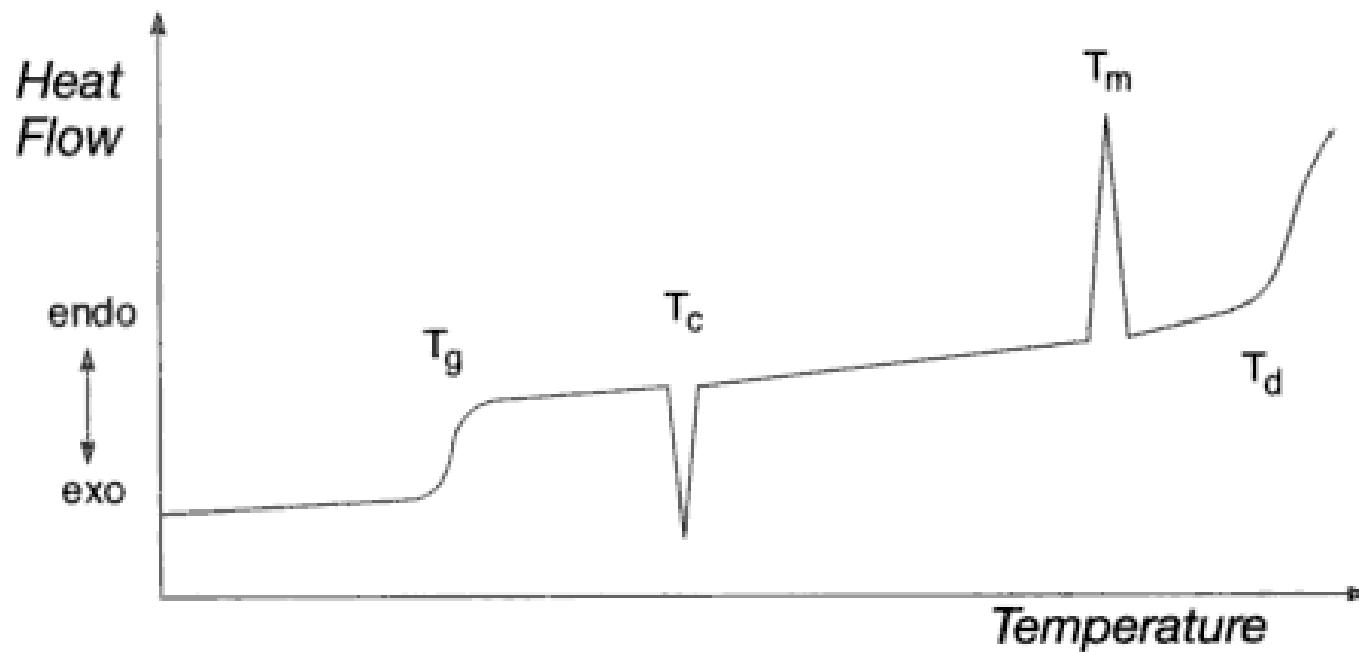
Melting vs. Glass Transition Temp.

What factors affect T_m and T_g ?

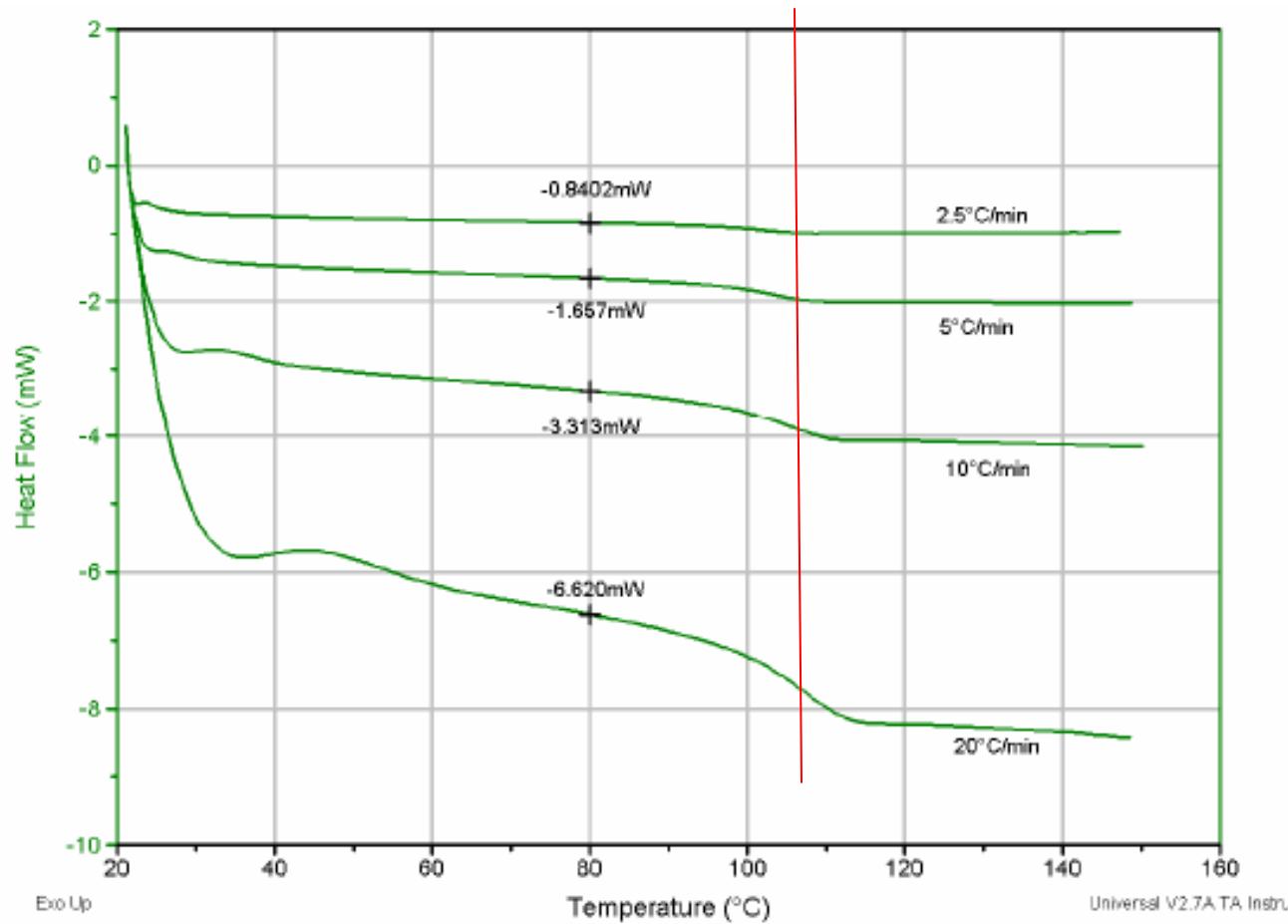
- Both T_m and T_g increase with increasing chain stiffness
- Chain stiffness increased by
 - Bulky sidegroups
 - Polar groups or sidegroups
 - Double bonds or aromatic chain groups
- Regularity – effects T_m only



DSC plot of semicrystalline polymers

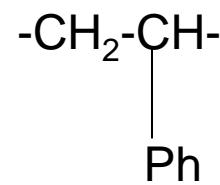
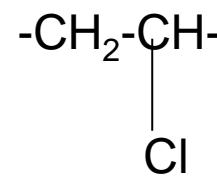
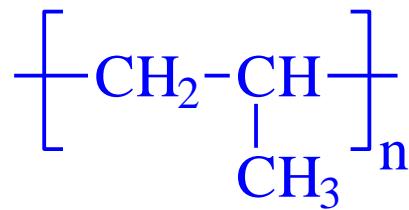


T_g of PMMA at different heating rate



T_g and T_m

<i>Material</i>	<i>Glass Transition Temperature</i> [°C (°F)]	<i>Melting Temperature</i> [°C (°F)]
Polyethylene (low density)	-110 (-165)	115 (240)
Polytetrafluoroethylene	-97 (-140)	327 (620)
Polyethylene (high density)	-90 (-130)	137 (279)
Polypropylene	-18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Polyester (PET)	69 (155)	265 (510)
Poly(vinyl chloride)	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)



Modulus of different calss of polymers w.r.t. temperature

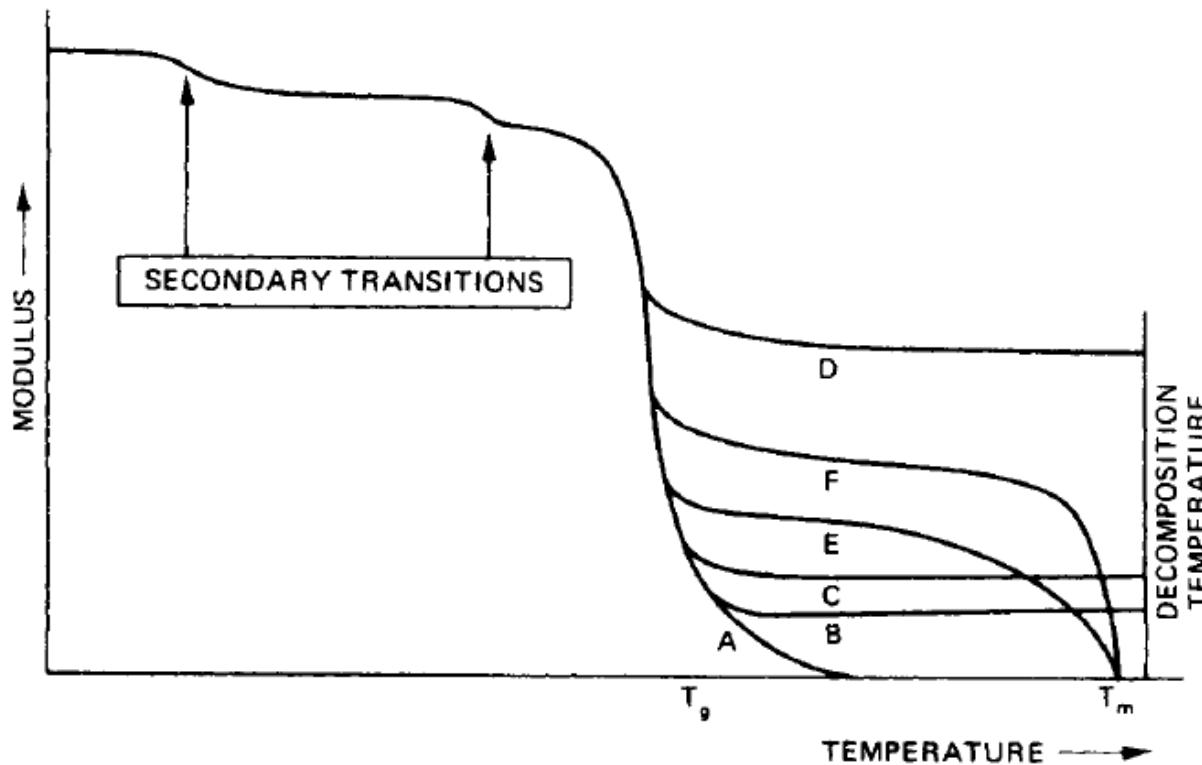


Figure 9.1. Schematic illustration of dependence of the modulus of a polymer on a variety of factors. A is an amorphous polymer of moderate molecular weight whereas B is of such a high molecular weight that entanglements inhibit flow. Similar effects are shown in C and D, where the polymer is respectively lightly and highly cross-linked. In E and F the polymer is capable of crystallisation, F being more highly crystalline than E

Applications of Polymers

It is difficult to find an aspect of our lives that is not affected by polymers. Just 70 years ago, materials we now take for granted were non-existent.

1. Polymers in daily life:
2. Polymers in automotive
3. Polymers in sports
4. Polymers in agricultural
5. Polymers in medicine
6. Polymers pharmacy and pharmaceutical formulations
7. Polymers in aero-space
8. Polymers in electronics
9. Polymers in defence



Electronic Packaging

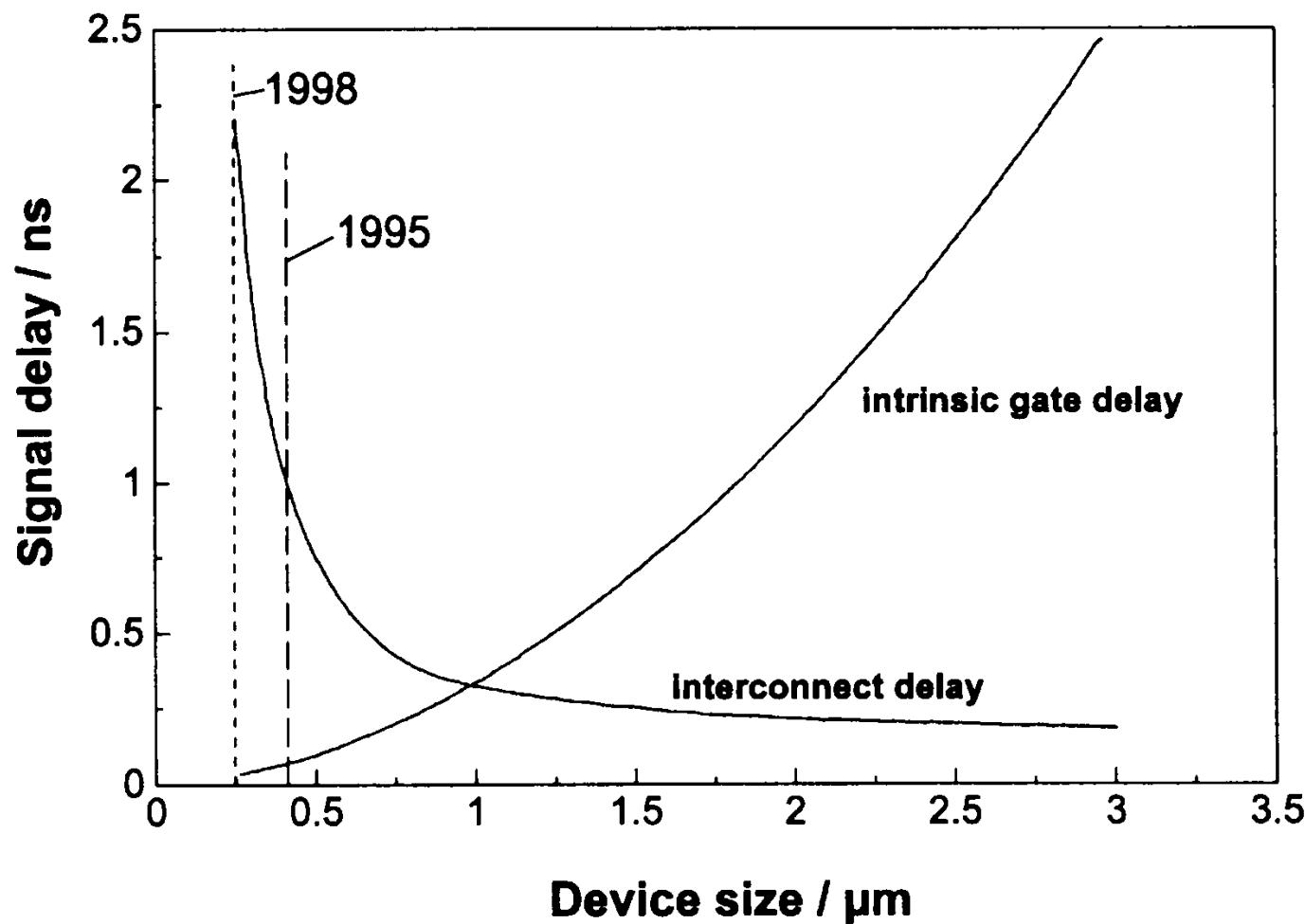
The need for low dielectric constant materials

- Smaller feature size in microelectronic devices leads to increasing line to line capacitance

$$\tau = RC = 2 \rho \epsilon \epsilon_0 [4L^2 / P^2 + L^2 / T^2]$$

R	= Total resistance
C	= Total Capacitance
ρ	= Specific resistance of the metal of the interconnect lines.
ϵ	= Dielectric constant of the insulator between the Inter connect lines.
ϵ_0	= Dielectric constants of vacuum.
L, P, T	= Length, pitch & thickness of the interconnect array.

Signal delay vs. device size in integrated circuitry



Ref: S.-P. Jeng et al. *Mat. Res. Soc. Symp. Proc.* 337, 25 (1994)].

SEMATECH roadmap for intermetal dielectric

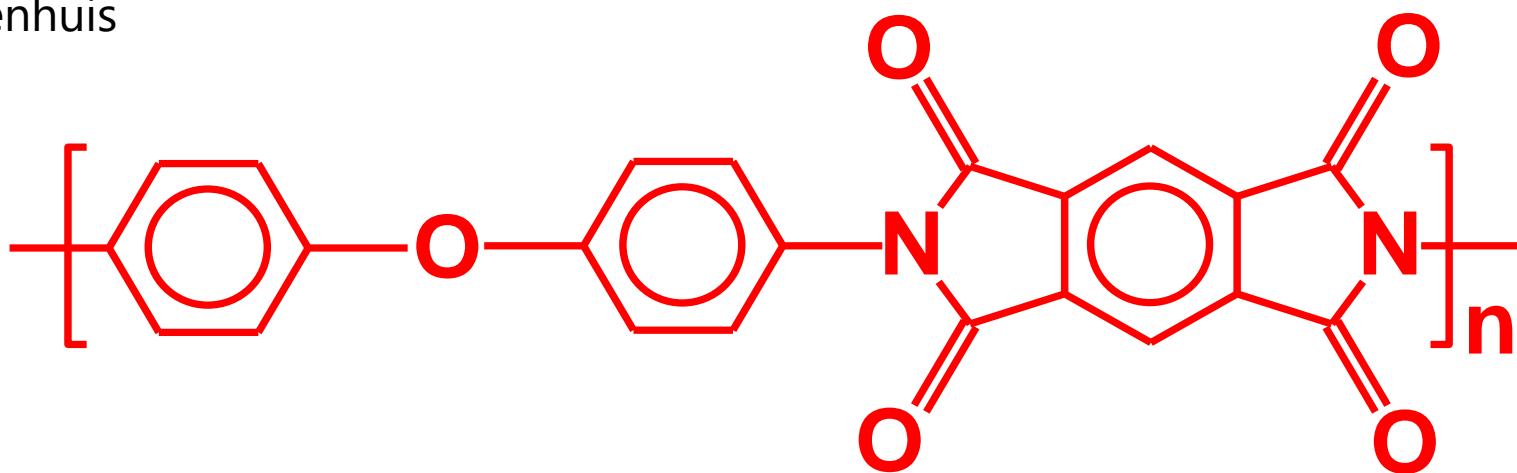
Required dielectric constant		
Technology year	Design rule (micron)	Required ϵ
1998	0.25	3.9
2001	0.18	2.9
2004	0.15	2.3
2007	0.12	1.9

Ref: Semiconductor Industry Association. International Technology Roadmap
for semiconductors (ITRS), 1998 update (<http://www.itrs.net/ntrs/publntrs.nsf>)

Book: Properties of Polymers, Fourth Edition Their Correlation with Chemical Structure their Numerical Estimation and Prediction from Additive Group Contributions

Authors: D.W. van Krevelen, Klaas te Nijenhuis

KAPTON



SiO_2 $\epsilon = 4$

$\epsilon = 3.4$
 $T_g > 300^\circ\text{C}$
 $TS = 158 \text{ MPa}$
 $YM = 3.2 \text{ GPa}$
Water Absorption = 3.5 %

Properties required for new intermetal Dielectrics

• Dielectric constant	< 3, preferably 2.5
• Dissipation factor at 1 MHz	< 0.005
• Thermal stability	400 - 450 °C
• Glass transition temperature	≥ 300 °C
• Thermal conductivity	<0.5 W/(m.K)
• Coefficient thermal expansion	< 50 ppm
• Tensile strength	>100 MPa
• Young modulus	>1 GPa
• Moisture absorption	< 1%
• Good adhesion to materials such as SiO ₂ , Si, Al, Cu, TiN	
• Good film forming ability	

Ref: P. Springer, *Semiconductor. Int.* 5 (1996) 88

Solutions

Spin-on

- Well defined chemical structure
- Good local planarization
- Post deposition cure

Plasma polymerization

- Solvent free
- Good uniformity
- Common equipment can be used

Concept

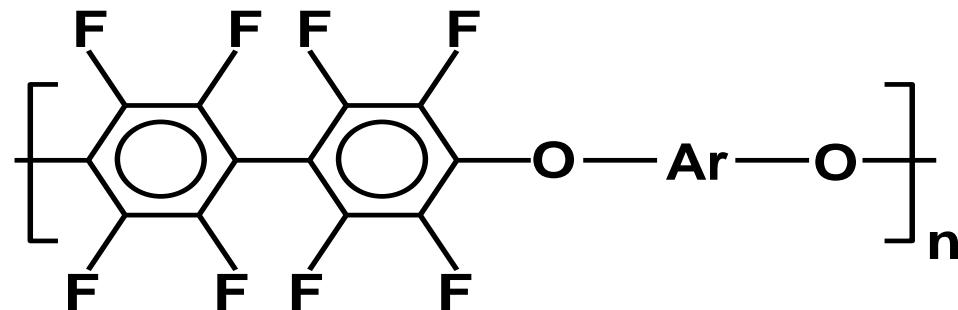
For low dielectric constant:

- Absence of polar groups
- Incorporation of fluorine as pendent CF_3 group

For high T_g and strength:

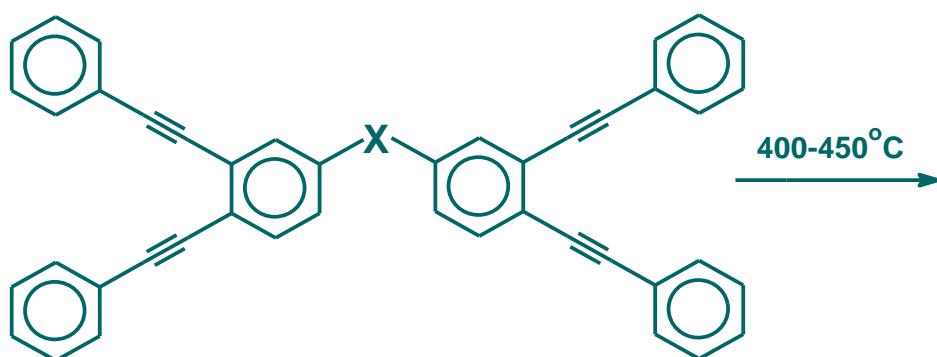
- Stiff repeat unit
- High molecular weight

FLARE

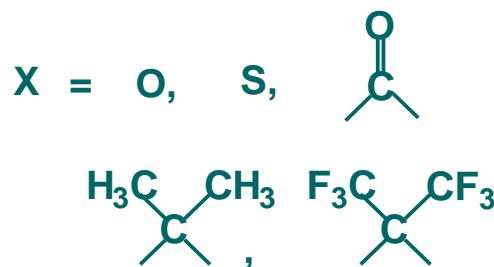


ϵ	= 2.5-3.1
T_g	= 189-285 °C
T_d	= 540 °C
TS	= 83-107 MPa
YM	= 2.45-2.95 GPa
CTE	= 65- 76 ppm / °C
Gap Fill Property	= < 0.8 μm

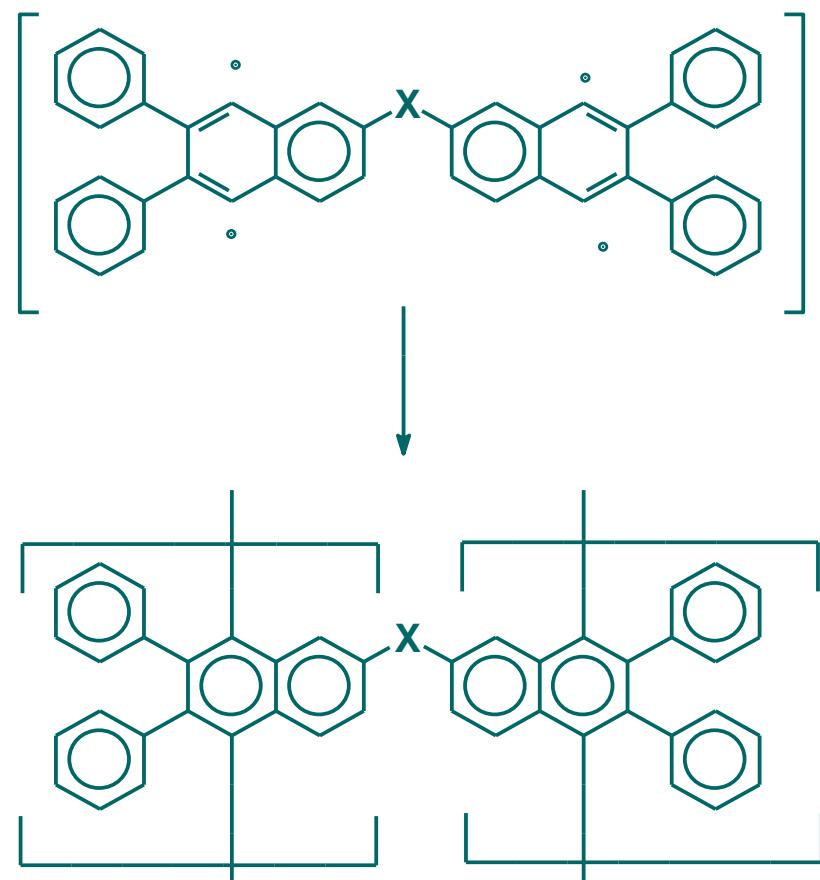
SiLK



Plasma polymerization

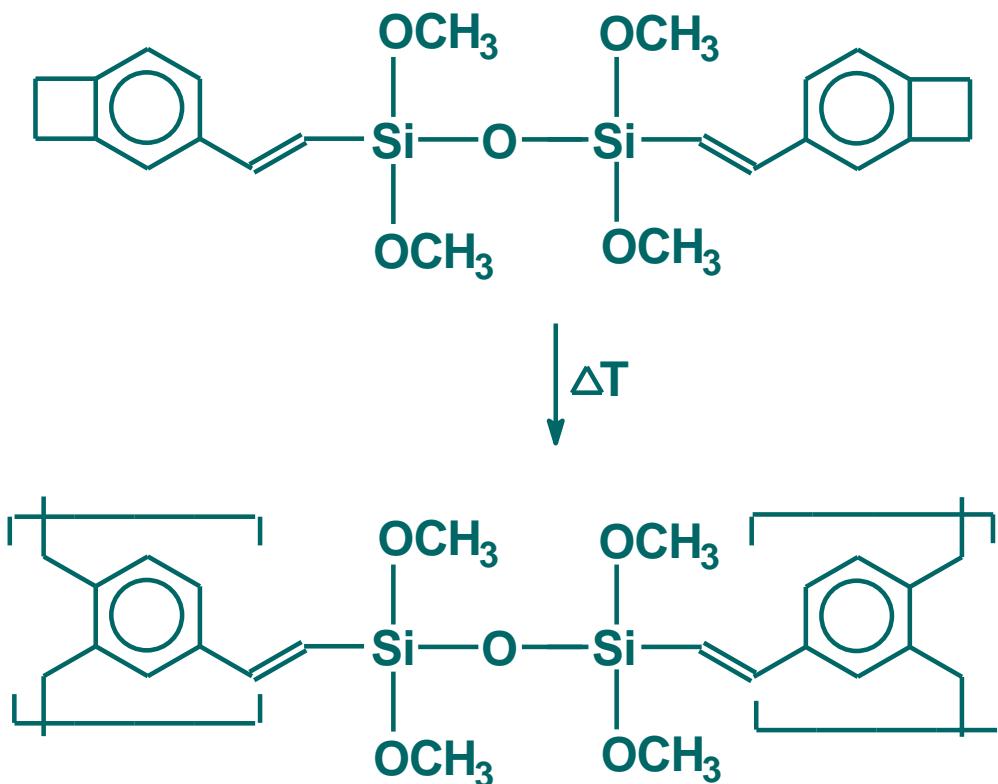


$$\varepsilon = 2.6 - 2.7$$



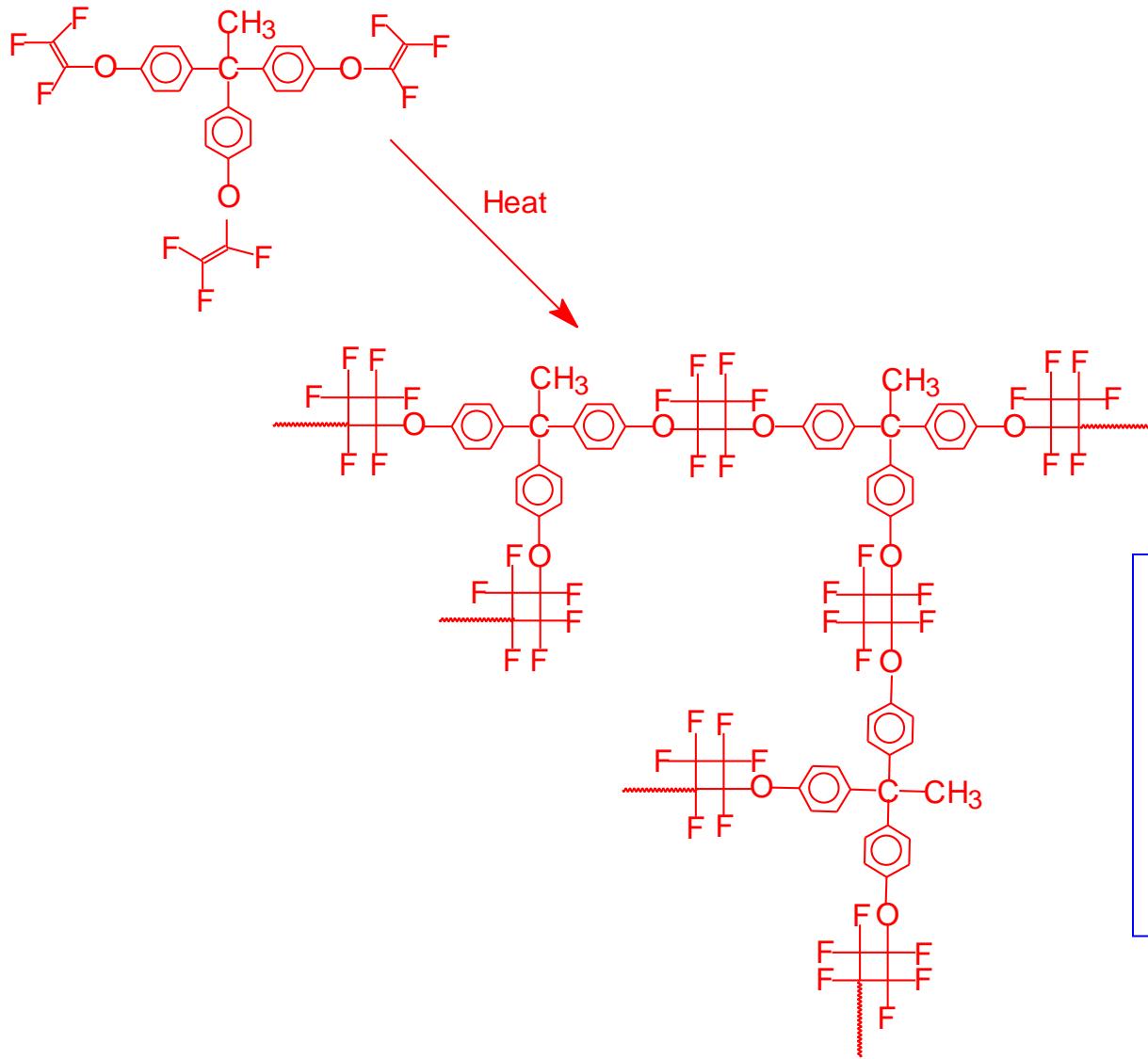
Plasma polymerization

Crosslinked BCB resins



ϵ	= 2.6-2.7
TS	= 85 MPa
YM	= 2 GPa
CTE	= 52 ppm / °C
Water absorption	= 0.2 %

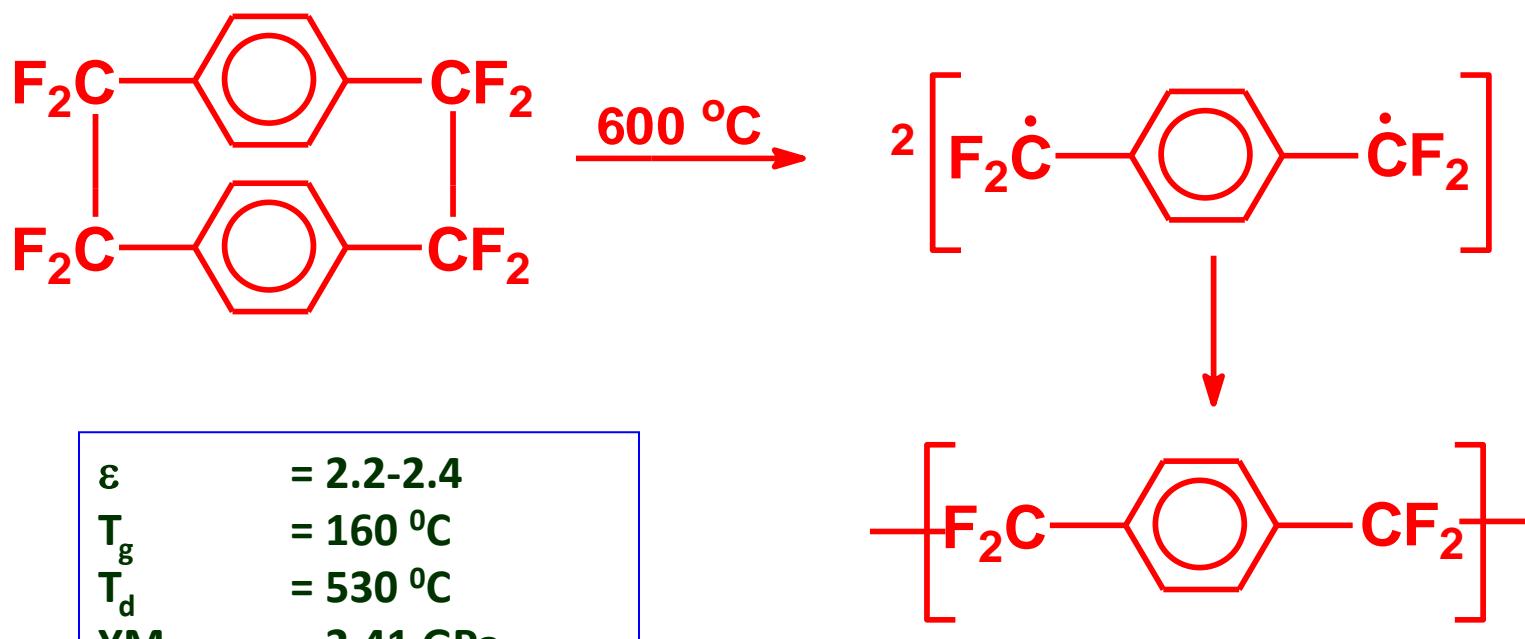
Poly(perfluorocyclobutane) (PFCB)



