Modern Techniques in Polymerization: 4582-605

Instructor: Jeff Pyun

Lecture 2-3: Aspects of Step-Chain-Living Polymerizations

September 6-8th, 2010

International Union of Pure and Applied Chemistry (IUPAC)

1) Polycondensation: condensation + step-reaction

Formation of low-mol-wt byproduct
Step-reaction polymerization

2) Polyaddition: addition + step-reaction

No byproducts
Step-reaction polymerization

3) Chain polymerization: addition + chain polymerization

No byproducts
Chain-reaction polymerization

4) Condensative chain polymerization: condensation + chain-reaction

Formation of low-mol-wt byproduct
Chain-reaction polymerization

1.7 Nomenclature

IUPAC name

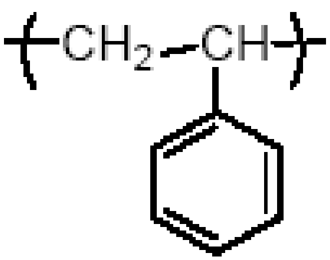
1) The smallest constitutional repeating unit (CRU) is identified

2) Substituent groups are assigned the lowest possible numbers

3) The name is placed in parenthesis, and prefixed with poly

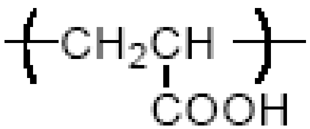
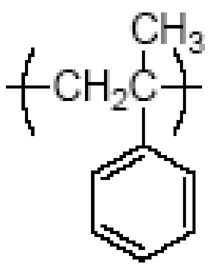
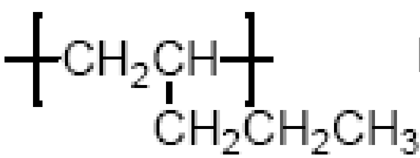
1.7.1 Vinyl polymers

poly + monomer name

	Source name = common name	IUPAC name
$-\!(\!-CH_2CH_2-\!)\!-$	polyethylene	poly(methylene)
$-\![\!-CF_2CF_2-\!]\!-$	polytetrafluoroethylene	poly(difluoromethylene)
	polystyrene	poly(1-phenylethylene)

poly + (monomer name)

more than one word **or letter or number**

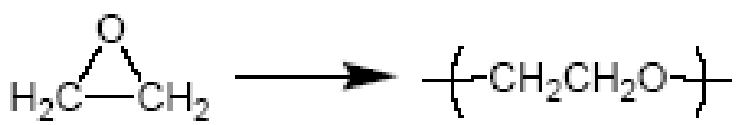
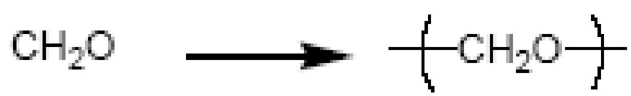
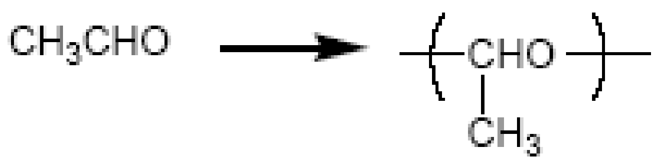
	Source name = common name	IUPAC name
	**poly(acrylic acid)**	**poly(1-carboxylatoethylene)**
	**poly(α-methylstyrene)**	**poly(1-methyl-1-phenylethylene)**
	**poly(1-pentene)**	**poly[1-(1-propyl)ethylene]**

1.7.3. Nonvinyl Polymers

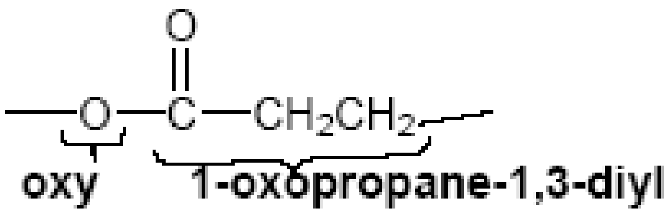
Polyethers, polyesters, polyamides

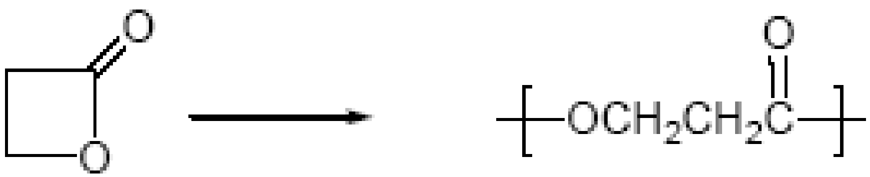
Heteroatoms Seniority: O, S, N, P

1) Polyethers

	Source name	IUPAC name
	Poly(ethylene oxide)	Poly(oxyethylene)
	Polyformaldehyde	Poly(oxymethylene)
	Polyacetaldehyde	Poly(oxyethylidene)

2) Polyesters



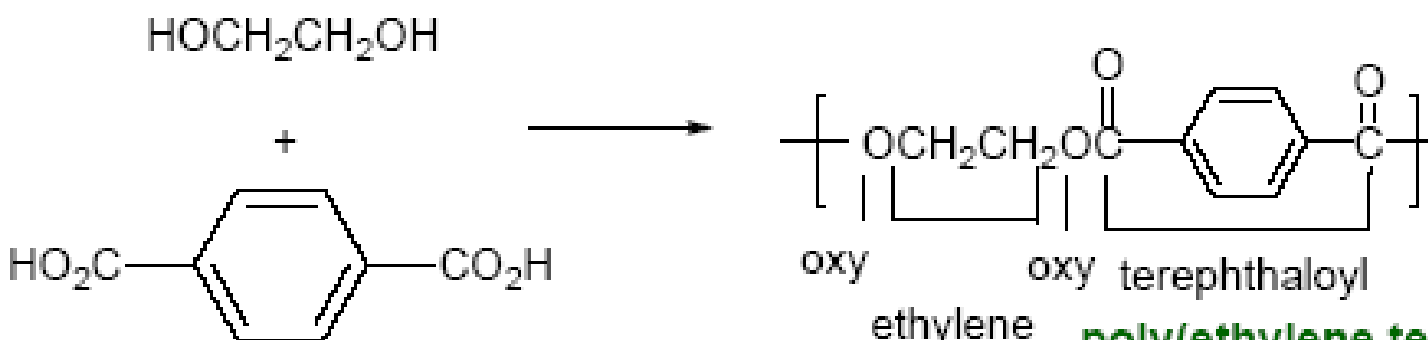


poly(β-propiolactone)
= poly(3-propionate)

poly[oxy(1-oxopropane-1,3-diyl)]

poly(10-decanoate)

poly[oxy(1-oxodecane-1,10-diyl)]

