What is polymer Chemistry

- Chemistry of large molecules (macromolecules).
- "**Macromolecules**" : molecules existed as a result of *covalently linked smaller units*, and possessed unique physical and chemical properties.
- Polymer is macromolecules, but macromolecules may not be a polymer.

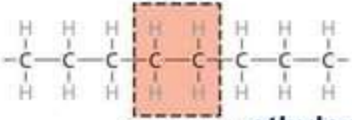
What is polymer

- Polymer is compound consisting of *long-chain molecules*, each molecule made up of *1000- 10 000 repeating units* connected together.
- The word *polymer* is Greek words *poly*: many, and *meros* (reduced to *mer*: part.
- *Molar mass* ranges from *10^4- 10^6 g/g-mole*.
- Most polymers are based on *carbon* and are therefore considered organic compounds.

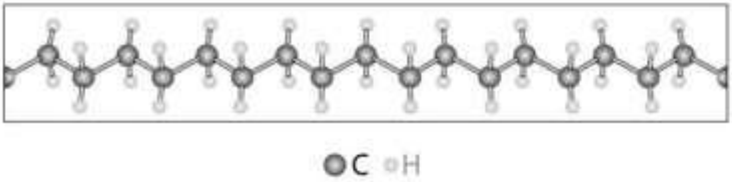
Polymer Chain Lengths

- Many polymer properties are affected by the length of the polymer chains. For example, the melting temperature increases with increasing molecular weight.
- At room temp, polymers with very short chains (roughly 100 g/mol) will exist as liquids.
- Those with weights of 1000 g/mol are typically waxy solids and soft resins.
- Solid polymers range between 10,000 and several million g/mol.
- The molecular weight affects the polymer's properties (examples: elastic modulus & strength).

Polymeric Materials, Repeating units

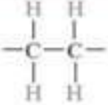
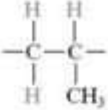


Repeat unit **ethylene**



polyethylene

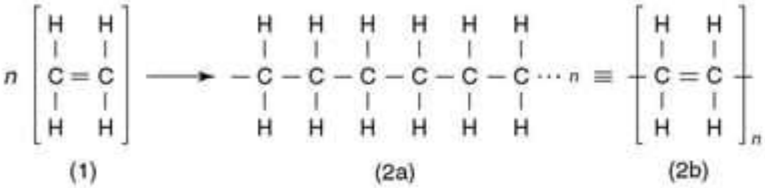
Polymeric Materials, Repeating units

Polymer		*Repeat Unit*
	Polyethylene (PE)	
	Poly(vinyl chloride) (PVC)	
	Polytetrafluoroethylene (PTFE)	
	Polypropylene (PP)	

Typical Values of DP and MW for Selected Polymers

Polymer	DP(n)	MW
Polyethylene	10,000	300,000
Polyvinylchloride	1,500	100,000
Nylon	120	15,000
Polycarbonate	200	40,000

Polymeric Materials & Notation



polyethylene of chain length n ; (2b) concise notation for depicting the polymer structure of chain length n

Applications

- Packaging/films (PE, PP, PET)
- Everyday household stuff
- Paint (Polyacrylate, Epoxy)
- Adhesives (Epoxy resin, Acrylic resin)
- Auto's,aerospace,etc.
- Fibres (polyester, nylon)

- Electronic applications
- Elastomers (Rubber, Butadiene)

Plastics and the environment

Most common plastics pose serious threats to human health and the environment

- *extreme pollution from production*
- *toxic chemical exposure during use*
- *hazards from fires* ($C_xH_y + O_2 \rightarrow CO_2 + H_2O$)
- *their contribution to the world's growing waste crisis*

Historical Background

Ages ago –Natural fibers Ex. wool, silk and cotton

1492 – *Columbus* discovered South America and found the use of natural rubber *(Hevea brasiliensis)*

Polyisoprene

"Crying trees"