ε	= 2.35
T_g	= 400 °C
TS	= 66 MPa
YM	= 2.27 GPa
EB	= 4 %
Poor Thermal Stability	

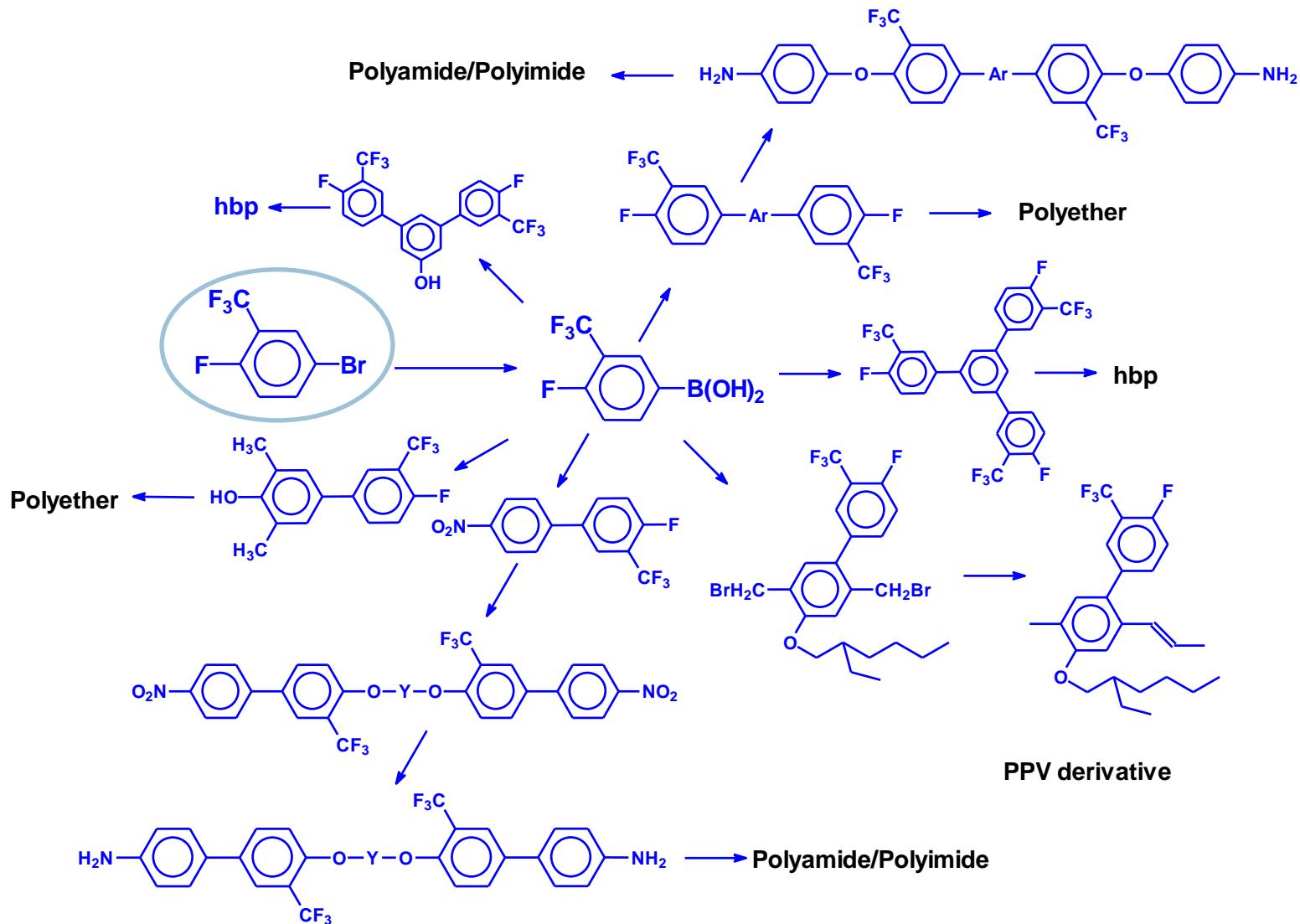
Plasma polymerization

Parylene F



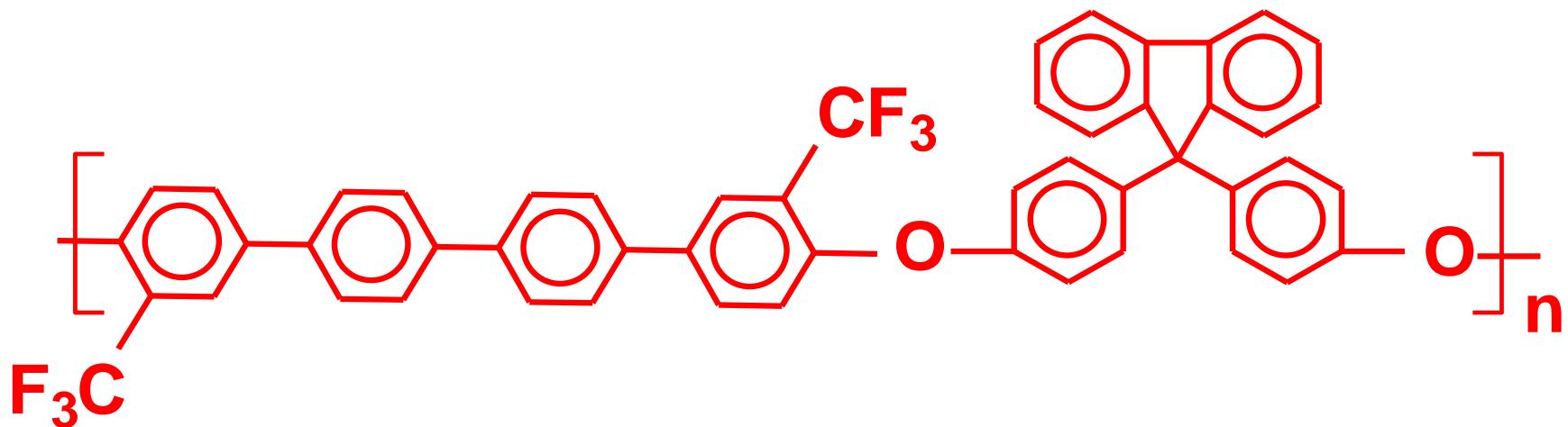
ϵ	= 2.2-2.4
T _g	= 160 °C
T _d	= 530 °C
YM	= 2.41 GPa
CTE	= 28 ppm / °C

Designing new polymers by molecular engineering



Courtesy of 5-bromo-2-fluoro benzotrifluoride

Poly(arylene ether)



$\varepsilon = 2.67$; $T_d = 534 \text{ }^\circ\text{C}$ (5 % wt. loss in air)

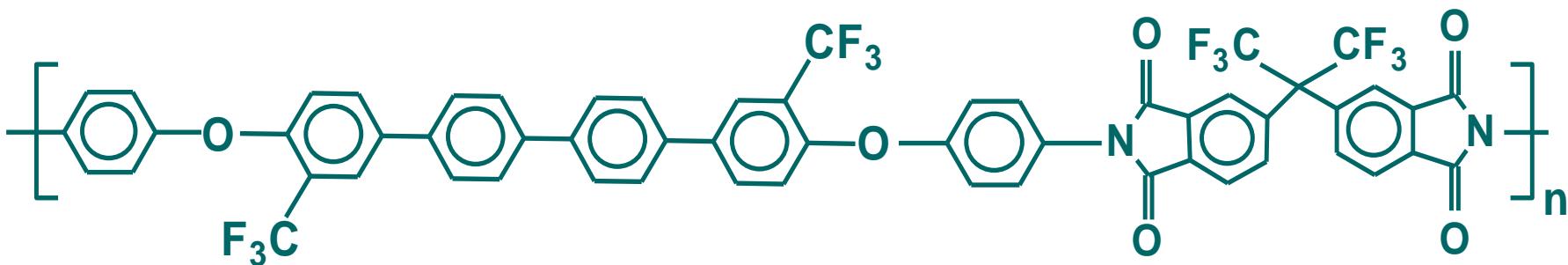
$T_g = 300 / 315 \text{ }^\circ\text{C}$ (DSC / DMTA)

TS = 75 MPa

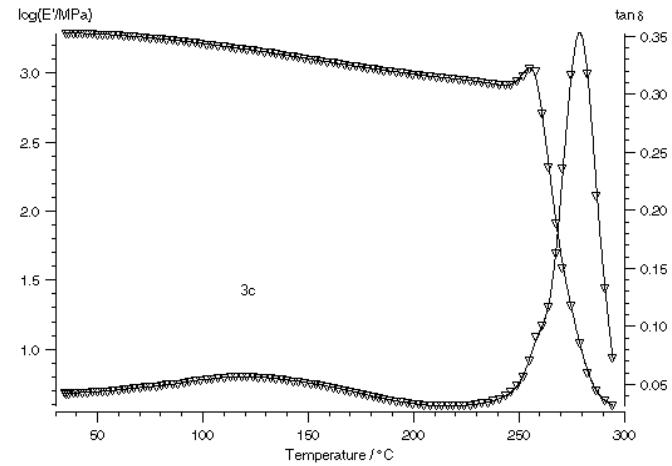
Water absorption rate = 0.2 wt %

Ref : S. Banerjee, et al. *Chem. Mater.* (1999)

Poly(ether imide)

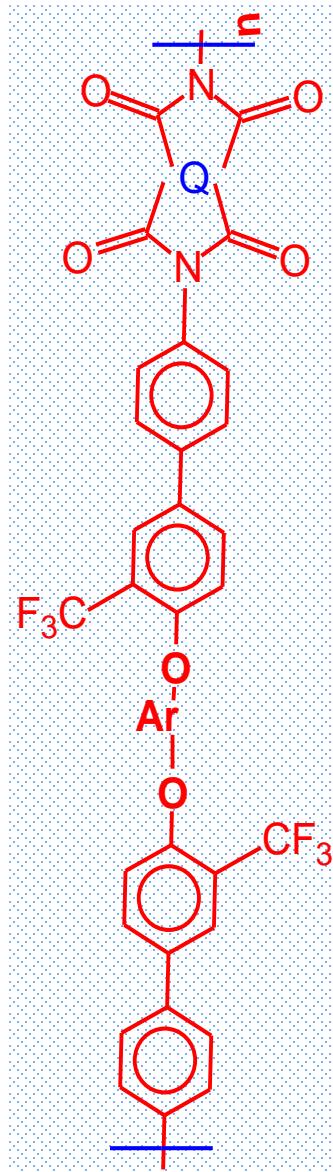


$\varepsilon = 2.60$;
Water abs. = 0.2 wt %;
 $T_d = 526^\circ\text{C}$; $T_g = 273^\circ\text{C}$;
 $T_s = 109 \text{ MPa}$; Mod.= 2.5 GPa;
 $E_b = 24 \%$



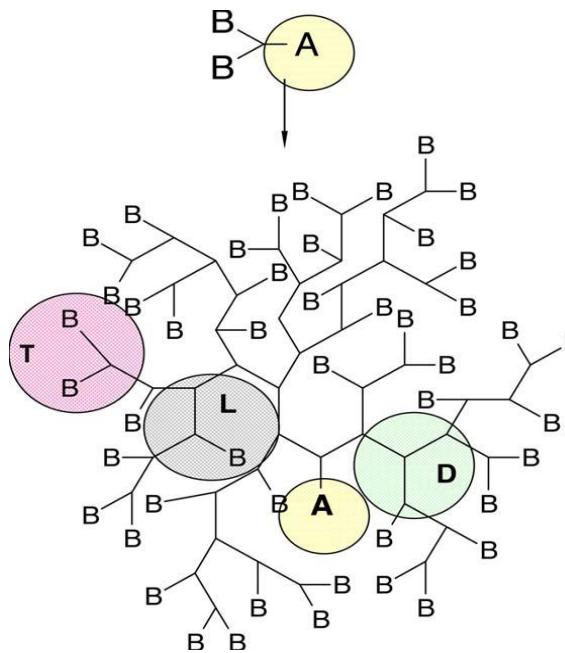
Ret. S. Banerjee, et al. J. Polym. Sci. Polym. Chem. (2002)

Summary of the polymer properties



Ar	Q	Tg / 0C	% Fluorine	Dielectric constant	% Water abs.
		262	12.94	3.12	0.45
		252	20.59	2.79	0.28
		239	11.57	3.09	0.48
		230	11.72	3.05	0.53
		268	23.05	2.92	0.21
		260	30.56	2.52	0.18
		245	20.86	2.62	0.28
		235	21.09	2.57	0.26
		311	11.36	2.81	0.48
		285	18.55	2.58	0.38
		282	10.29	2.92	0.51
		275	10.41	2.90	0.47

Hyperbranched polymers



Schematic representation of a hyperbranched polymer by AB_2 monomer

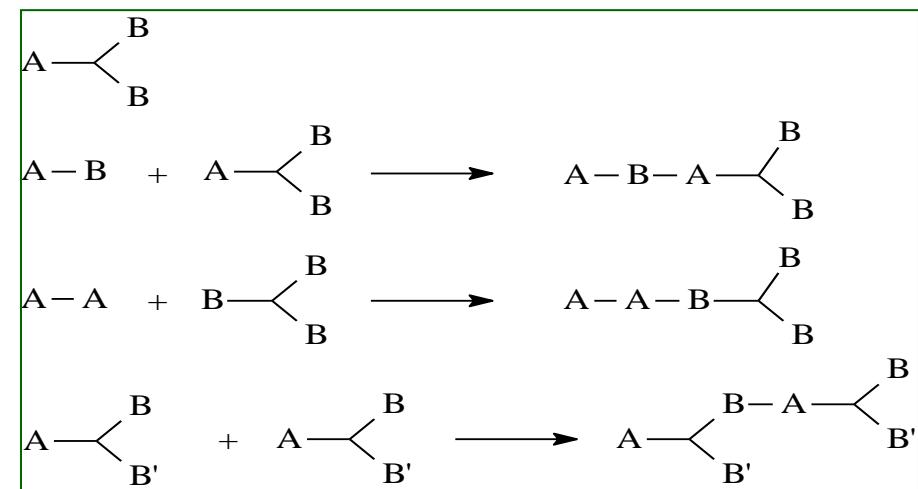
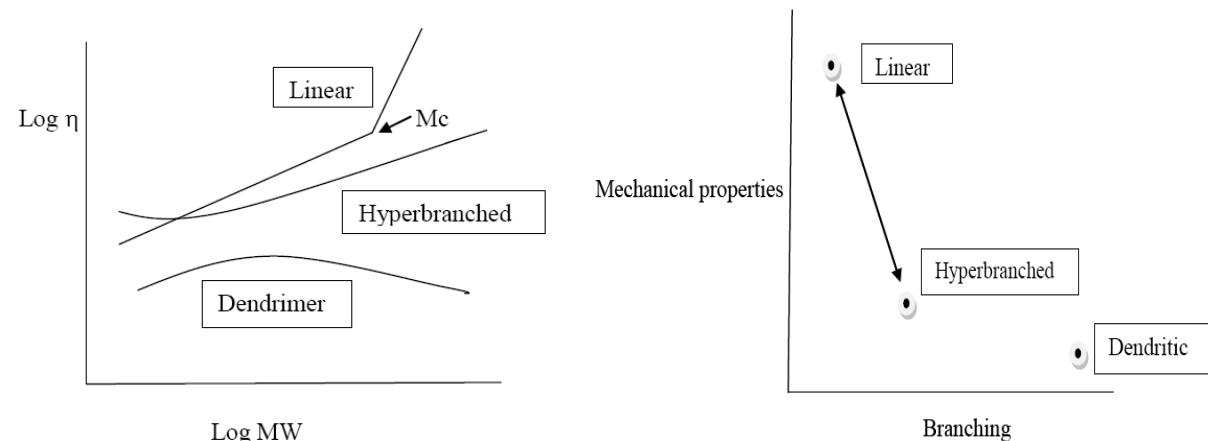
$$[\text{DB}_{\text{Fréchet}} = (t+d)/(t+l+d)]$$

$$[\text{DB}_{\text{Frey}} = 2d/(2d+l)]$$

DB for perfect dendrimer = 1

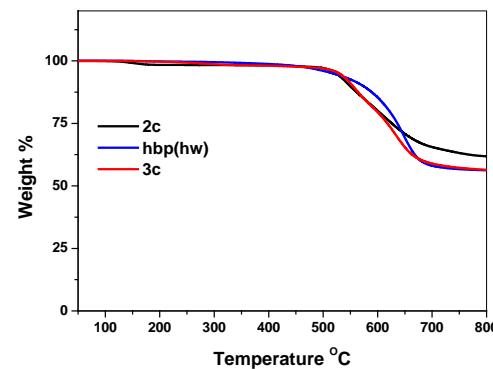
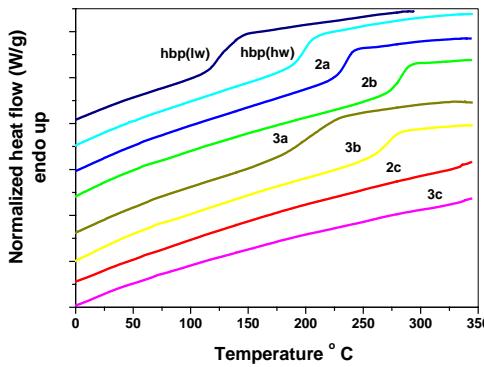
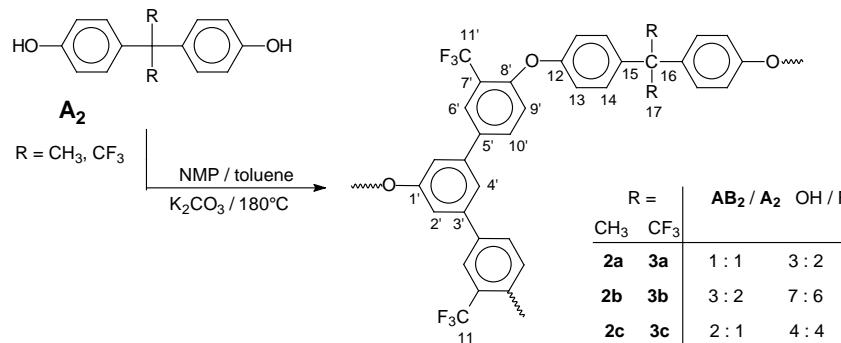
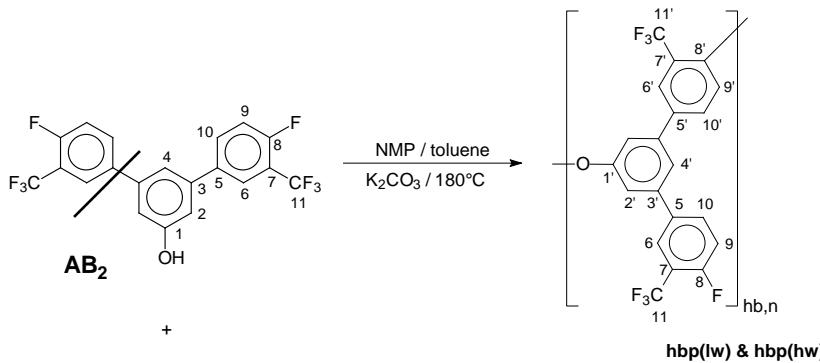
DB for linear polymer = 0

DB for hyperbranched polymer = 0-1



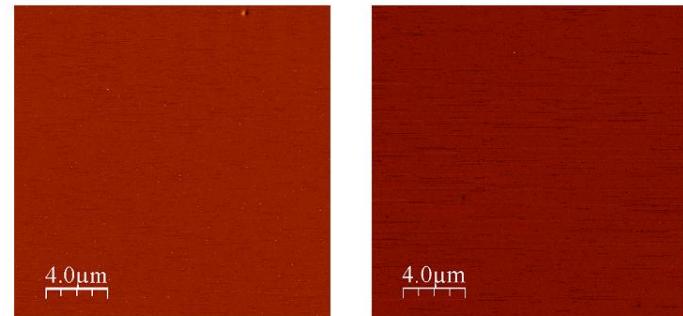
Schematic routes for hyperbranched polymers

Hyperbranched polymer



Concept

- Higher fractional free volume
- Higher fluorine content



$T_{d10\%} = 573^{\circ}\text{C}$
 $T_g > 350^{\circ}\text{C}$
 $M_w = 44,70,000 \text{ gmol}^{-1}$
 $\text{PDI} = 2.2$



Energy Saving

Membrane Based Separation Processes

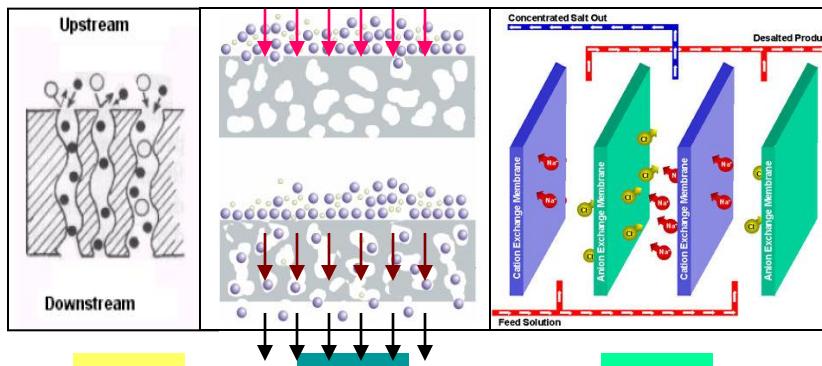
Process	Pore size/ mol wt	Driving Force	Mechanism
Microfiltration	0.02-10µm	ΔP 0-1 bar	Sieving
Ultrafiltration	0.001-0.02µm mol wt 10^3 - 10^6	ΔP 0-10 bar	Sieving
Nanofiltration	<2 nm mol wt 10^2 - 10^3	ΔP 10-25 bar	Solution Diffusion
Reverse Osmosis	non porous	ΔP 10-100 bar	Solution Diffusion
Gas Separation	non porous	ΔP 10-100 bar	Solution Diffusion
Dialysis	10-30 A	Concentration difference	Sieving plus Diffusion
Pervaporation	non porous	Partial pressure difference	Solution Diffusion
Electrodialysis	mol wt <200	Electrical potential	Ion Migration

Advantages

- Low energy consumption.
- Low investment cost.
- Better selectivity without thermodynamic limitations.
- Clean and close operation.
- No process wastes.
- Compact and scalable units.

Drawbacks

- Scarce membrane market.
- Lack of information.
- Low permeate flows.
- Limited application

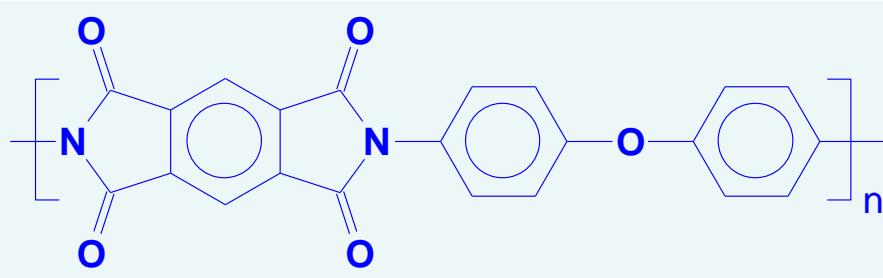


Organic substances dehydration

Recovery of volatile compounds at low concentrations

Separation of close boiling as well as azeotropic mixtures

Polyimides



Kapton®

Strengths

- High thermal stability
- High glass transition temperatures (above 350 °C)
- High mechanical properties
- Good chemical resistance
- Low dielectric constant



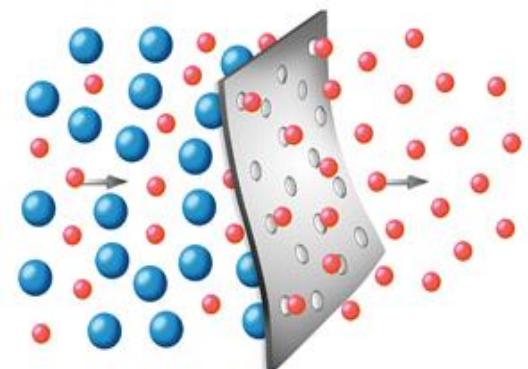
Industrial Applications



- Insulating films for flexible cables in electrical industry
- High temperature adhesive in semiconductor industry
- High temperature resistive cables for aerospace application
- Machinery parts and shapes for automobile application
- Photoresist material in photolithography

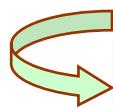


Membrane based gas separation application



Ref. N.L. Norman, G.F. Anthony, W.S. Winston Ho, Advanced membrane technology and applications. John Wiley & Sons Inc; 2008.

Scope of gas separation process

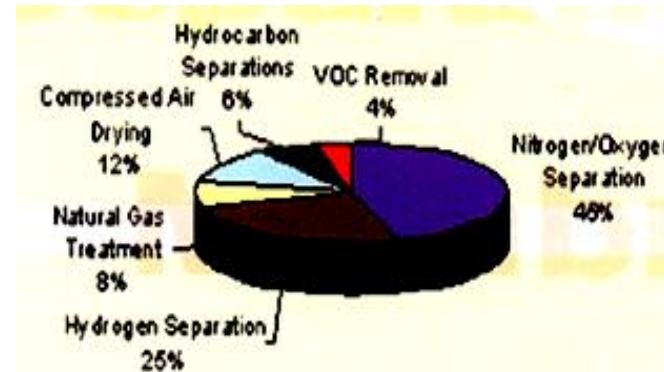


- Recovery of excessive flue gases from heavy industries effluents.
- Removal of CO₂, H₂S and H₂O from natural gas to increase the fuel efficiency and decrease pipe corrosion.
- Preparation of oxygen enriched air.



Other technologies

- ✓ Amine adsorption process
- ✓ Cryogenic distillation process



Gas Separation Membrane Market Value, 2000
Total Value : \$127 million

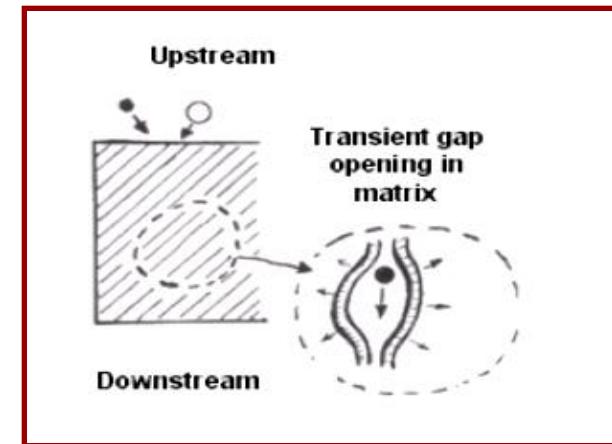
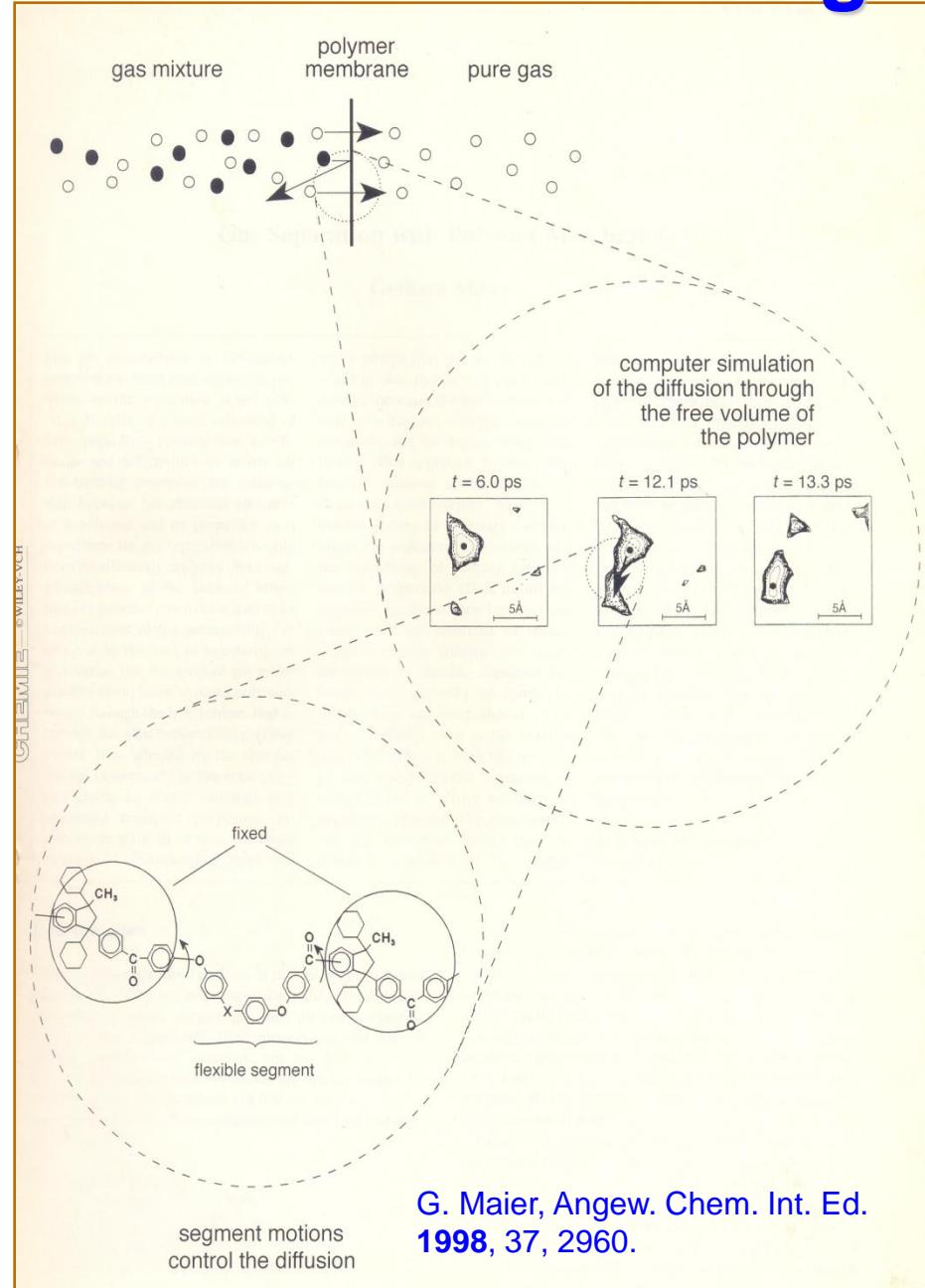


Hydrogen Purification Skid
– Membrane type

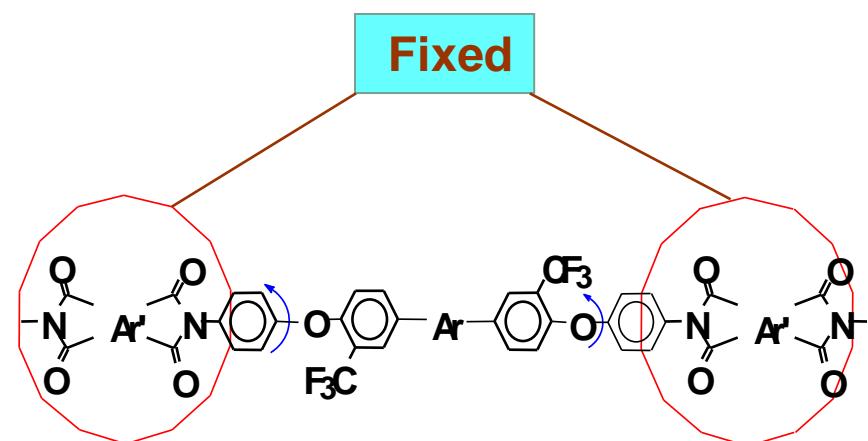
Commercially Used Polymers for Gas Separation

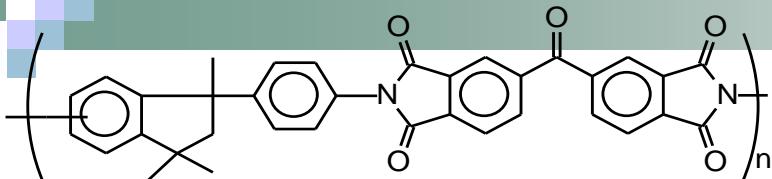
Polymer	Permeability (Barrers)		Ideal permselectivity α (CO_2/CH_4)	Ideal permselectivity α (O_2/N_2)
	CO_2	O_2		
<p>Matrimid</p>	9.0	1.90	37.5	7.0
<p>Ultem</p>	1.33	0.41	36.9	8.0
<p>Extem</p>	3.28	0.81	25.2	6.2
<p>Polysulfone</p>	5.6	1.4	22.4	5.6
<p>Cellulose acetate</p>	6.56	1.46	32.8	6.4

Design concept



Solution diffusion mechanism





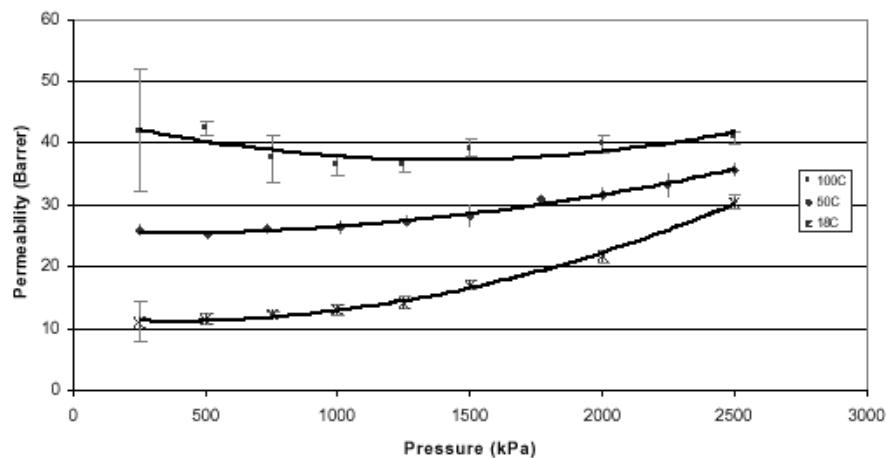
Matrimid® 5218 Resin

Table 1. A Comparison of transport performances for Matrimid membranes between the mixed gas and pure gas measurements.