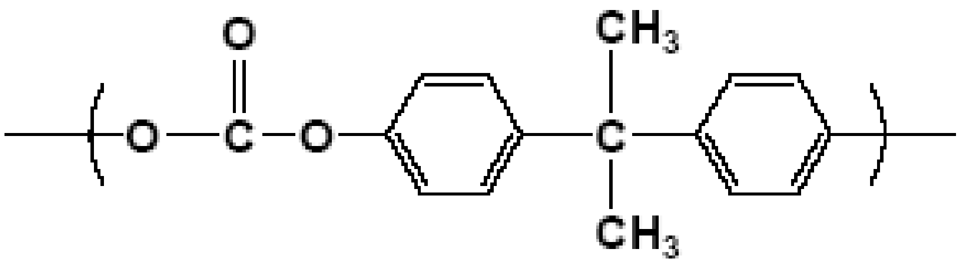


poly(ethylene terephthalate)

poly(oxyethyleneoxyterephthaloyl)

3) Polycarbonate

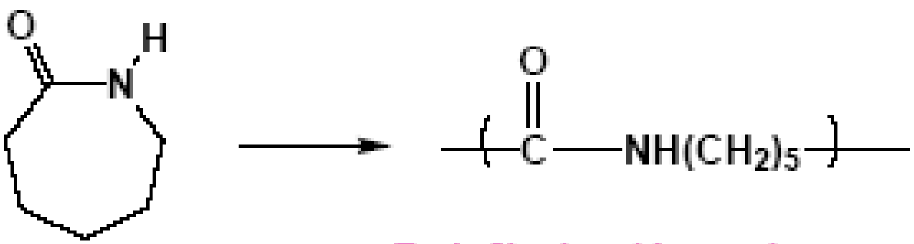
Heteroatoms Seniority: O, S, N, P



Bisphenol A polycarbonate

poly(oxycarbonyloxy-1,4-phenyleneisopropylene-1,4-phenylene)

4) Polyamide



Polycaprolactam
= nylon 6

caprolactam

Poly[imino(1-oxohexane-1,6-diyl)]

Poly(undecanoamide)
= nylon 11

11-aminoundecanoic acid

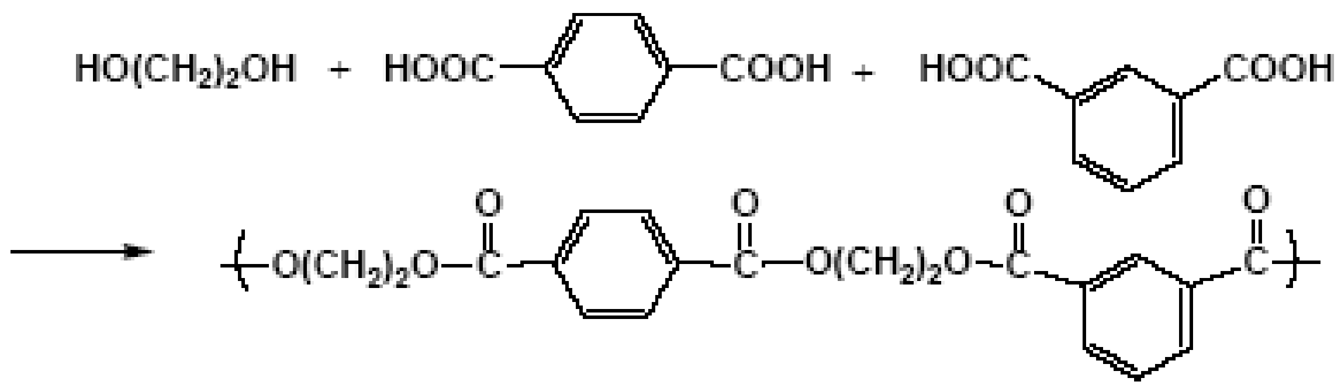
Poly[imino(1-oxoundecane-1,11-diyl)]

1.7.4 Nonvinyl copolymers

IUPAC source-based nomenclature for nonvinyl copolymers

2:1:1 –molar ratio of the monomers
ethylene glycol, terephthalic acid, and isophthalic acid

⟶ poly(ethylene terephthalate-co-ethylene isophthalate)



6-aminohexanoic acid + 11-aminoundecanoic acid

⟶ poly[(6-aminohexanoic acid)-co-(11-aminoundecanoic acid)]

poly[(6-hexanoamide)-co-(11-undecanoamide)]

$$H_2N(CH_2)_5COOH + H_2N(CH_2)_{10}COOH$$

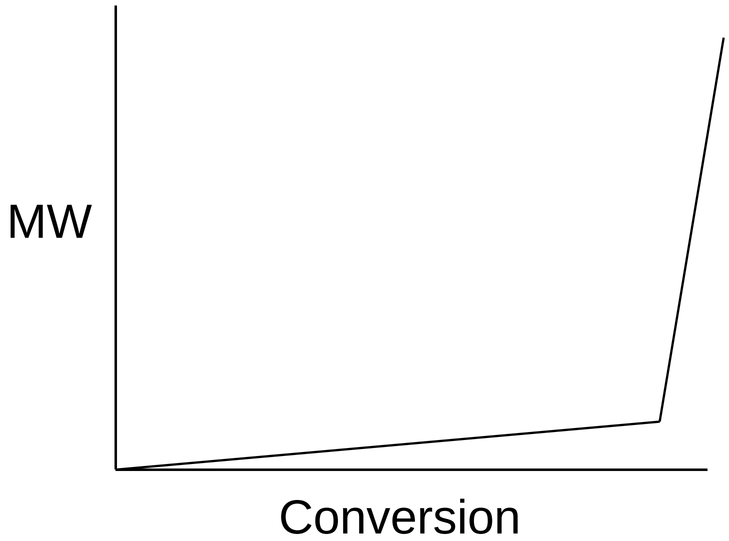
$$\longrightarrow -\!\!\left(HN(CH_2)_5CO-NH-(CH_2)_{10}CO\right)\!\!-$$