Para rubber

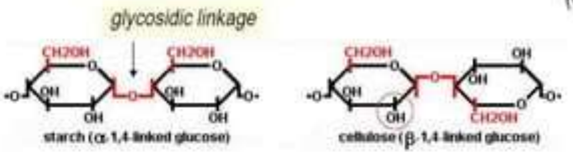
Uses:
Latex coating

Classification of Polymers 1. By Source:

1.1 Natural polymers (including macromolecules)

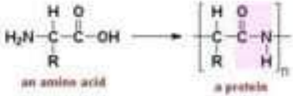
- Polysaccharide <u>Ex.</u> starch, glycogen, cellulose, chitin, c

$(C_6H_{10}O_5)_n$, where n = 300 and 3000.



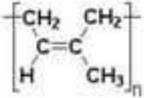
-NHCO-CH_3 for chitin
-NH_2 for chitosan

- Protein



(Polyamide)

- *cis*-polyisoprene (natural rubber)



1.2 Synthetic polymers

<u>Ex.</u> plastics, synthetic rubbers, synthetic fibers ect.

Classification of Polymer
2. by Skeletal Structure

Polymers can exist with various **skeletal structures** - such as:

1. **Linear polymers.**
2. **Branched polymers.**
3. **cross-linked polymers.**
4. **Network polymers.**
5. **Dendiemer Polymer**

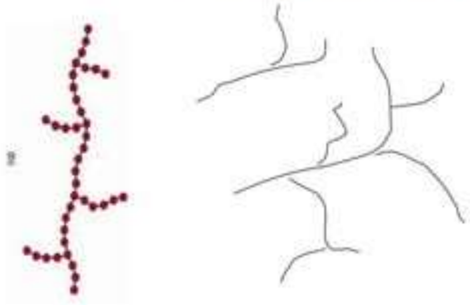
Classification of Polymer by Structure:

***Linear* structure :** chain-like structure
Characteristic of thermoplastic polymers.

Linear

Polymer Structure

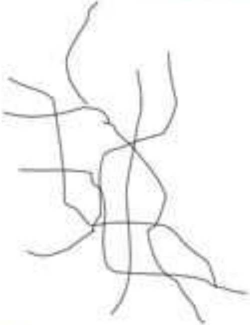
- ***Branched*** structure that includes side branches along the chain, also found in thermoplastic polymers.



Branched

Polymer Structure

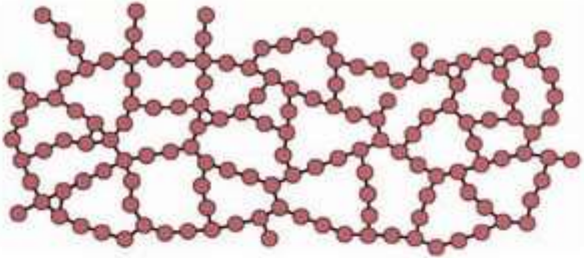
- ***Loosely Cross-linked***: bonding occurs between branches and other molecules at certain Connection points. As ***in an elastomer***



Loosely Cross- Linked

Polymer Structure

Tightly cross-linked or ***network structure*** - in effect, the entire mass is one gigantic macromolecule. As in a **thermoset.**

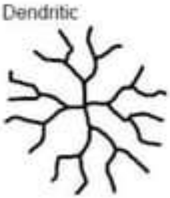


network structure

Polymer Structure

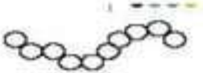
Dendrimer Polymer: from the Greek word means tree- like polymer, dendrimer structure has:

1. Symmetric around the core.
2. Spherical three-dimensional morphology.

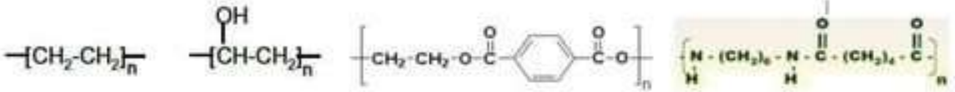


Dendrimer Structure

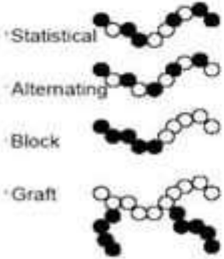
Classification of Polymer: 3. by Composition