Matrimid Membrane	Mixed Gas (40% CO ₂ in CH ₄)			Pure Gas		
	Total Upstream Pressure (atm)	Permeability (Barrel ^a)		Selectivity	Permeability (Barrel ^a)	Ideal Selectivity
		CO ₂	CH ₄			
Untreated Film	10	7.26	0.23	31.6	8.50	0.24
	15	6.72	0.22	30.5	8.16	0.23
7-days cross-linked Film	10	3.34	0.089	37.5	5.70	0.16
	15	3.26	0.081	40.2	5.23	0.15

^a 1 Barrer = $1 \times 10^{-10} \text{ cm}^3 (\text{STP}) \cdot \text{cm}/\text{cm}^2 \text{ s cmHg}$

CO₂ Permeability of As - Cast Matrimid
Temperature Range 18 - 100C



Scope of membrane research

CO₂ recovery from land fill gas

CO₂ ~ 40-45 mol %

CH₄ ~ 54 – 59 mol %

N₂ ~ 4 %, O₂ ~ 1 %

Water vapor ~ 1 %

H₂S & CFC ~ trace

Capture of CO₂ from the flue gas

(CO₂ ~ 15 %, water ~ 7 %, O₂ ~ 3 %, Nitrogen ~74 %, NOx + SOx ~ 1 %)

- Commercial membranes are limited to ambient temperature
- Matrimid offers high temperature separation of CO₂
- Mixed matrix membranes CMS dispersed within polymer matrices showed manifold increase in CO₂ permeability and CO₂ / CH₄ selectivity

Present need:

- Membrane that can operate at high temperature and pressure
- Higher flux and selectivity
- Low cost (for large scale application)

Measurement of Gas Transport Properties

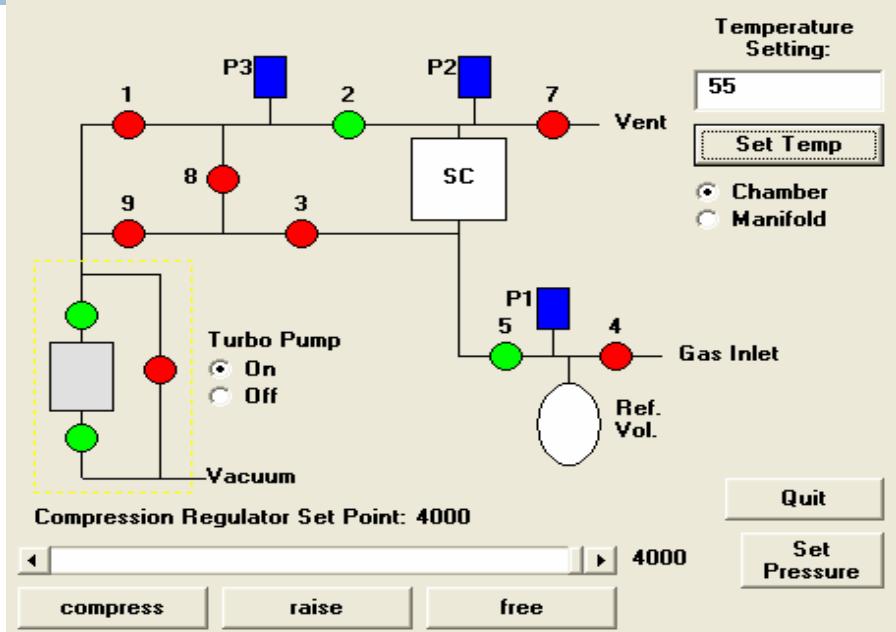


Figure: Schematic diagramme of the instrumental setup

P = Permeability coefficient

$$P = \left[\frac{VdT_0}{Ap_0 p_i T} \right] \left(\frac{dp}{dt} \right)_s$$

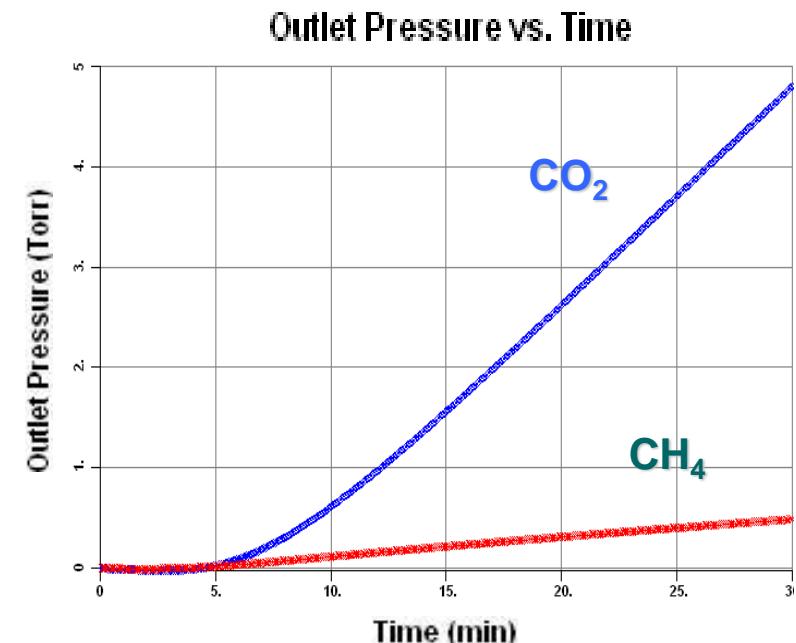
D = Diffusion coefficient (cm²/sec)

$$D = \frac{d^2}{6\theta}$$

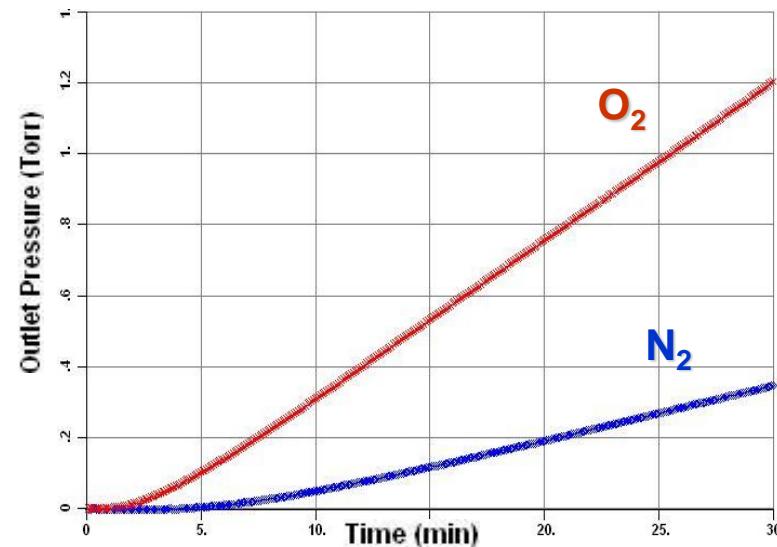
$\alpha_{A/B}$ = Ideal permselectivity towards gas 'A' relative to gas 'B'

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

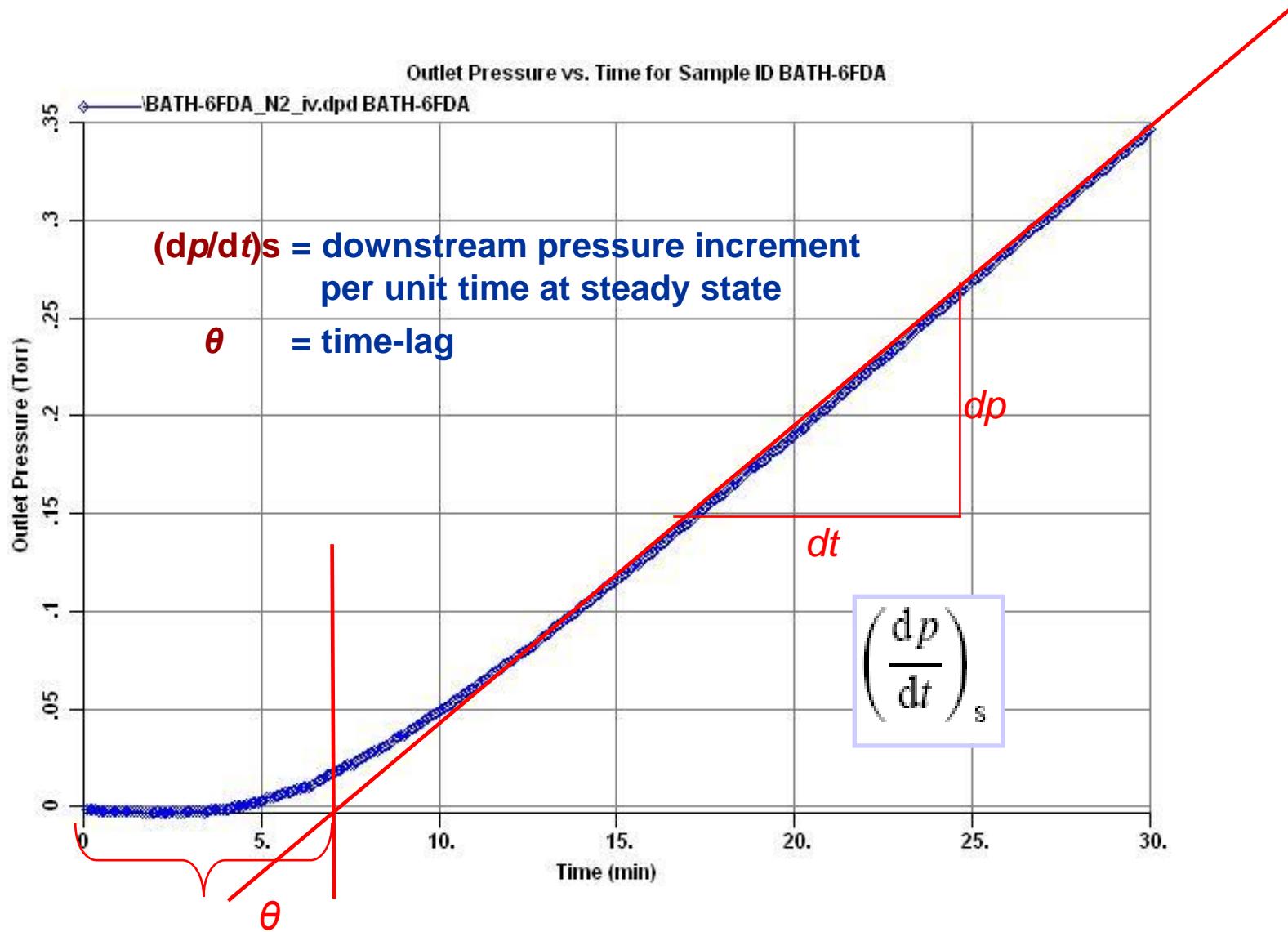
1 Barrer = 10^{-10} cm³ (STP) cm/cm² s cm Hg



Outlet Pressure vs. Time



Calculation of Gas Transport Coefficients





Where we stand?

Membrane type	Structure	Permeability (barriers)		Ideal selectivity $P(CO_2)/P(CH_4)$
		CO_2	CH_4	
BAPY-6FDA		51.92	1.95	26.6
BPI-6FDA		51.91	2.11	24.6
SBPDA-6FDA		52.98	1.21	43.8
BAPA-6FDA		53.85	1.01	53.3
BIDA-6FDA		71.32	1.99	35.8

S. K. Sen, Banerjee et al., *J. Membr. Sci.* Vol. 343, pages 97-103(2009)

S. K. Sen, Banerjee et al., *J. Membr. Sci.* Vol. 350, pages 53-61 (2010)

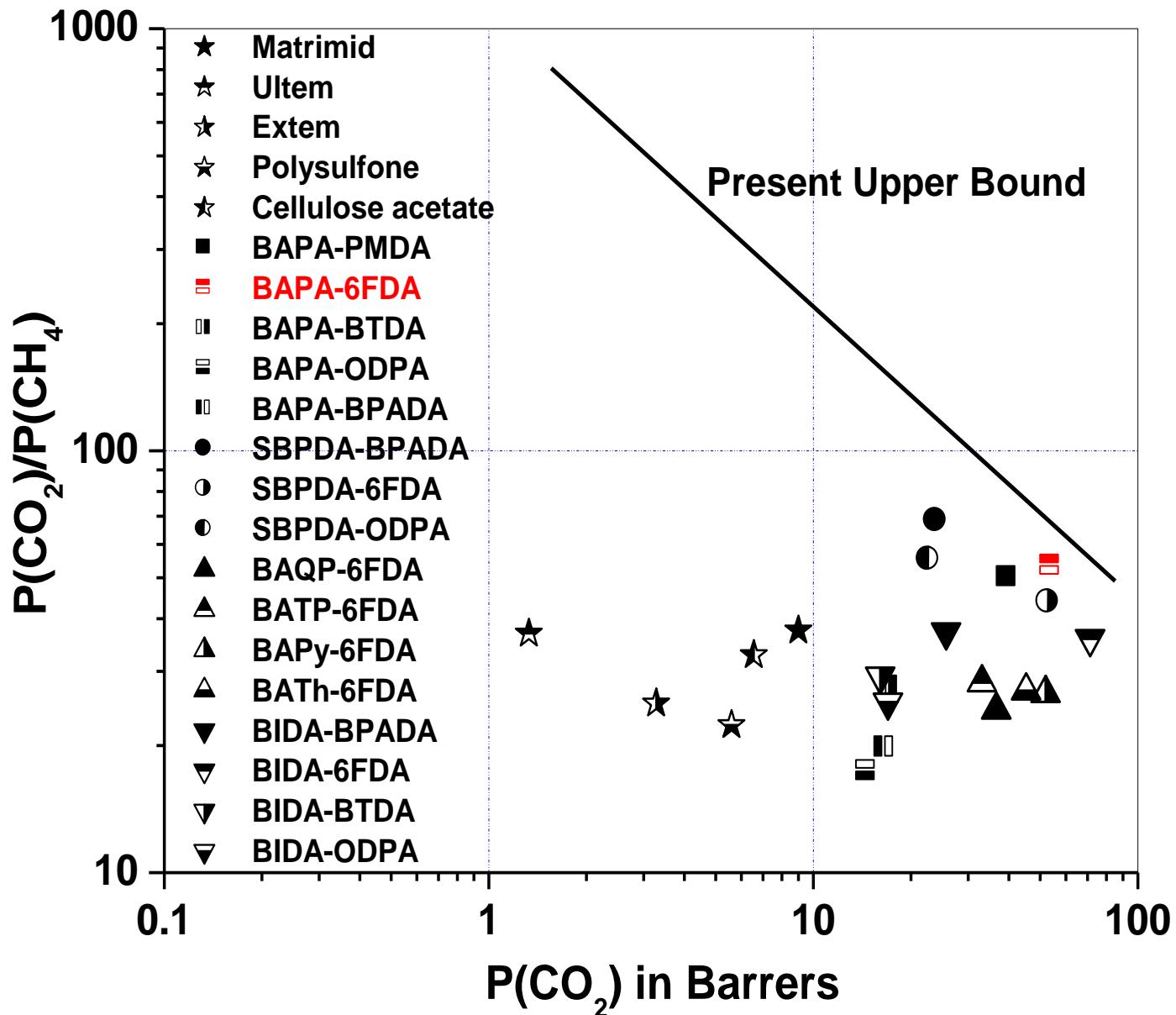
B. Dasgupta , Banerjee et al., *J. Membr. Sci.* Vol. 345, pages 249-256 (2009)

A. Bos et al., *Sep Purif Technol.* 1998, 14, 27;

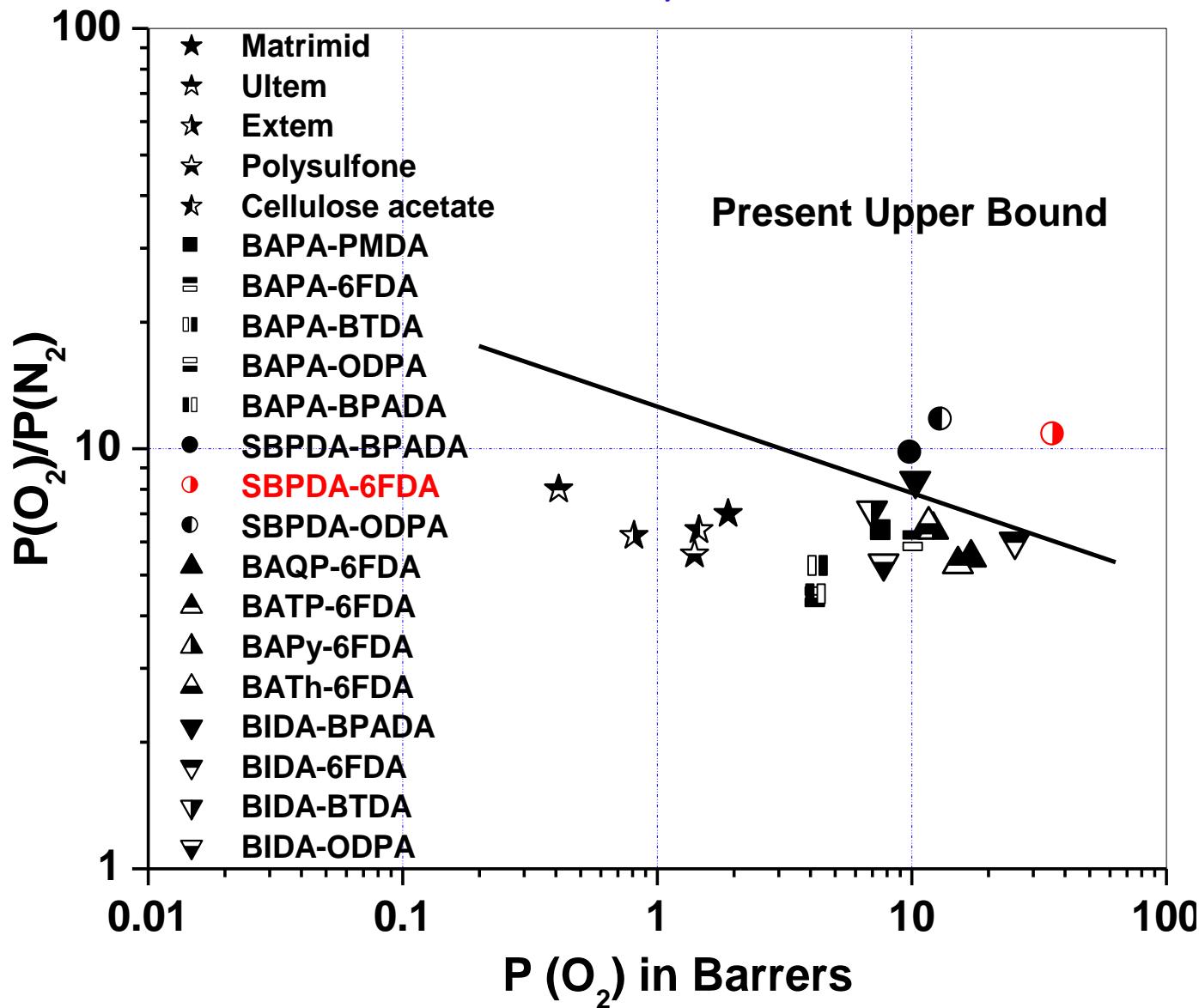
W. J. Koros et al., *J. Membr. Sci.* 2008, 175, 181;

and H. Yamamoto et al., *J. Polym. Sci. Part B: Polym. Phys.* 1990, 28, 2291.

Comparison of CO₂/CH₄ Separation Performances with Commercially Used Polymers



Comparison of O₂/N₂ Separation Performances with Commercially Used Polymers





Sulzer Chemtech

Mass Transfer Technology

Sulzer Chemtech AG, P.O. Box 65
CH-8404, Winterthur, Switzerland

BORSIG MEMBRANE TECHNOLOGY

BORSIG Membrane Technology GmbH
Egellsstraße 21, 13507 Berlin, Germany



Study #2307
March 2008
\$4600
349 Pages

Membrane Separation Technologies

US Industry Study with Forecasts for 2012 & 2017

Freedonia

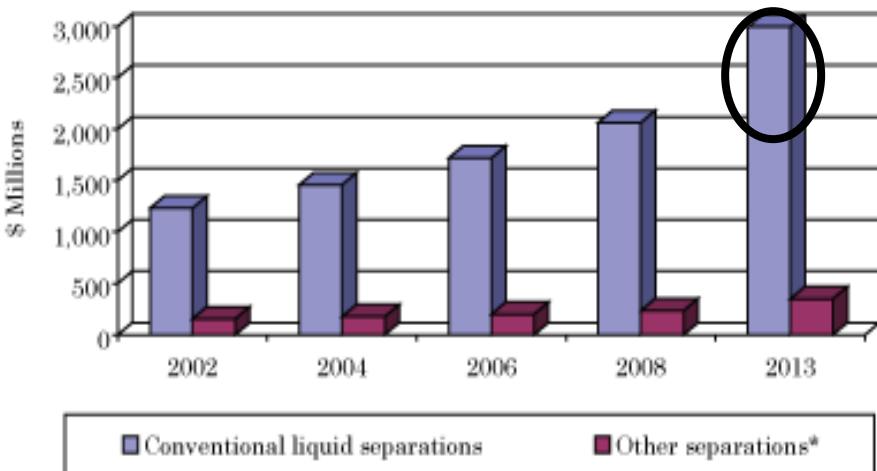
US demand to grow 8.2% annually through 2012

Demand for membrane materials is expected to increase 8.2 percent per year to \$4.3 billion in 2012. Growth will be driven by ongoing interest in process fluids with higher purity levels in a variety of markets, as well as the introduction of increasingly strict environmental regulations concerning the quality of water and wastewater streams. These factors are leading to the rising penetration of membranes into markets such as water and wastewater treatment, and food and beverage processing, as industry requirements surpass levels that can be achieved with conventional filtration equipment alone. Additionally, a growing number of industries are using membranes to reduce water use and waste.



SUMMARY FIGURE

PROJECTED VALUE OF THE U.S. MARKET FOR MEMBRANE MODULES USED IN GAS AND LIQUID SEPARATIONS, 2002-2013
(\$ MILLIONS)

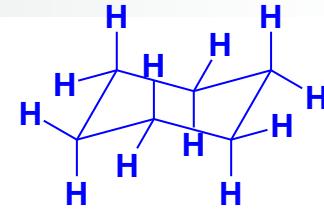
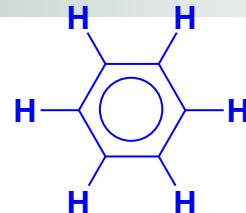


Source: BCC Research

Pervaporation

Why Benzene/Cyclohexane?

- ✓ Industrial demand
- ✓ Close boiling mixtures
- ✓ Form azeotropes
- ✓ Easily detected by GC



bp (°C): 80.100
fp (°C): 5.533

bp (°C): 80.738
fp (°C): 6.554

Bz + Cy (45 wt%): bp 77.5 (°C)

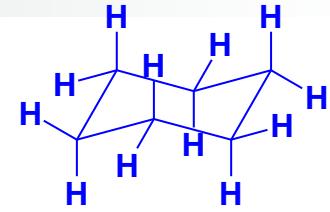
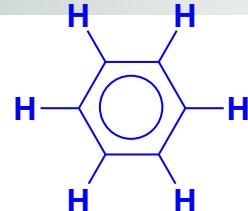
Different polymers used for Benzene/Cyclohexane

Membrane	Benzene in feed	Temperature (°C)	Normalized Flux (J) (kg μm/m²h)	Separation factor (α)	Reference
LDPE	50	25	10.8	1.6	Huang et al 1968
PVDF	53	56	1.5	5.4	McCandless et al 1974
PVA/PAAm	50	25	2.3	11.9	Park et al 1994
Modified nylon 6	50	50	0.057	4.5	Yoshikawa et al 1997
PAS	50	50	2.6	22.5	Ray et al 1997
PU-TEOS	50	50	0.65	19	Kusakabe et al 1998
BAPPP-TIPA	50	50	16.3	4.9	Wang et al 2001
BAPPH-TIPA	50	50	29.4	4	Wang et al 2001

LDPE: Low density polyethylene; **PVDF:** Poly(vinylidene fluoride); **PVA/PAAm:** Polyvinyl alcohol/ Polyallyl amine; **PAS:** Poly(acrylonitrile-co-styrene); **PU-TEOS:** Polyurethane-tetraethyl-ortho-silicate); **BAPPP:** 2,2-Bis[4-(4-amionphenoxy)phenyl]propane; **BAPPH:** 2,2-Bis[4-(4-amionphenoxy)phenyl]hexafluoro propane; **TIPA:** 5-t-butyl-isophthalic acid.

Why Benzene/Cyclohexane?

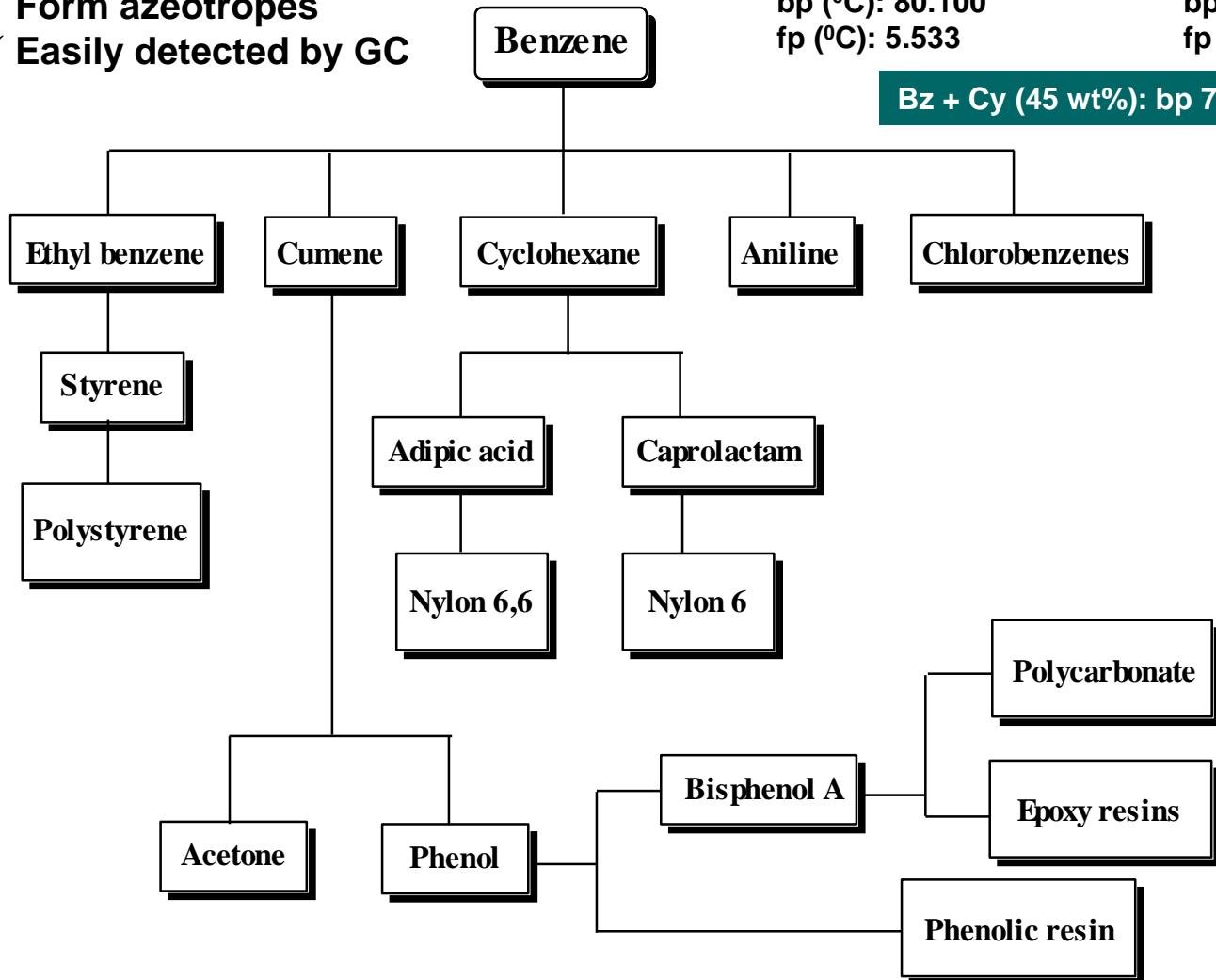
- ✓ Industrial demand
- ✓ Close boiling mixtures
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bp (°C): 80.100
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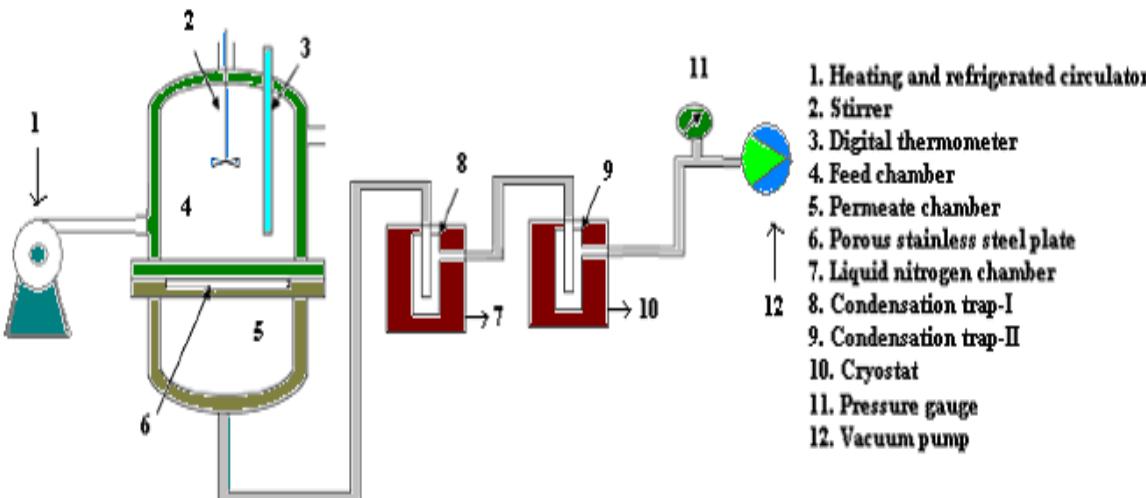




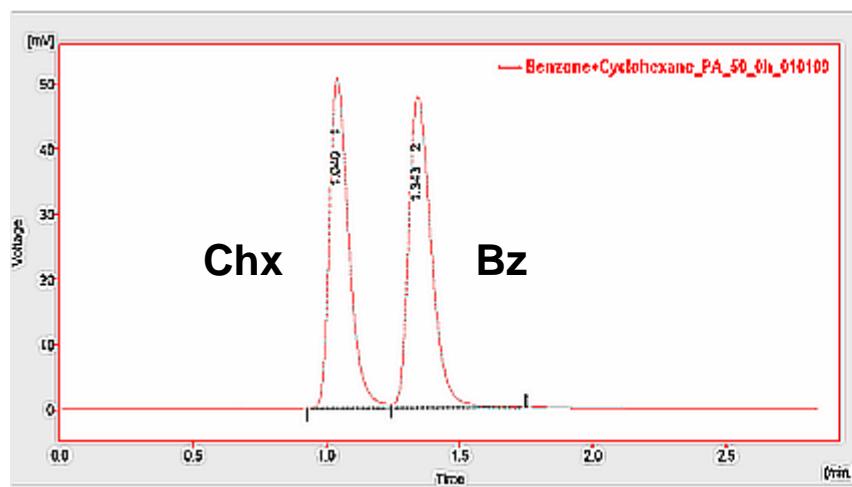
Goal of the present research

- **Design and preparation of new diamine monomers**
- **Preparation of processable PEAs**
- **Systematic investigation of pervaporation study of the PEAs for benzene (Bz)/cyclohexane (Chx) mixture at different temperatures (50, 60 and 70 °C)**
- **Establishment of structure property correlation**

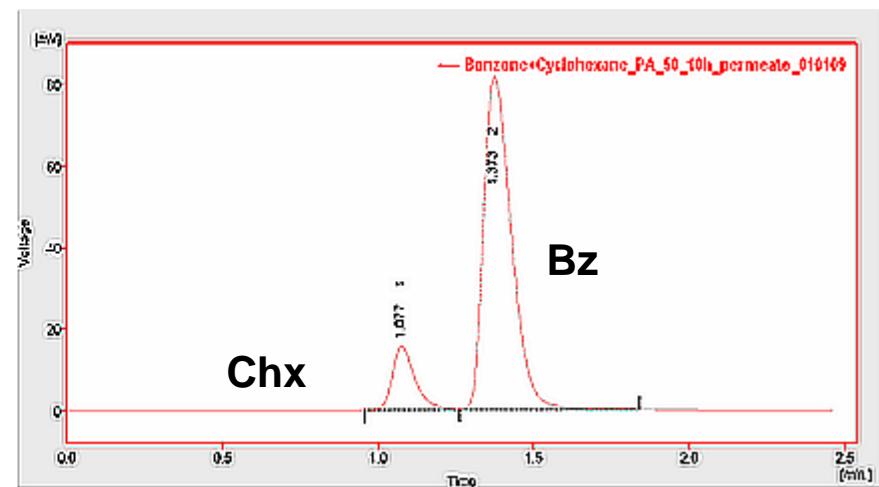
Pervaporation application



- 10% OV-17 packed column
- Flame ionization detector (FID)
- Temperature of the oven, injector and detector 80, 100 and 200 °C