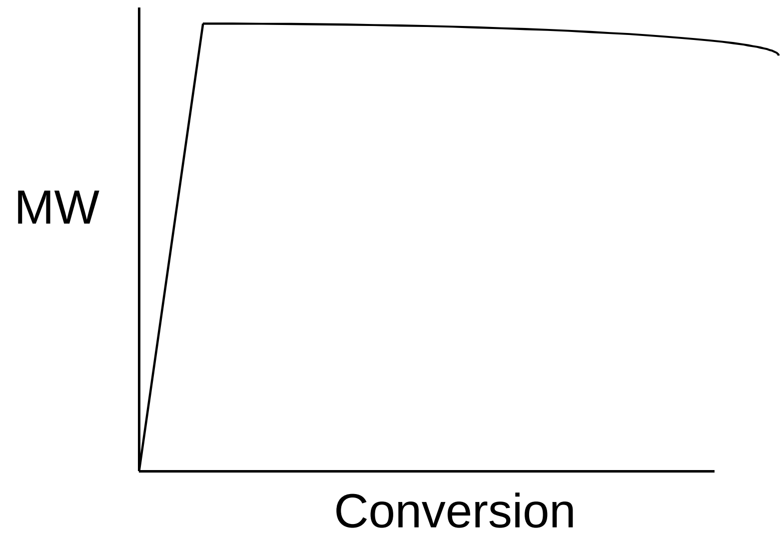
1.7.2. Vinyl Copolymers

IUPAC recommends source-based nomenclature for copolymers.

Systematic	Concise
Poly[styrene-*co*-(methyl methacrylate)]	Copoly(styrene/methyl methacrylate)
Poly[styrene-*alt*-(methyl methacrylate)]	Alt-copoly(styrene/methyl methacrylate)
Polystyrene-*block*-poly(methyl methacrylate)	Block-copoly(styrene/methyl methacrylate)
Polystyrene-*graft*-poly(methyl methacrylate)	Graft-copoly(styrene/methyl methacrylate)
Poly(styrene-*co*-ethylene-*co*-propylene)	Copoly(styrene/ethylene/propylene)

MW Evolution of Step vs. Chain Growth Polymerization





Step Growth Evolution of MW

Reaction of difunctional monomers
With complementary functional groups
(A_2 + B_2)

High polymer formed only at very high conversion

Heteroatom backbones

Chain Growth Evolution of MW

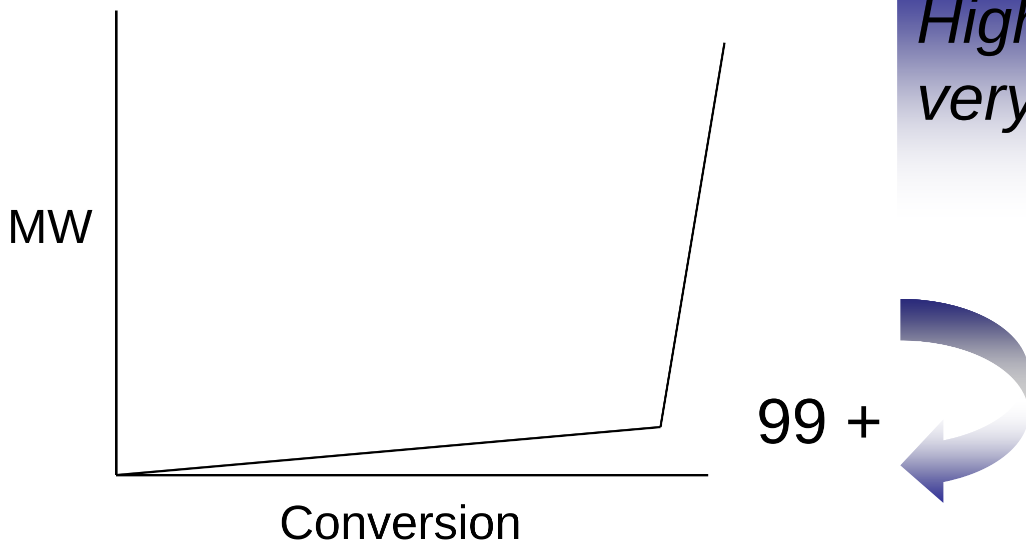
4-Elementary reactions (initiation, propagation, termination, transfer) of reactive monomer + initiator
(vinylic- π-systems, strained rings)

High polymer formed at low conversion

C-C bonds for vinylic monomers,
Heteroatom backbones for cyclic monomers

Requirements for Step-Growth Polymerization

High polymer formed only at very high conversion!!!



- High monomer purity
- Difunctionality
- Stoichiometry
- Quantitative conversion of monomer to polymer!
- No side Reactions

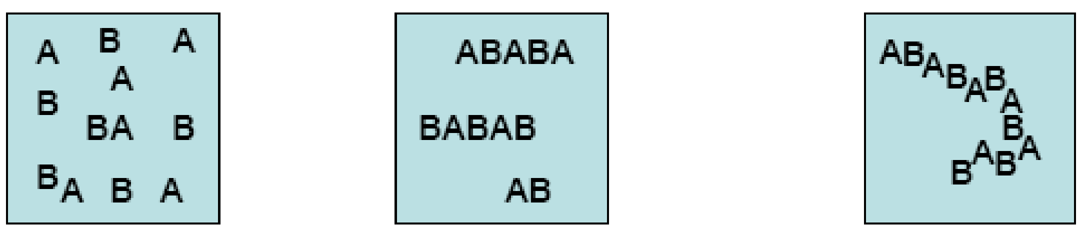
Step Growth/Condensation Polymerization

TABLE 2.1 *A schematic illustration of the fundamental differences in reaction mechanism between step polymerization and chain polymerization**

Formation of	Step polymerization	Chain polymerization
Dimer	o + o → o–o	I + o → I–o I–o + o → I–o–o
Trimer	o–o + o → o–o–o	I–o–o + o → I–o–o–o
Tetramer	o–o–o + o → o–o–o–o o–o + o–o → o–o–o–o	I–o–o–o + o → I–o–o–o–o
Pentamer	o–o–o–o + o → o–o–o–o–o o–o + o–o–o → o–o–o–o–o	I–o–o–o–o + o → I–o–o–o–o–o
Hexamer	o–o–o–o–o + o → o–o–o–o–o–o o–o + o–o–o–o → o–o–o–o–o–o o–o–o + o–o–o → o–o–o–o–o–o	I–o–o–o–o–o + o → I–o–o–o–o–o–o
Heptamer	o–o–o–o–o–o + o → o–o–o–o–o–o–o o–o + o–o–o–o–o → o–o–o–o–o–o–o o–o–o + o–o–o–o → o–o–o–o–o–o–o	I–o–o–o–o–o–o + o → I–o–o–o–o–o–o–o
Octomer	o–o–o–o–o–o–o + o → o–o–o–o–o–o–o–o o–o + o–o–o–o–o–o → o–o–o–o–o–o–o–o o–o–o + o–o–o–o–o → o–o–o–o–o–o–o–o o–o–o–o + o–o–o–o → o–o–o–o–o–o–o–o	I–o–o–o–o–o–o–o + o → I–o–o–o–o–o–o–o–o

* Definition of symbols used : o, molecule of monomer; –, chemical link; I, initiator species

[Young & Lovell, "Introduction to Polymers" 2nd ed.]