3.1 Homopolymers (contain one type of repeat unit)

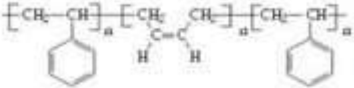


3.2 Copolymers (contain at least 2 repeat units)

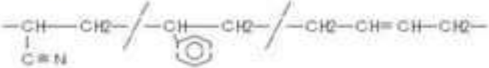


Ex. Styrene-Butadiene-Styrene block copolymer (SBS)

"Thermoplastic Elastomer"



Ex. Acrylonitrile-butadiene-styrene copolymer (ABS)



Nomenclature of Polymer

Nomenclature of Polymers

Source-based name: base on name of monomer

Poly + name of monomer   **Note**: use ( ) if monomer has a multi-worded name

Structure-based name: base on structure of repeat unit

Poly(name of structure of repeat unit)

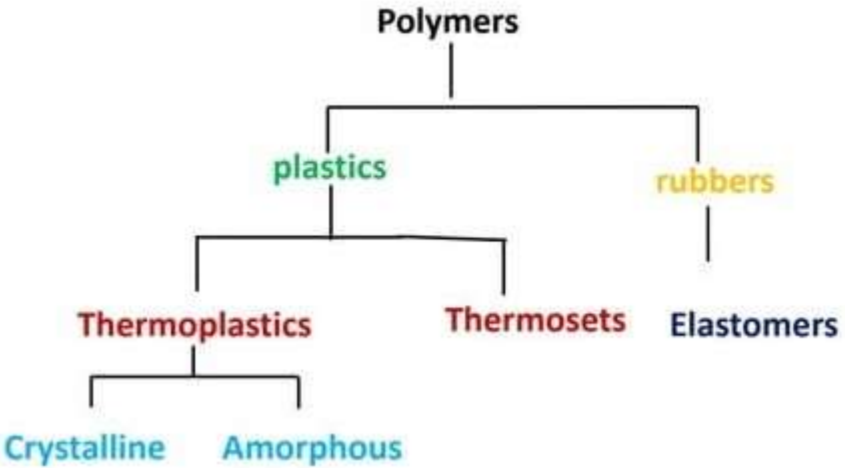
Monomer	Polymer	Structure-based name	Source-based name
$CH_2=CH_2$	$-\!\left(CH_2\right)_n\!-$	Poly(methylene)[a]	Polyethene; polyethylene In UK called polythene
$CH(OH)=CH_2$	$-\!\left(CH(OH)-CH_2\right)_n\!-$	Poly(1-hydroxyethylene)	Poly(vinyl alcohol)
$CH(CH_3)=CH_2$	$-\!\left(CH(CH_3)-CH_2\right)_n\!-$	Poly(1-methylethylene)	Polypropylene; polypropene

Types of Polymers

- Polymers can be separated into *plastics* and *rubbers.*
- It can be classified into the following three categories:
- *1. Thermoplastic* polymers
- *2. Thermosetting* polymer } plastics
- *3. Elastomers* → rubbers

Polymer Classification

Polymers are commonly classified according to thermal effect as follows:



Thermoplastics
Thermosetting plastics

- Thermoplastics: Thermoplastics soften when heated, and they become hard and rigid once again when cooled.
- Example: Polyethylene, PVC, Nylon Uses: Bags, Toys
- Thermosetting plastics: Thermosetting materials do not become softy on heating.
- Example: Bakelite Uses: Electric switches, Telephone parts, Cooker handles

Effect of Branching on Properties

branched structures, or a mixture of the two

- If Branches increase among the molecules, the polymer becomes:

- Stronger in the solid state.

- More viscous in liquid state.

•

Crystalinity and Properties

As crystallinity is increased in a polymer:

- Density increases.
- Stiffness, strength, and toughness increases.
- Heat resistance increases.
- It becomes opaque (Not transparent).