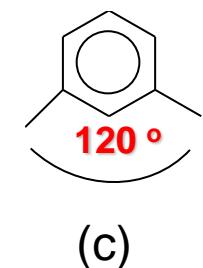
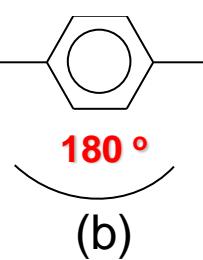
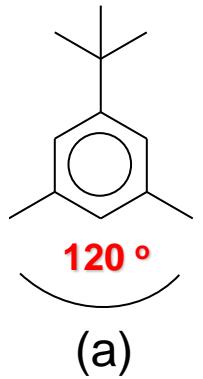
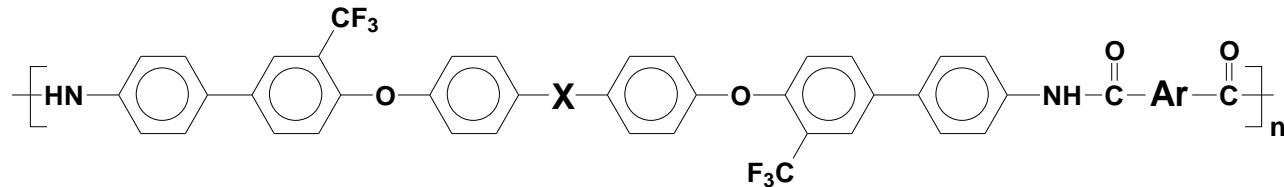


	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	1.040	253.907	50.603	47.5	51.4	0.08
2	1.343	281.088	47.803	52.5	48.6	0.09
Total		534.995	98.406	100.0	100.0	



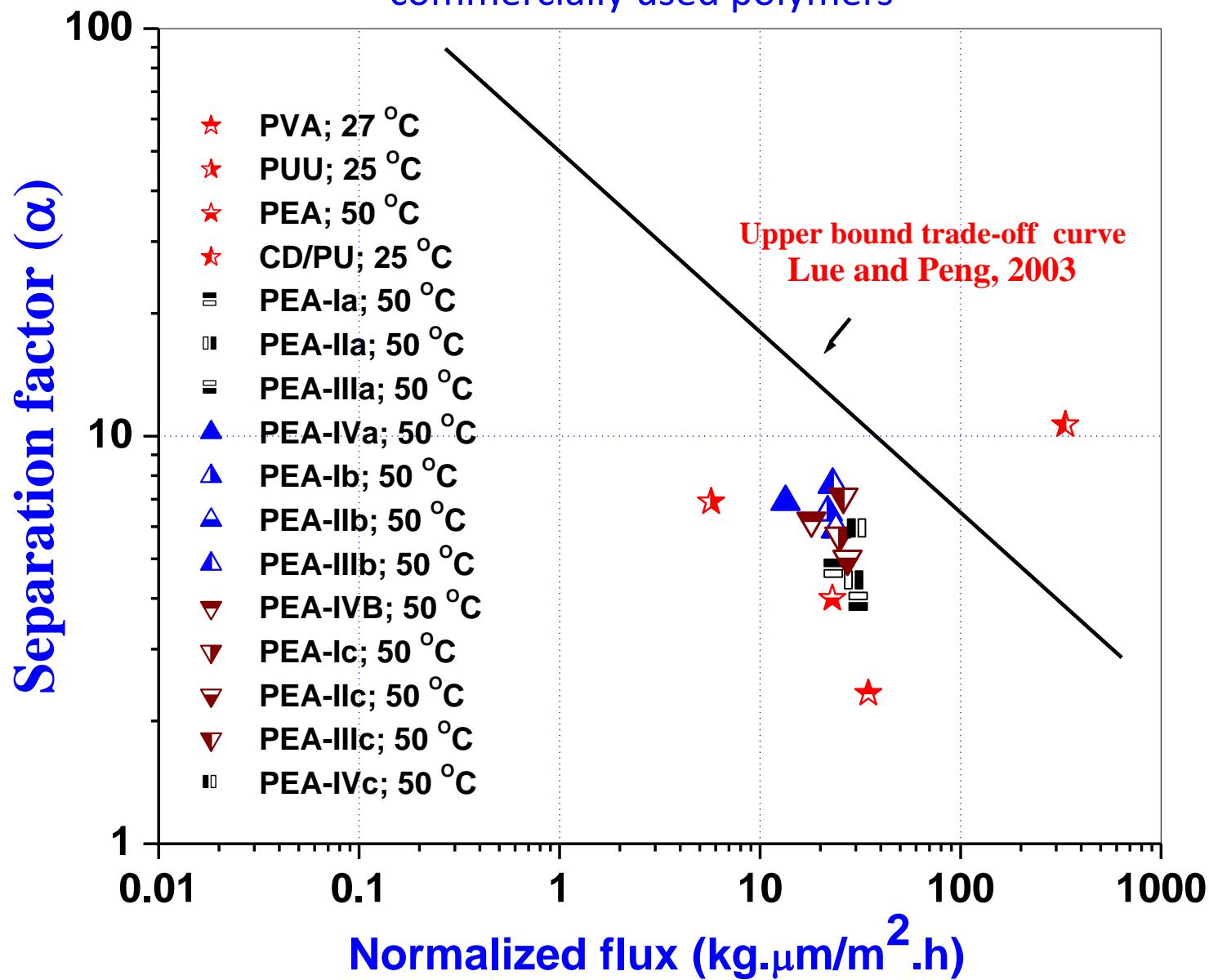
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	1.077	78.097	15.546	13.3	16.0	0.08
2	1.373	507.950	81.651	86.7	84.0	0.10
Total		586.047	97.197	100.0	100.0	

Polymer Structure vs. Properties



PEAs		T_g (°C)	FFV	Separation factor (α)	Normalized flux (kg. $\mu\text{m}/\text{m}^2.\text{h}$) at 50 °C	PSI (g/ $\text{m}^2.\text{h}$) at 50 °C
X	Ar					
- $(\text{CH}_3)_2-$	a	250	0.188	4.7	23.66	2087
- $(\text{CF}_3)_2-$		252	0.287	4.4	29.89	2421
		273	0.293	3.9	31.42	2169
		310	0.254	5.9	30.85	3601
- $(\text{CH}_3)_2-$	b	233	0.143	6.9	13.41	1888
- $(\text{CF}_3)_2-$		240	0.176	6.5	21.77	2849
		294	0.173	5.9	23.91	2788
		300	0.145	7.6	23.03	3616
- $(\text{CH}_3)_2-$	c	230	0.167	6.2	18.04	2236
- $(\text{CF}_3)_2-$		233	0.201	5.7	24.86	2782
		285	0.199	5.0	27.31	2600
		290	0.168	7.1	26.04	3782

Pervaporation performances in comparison with commercially used polymers

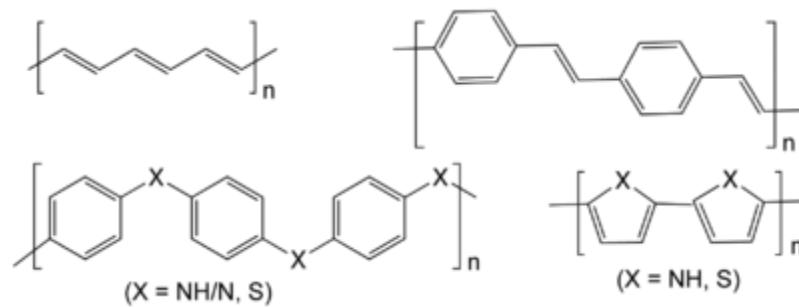




Renewable Energies

Conjugated polymers

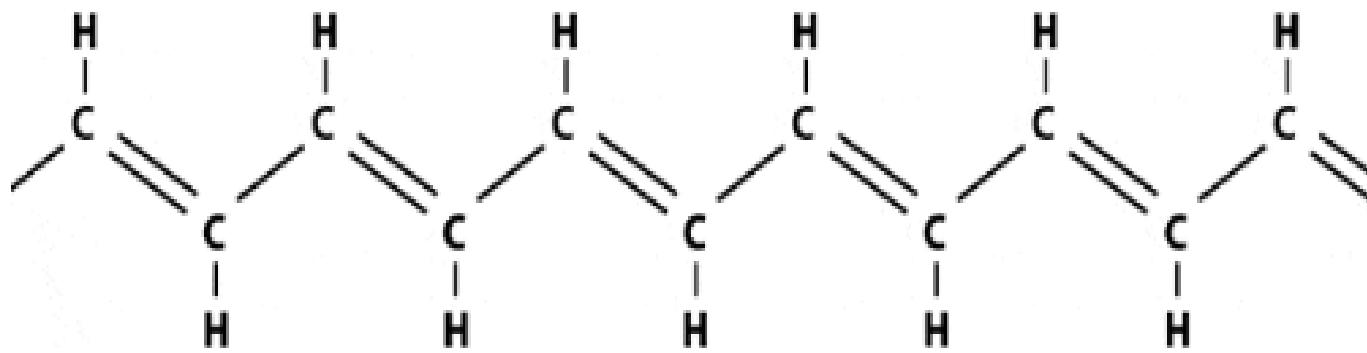
Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity



1. Conjugated organic polymers can be doped, via oxidation or reduction chemistry or via acidbase chemistry, to induce very high electrical conductivity.
2. Conjugated polymers are beginning to find uses, in both the neutral and the doped states, in prototype molecular-based electronics applications and in electronic and opto-electronic devices.

Two conditions to become conductive:

1. The first condition for this is that the polymer consists of alternating single and double bonds, called conjugated double bonds. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised “sigma” (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localised “pi” (π) bond which is weaker.



2. The second condition is that the plastic has to be disturbed - either by removing electrons from (oxidation), or inserting them into (reduction), the material. The process is known as doping.

Discovery of conducting polymers

1862

Lethby (College of London Hospital)
Oxidation of aniline in sulfuric acid

1970's

Shirakawa (Japan)

Acetylene gas



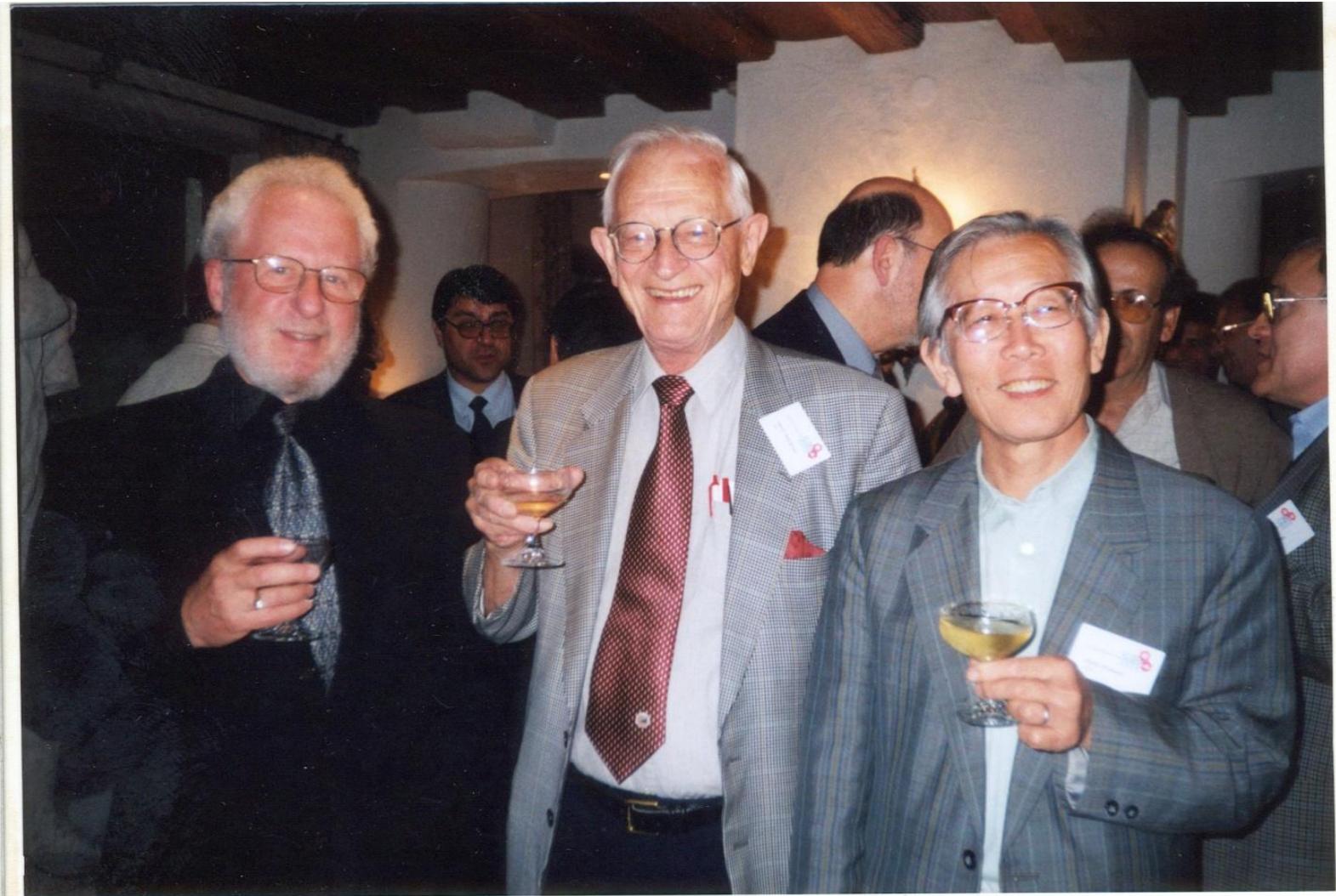
Ti(OBu)₄ & Et₃Al
Toluene
−78°C

Ti(OBu)₄ & Et₃Al
Hexadecane
150°C

copper-coloured film
cis-polyacetylene

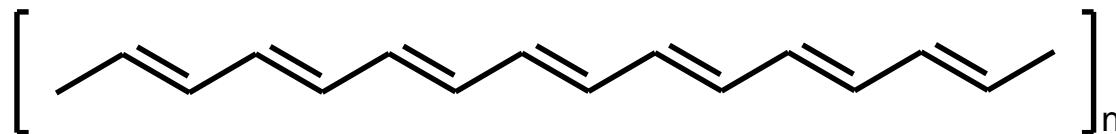
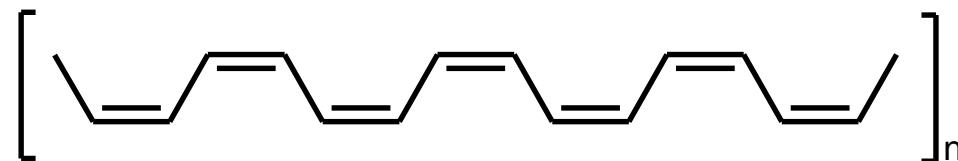
silvery film
trans-polyacetylene

Discoverers - Nobel Prize 2000



A. Heeger, A. McDiarmid, H. Shirakawa

Polyacetylene (PA)



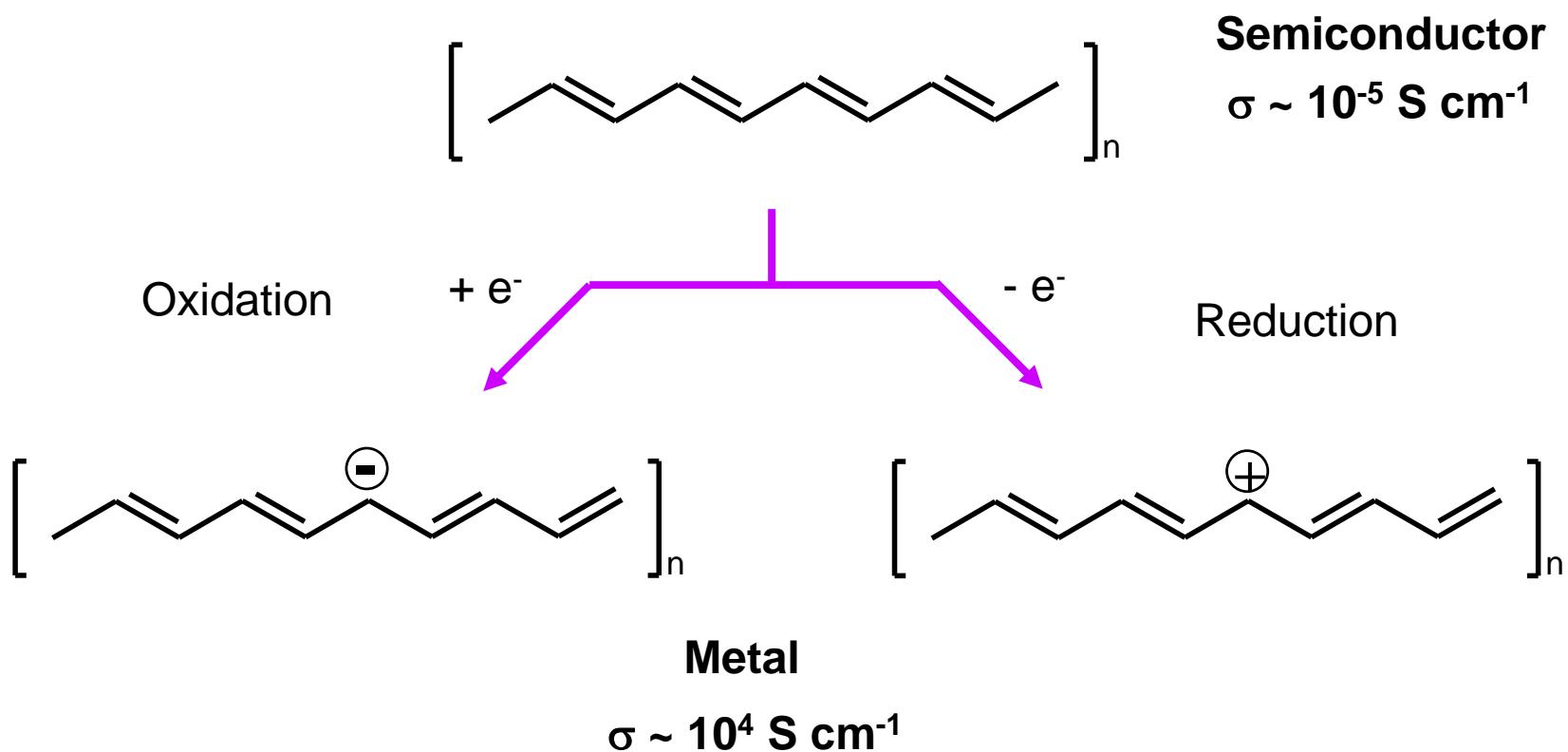
Electrical conductivity (σ)

cis PA $10^{-10} - 10^{-9} \text{ S cm}^{-1}$

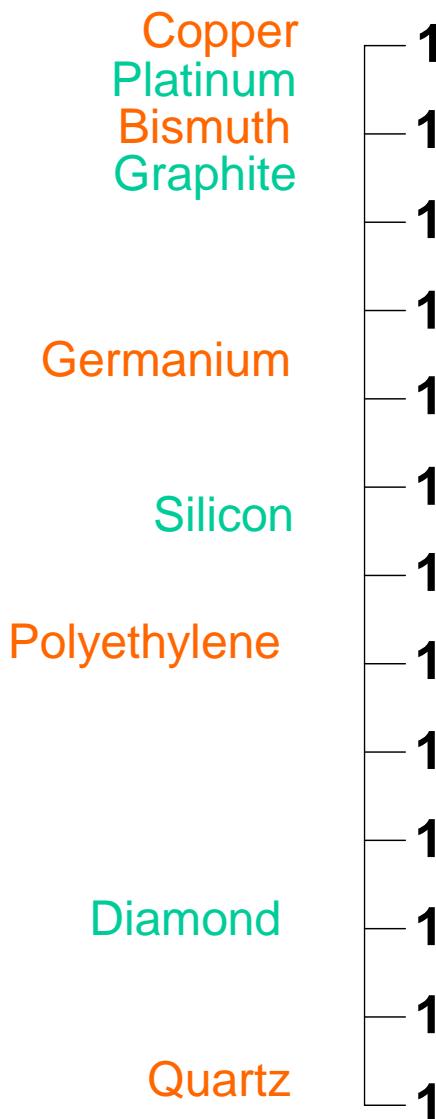
trans PA $10^{-5} - 10^{-4} \text{ S cm}^{-1}$

For comparison : σ (copper) $\sim 10^6 \text{ S cm}^{-1}$
 : σ (teflon) $\sim 10^{-15} \text{ S cm}^{-1}$

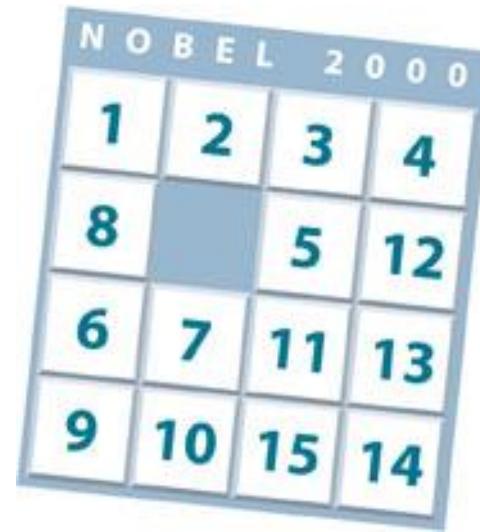
Doping leads to enhanced conductivity



Electrical conductivities



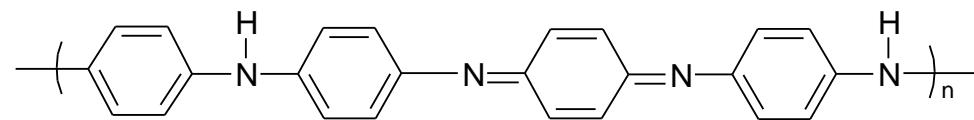
Doped polyacetylene is, e.g., comparable to good conductors such as copper and silver, whereas in its original form it is a semiconductor.



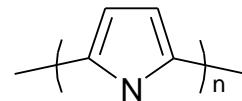
The game offers a simple model of a doped polymer. The pieces cannot move unless there is at least one empty "hole". In the polymer each piece is an electron that jumps to a hole vacated by another one. This creates a movement along the molecule - an electric current

Examples of conducting polymers

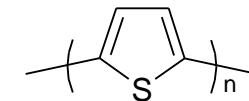
Polyaniline
(PANI)



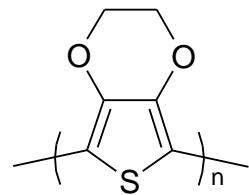
Polypyrrole
(PPy)



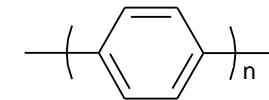
Polythiophene
(PT)



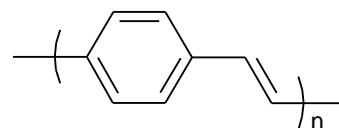
Polyethylene
dioxythiophene
(PEDOT)



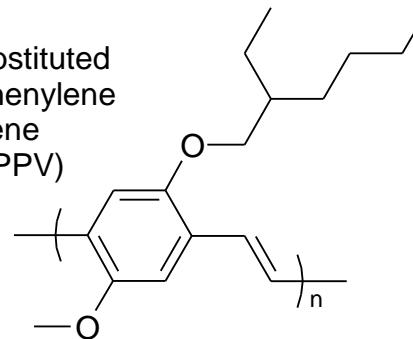
Polyparaphenylene
(PPP)



Polyparaphenylene
vinylene
(PPV)

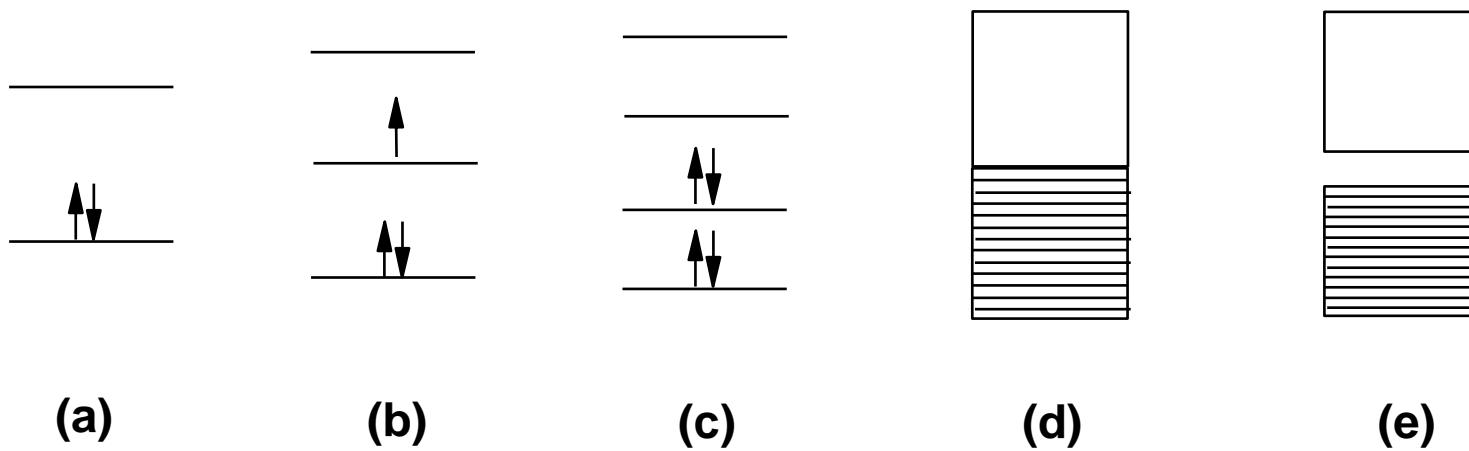


Alkoxy-substituted
polyparaphenylene
vinylene
(MEH-PPV)



Polyacetylene - electronic structure

π -electronic energy levels and electron occupation



(a) ethylene

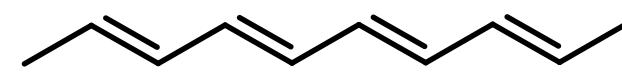
(d) regular *trans*-PA



(b) allyl radical

(c) butadiene

(e) dimerised *trans*-PA

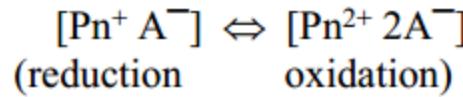


Conducting Mechanism

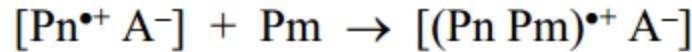
- While the addition of a donor or an acceptor molecule to the polymer is called "doping ", the reaction that takes place is actually a redox reaction.
- The first step is the formation of a cation (or anion) radical, which is called a soliton or a polaron.



- This step may then be followed by a second electron transfer with the formation of a dication (or dianion) known as a bipolaron.

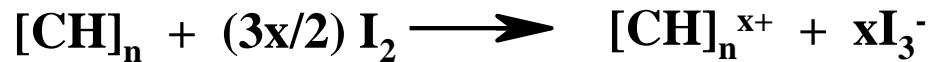
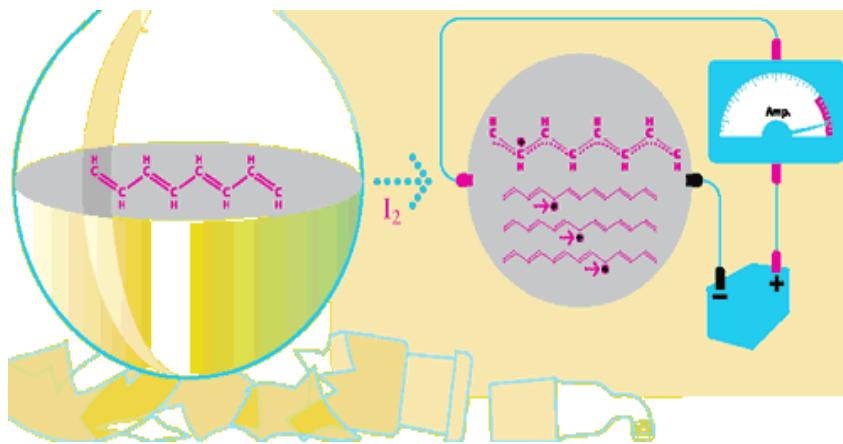


- Alternatively after the first redox reaction, charge transfer complexes may form between charged and neutral segments of the polymer when possible.

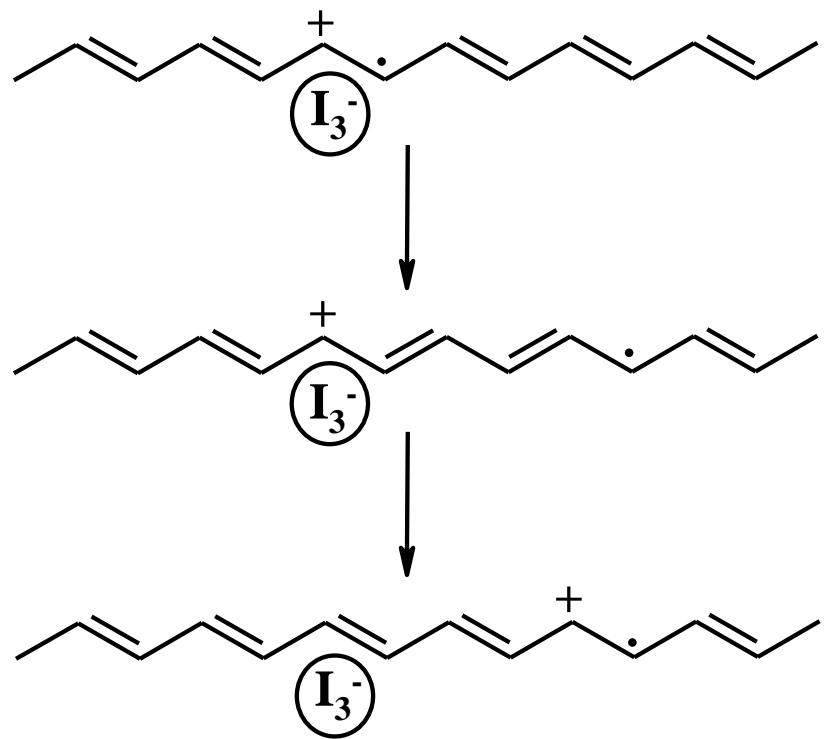


How does a conducting polymer work ?

Oxidative doping of polyacetylene by iodine

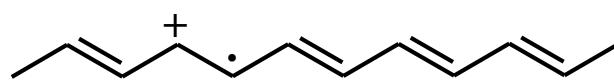


Polaron and its delocalisation

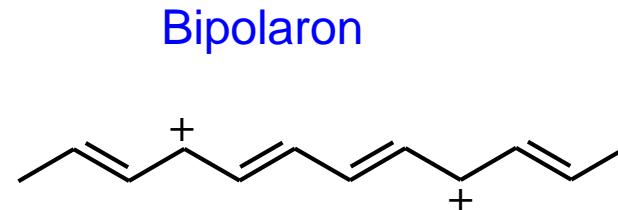


Oxidation with iodine causes the electrons to be jerked out of the polymer, leaving "holes" in the form of positive charges that can move along the chain.

Excitations



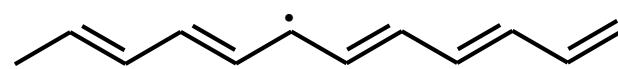
oxidation
→



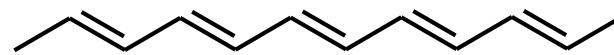
Bipolaron



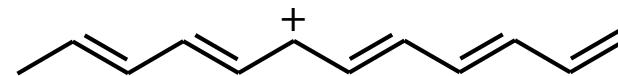
isomerisation
→



Neutral Soliton



oxidation
→



Positive Soliton

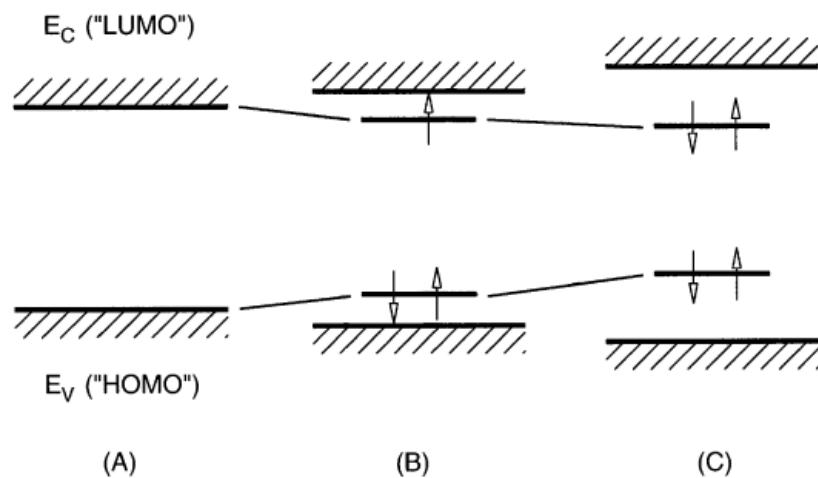
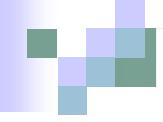


Fig. 2. Energy level scheme of the self-localized states in conjugated polymers: (A) Band edges of a neutral polymer, where both physics and chemistry terminologies are used to label the band edges; (B) polaron state formed upon the addition of an extra electron; and (C) spinless bipolaron state formed upon the addition of a second electron, which also corresponds to the combination of two polarons.



Applications of conducting polymers

Polyaniline (PANI)

Transparent conducting electrodes
Electromagnetic shield
Corrosion inhibitor
'Smart windows' (electrochromism)

Polypyrrole (Ppy)

Radar-invisible screen coating
(microwave absorption)
Sensor (active layer)

Polythiophene (PT)

Field-effect transistor
Anti-static coating
Hole injecting electrode in OLED

Polyphenylenevinylene (PPV)

Active layer in OLED

Organic light emitting diodes (OLED's)

An OLED is any light emitting diode (LED) which emissive electroluminescent layer is composed of a film of organic compounds.