Time zero:
6 A monomers
6 B monomers

75% conversion
6/24 functional groups left
oligomers

92% conversion
2/24 functional groups left
polymer

Monomer Functionality and Polymer Architecture

Step-Growth

Difunctional monomers:
linear polymers

$A_2 + B_2$; AB monomers

multifunctional monomers:
branched, network polymers

$A_3 + B_2$; $A_2 + B_3$; $A_x + B_x$ -gelation
AB_2; AB_x monomers: (hyper)branched

For multifunctional monomers
Onset of gelation strongly dependent
on functionality of crosslinkers

Chain-Growth

monofunctional monomers:
linear polymers

Vinylic: styrene, acrylates

Di-, multifunctional monomers:
Crosslinked-networks

Dimethacrylates, divinylbenzene

multifunctional initiators:
In living processes with fast
Controlled initiation

Stars, branched polymers

Carother's Theory for Molar Mass Prediction in Step-Growth Polymerization

$$\overline{X_n} = \frac{N_o}{N} \quad \text{(eq. 1)}$$

$$p = \frac{\text{\# of functional groups that have reacted}}{\text{\# of functional groups initially present}}$$

$$p = \frac{N_o - N}{N_o} \qquad \frac{N_o}{N} = \frac{1}{1 - p} \quad \text{(eq. 2)}$$

Combine (eq's.1&2)

$$\overline{X_n} = \frac{1}{1 - p} \quad \textit{Carothers Eq.}$$

$\overline{X_n}$ — Defined as number average degree of polymerization

N_o — Number of molecules present initially at T = 0 (i.e., monomers)

N — Number of molecules present initially at T = t (both polymer and monomers)

p — Extent of reaction (fractional, 100% = 1.0) ***AND*** the probability that any functional group has reacted (i.e., formed bonds)

Theory applicable to polymerizations of: A_2 + B_2; AB, A_2-with stoichiometric balance

Requires perfect stoichiometric balance; high MW only at very high conversion!

MW distributions for Step-Growth

Carother's theory only provides X_n, M_n average values, no MW distributions!

Flory developed statistical theory to derive both number and weight fraction distributions

<u>Mole fraction distributions</u>

P(x) = probability distribution = number fraction distribution = mole fxn distrib.
"probability of a molecule possessing **x** monomer units at some time = t and *p*, where *p = extent of reactioni and probability of functional group reacted*

$$P(x) \equiv \frac{\#\ of\ polymers\ of\ X_n = x}{total\ \#\ of\ macromolecules}$$

1000 total polymer chains
10 trimeric molecules
P(trimer) = 0.010

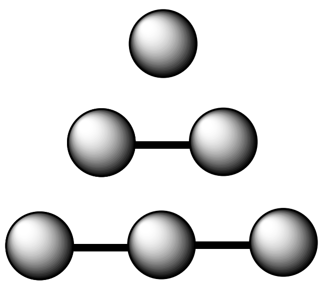
<u>Weight fraction distributions</u>

$$W(x) \equiv \frac{total\ mass\ polymers\ of\ X_n = x}{total\ mass\ of\ macromolecules}$$

1000g polymer chains
10g trimeric molecules
W(trimer) = 0.010

Most Probable Distributions: Number Fraction

p = extent of reaction and probability that functional groups have reacted
p = probability of finding bonds between monomers



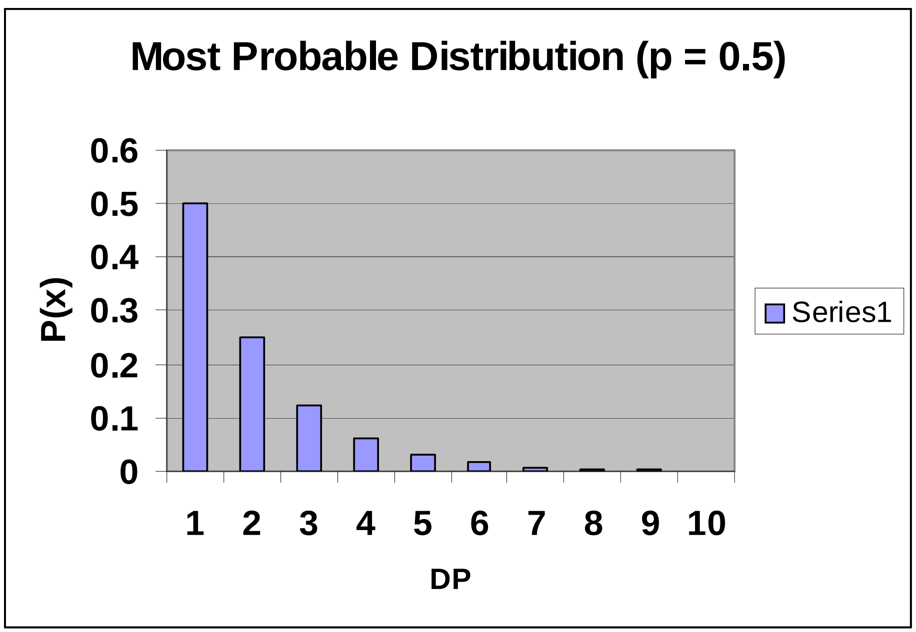
Probability of “finding” a monomer: **$P(1) = 1 - p$**

Probability of “finding” a dimer: **$P(2) = p(1 - p)$**

Probability of “finding” a trimer: **$P(3) = p^2(1 - p)$**

Probability of “finding” an *x*-mer: **$P(x) = p^{x-1}(1 - p)$**

This type of MW distribution referred to as a “most probable distribution” or “Flory-Schulz distribution”