THERMOPLASTICS PROPERTIES

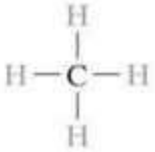
- 1. Formed by addition Polymerization.
- 2. Long chain linear polymers.
- 3. Soften on heating and stiffen on cooling
- They can be moulded into any shape.
- Less than 100% crystallinity, but instead **amorphous**.

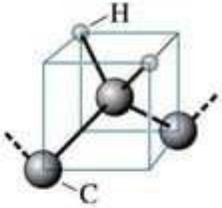
THERMOSETTING PLASTICS

- 1. Formed by condensation Polymerization.
- 2. Three dimensional network structure joined by strong covalent bonds
- 3. Do not soften on heating
- 4. Rigid materials
- 5. At high temperature, thermoset plastics degrade rather than melt.

Hydrocarbon Molecules

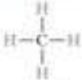
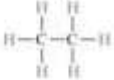
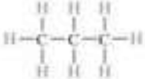
- Many organic materials are hydrocarbons
- Most polymers are made up of H and C.
- The bonds between the hydrocarbon molecules are covalent.
- Each carbon atom has 4 electrons that may be covalently bonded, the hydrogen atom has 1 electron for bonding.
- A single covalent bond exists when each of the 2 bonding atoms contributes one electron (ex: methane, CH_4).





Saturated Hydrocarbons

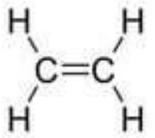
- Each carbon has a single bond to 4 other atoms; the 4 valence electrons are bonded, the molecule is stable.
- The covalent bonds in each molecule are strong, but only weak hydrogen and van der Waals bonds exist between the molecules.

Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

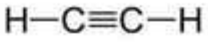
- Most of these hydrocarbons have relatively low melting and boiling points.
- However, boiling temperatures rise with increasing molecular weight.

Unsaturated Hydrocarbons

- Double & triple bonds are somewhat unstable : involve sharing 2 or 3 pairs of electrons, respectively. They can also form new bonds
  - Double bond found in ethylene - C_2H_4



  - Triple bond found in acetylene - C_2H_2

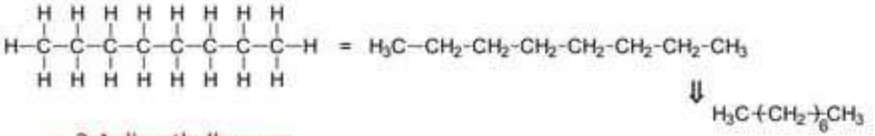


Isomerism

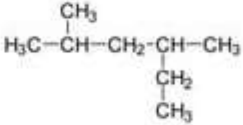
- *Two* compounds with same chemical formula can have different structures (atomic arrangements).

  for example: C_8H_{18}

  - normal-octane



  - 2,4-dimethylhexane



Synthesis of Polymers

- **There are a number different methods of preparing polymers from suitable monomers, these are**
  - **1. step-growth (or condensation) polymerization**
  - **2. Chain growth (addition) polymerization**

Synthesis of Polymers

Polymerization is a process of reacting monomer molecules together in a chemical reaction to form linear chains or a three-dimensional network of polymer chains.

1. Addition: repeating units and monomers are same

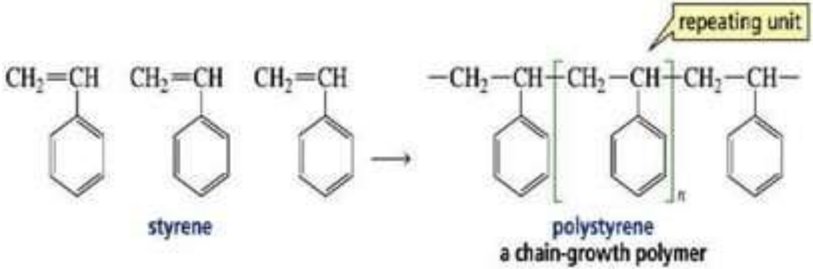
- Addition polymerization involves the linking together of molecules, double or triple chemical bonds

2. Condensation: "step-growth polymerization,

Condensation: repeating units and monomers are not equal,
Example: Reactions of alcohol, amine, or carboxylic acid (or other carboxyl derivative) functional groups.