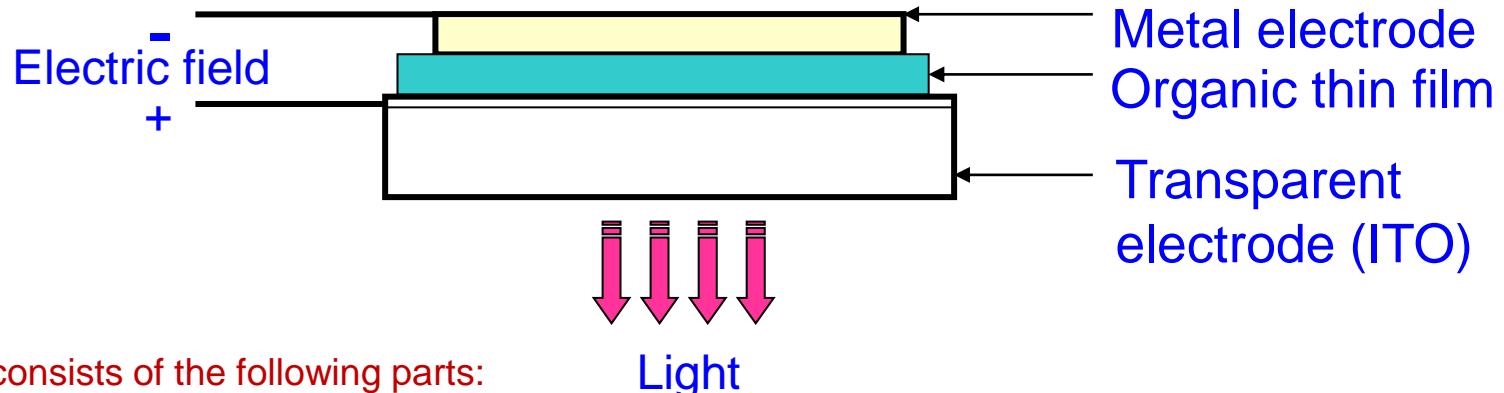
- A light emitting polymer is an electro-luminescent plastic. The molecules of this plastic emit light when an electric field is applied.
- Polymer based light-emitting diodes (LED) were discovered in 1990.
- Cambridge Display Technology has the core patents for the Technology of LEP.



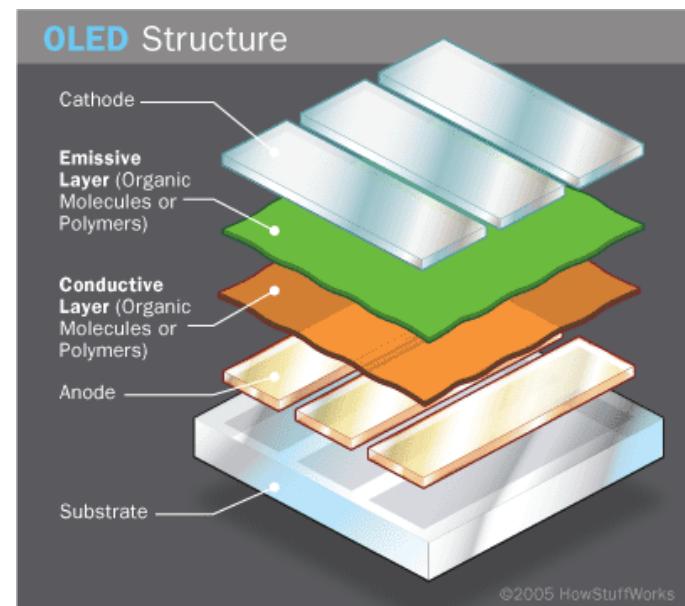
Flexible plastic serves as home to new, highly efficient organic light-emitting diodes.

OLEDs provide high-contrast and low-energy displays that are rapidly becoming the dominant technology for advanced electronic screens.

OLED Structure

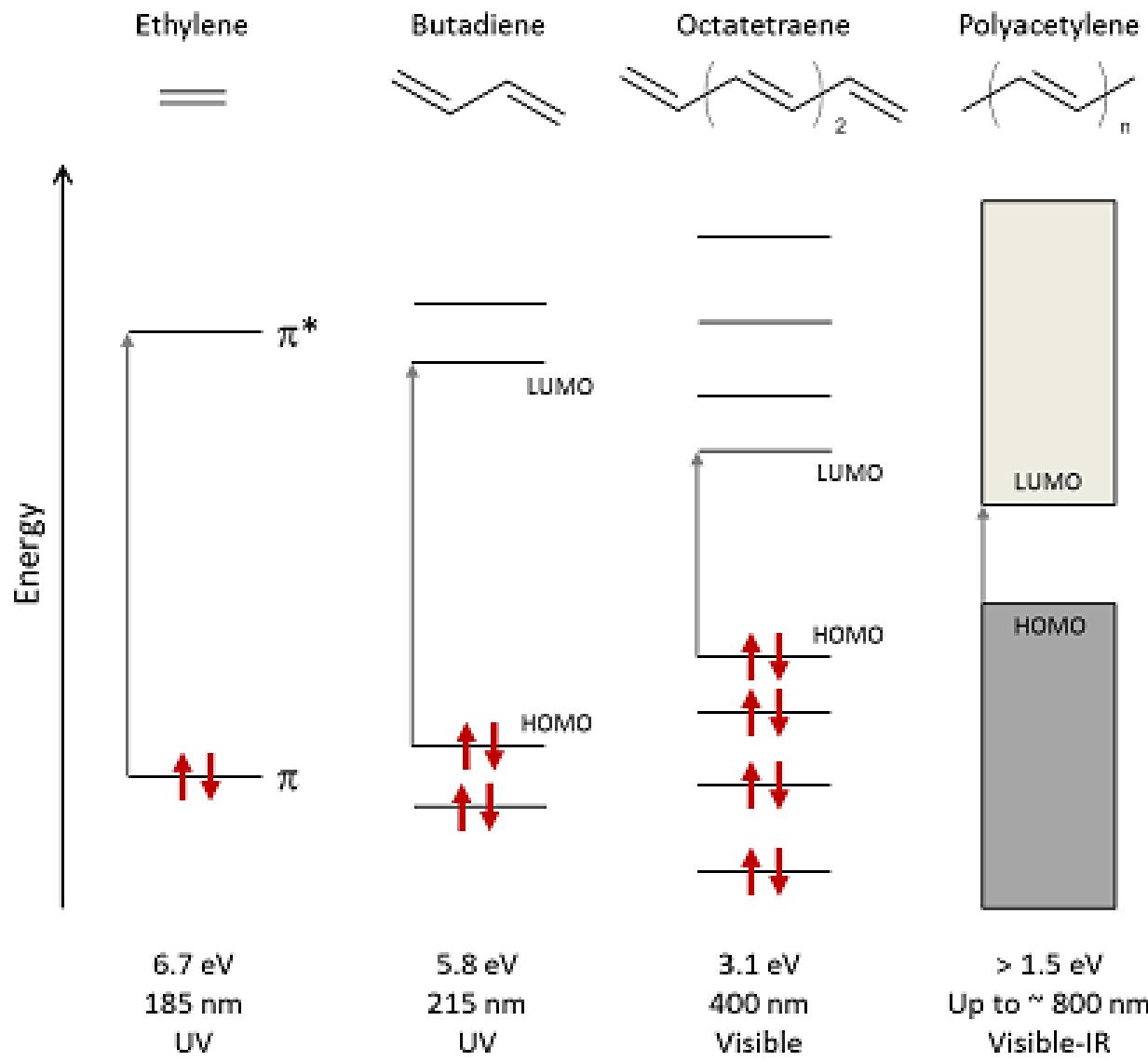


- 1. Substrate** (clear plastic, glass, foil) - The substrate supports the OLED.
- 2. Anode** (transparent) - The anode removes electrons (adds electron "holes") when a current flows through the device.
- 3. Conducting layer** - This layer is made of organic plastic molecules that transport "holes" from the anode. One conducting polymer used in OLEDs is polyaniline.
- 4. Emissive layer** - This layer is made of organic plastic molecules (different ones from the conducting layer) that transport electrons from the cathode; this is where light is made. One polymer used in the emissive layer is polyfluorene.
- 5. Cathode** (may or may not be transparent depending on the type of OLED) - The cathode injects electrons when a current flows through the device.

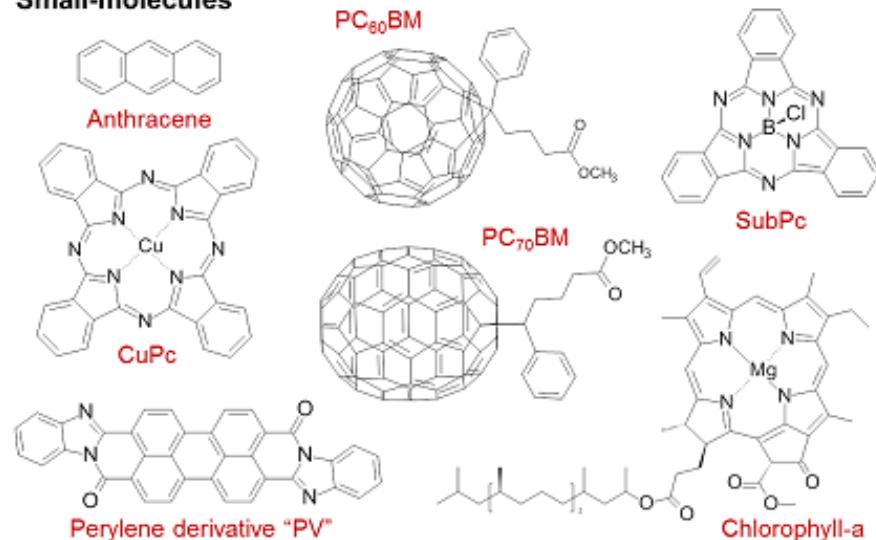


OLED Operation

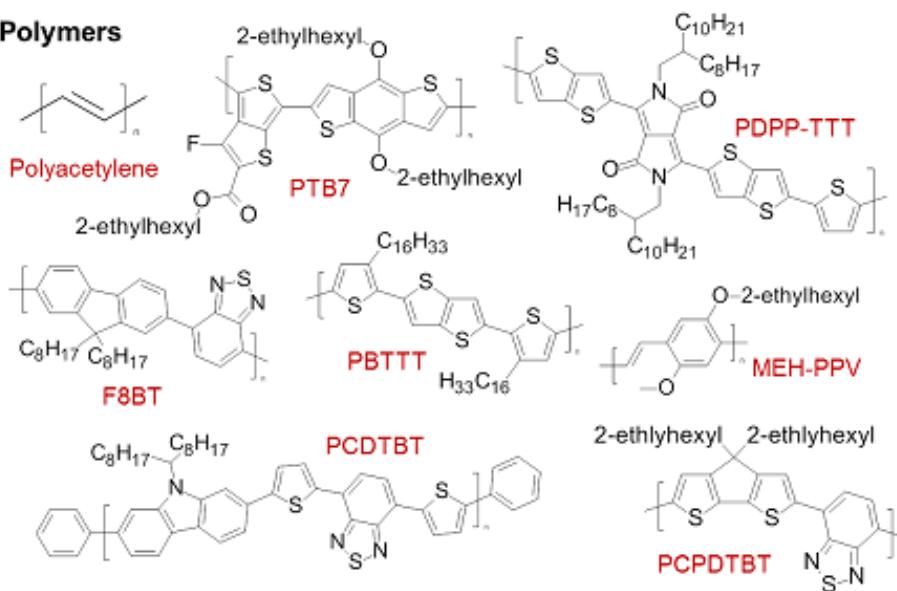
- A typical OLED is composed of a layer of organic materials situated between two electrodes, the anode and cathode, all deposited on a substrate. The organic molecules are electrically conductive as a result of delocalization of pi electrons caused by conjugation over all or part of the molecule
- During operation, a voltage is applied across the OLED such that the anode is positive with respect to the cathode.
- A current of electrons flows through the device from cathode to anode, as electrons are injected into the LUMO of the organic layer at the cathode and withdrawn from the HOMO at the anode.
- This latter process may also be described as the injection of electron holes into the HOMO.
- Electrostatic forces bring the electrons and the holes towards each other and they recombine forming an exciton, a bound state of the electron and hole.
- This happens closer to the emissive layer, because in organic semiconductors holes are generally more mobile than electrons.
- The decay of this excited state results in a relaxation of the energy levels of the electron, accompanied by emission of radiation whose frequency is in the visible region.
- The frequency of this radiation depends on the band gap of the material, in this case the difference in energy between the HOMO and LUMO.



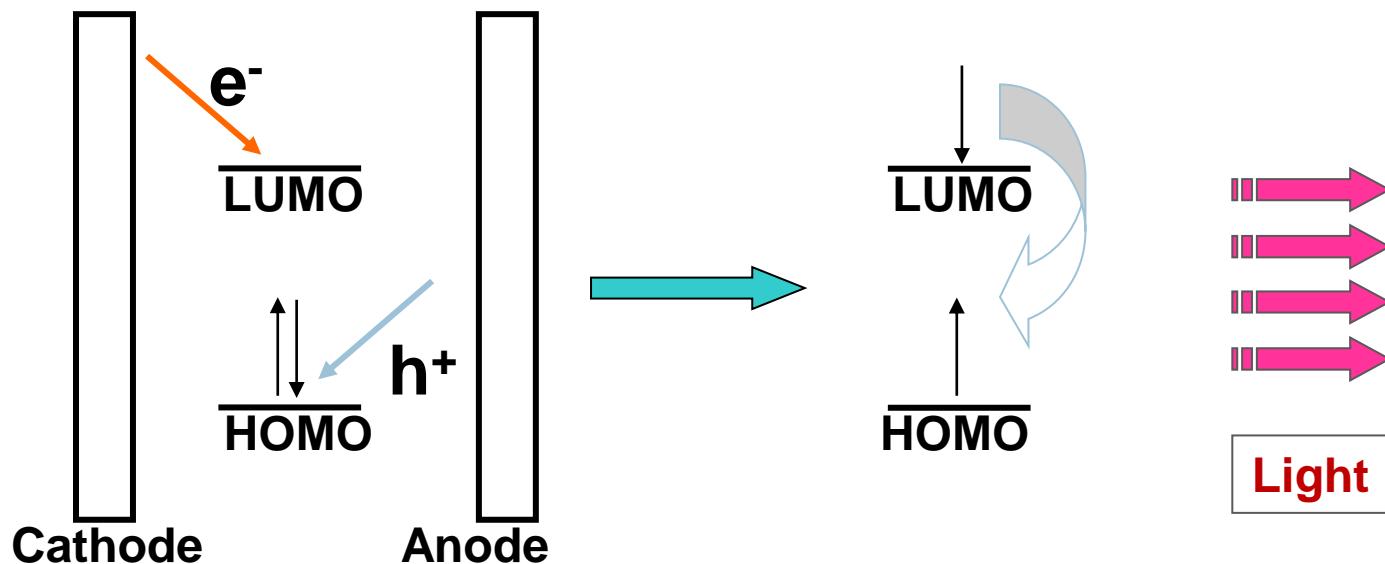
Small-molecules



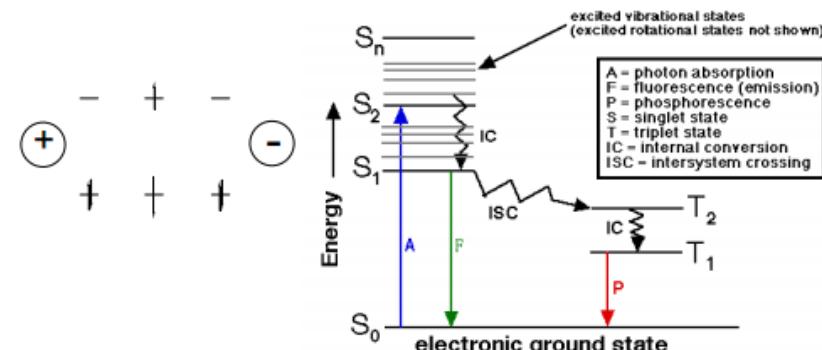
Polymers



Principle of EL

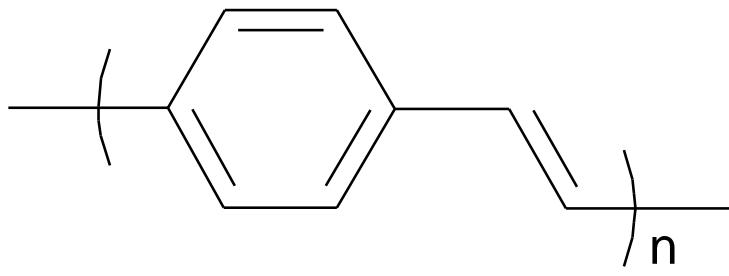


OLEDs - when electrons and holes meet

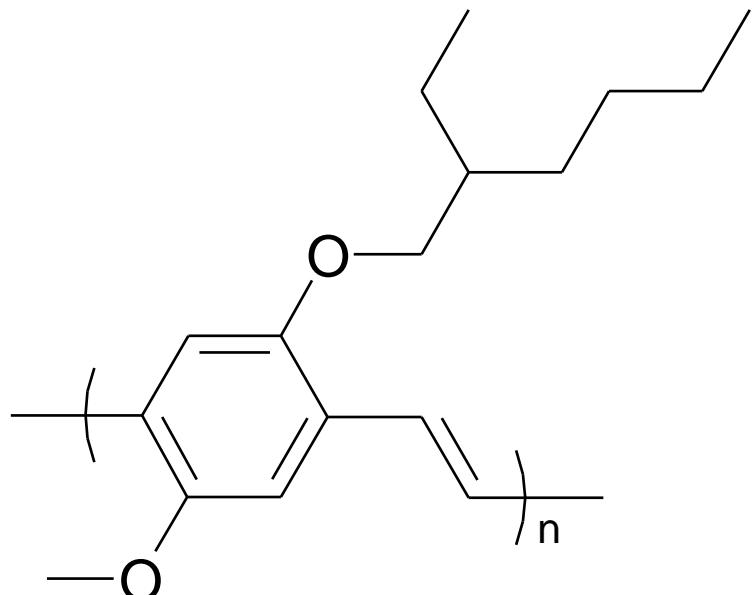


Jablonski Diagram

Polymers for Organic Light Emitting Diodes (OLED)



PPV



MEH-PPV

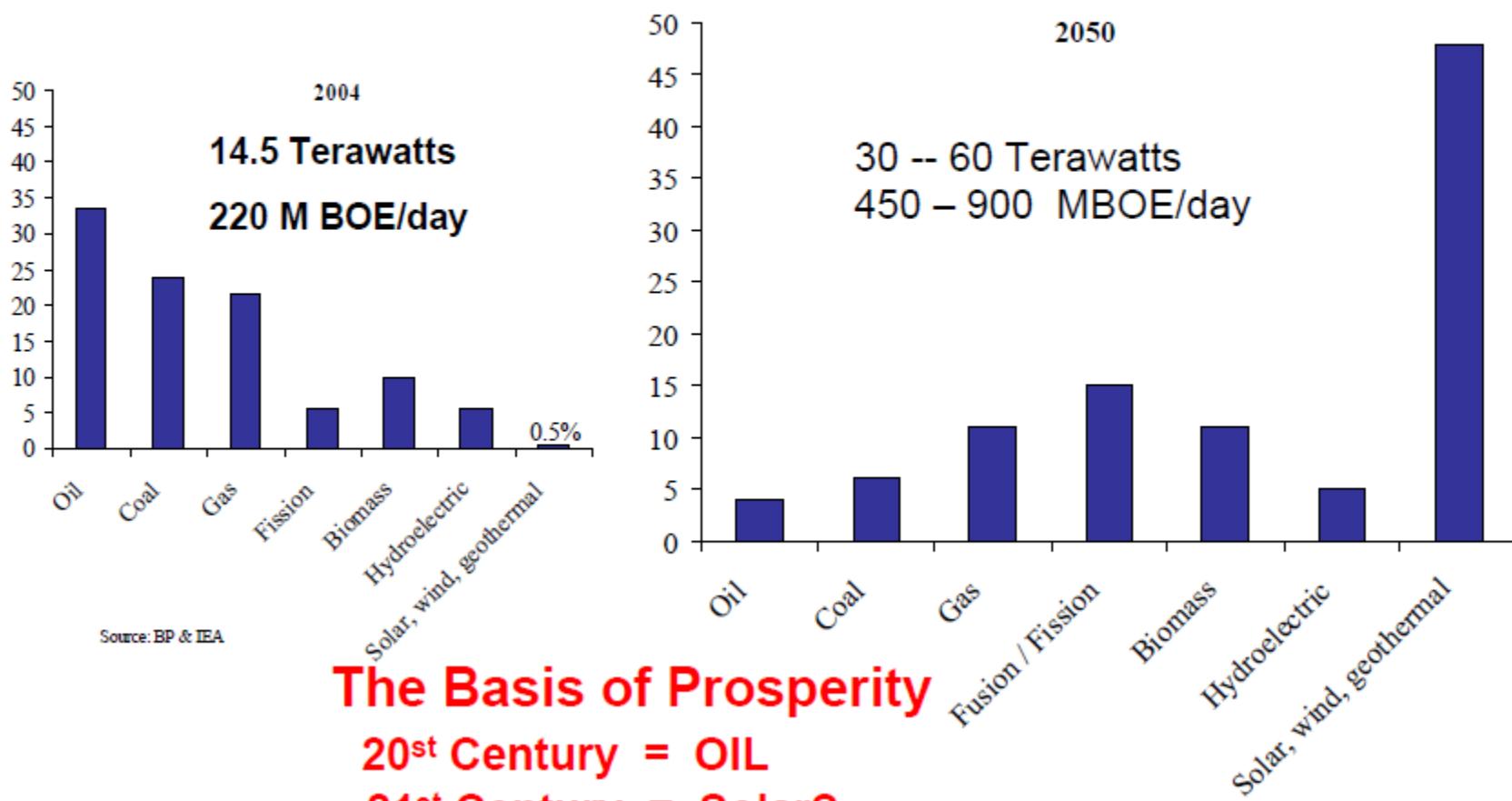
Commercial materials like Mn²⁺ in ZnS require 100V DC

PPV : requires 5 - 10V DC

runs even with AC

brightness ~40,000 cd/m² ie. ~100 times brighter than a TV screen

The ENERGY REVOLUTION (The Terawatt Challenge)





Sustainable Energy Production

- We need **clean, efficient, renewable, reliable** energy production technology
- Current major source of energy production: Fossil fuel (example: natural gas, oil)
- Fossil fuel: organic compounds composed of **C** and **H**
- Energy production from fossil fuel :
 - not clean, not renewable
 - smog, green house gas, regional instability, limited resource
- We are consuming fossil fuel about a million times more rapidly than the rate at which it was produced
- World petroleum production cannot be sustained, and will begin to decline in the future

Major Petroleum-Consuming Nations

	Consumption million barrels/day	Barrels per person-day	Imports, mb/day
United States	19.7	0.0702	10.40
Japan	5.4	0.0425	5.30
China	4.9	0.0038	1.60
Germany	2.7	0.0326	2.60
UK	1.7	0.0284	–
France	1.9	0.0328	1.85
Saudi Arabia	1.36	0.0284	–

* Energy Information Administration, DOE; www.nationmaster.com

United States: 4% population but 25% energy consumption of the world
Among developed countries US people consumes almost two times more oil than others

Alternative Energy for Our Future

Energy from non-fossil fuels

Solar energy

Wind, geothermal energy

Hydrogen fuel cells

Biomass



Interdisciplinary Research

Physics, Chemistry, Biology,

Materials Science,

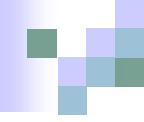
Mechanical Engineering,

Electric Engineering, etc



Renewable Technologies: Need

- It is expected that the global energy demand will double within the next 50 years.
- Fossil fuels are running out and are held responsible for the increased concentration of carbon dioxide in the earth's atmosphere.
- Hence, developing environmentally friendly renewable energy is one of the challenges to society in the 21st century.
- One of the renewable technologies is the hydrogen fuel cell that generates electricity from the chemical reaction of hydrogen and oxygen as a byproduct water.
- Similarly photovoltaics (PV), is the other renewable energy technologies is the technology that directly converts daylight into electricity.
- Thus, hydrogen fuel cells and photovoltaic (PV) energy technologies can contribute to environmentally friendly renewable energy production and mitigate the issues associated to carbon dioxide emission.....Global warming!!!

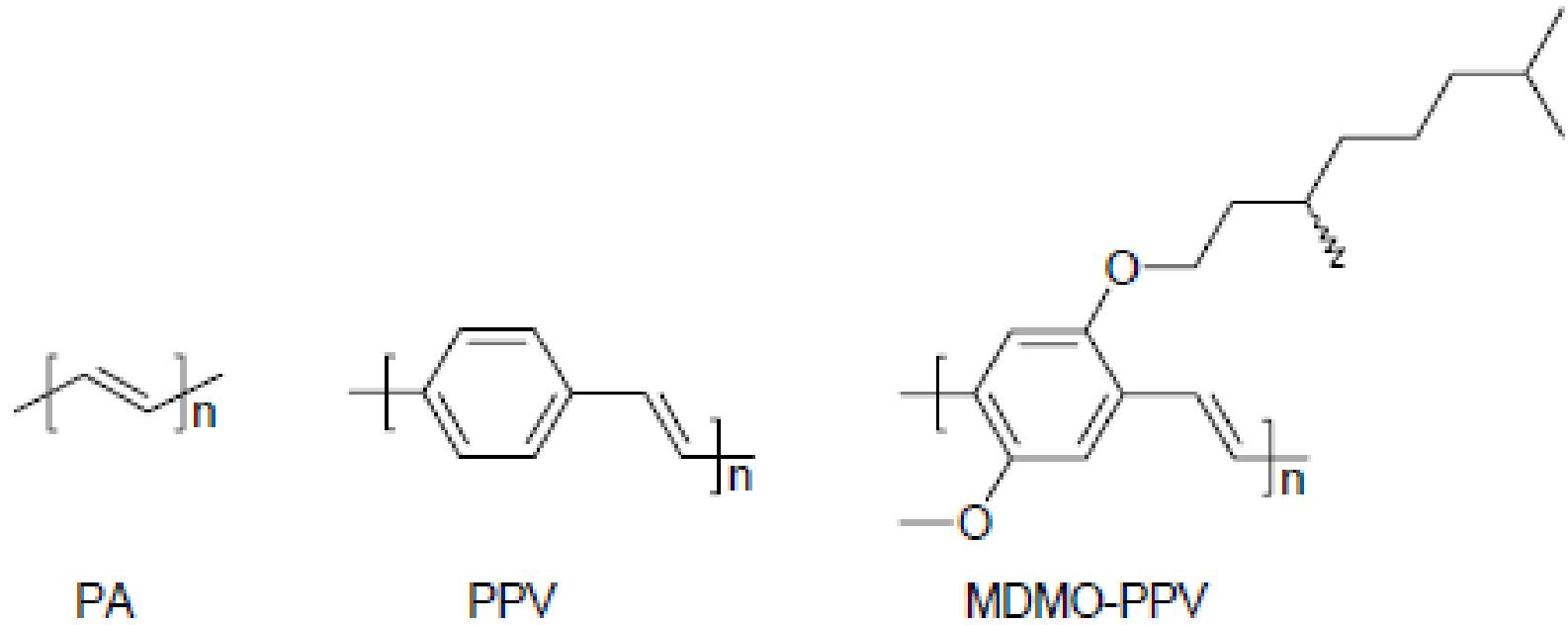


Photovoltaics



Using the sun
to generate
electricity

Molecular structures of the conjugated polymers trans-polyacetylene (PA), poly(pphenylenevinylene) (PPV), and a substituted PPV (MDMO-PPV)



Basic processes in an organic solar cell

Various architectures for organic solar cells have been investigated in recent years. In general, for a successful organic photovoltaic cell four important processes have to be optimized to obtain a high conversion efficiency of solar energy into electrical energy.

-Absorption of light

-Charge transfer and separation of the opposite charges

-Charge transport

- Charge collection

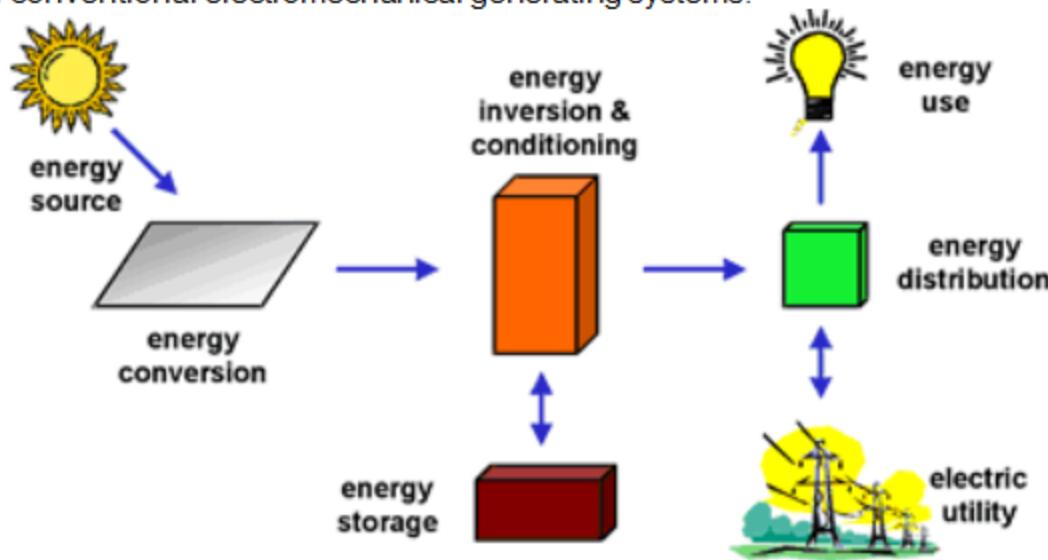
For an efficient collection of photons, the absorption spectrum of the photoactive organic layer should match the solar emission spectrum and the layer should be sufficiently thick to absorb all incident light. A better overlap with the solar emission spectrum is obtained by lowering the band gap of the organic material.



PV technology basics

How a PV System Works

PV systems are like any other electrical power generating systems, just the equipment used is different than that used for conventional electromechanical generating systems.



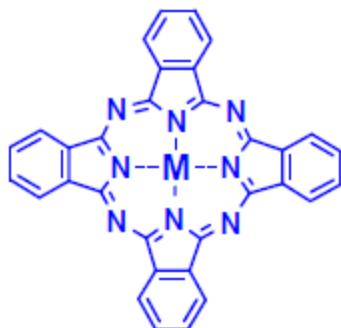
The need for two semiconductors:

Photovoltaic cell configurations based on organic materials differ from those based on inorganic semiconductors, because the physical properties of inorganic and organic semiconductors are significantly different.

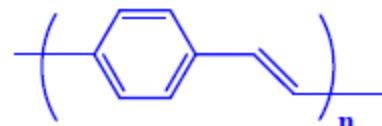
- Lower dielectric constant
- Exciton binding energy is larger than inorganic semiconductors energy (for GaAs the exciton binding energy is 4 meV, for polydiacetylene 0.5 eV)
- Dissociation into free charge carriers does not occur at room temperature in case of organic conducting polymers. Hence, low mobility of the charge carriers and the internal field of the p-n junction.