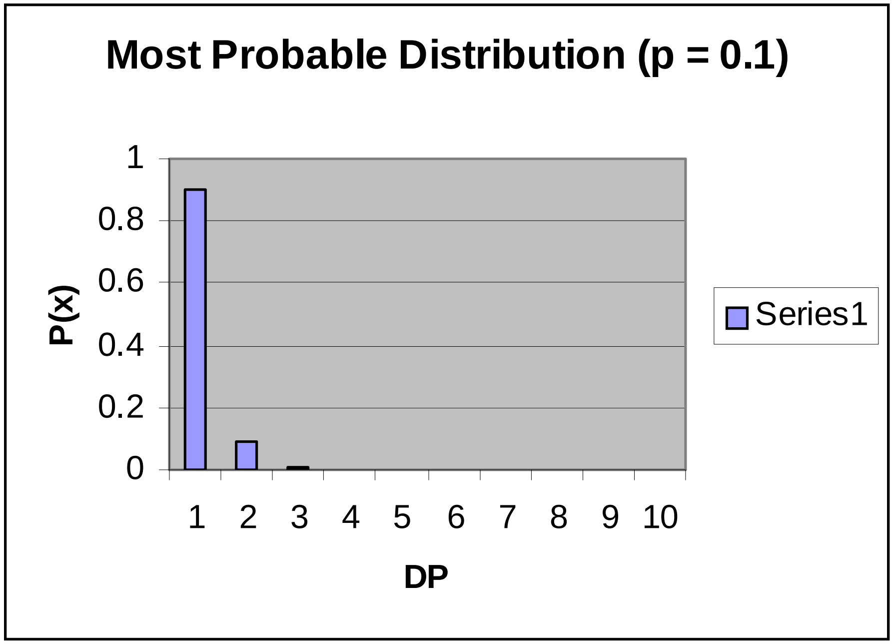


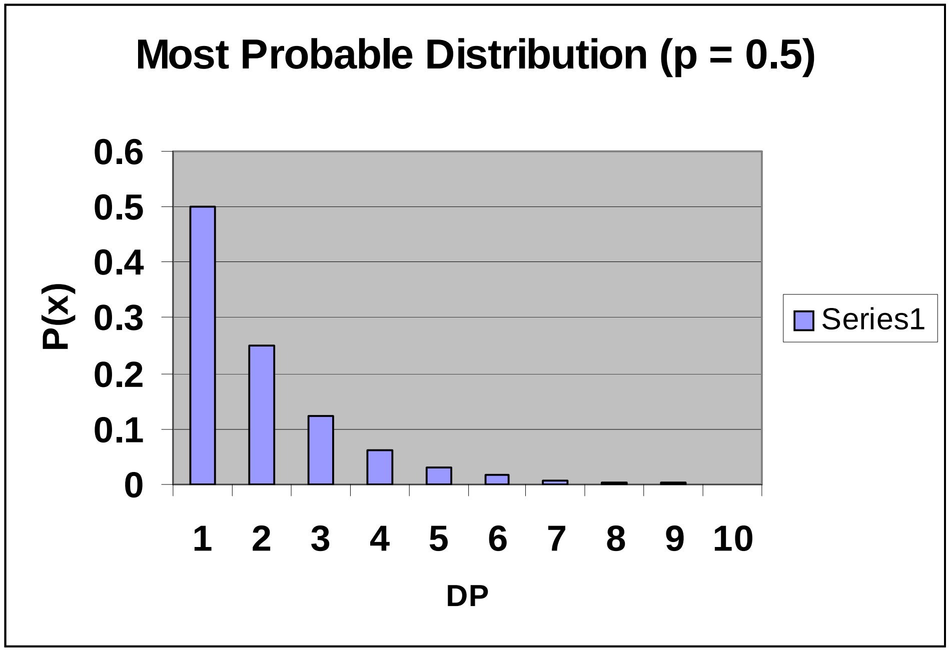
P(x) decreases monotonically with DP
Characteristic of step-growth polym.

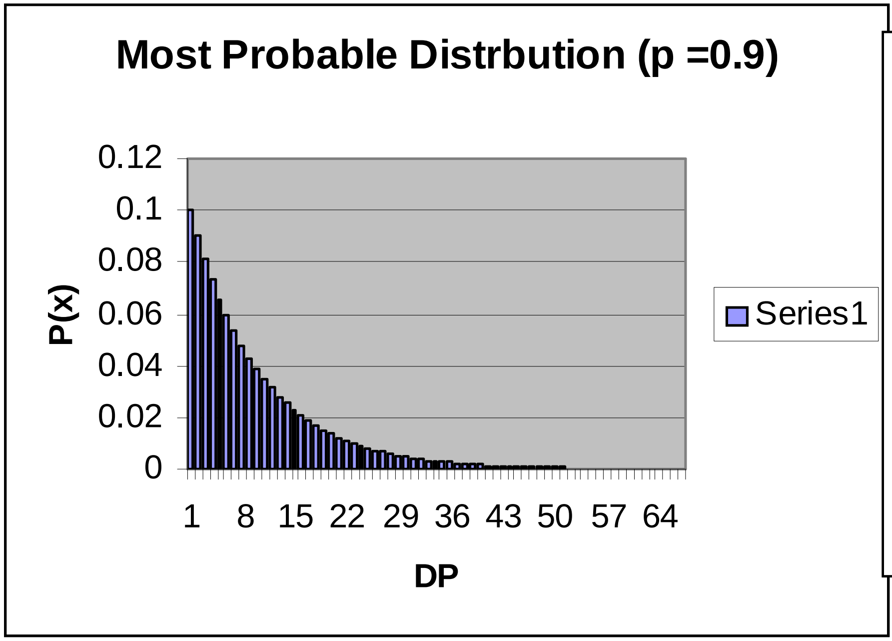
$P(x) = p^{x-1}(1 - p)$ *is discrete distr.*