Types of Polymerization

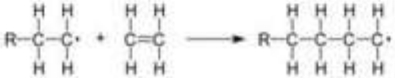
- 1. Chain-growth polymers, also known as addition polymers, are made by chain reactions



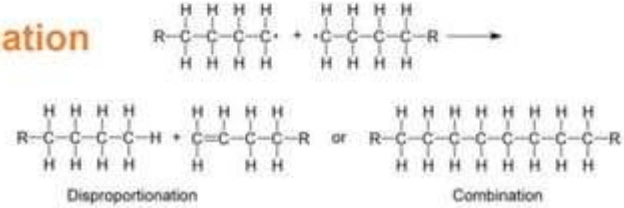
Addition (Chain) Polymerization

– **Initiation**

– **Propagation**

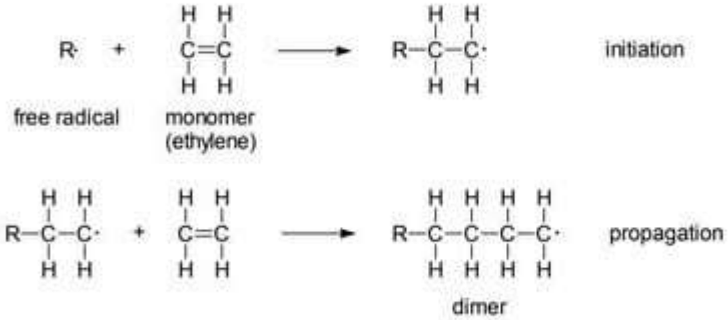


– **Termination**



Addition

Free radical polymerization: ethylene gas reacts with the initiator(catalyst) ("R." is the unpaired electron)