Both p-type (donor) and n-type (acceptor) material is required for organic PV technology

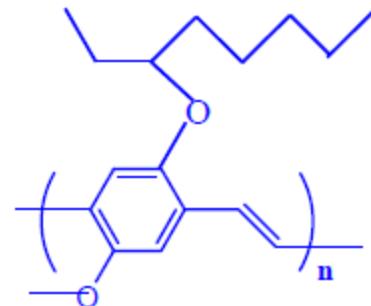
Representative Organic Donors



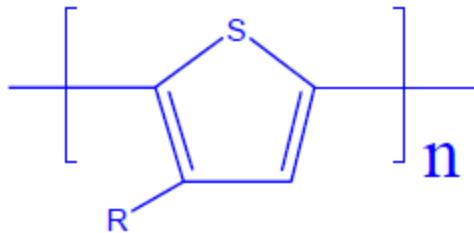
Phthalocyanines (MPc)
e.g., H₂Pc when M=H₂



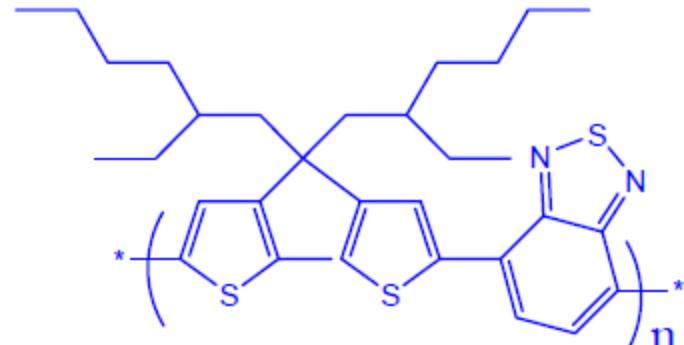
PPV



MEH-PPV



PT, e.g., P3HT when R=C₆H₁₃



PCPDTBT

Representative Organic Acceptors



Perylenes

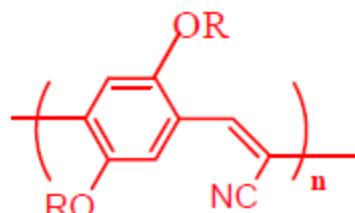
e.g., Me-PTC when R=Me



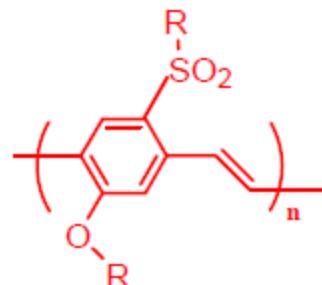
C₆₀



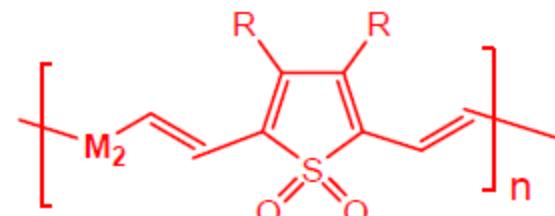
PCBM



CN-PPV



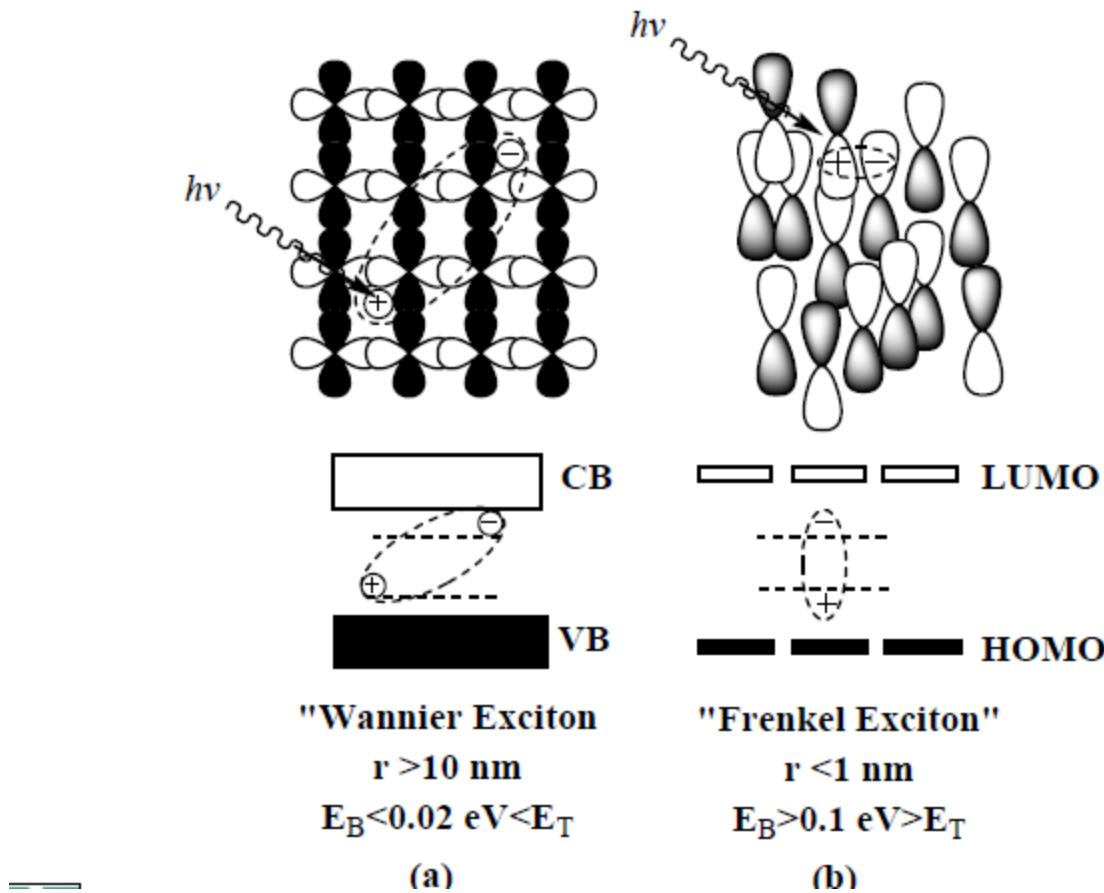
SF-PPV



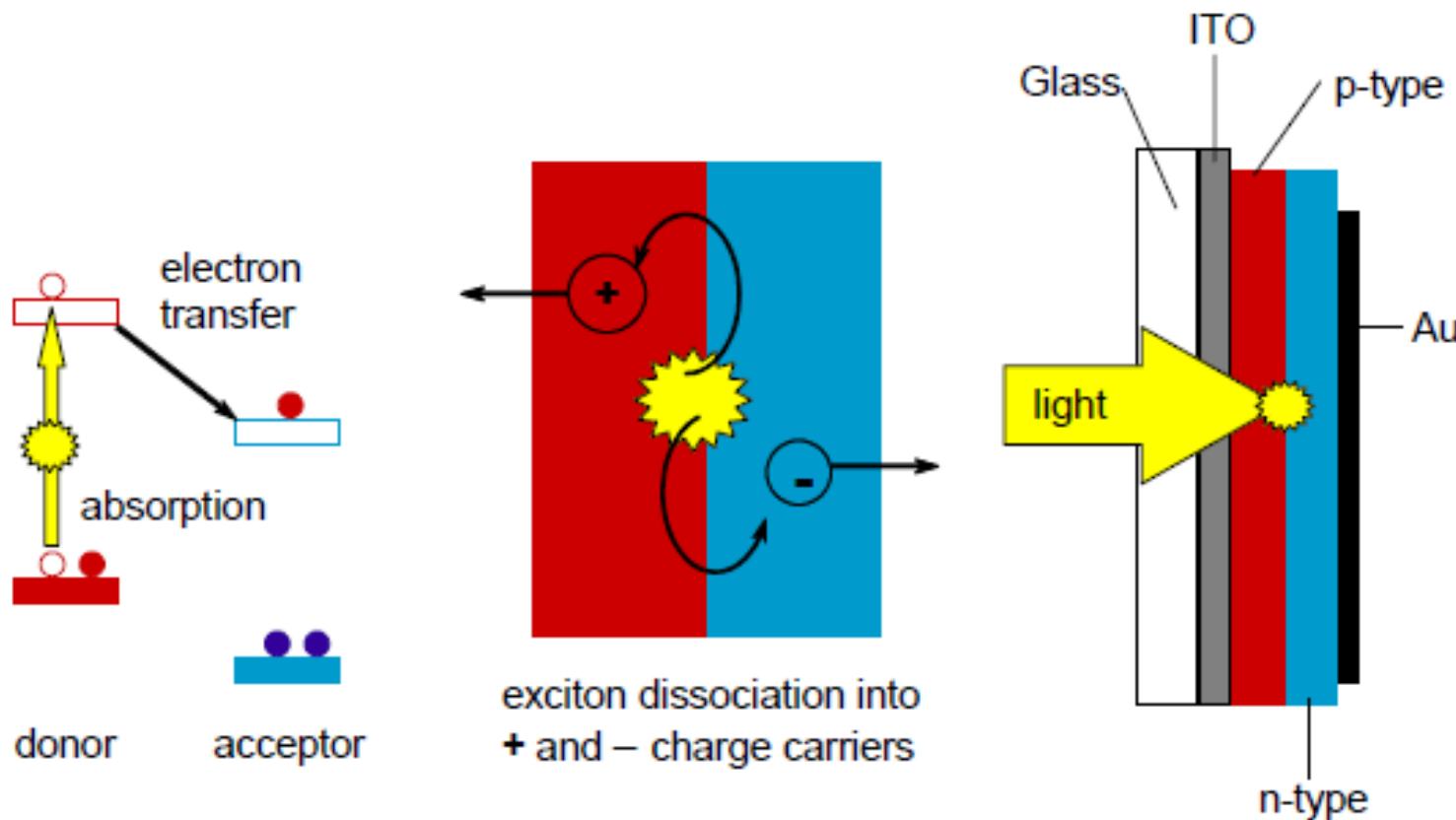
SF-PTV

Inorganic vs. Organic Excitons

(Sun, S. "Organic and Polymeric Solar Cells", in *Handbook of Organic Electronics and Photonics*, edited by S. H. Nalwa, American Scientific Publishers, Los Angeles, California, 2008, Vol. 3, Chapter 7).

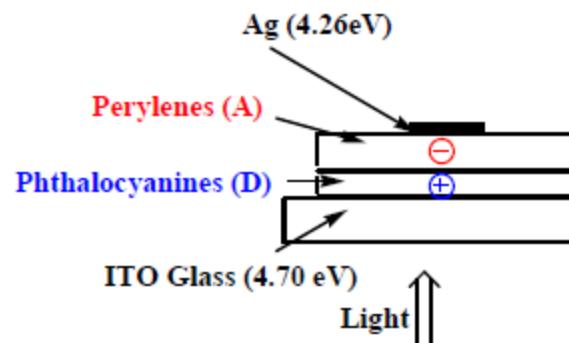


Schematic drawing of the working principle of organic photovoltaic cell



Organic D/A Bilayer Solar Cell ‘Tang Cell’

First Organic D-A Type Solar Cell



C. W. Tang

Eastman Kodak Co.

Appl. Phys. Lett., 48(2), 183(1986)

Efficiency 1%

0.75 Sun @ AM 2

Voc = 0.45 V

Isc = 2.3 mA/cm²

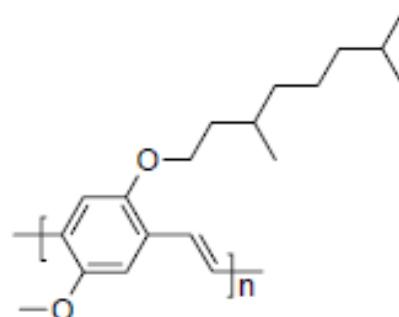


Phthalocyanines (Donor)

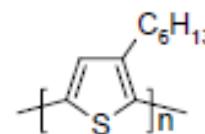


Perylenes (Acceptor)

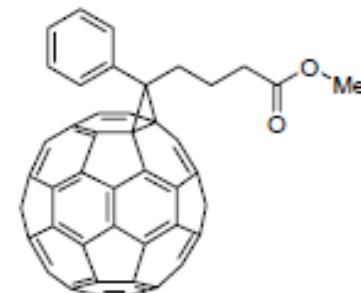
Bulk-heterojunction solar cells



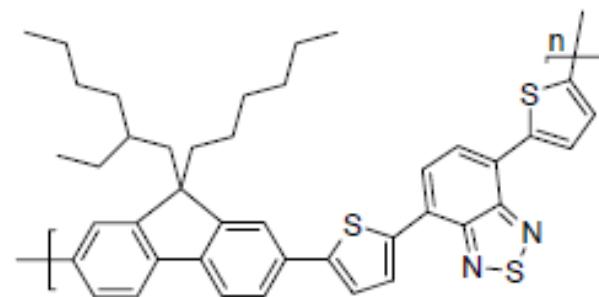
MDMO-PPV



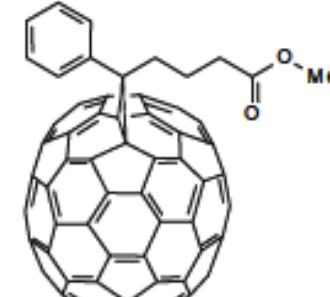
P3HT



PCBM



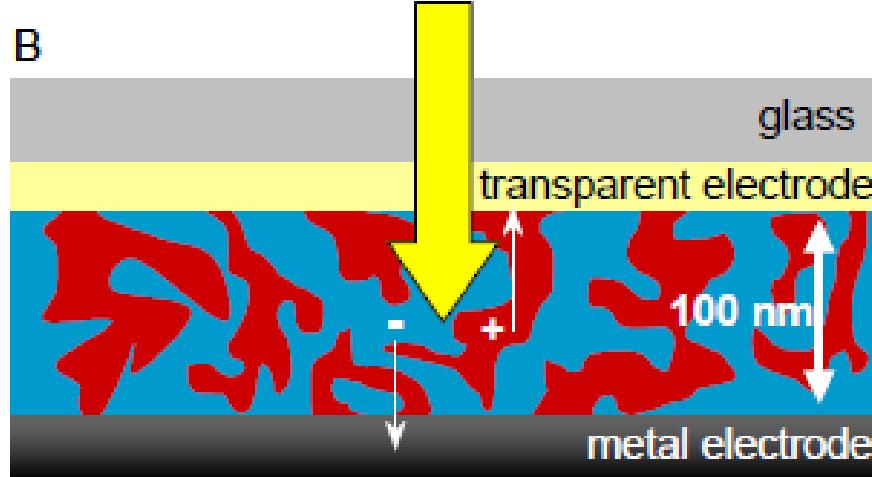
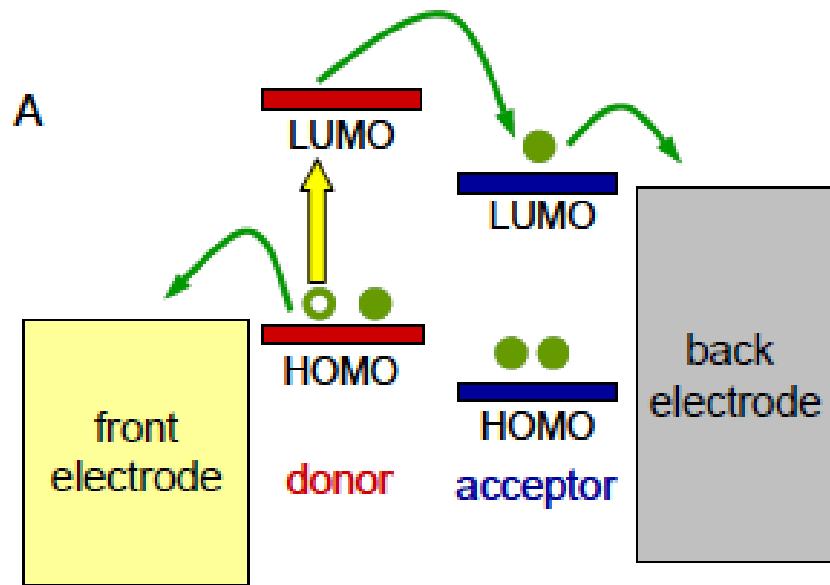
PFDTBT



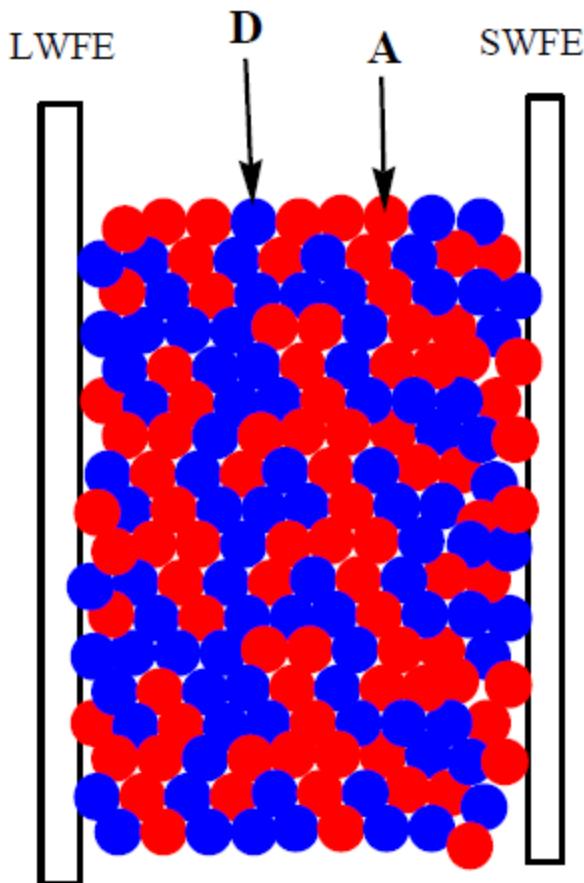
[70]PCBM

Power conversion efficiencies exceeding 2.5% (MDMO-PPV as a donor and PCBM as an acceptor)

The bulk-heterojunction concept.



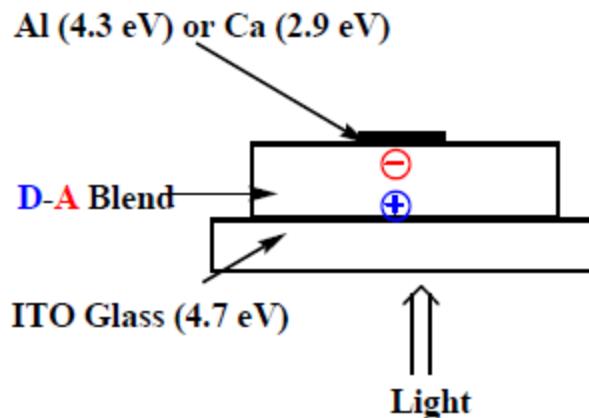
D/A Blend Solar Cells: “Bulk Heterojunction”



G. Yu, J. Gao, J. Hummelen, F. Wudl,
and A. Heeger, Science, **270**, 1789 (1995).

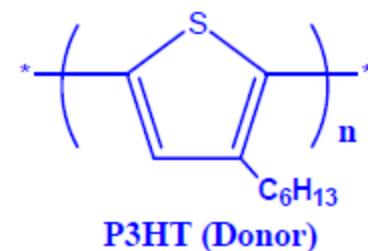
Current State-of-the-Art Polymer Solar Cells

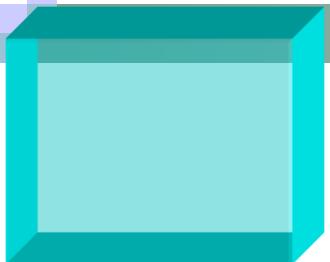
"Bulk D-A Heterojunctions" Single Layer Organic Solar Cell



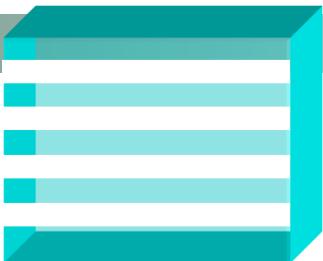
Y. Yang, et. al. at UCLA
Nature Materials, 4, 864 (2005)
 $\eta \sim 5\%$

A. Heeger, et. al. at UCSB
Science, 317, 222 (2007)
 $\eta = \sim 6\%$

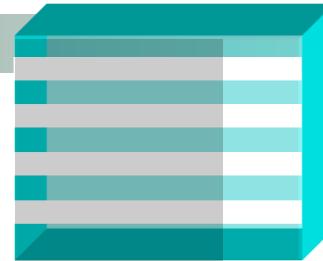




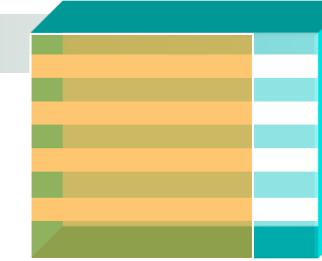
ITO substrate



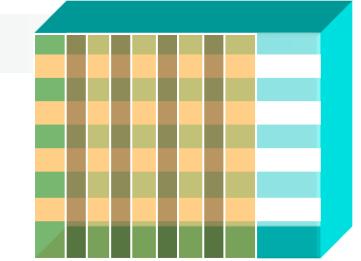
Pattern generated in
Aqua regia



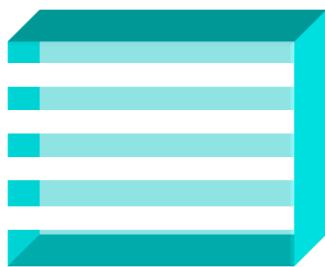
PEDOT PSS layer
Spin coated



Polymer +PCBM
deposition
by spin coating



Deposition of metal
cathodes by
thermal evaporation



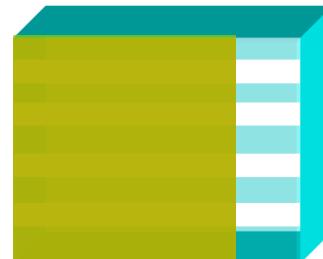
PEDOT
PSS layer
Spin coated



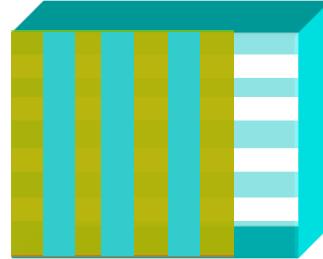
Bilayer



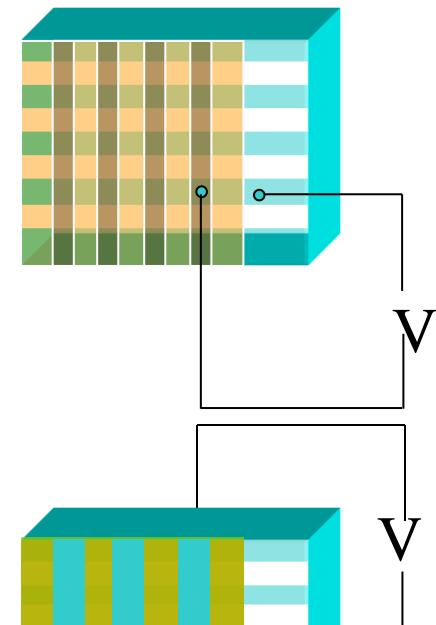
polymer layer
Spin coated
166



PCBM layer
Spin coated

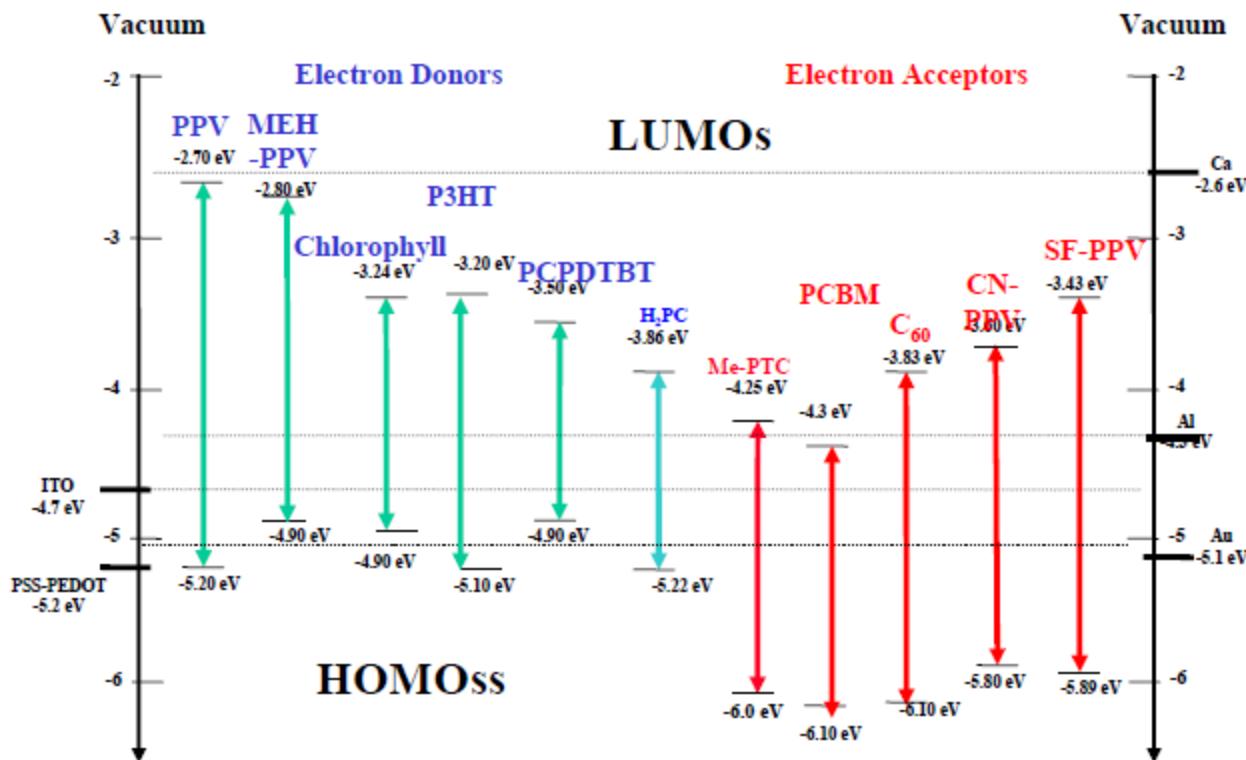


Deposition of metal
cathodes by
thermal evaporation



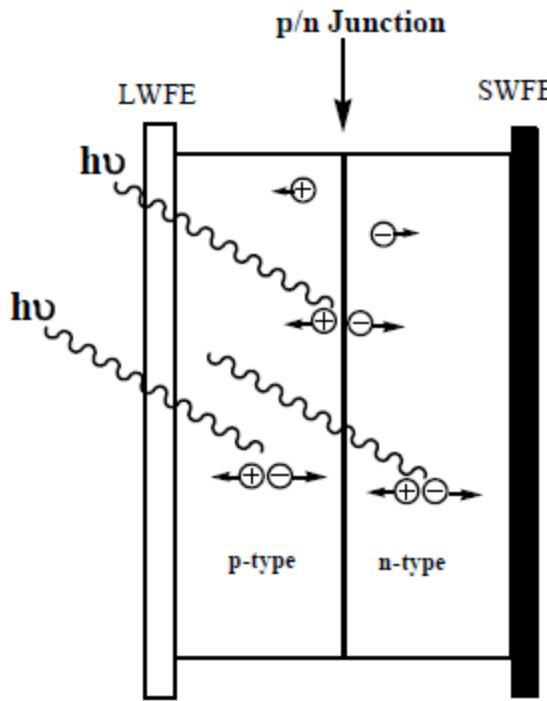
HOMO/LUMO Levels

(Sun, S. et al. "Sunlight Energy Conversion via Organics", an invited review article in *Handbook of Photovoltaic Science and Engineering*, Luque, A and Hegedus, S., eds., Wiley, the Atrium, England, 2009 .



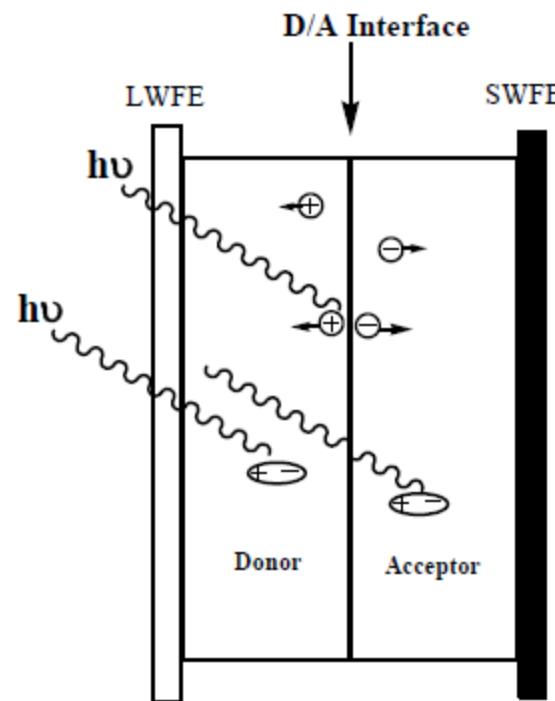
Double Layer Solar Cell Device Structures

(Sun, S. "Organic and Polymeric Solar Cells", in *Handbook of Organic Electronics and Photonics*, edited by S. H. Nalwa, American Scientific Publishers, Los Angeles, California, 2008, Vol. 3, Chapter 7) .



(a)

"Bell Lab Cell" 1954



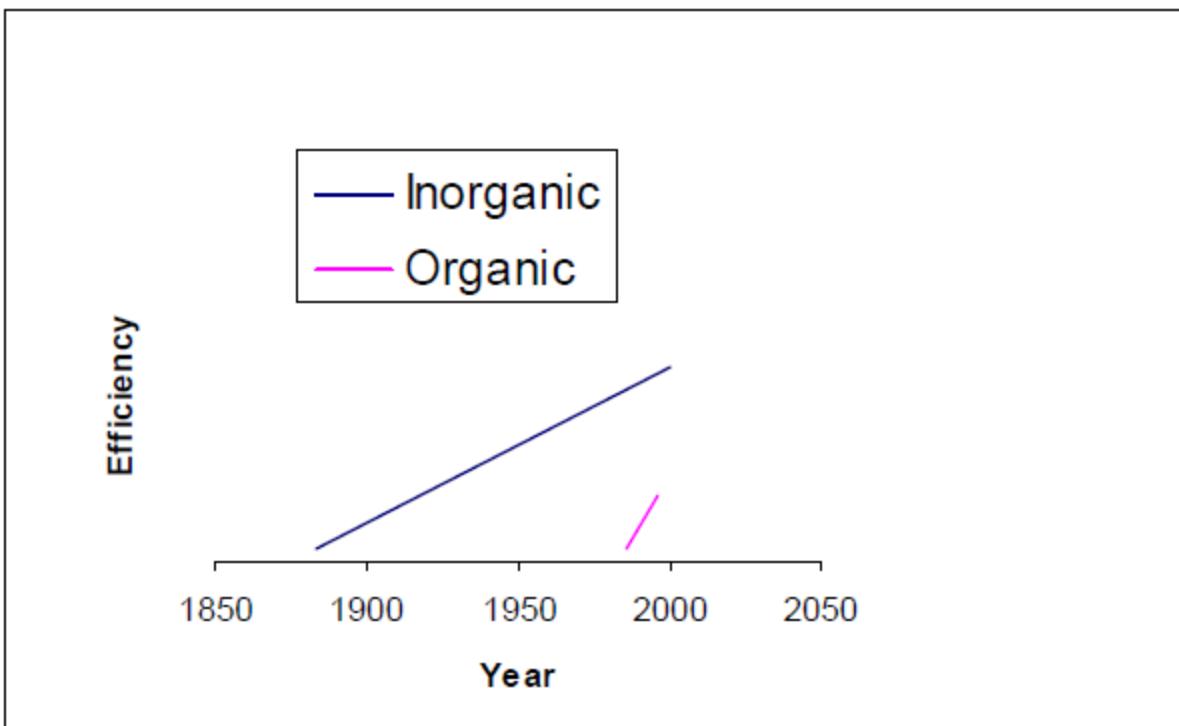
(b)

"Tang Cell" 1986

**165,000 TW of sunlight
hit the earth**



PV Efficiencies of Inorganic vs. Organic Cells





Five Critical Steps in Organic Photovoltaic

1. Photon Capture (Solar radiation: 1.0-2.0 eV on surface of the earth, 2.0-3.0 eV in space, Materials Engineering at Energy Domain).
2. Exciton Diffusion (D/A interface within 5-50 nm region, Materials Engineering at Spatial Domain).
3. Charge Separation (Orbital Couplings, Offsets, Materials Engineering at Spatial Domain and Energy Domain).
4. Charge Transportation (Morphology, Materials Engineering at Spatial Domain)
5. Charge Collection at Electrodes (Engineering at Energy Domain)

Three Key ‘Losses’ of Organic Photovoltaics

(Sun, S., *Sol. Energy Mater. Sol. Cells*, 2003, 79(2), 257-264)

- 1. Photon Loss**

(Materials Excitation Energy Gaps vs. Sunlight Spectrum)

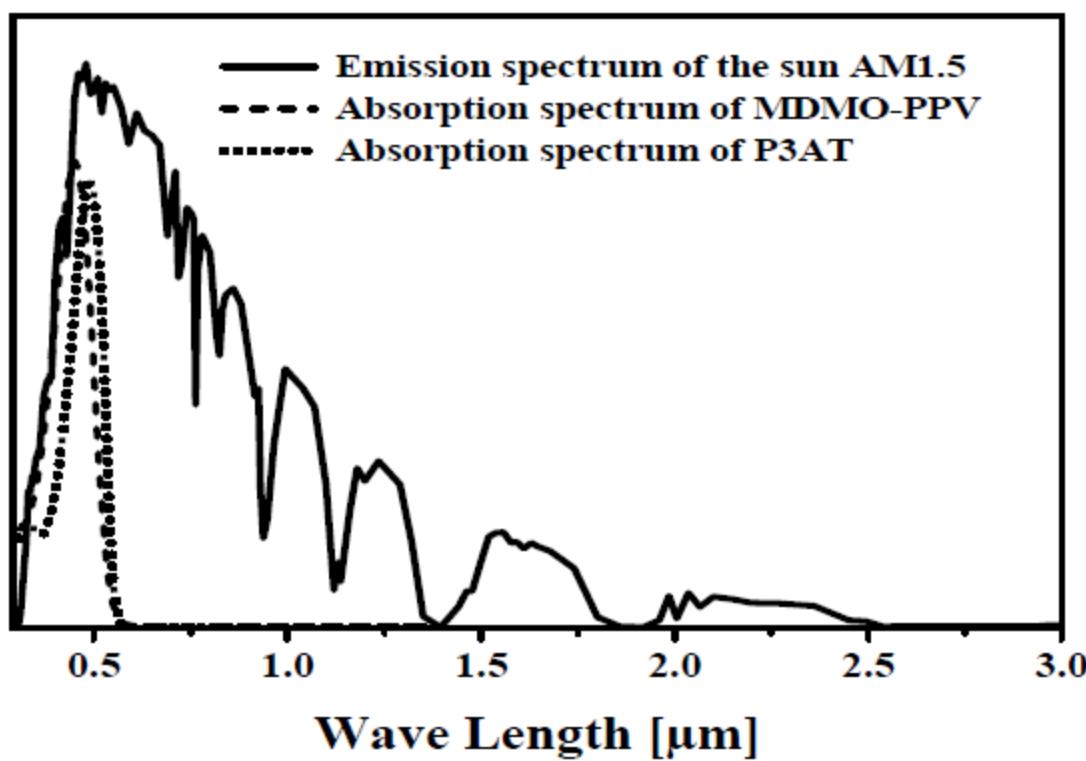
- 2. Exciton Loss**

(D/A Domain Size, Morphology, D/A Orbital Coupling and Energy Offsets)

- 3. Carrier Loss**

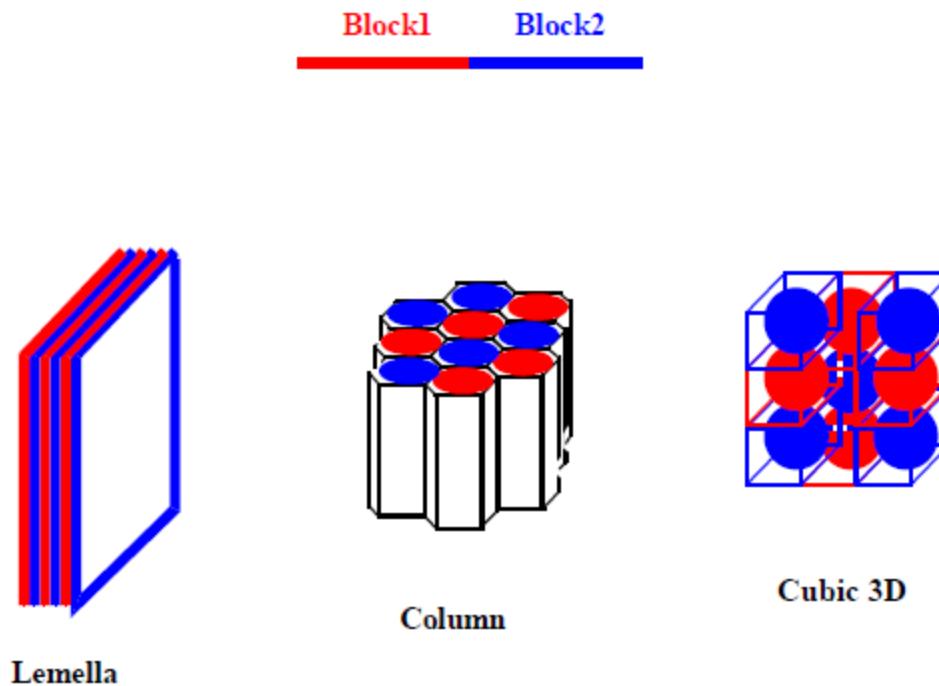
Carrier Transport Pathways, Morphology, Electrodes