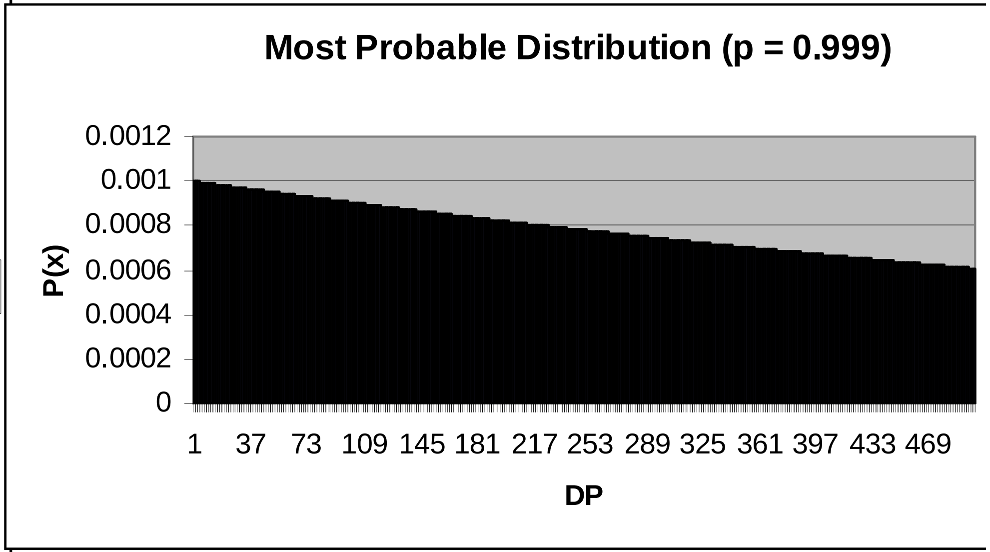
$P(x) = (1/X_n)e^{-x/X_n}$ continuous form

Most Probable Distributions with Higher Conversion









Most Probable Distributions: Weight Fraction

Probability Distribution-Mole Fraction Distribution

$$P(x) = p^{x-1}(1 - p)$$

$$P(x) = \text{mole fraction} = \frac{N_x}{N}$$

N_x = total number of X-mers

N = total number of molecules (monomer & polym) at some Time = t

$$N_x = N\,(1 - p)\,p^{x-1}$$

However, **N** is cumbersome to determine

$$N = N_o\,(1 - p)$$

N_o = total number of molecules at T = 0

$$N_x = N_o(1 - p)^2\,p^{x-1}$$

$$W(x) \equiv \frac{\textit{total mass polymers of } X_n = x}{\textit{total mass of macromolecules}} = \frac{N_x(x\,\overline{M_o})}{N_o\,\overline{M_o}}$$

$\overline{M_o}$ = ave. MW of repeat unit

$$W(x) = \frac{x\,N_x}{N_o} = x\,(1 - p)^2\,p^{x-1}$$

Other eq. which defines Flory-Schulz Distribution!

HW Problem Set: Create W(x) distributions as a function of conversion

Polydispersity in Step-Growth Polym.

Polydispersity = M_w/M_n index for MW distribution

$$\overline{M}_n = \Sigma P(x)\,\overline{M}_x = \Sigma x\,\overline{M}_o\,(1 - p)\,p^{x-1}$$

remember
$P(x) = (1 - p)\,p^{x-1}$
$M_x = x\,M_o$

$$\Sigma x\,p^{x-1} = (1 - p)^{-2} \text{ when } p < 1$$

$$\overline{M}_n = \frac{\overline{M}_o}{(1 - p)} = \overline{X}_n\,\overline{M}_o$$

remember
$X_n = 1/(1 - p)$

$$\overline{M}_w = \Sigma W(x)\,\overline{M}_x = \Sigma x^2\,\overline{M}_o\,(1 - p)^2\,p^{x-1}$$

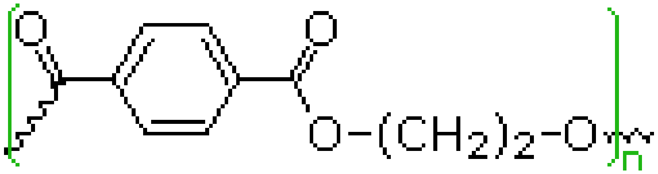
remember
$W(x) = p^{x-1}\,x(1 - p)^2$
$M_x = x\,M_o$

$$\Sigma x^2\,p^{x-1} = (1 + p)(1 - p)^{-3} \text{ when } p < 1$$

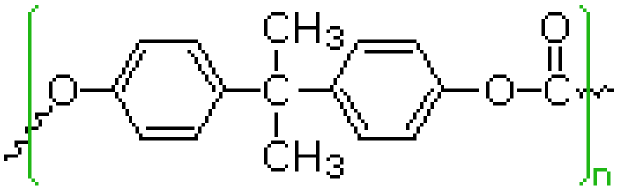
$$\overline{M}_w = \overline{M}_o\,\frac{(1 + p)}{(1 - p)}$$

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + p$$

Examples of Step-Growth Polymers



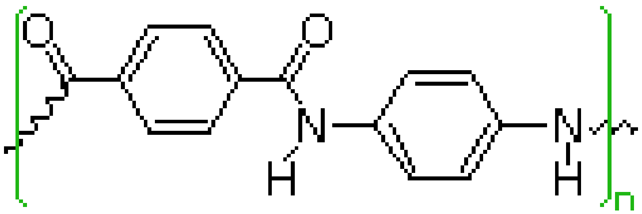
Polyester
Dacron, Mylar



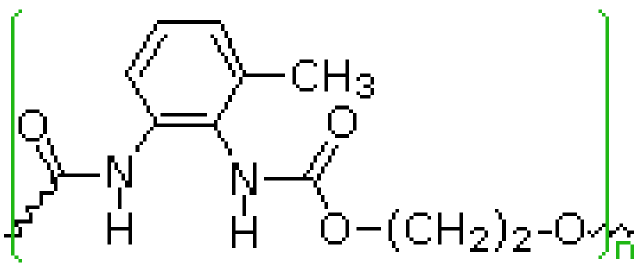
polycarbonate

~[CO(CH2)4CO-NH(CH2)6NH]n~

Polyamide
Nylon 6,6



Polyaromatic amide
Kevlar



Polyurethane
Spandex

Key Features of Step-Growth Polymers

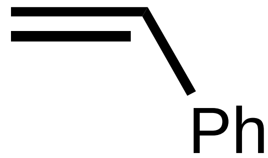
More expensive than chain-growth poylmers

Improved mechanical properties

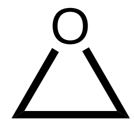
Wider range of optical, electronic magnetic properties