Solar Spectrum on Earth Surface (AM 1.5)



Optimizations at Spatial Domain

AB Diblock Copolymer Morphologies

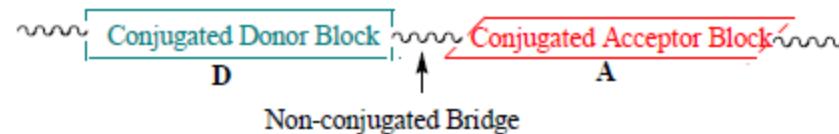


Representative Block Copolymer Morphologies

A 'Tertiary' Nano Structured Polymer Solar Cell

(Sun, S., *Sol. Energy Mater. Sol. Cells*, 2003, 79(2), 257-264)

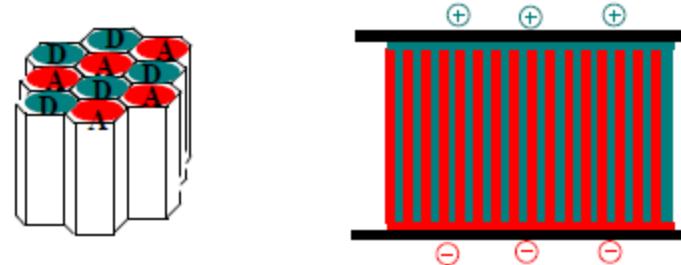
i) "Primary Structure"



ii) "Secondary Structure"



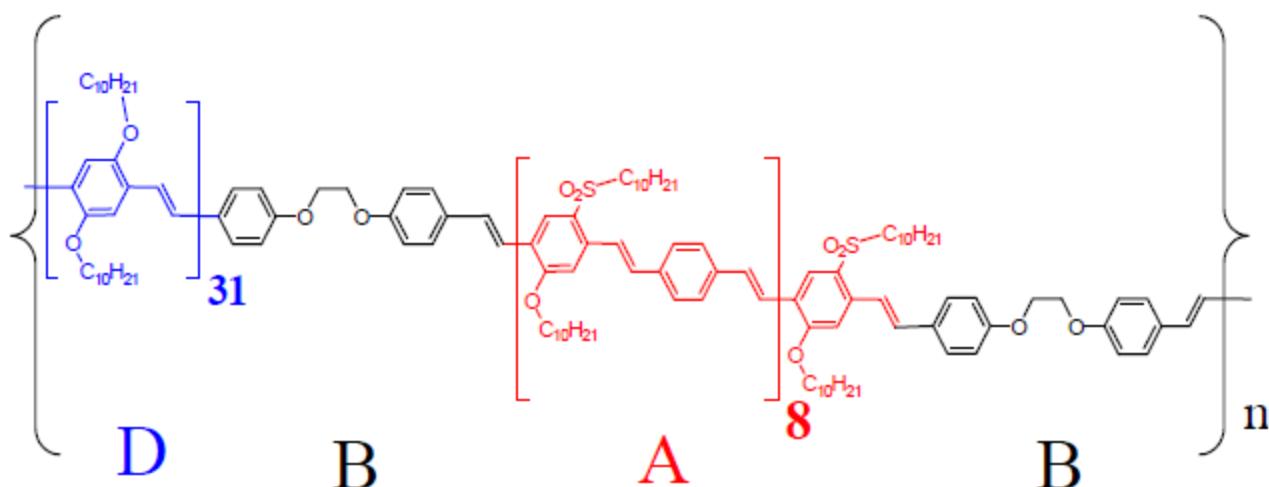
iii) "Tertiary Structure"



iii-a) Columnar 'HEX' Morphology iii-b) PV Device Architecture

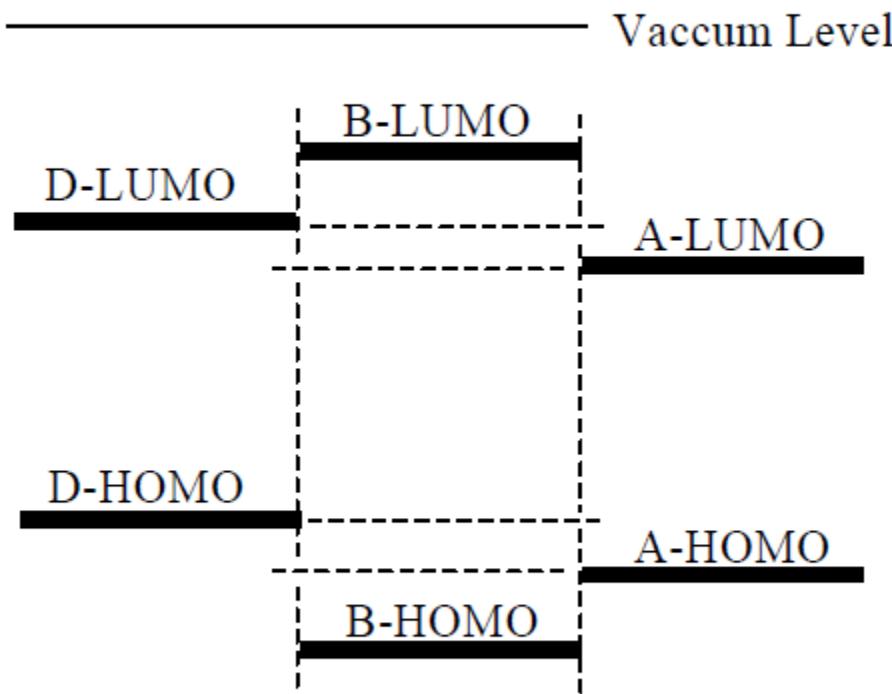
Most Recent Block Copolymers Developed at NSU

Zhang, C., et al. *Macromolecules*, 2006, 39, 4317-4326.

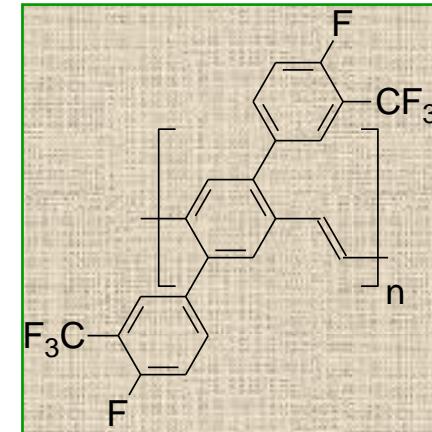
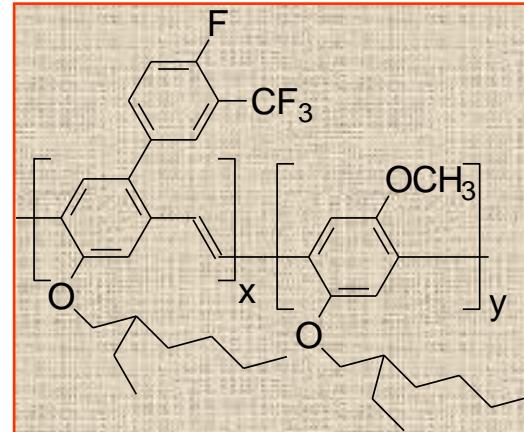
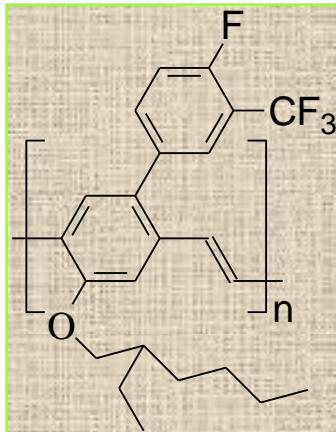
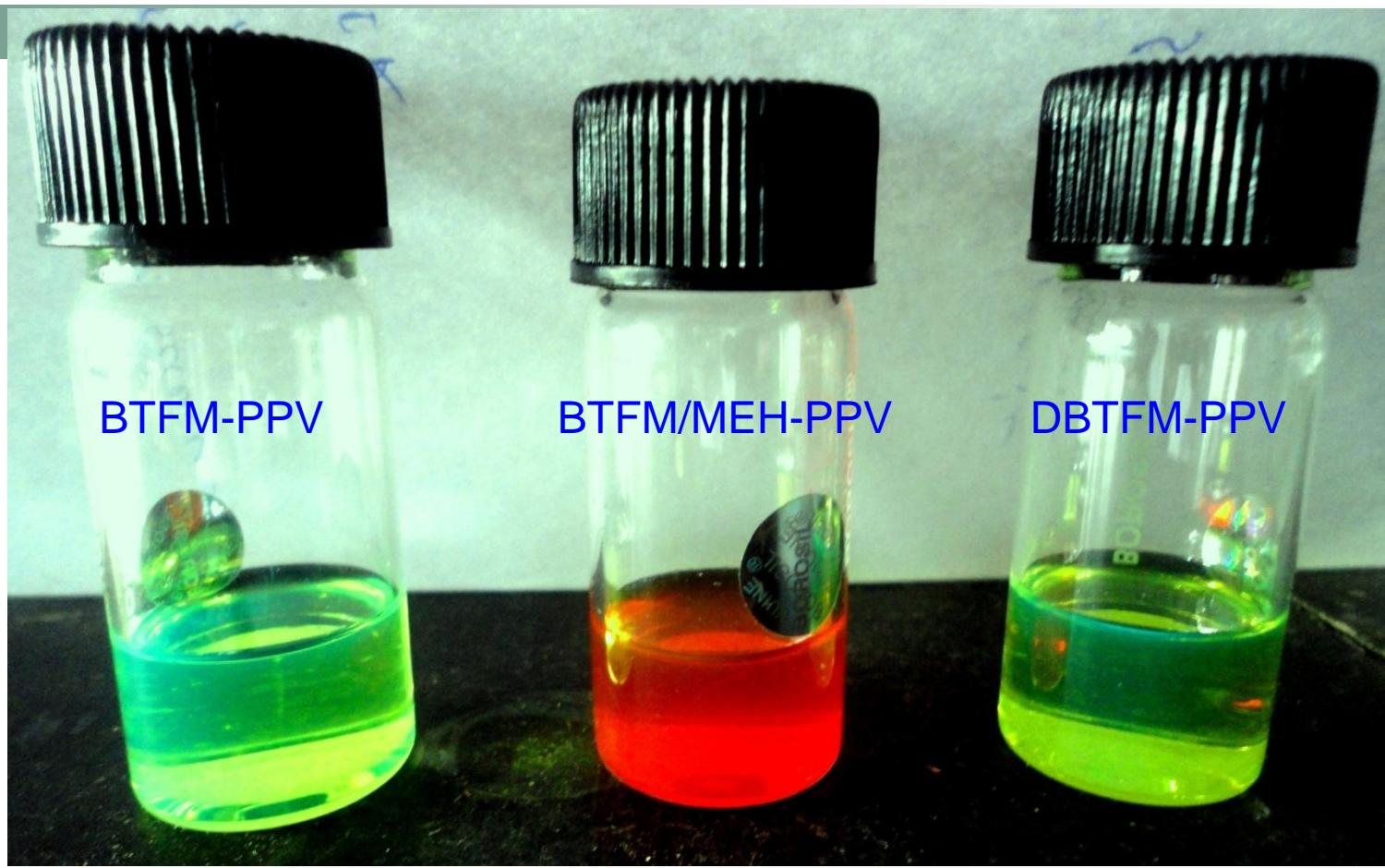


Energy Levels of -DBAB- Block Copolymer

(Sun, S.; et al., *J. Mater. Sci.*, 2005, 40, 1429-1443.)



Intra-chain energy level schematic diagram
of -DBAB- type block copolymer



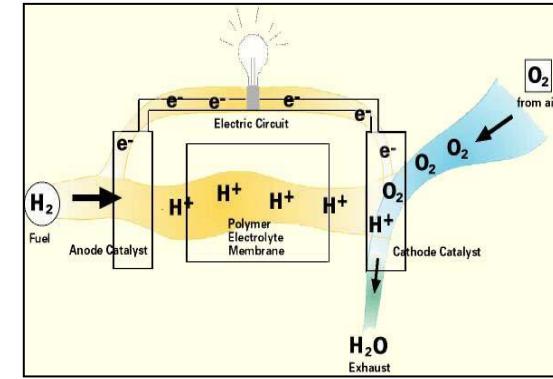
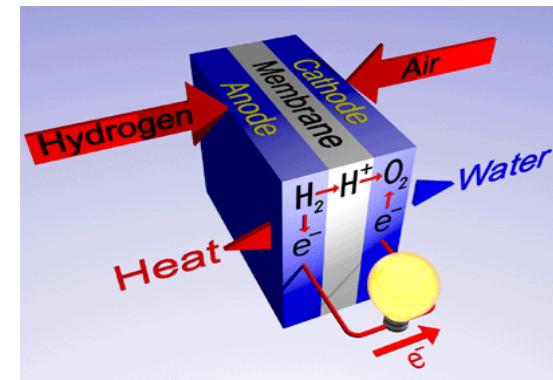


Introduction

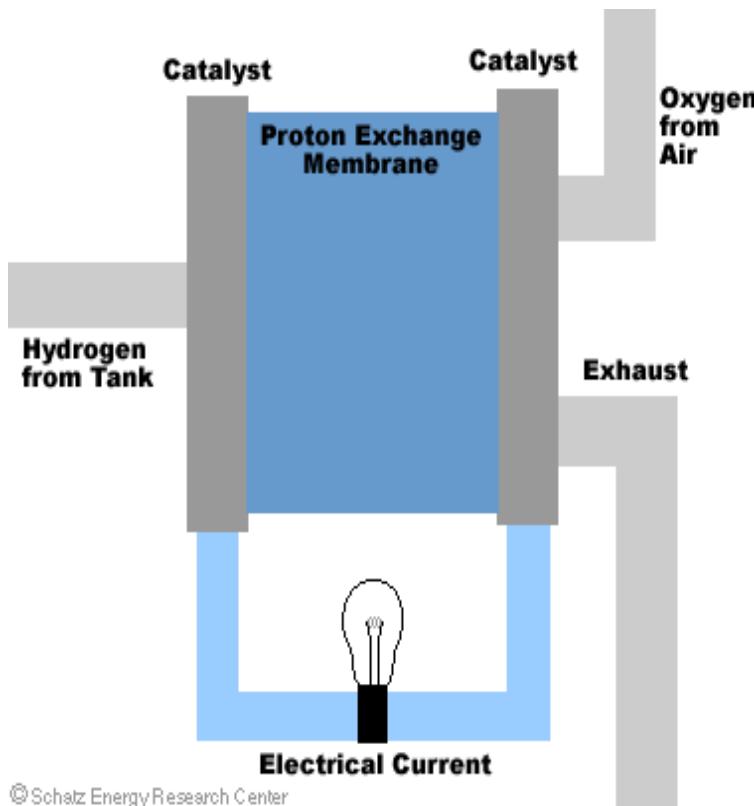
- The global energy demand expected to be double within the next 30-40 years
- 90% of present global energy is supplied by fossil fuels
 - Non-sustainable
 - Negative environmental impacts
- Need sustainable, environmentally-friendly energy sources
- Fuel cells are a promising technology

Introduction

- PEMFCs are considered as reliable alternate energy converting device because of
 - high power density
 - high efficiency
 - low operating temperatures
 - solid non-corrosive electrolyte
 - long life
 - ease of design and adaptable size
 - environmentally friendly
- Polymer electrolyte membranes (PEMs) are key materials for proton exchange membrane fuel cells (PEMFCs)
- **Applications:**
 - Automobiles
 - portable devices
 - Stationary systems



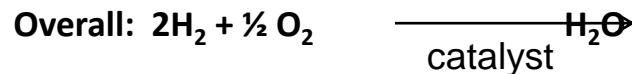
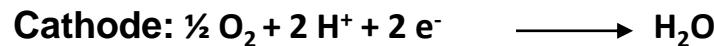
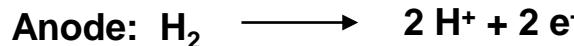
Working Principle of PEMFC



© Schatz Energy Research Center

1. When hydrogen is fed to the first catalyst layer, at anode, the hydrogen molecules are split into their basic elements, i.e. protons and electrons.
2. The protons migrate through the electrolyte membrane to the second catalyst layer, the cathode. Here they react with oxygen to form water.
3. At the same time the electrons are forced to travel through external circuit to the cathode side, because they can not pass the membrane
4. This movement of electrons thus creates an electrical current

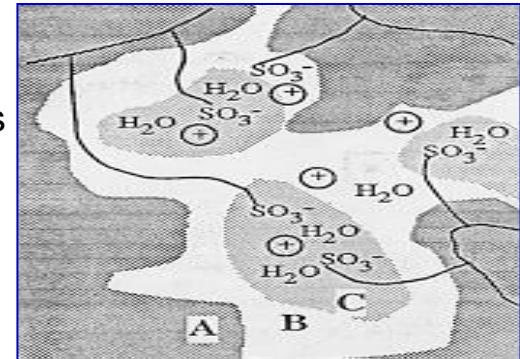
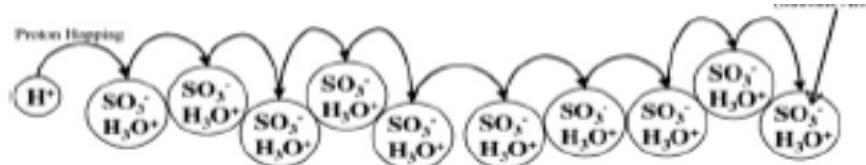
Electrode reaction:



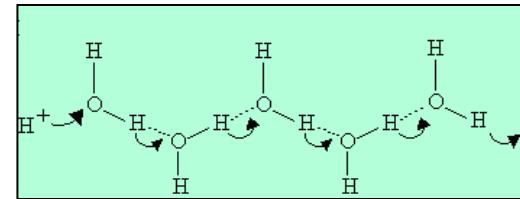
Proton transport mechanism

“Grotthus mechanism”

- Protons hop from one hydrolyzed ionic site ($\text{SO}_3^- \text{H}_3\text{O}^+$) to another across the membrane

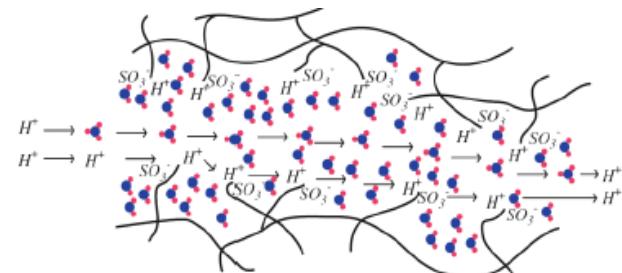


- It involves conversion of H-bonds to covalent bonds between water molecules and vice versa; only the charge of the proton is transported and not its mass.



“Vehicular mechanism”

- Hydrated proton (H_3O^+) diffuses through the aqueous medium in response to the electrochemical difference
- The water connected protons ($\text{H}^+ (\text{H}_2\text{O})_x$) in the result of the electro-osmotic drag carry the one or, more molecules of water through the membrane and itself are transferred with them.

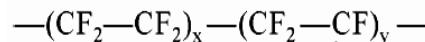


Scope of the Work

❖ Required and desirable characteristics

- ✓ High ionic conductivity (and zero electronic conductivity)
- ✓ Good mechanical strength
- ✓ Long-term chemical stability i.e. good oxidative and hydrolytic stability
- ✓ Good thermal stability
- ✓ Low oxidant and fuel cross-over
- ✓ Low cost and ready availability

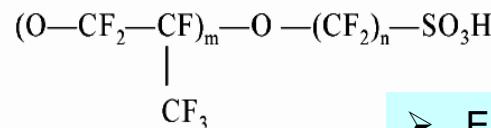
❖ DuPont's Nafion®: A state of art PEM material for fuel cell



Advantage:

- Excellent Proton Conductivity up to 10^{-2} - 10^{-1} S/cm
- Good chemical & oxidative stability
- Long term stability

Nafion®117 : m ≥1, n=2, y=1, x=7-20



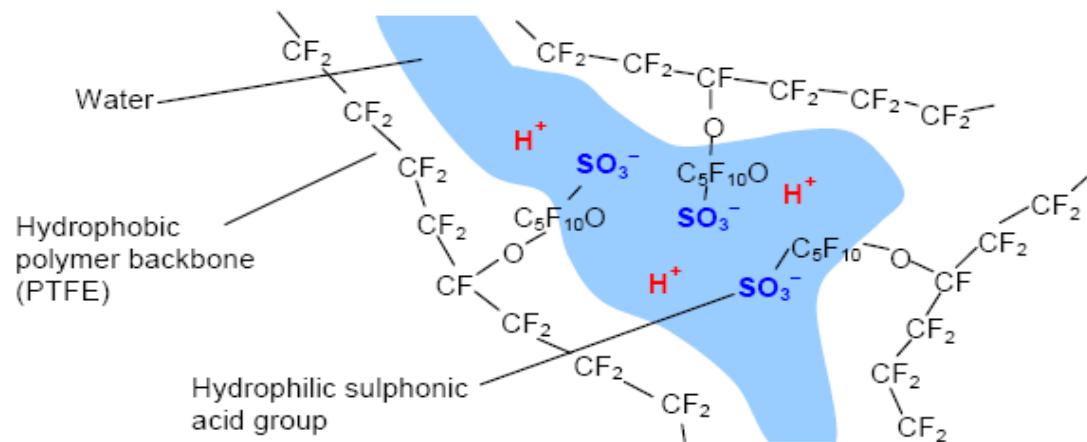
Disadvantage:

- Expensive (up to US\$ 700 per square meter).
- High methanol permeability
- Loss of membrane performance at elevated temperature ($>80^{\circ}\text{C}$)

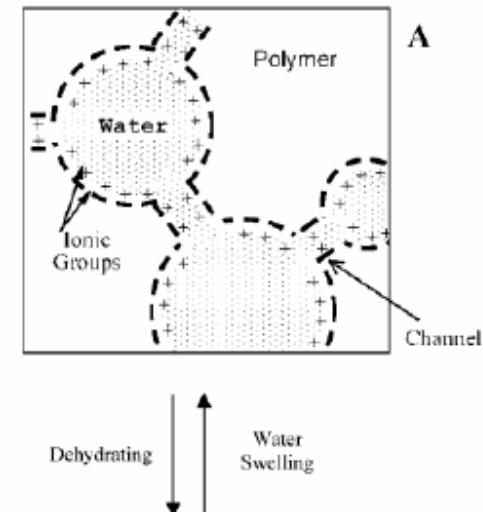
- ❖ The current state-of-the-art performance is not high enough for the practical applications

Why does Nafion® possess high proton conductivity?

- nano scale phase separation between hydrophilic and hydrophobic domains
- connectivity between the hydrophilic don

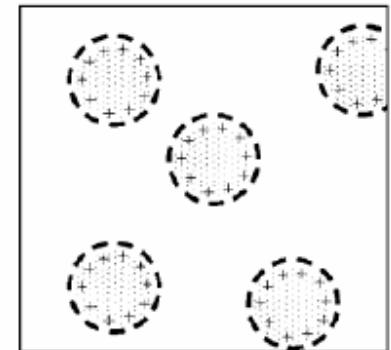


PERCOLATION
(HWLN)



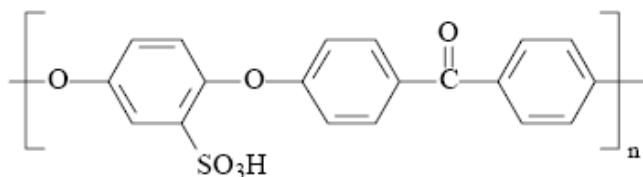
A

ISOLATED CLUSTERS
(LWLN)

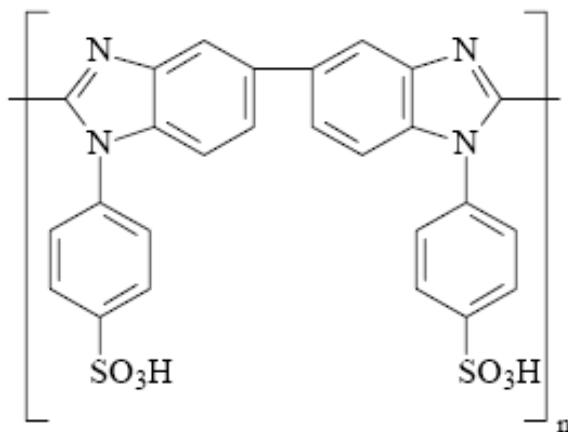


B

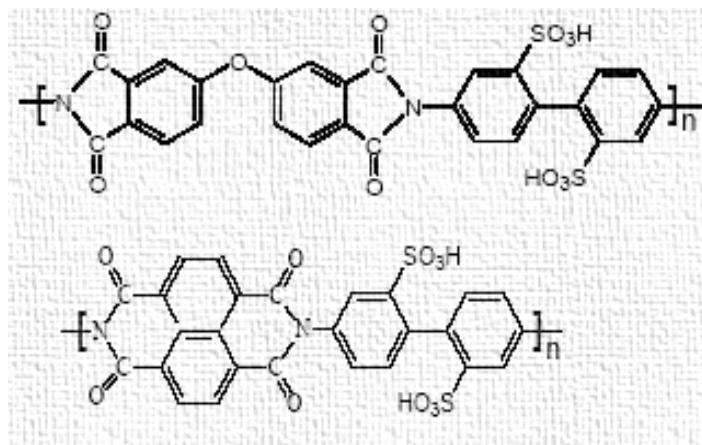
Hydrocarbon based alternative PEM materials



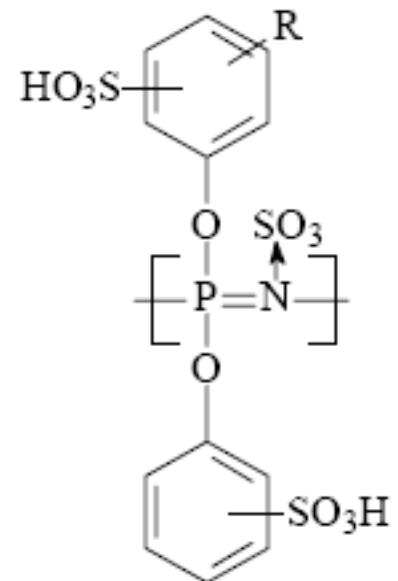
Sulfonated PEEK



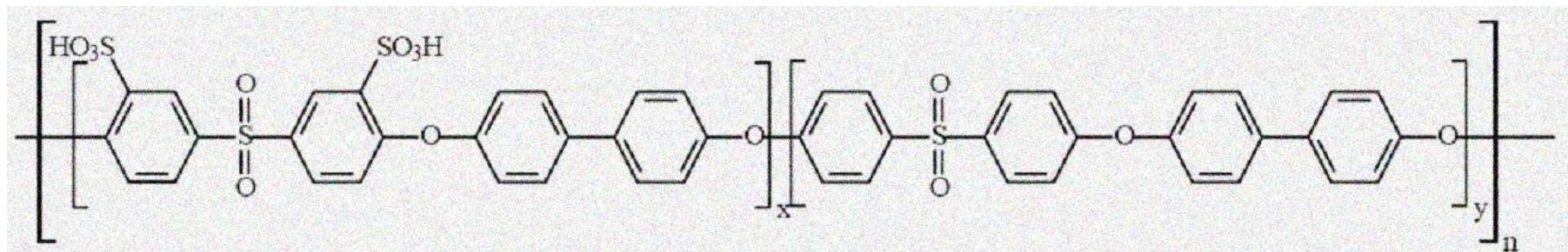
Sulfoarylated PBI



Sulfonated Polyimide



Sulfonated Poly[(3-methylphenoxy)-(phenoxy)phosphazene]



Sulfonated Poly(arylene ether sulfone)

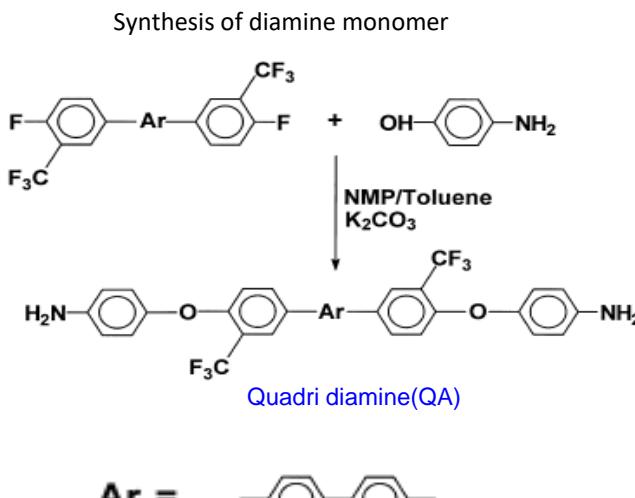
General understanding about hydrocarbon based PEM materials

- Increase in IEC results in increase in proton conductivity.
- A trade-off relation exists between IEC and stability related properties (like dimensional stability, hydrolytic- oxidative stability) & also with mechanical strength.
- Control of polymer morphology and ionic nanostructure is effective to obtain PEMs which have moderate IEC values and high proton conductivity.

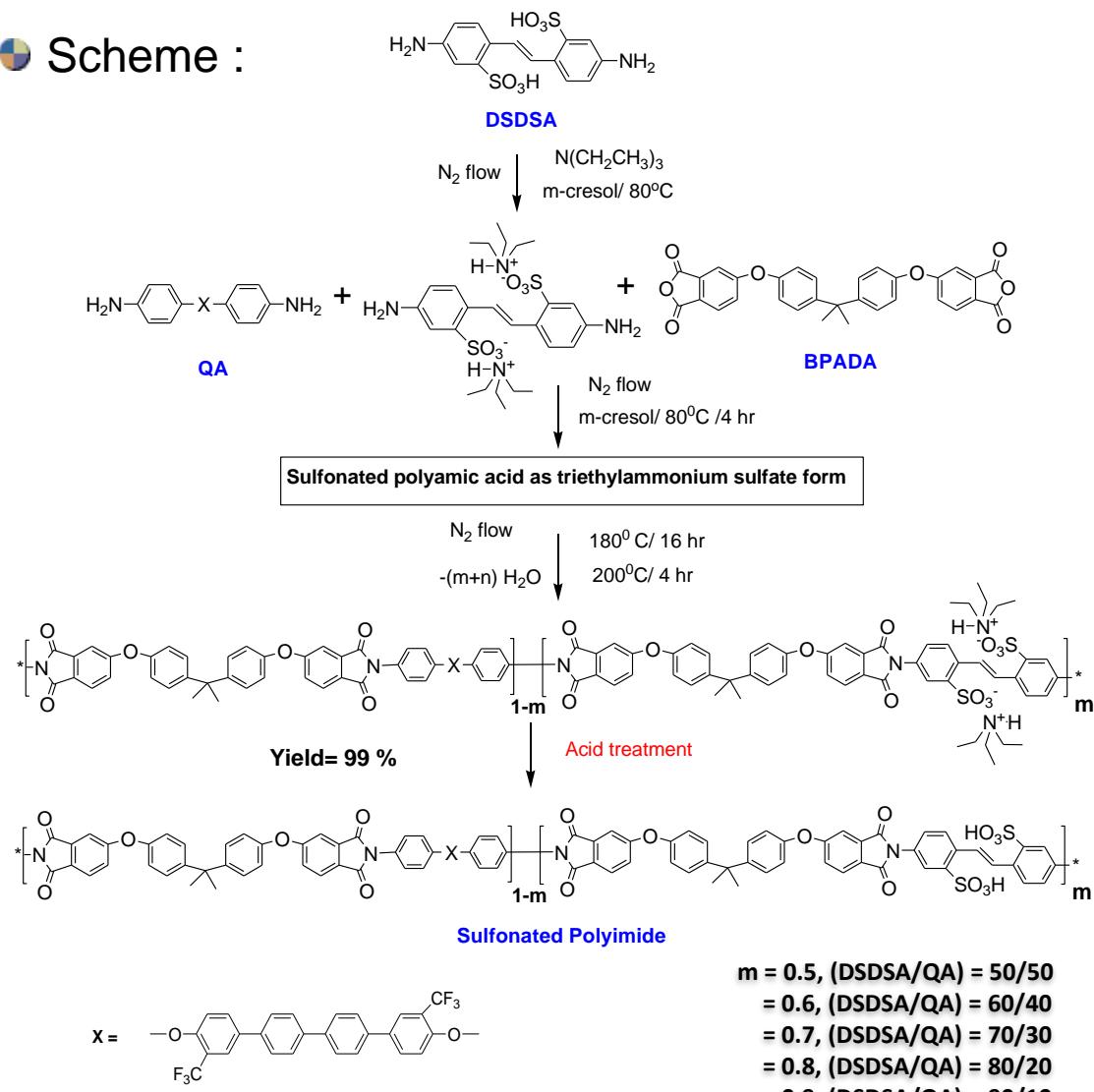
Methodologies to obtain desired properties

- ✓ Introduction of polar and flexible ether linkages to have better solubility & processability.
- ✓ Inclusion of hydrophobic pendant $-CF_3$ groups to have better phase separated morphology and stability.
- ✓ Copolymerization to control IEC and other properties.

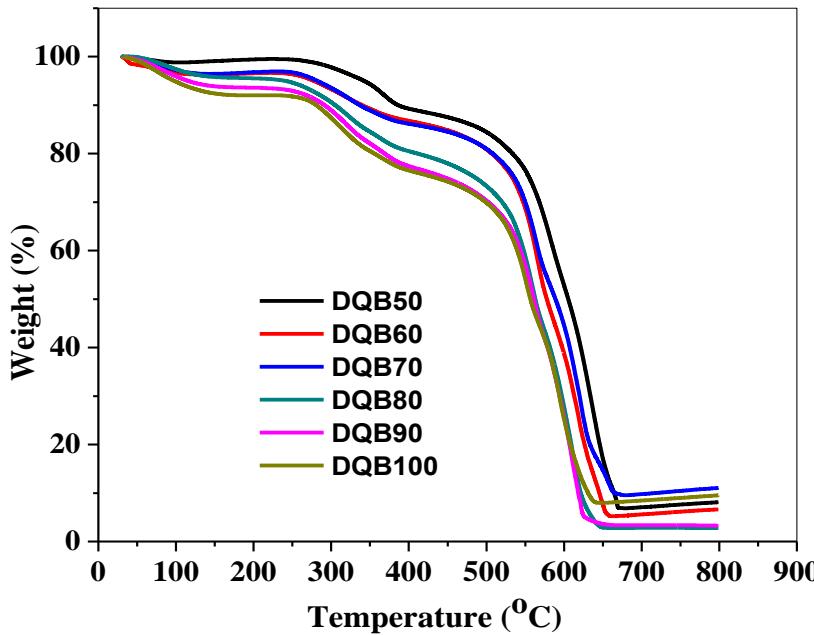
Synthesis of semifluorinated 5-Membered SPIs



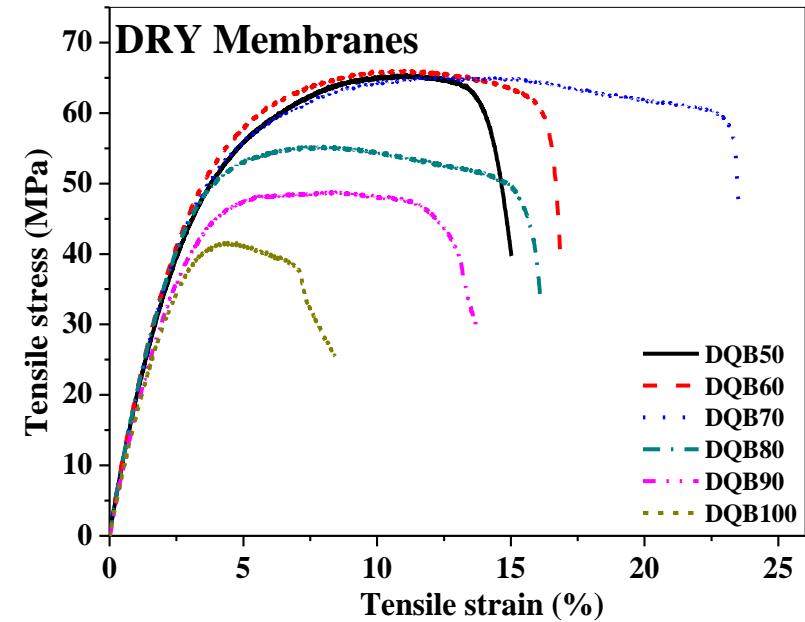
Scheme :



Good thermo-mechanical properties



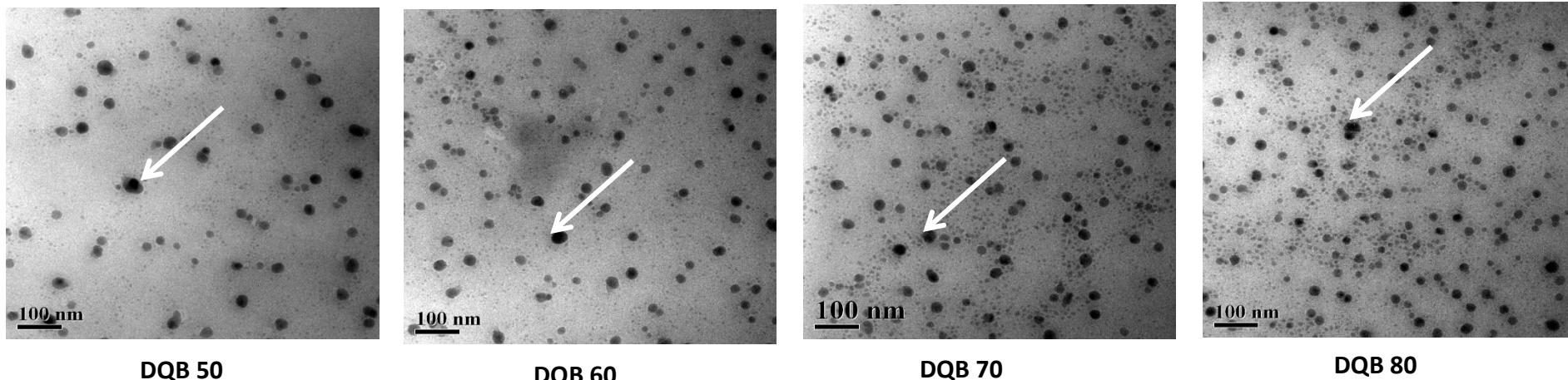
TGA plots of the SPIs; heating rate: 10 $^{\circ}\text{C min}^{-1}$



(Stress-strain plot of DQB membranes;
strain rate 5%/min, at 25 $^{\circ}\text{C}$ and 65% RH)

- Initial weight loss ~ 100 $^{\circ}\text{C}$
→ evaporation of the absorbed water.
- 2nd weight loss ~ 285 $^{\circ}\text{C}$
→ decomposition of sulfonic acid groups.
- 3rd weight loss around 580 $^{\circ}\text{C}$ -600 $^{\circ}\text{C}$
→ pyrolysis of the SPI backbones.
- Good mechanical properties (tensile strength ranging from 42 – 66 MPa and Young's moduli of 1.45–1.67GPa).

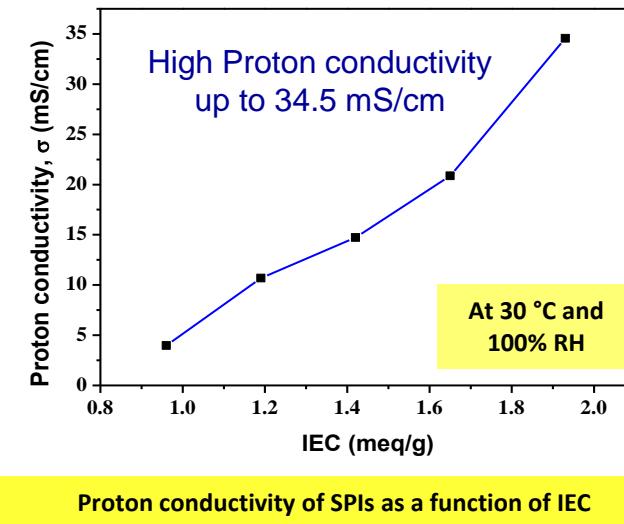
Microstructure, IEC & proton conductivity



TEM micrographs of SPI membranes (cross section, Ag⁺ form)

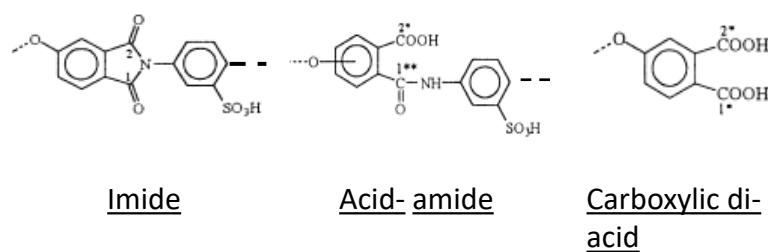
❖ PEM properties :

Polymer membranes	DSSDA mole %	IEC (meq/g)		WU (wt %)	Proton conductivity (S.cm ⁻¹)
		Theo.	Exp.		
DQB50	50	1.00	0.96	14.0	3.96×10^{-3}
DQB60	60	1.24	1.19	20.55	1.07×10^{-2}
DQB70	70	1.49	1.42	25.29	1.47×10^{-2}
DQB80	80	1.75	1.65	30.0	2.09×10^{-2}
DQB90	90	2.04	1.93	35.17	3.45×10^{-2}
DQB100	100	2.34	2.20	41.27	-



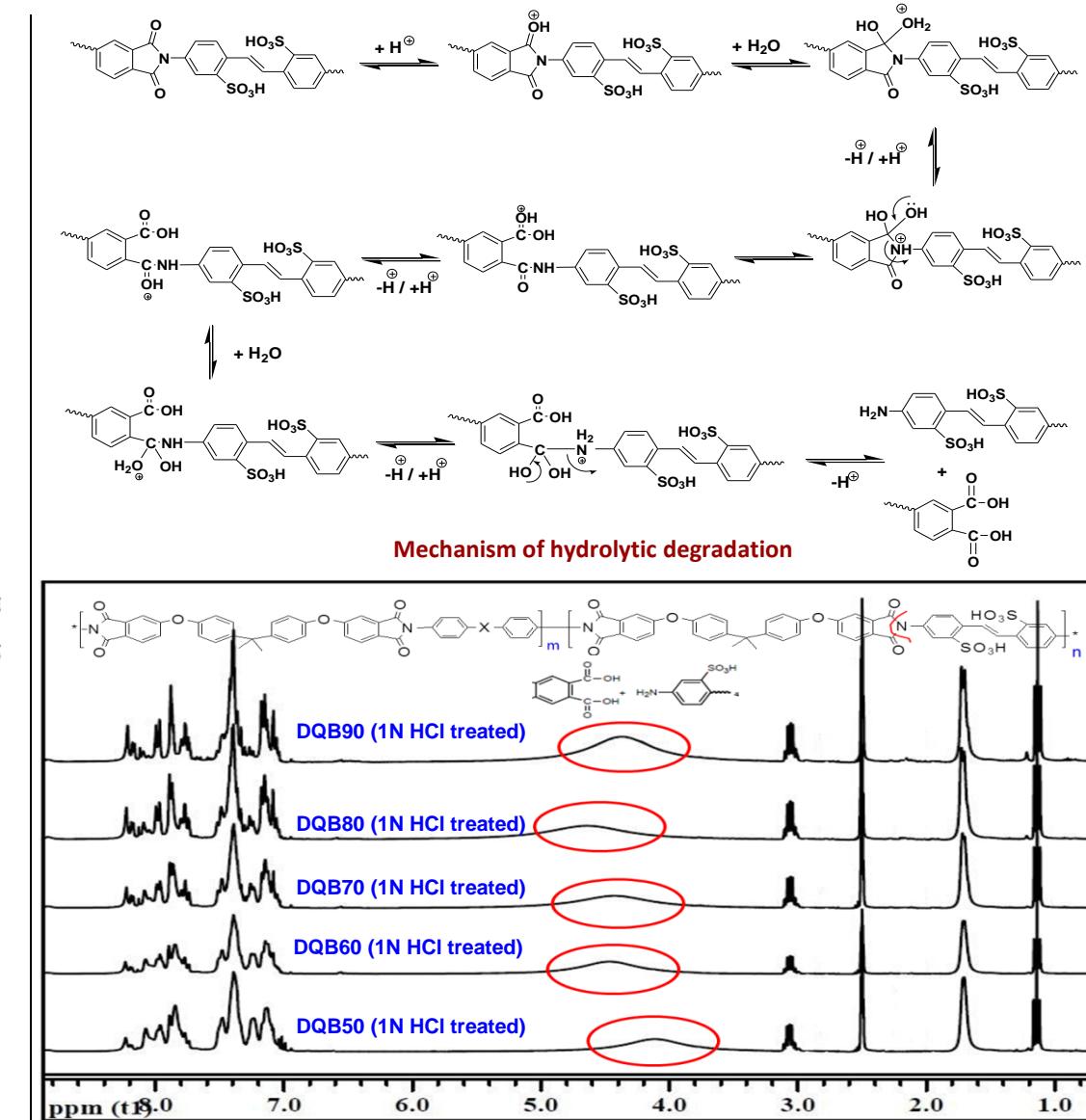
Limitation: Suffers with poor hydrolytic stability

The major concern of the synthesized sulfonated polyimide membranes is that they suffer from hydrolytic degradation in acidic medium during acid treatment and subsequently all the membrane becomes brittle after a certain time.

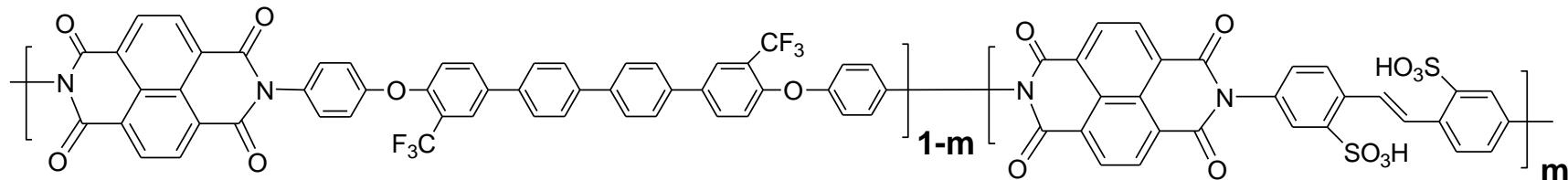


Acid-hydrolysis of 5-membered imide ring leads to chain scission and subsequently,

- ✓ Membrane becomes brittle
- ✓ Mw of the polymer decreases



Studies on semifluorinated 6-Membered SPIs

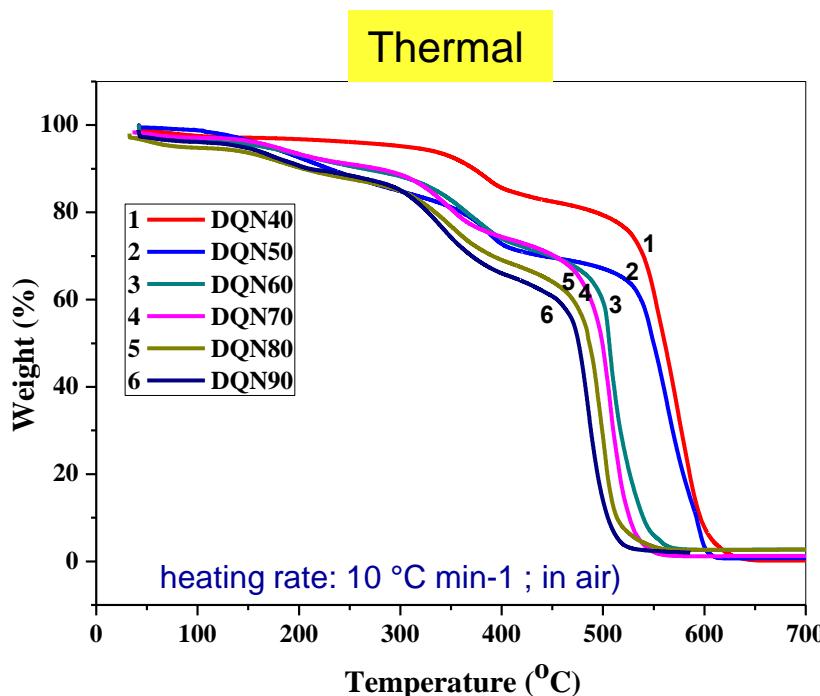


DQN XX series

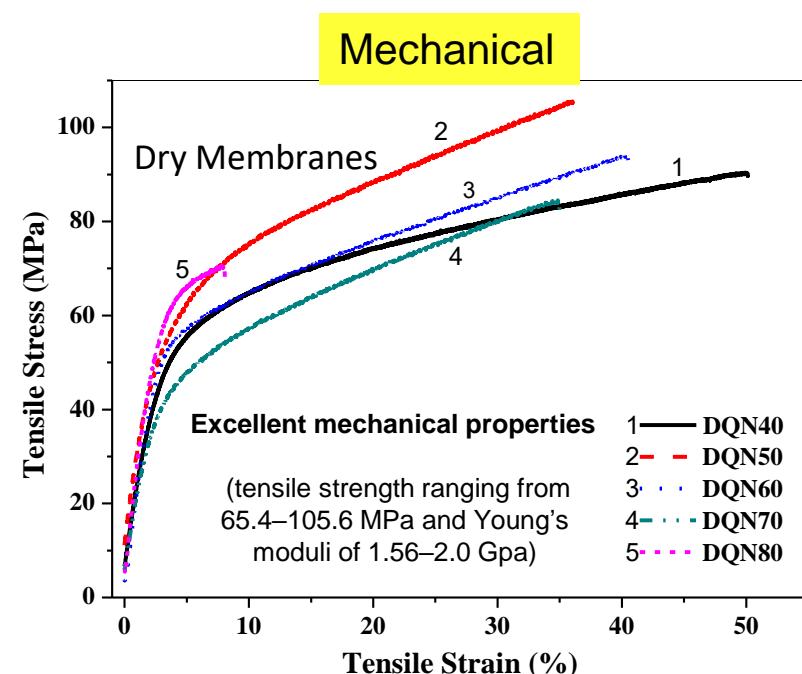
m=0.4, DQN 40
=0.5, DQN 50
=0.6, DQN 60
=0.7, DQN 70
=0.8, DQN 80
=0.9, DQN 90

- Possess good solubility in common organic solvents
 - High molecular weight
 - Excellent thermal and mechanical properties
 - Good dimensional stability with decent hydrolytic-oxidative stability
 - Nano-scale phase separated structure
 - High proton conductivity.

Physical Properties



TGA thermograms of the DQN polymers;



Stress-strain plot of DQN membranes

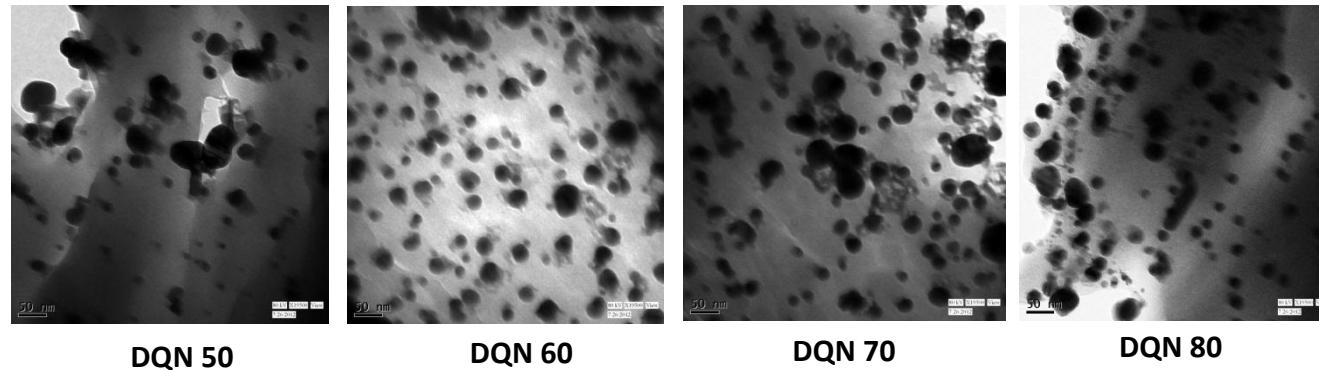
Chemical stability

Polymer membrane	Hydrolytic stability ^a (h)	Oxidative stability ^b (h)	
		τ_1	τ_2
DQN40	>250	3.8	>24
DQN50	>250	3.5	>24
DQN60	>250	3	20
DQN70	>250	1.2	9
DQN80	~120	0.8	4.5

^a Time that the membrane is completely dissolved in deionized water at 80 °C.

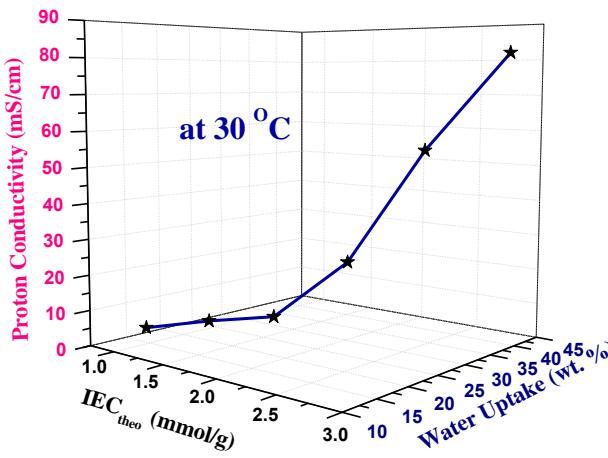
^b Tests performed in Fenton's reagent at 80 °C. τ_1 and τ_2 are the elapsed times in which the membranes start to break and dissolve completely.

Microstructure IEC and proton conductivity



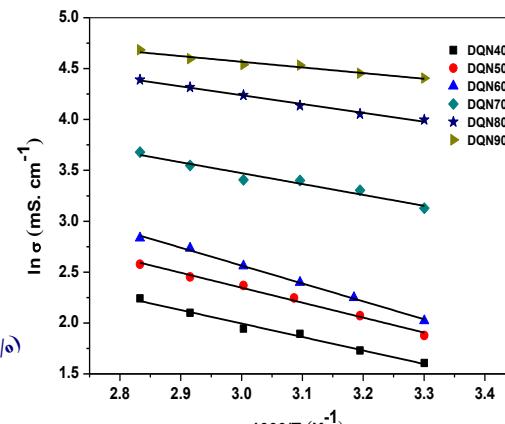
TEM micrographs of SPI membranes (cross section, Ag⁺ form)

- PEM properties:



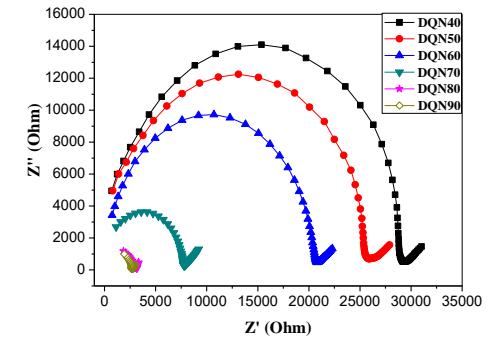
Correlation plot of IEC_{theo}, WU and proton conductivity

$$\text{Arrhenius equations, } \sigma = A e^{-E_a/RT}$$



Temperature dependence of proton conductivity

- Excellent nano phase separated structure
- High proton conductivity in the range of Nafion at 100 % relative humidity

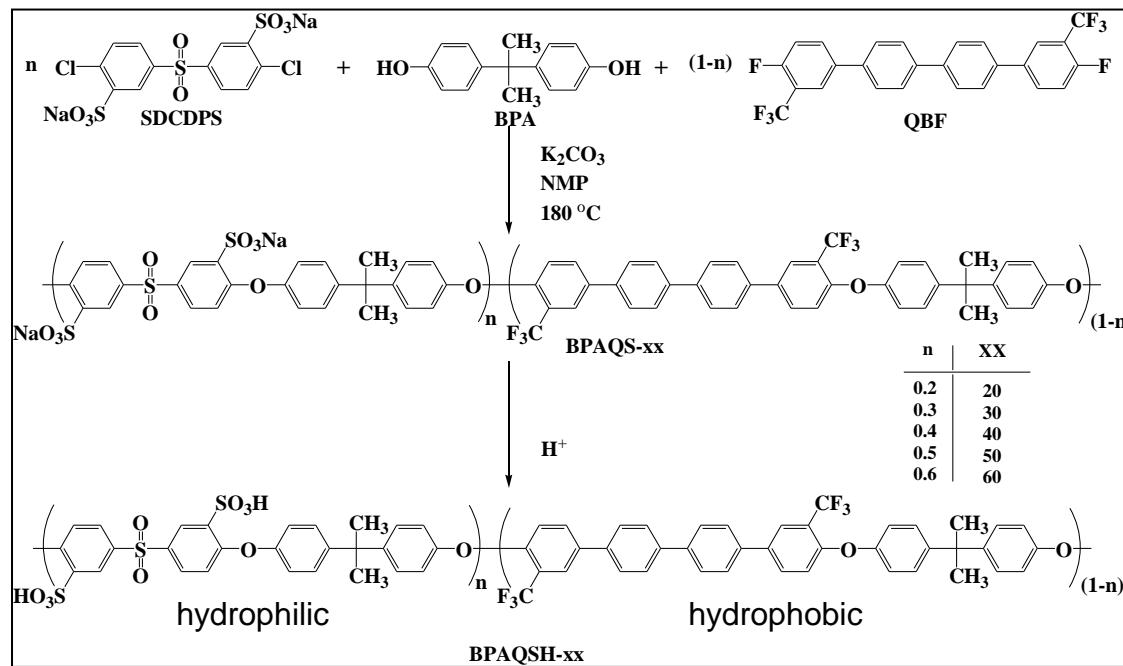


Variation in the impedance behaviour

Polymer membrane	IEC (meq/g)		Proton conductivity (mS cm⁻¹)		E _a (kJ/mol)
	theo. ^a	exp. ^b	30 °C	80°C	
DQN40	1.03	0.98	5	9.4	11
DQN50	1.34	1.36	6.5	13.2	12.2
DQN60	1.67	1.67	7.6	17	14.6
DQN70	2.03	n.d.	22.8	39.6	8.9
DQN80	2.42	n.d.	54.5	80.6	7.2
DQN90	2.85	n.d.	81.9	108.2	4.6

Studies on semifluorinated sulfonated poly(arylene ether sulfone)s

Reaction scheme:



Approach to the structural designing:

- QBF is incorporated to control the DS of the random copolymer BPAQSH-xx
- CF₃ group in QBF increases the hydrophobicity of non-sulfonated backbone segment over sulfonated segment which may help for good phase separated morphology
- SDCDPS with features of localized sulfonic acid density and rigid QBF moiety are incorporated into the backbone structure of polymer to increase the statistical length of non-sulfonated segment which may help to obtain good mechanical property, high hot water stability and high proton conductivity.
- rigid structure with pendant -CF₃ group of QBF moiety will help to attain good solubility, thermal, oxidative stability

Thermal properties, mechanical properties and oxidative stability

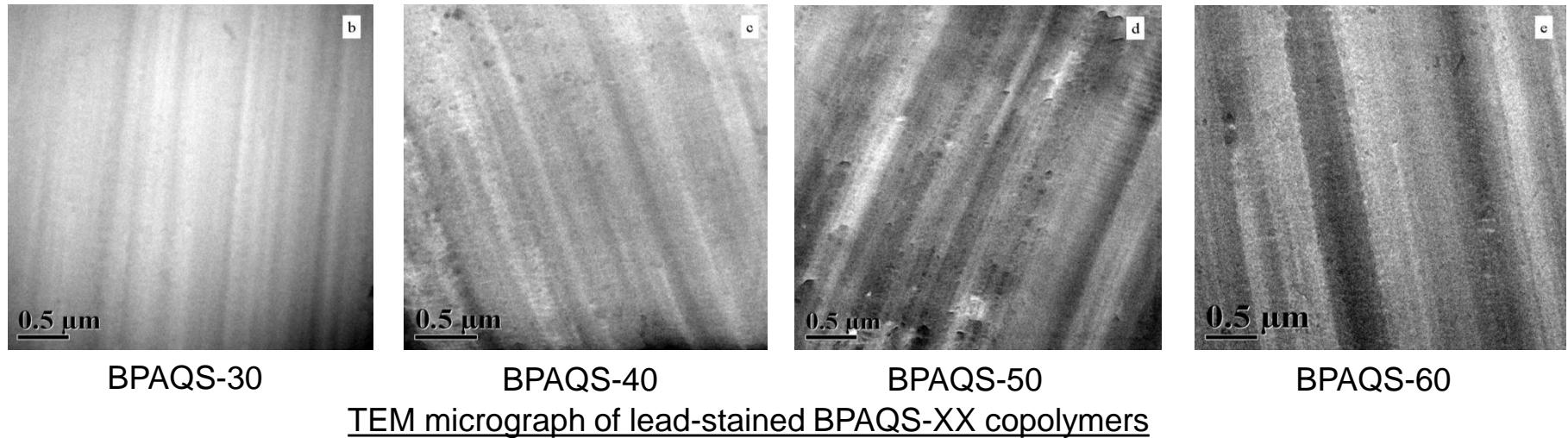
Polymer	T _g ^a (/°C)	T _{d5%} ^b (/°C)	T _{d1} ^b (/°C)	T _{d2} ^b (/°C)	TS (/Mpa)	Y (/GPa)	EB (/%)	Oxidative stability, t ^c (/h)
BPAQ	216	476	431	-	40	1.04	59	-
BPAQSH-20	245	365	393	546	57	1.55	18	29.6
BPAQSH-30	257	355	389	533	49	1.25	21	25.8
BPAQSH-40	ND	347	368	528	37	1.05	19	4.5
BPAQSH-50	ND	310	366	526	35	1.02	18	4.3
BPAQSH-60	ND	283	261	512	27	0.91	4	3.8

^a glass transition temperature determined by DSC, heating rate 10 °C/min under nitrogen.

^b t_d refers to decomposition temperature measured by TGA, heating rate 10 °C/min under air.

^c 't' refers to the time expended for the membrane beginning to break in Fenton's reagent (2ppm FeSO₄ in 3% H₂O₂) at 80 °C.

Microstructure and PEM properties



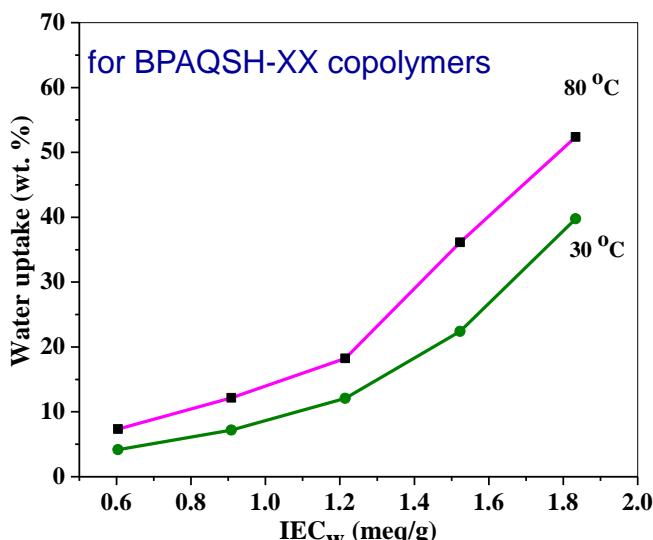
PEM properties:

Polymer	η_{inh}^a (dL/g)	IEC _w (meq/g)	WU _w (%)		Swelling (%)		σ (mS/cm)		E_a^b (KJ/mol)
			Titr.	30 °C	80 °C	30 °C	80 °C	30 °C	
xx=20	1.28	0.58	4	7	2.2	2.6	9	25	17.26
xx=30	1.25	0.84	7	12	2.8	3.3	13	31	16.44
xx=40	1.23	1.18	12	18	4.0	5.3	16	40	15.72
xx=50	1.21	1.46	22	36	4.6	6.3	31	71	13.96
xx=60	1.19	1.70	40	52	6.2	10.2	40	80	11.34

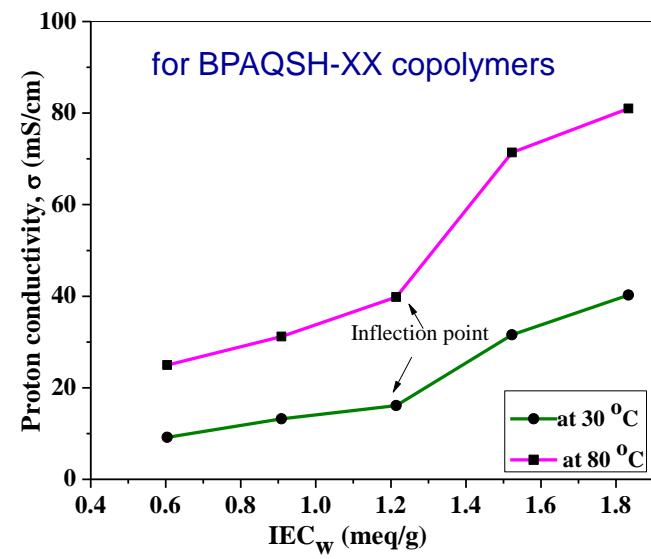
^a inherent viscosity of BPAQS-XX copolymers in NMP at 30 °C;

^b activation energy determined in the temperature range: 30-90 °C and heating rate 1-2 °C/min.

PEM properties



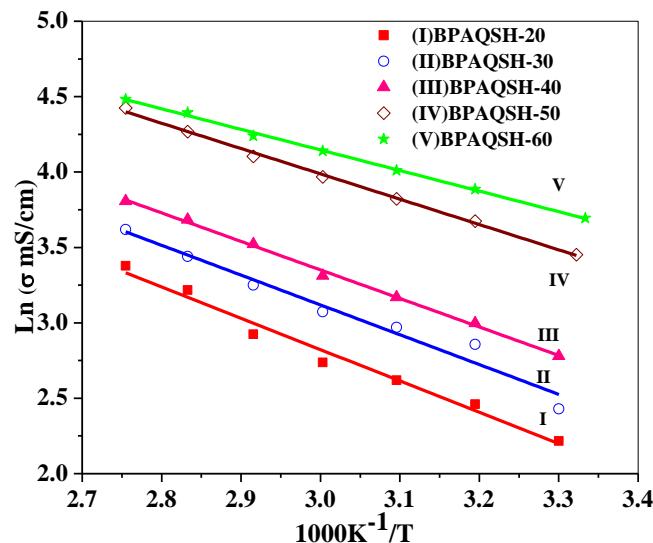
Water uptake as a function of IEC



Proton conductivity as a function of IEC

Arrhenius equation:

$$\sigma = A e^{-E_a/RT}$$



Arrhenius temperature dependence of proton conductivity (σ) of BPAQSH-XX membranes

Summary

- ❑ Both the synthesized aromatic SPIs and poly(arylene ether sulfone)s draw special attention as high performance polymeric materials with ease of processability and possessing an excellent balance between thermal , mechanical properties and proton conductivity.
- ❑ The synthesized 5-membered SPI (DQB XX) membranes are hydrolytically unstable and all the membranes undergoes hydrolysis upon long treatment with acid solution or long term keeping in water at room temperature but the 6-membered SPI (DQN XX) possess excellent hydrolytic-oxidative stability.
- ❑ Introduction of ether linkages (—O—) and bulky (—CF₃) pendent group into polymer chain resulted in increase in many physical properties like solubility, processability, dimensional stability and chemical stability.
- ❑ Hydrophobic (—CF₃) group also helps to form well phase separated structure responsible for better proton conductivity.
- ❑ High proton conductivity have been achieved for the membranes having moderately high IEC (88mS/cm at 90 °C for BPAQSH-60 and 108.2 mS/cm at 80 °C for DQN-90 sample).
- ❑ Overall combination of good PEM properties renders BPAQSH-50, BPAQSH-60 and DQN-70, DQN-80 as potential candidate for use as PEM materials.



End-of-life
Is there life after?