Examples of Monomers Chain-Growth Polymerization

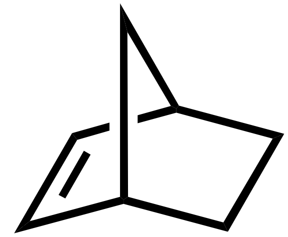
Ethylene



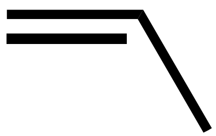
Styrene



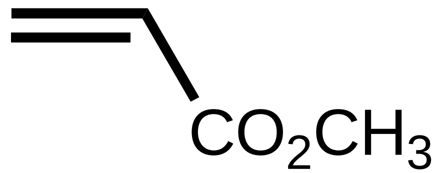
Ethylene oxide



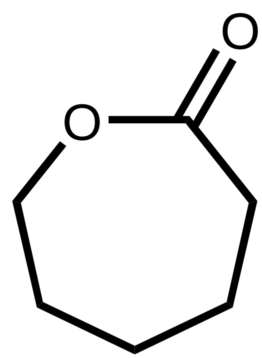
Norbornene

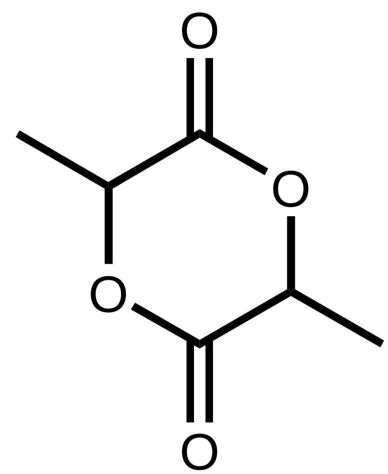


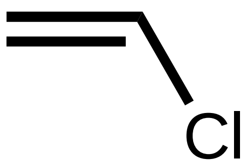
Propylene



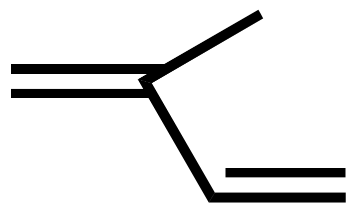
Methyl methacrylate







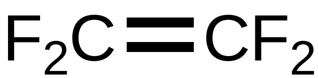
Vinyl chloride



Isoprene

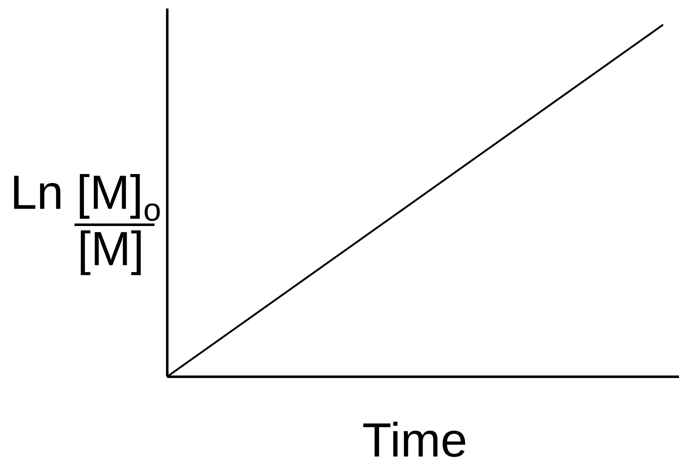
ε-Caprolactone

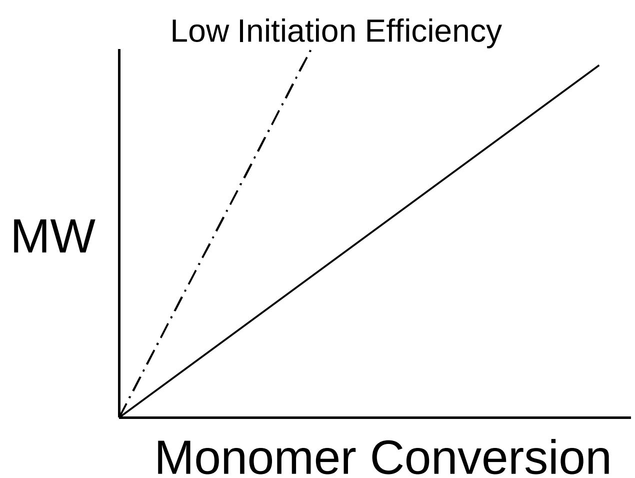
Lactide



Tetrafluoroethylene

Definition and Criteria for Living Polymerizations





Definition: Chain polymerization that proceeds in the absence of chain breaking processes (termination, transfer

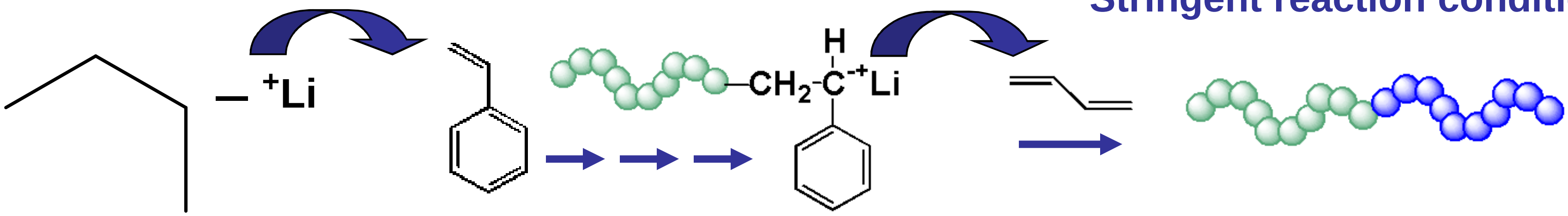
Criteria*: (Quirk et al., Polym. Int. **1992**, *27*, 359)

1) Polymerization proceeds until all monomer consumed, further addition of monomer results in chain extension
2) Number average MW (M_n, X_n) linear relationship with monomer conversion
3) # of initiator molecules = # of polymer chains, which is constant throughout reaction
4) DP = $[M]_o/[I]_o$ x conversion
5) Polymers of low polydispersity formed $M_w/M_n = 1 + 1/DP_n$
6) Block Copolymers formed from sequential monomer addition to living polymer chain
7) Facile chain end functionalization
8) Linearity of $\ln([M]_o/[M])$ vs. time (constant # of active centers

Controlled/Living Polymerizations

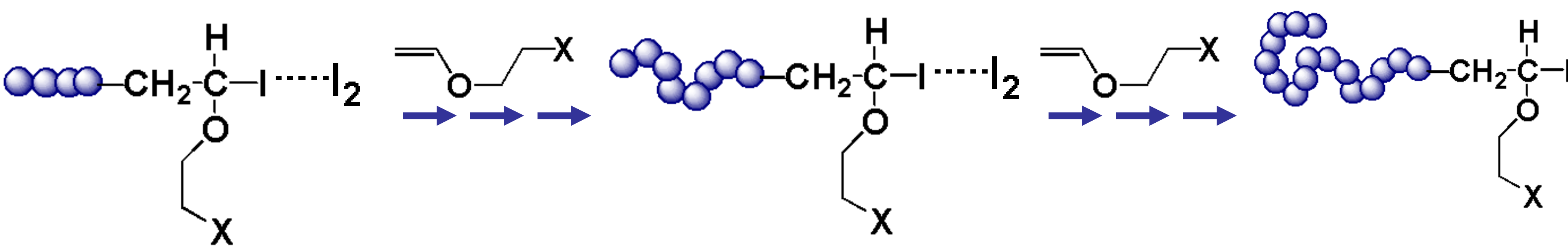
***Living polymerization*:** **a chain growth process without chain-breaking reactions (termination, transfer)**
Anionic, Insertion (ROMP)

Features: **precise DP_n ($\Delta[M]/[I]_o$)**
Low polydispersity
Active chain ends-Blocks
Control of architecture
Stringent reaction conditions



***Controlled/"Living" polymerization*:** **a chain growth process with chain-breaking reactions**
$R_{propagation}$ >> $R_{termination}$, $R_{transfer}$
Reversible deactivation

Features: **precise DP_n ($\Delta[M]/[I]_o$)**
Low polydispersity*
Active chain ends-Blocks
Control of architecture



Free Radical Chemistry: 1990's

Greater functional group tolerance
Range of monomers

Controlled/Living Polymerizations

Living Anionic Polymerization

Initiators: ex. organolithium compounds (sec-butyl lithium; n-butyl lithium) Grignard reagents, alkali bases

Monomers: *ex. Styrenes, dienes, (meth)acrylates, pyridines, epoxides: Functional monomer require protecting groups; alkyl esters cannot be polym*

Features: exquisite control of MW, block copolymers, low functional group tolerance

Controlled Cationic Polymerization

Initiators: ex. Alkyl halides, acetates, inorganic/organic acids, water

Monomers: *ex. Vinyl ethers, alkenes(butylene), styrene, cyclic ethers Functional monomer require protecting groups; alkyl esters cannot be polym*

Features: highly reactive cation species susceptible to chain transfer Controlled MW, block copolymers

Controlled Radical Polymerization

Initiators: ex. Alkyl halides, alkoxyamines, thioesters

Monomers: *ex. (meth)acrylates, (meth)acrylamides, styrenes, acrylonitrile, Pyridines, dienes,*

High functional group tolerance, widest scope of polymerizable monomers

Features: controlled MW, blcck copoylmers, functionality, bimolecular termination

Ring-Opening Polymerization

Coordination-Insertion Polym.

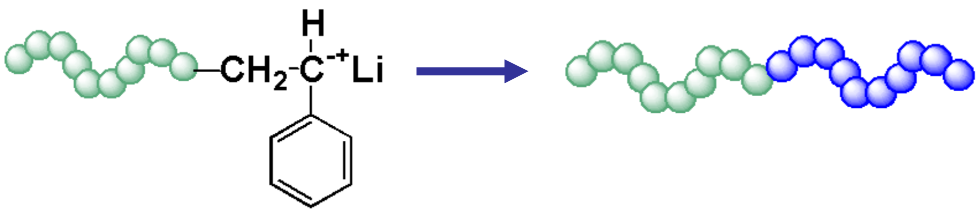
Ring-opening metathesis Polymerization (ROMP)

Initiators/catalysts:
Transition metal alkyldenes (Ru, Mo)

Monomers:
Cyclic alkenes (norbornylene Cyclooctadiene, dicyclopenta-dienes)

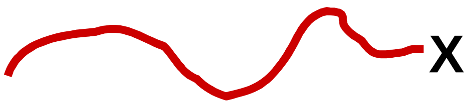
Controlled/Living Polymerizations: Materials

Block copolymers & Functionalization

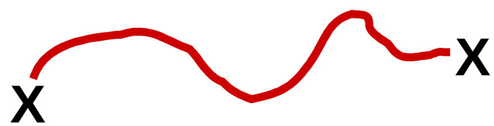


Living Polymer Chain

Block Copolymer

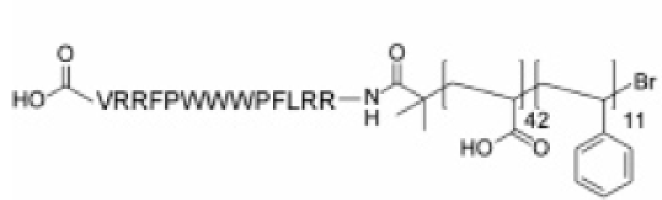


End-Functional Polym.

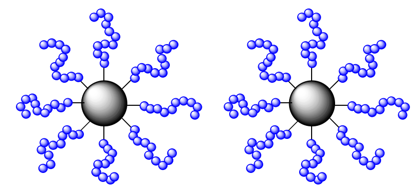


Telechelic

Biohybrids, Nanocomposites

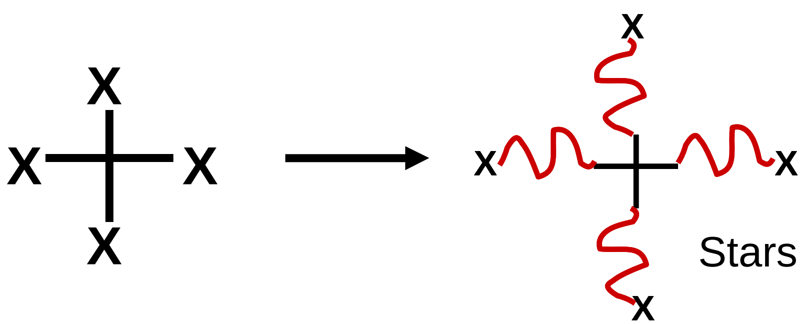


Peptide Conjugates

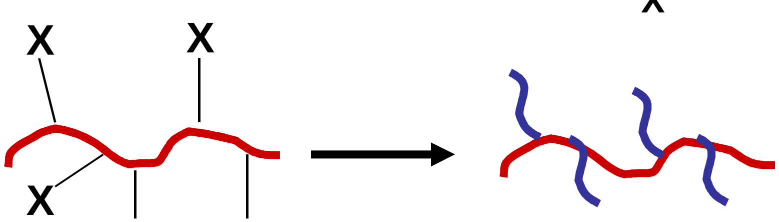


Organic/Inorganic Composite

Well-defined initiators: Stars, graft



Stars



Graft Copolymer

Surface Modification