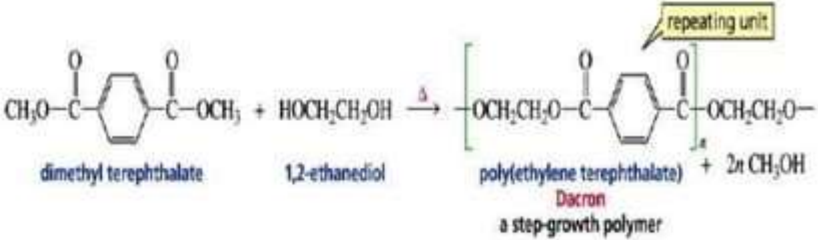


Some Common Addition Polymers

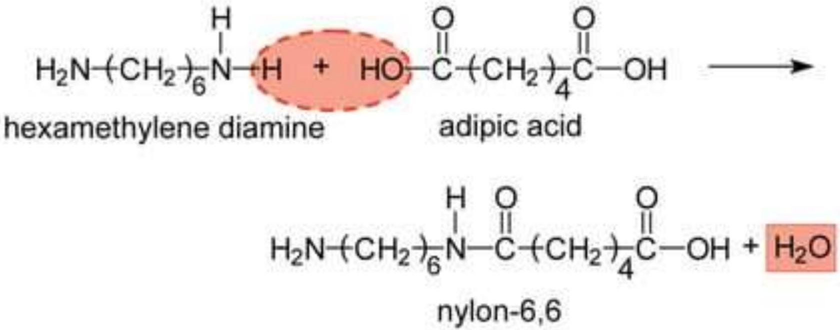
Name(s)	Formula	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	soft, waxy solid	film wrap, plastic bags
Polyethylene high density (HDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	rigid, translucent solid	electrical insulation bottles, toys
Polypropylene (PP) different grades	$-[CH_2-CH(CH_3)]_n-$	propylene $CH_2=CHCH_3$	atactic: soft, elastic solid isotactic: hard, strong solid	similar to LDPE carpet, upholstery
Poly(vinyl chloride) (PVC)	$-(CH_2-CHCl)_n-$	vinyl chloride $CH_2=CHCl$	strong rigid solid	pipes, siding, flooring
Poly(vinylidene chloride) (Saran A)	$-(CH_2-CCl_2)_n-$	vinylidene chloride $CH_2=CCl_2$	dense, high-melting solid	seat covers, films
Polystyrene (PS)	$-[CH_2-CH(C_6H_5)]_n-$	styrene $CH_2=CHC_6H_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets packaging (foamed)
Polyacrylonitrile (PAN, Orlon, Acrilan)	$-(CH_2-CHCN)_n-$	acrylonitrile $CH_2=CHCN$	high-melting solid soluble in organic solvents	rugs, blankets clothing
Polytetrafluoroethylene (PTFE, Teflon)	$-(CF_2-CF_2)_n-$	tetrafluoroethylene $CF_2=CF_2$	resistant, smooth solid	non-stick surfaces electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$-[CH_2-C(CH_3)CO_2CH_3]_n-$	methyl methacrylate $CH_2=C(CH_3)CO_2CH_3$	hard, transparent solid	lighting covers, signs skylights
Poly(vinyl acetate) (PVAc)	$-(CH_2-CHOCOCH_3)_n-$	vinyl acetate $CH_2=CHOCOCH_3$	soft, sticky solid	latex paints, adhesives
cis-Polyisoprene natural rubber	$-[CH_2-CH=C(CH_3)-CH_2]_n-$	isoprene $CH_2=CH-C(CH_3)=CH_2$	soft, sticky solid	requires vulcanization for practical use
Polychloroprene (cis + trans) (Neoprene)	$-[CH_2-CH=CCl-CH_2]_n-$	chloroprene $CH_2=CH-CCl=CH_2$	tough, rubbery solid	synthetic rubber oil resistant

Types of Polymerization

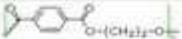
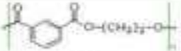
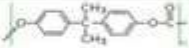
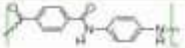
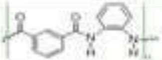
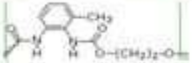
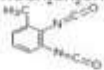
- 2. Step-growth polymers, also called condensation polymers, are made by combining two molecules by removing a small molecule



Condensation (Step) Polymerization



Condensation Polymers

Formula	Type	Components
$-[CO(CH_2)_4CO\text{-}OCH_2CH_2O]_n-$	**polyester**	$HO_2C\text{-}(CH_2)_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$
	**polyester** Dacron Mylar	para $HO_2C\text{-}C_6H_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$
	**polyester**	meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$
	**polycarbonate** Lexan	$(HO\text{-}C_6H_4\text{-})_2C(CH_3)_2$ (Bisphenol A) $X_2C{=}O$ ($X = OCH_3$ or Cl)
$-[CO(CH_2)_4CO\text{-}NH(CH_2)_6NH]_n-$	**polyamide** Nylon 66	$HO_2C\text{-}(CH_2)_4\text{-}CO_2H$ $H_2N\text{-}(CH_2)_6\text{-}NH_2$
$-[CO(CH_2)_5NH]_n-$	**polyamide** Nylon 6 Perlon	
	**polyamide** Kevlar	para $HO_2C\text{-}C_6H_4\text{-}CO_2H$ para $H_2N\text{-}C_6H_4\text{-}NH_2$
	**polyamide** Nomex	meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$ meta $H_2N\text{-}C_6H_4\text{-}NH_2$
	**polyurethane** Spandex	$HOCH_2CH_2OH$ 

Addition Vs. Condensation Polymerization

- In **addition polymerization** although x may assume any value, y is confined to unity
- the growing chain can react only with a monomer molecule and continue its growth

Addition Vs. Condensation Polymerization

- Polymerization reactions can generally be written as

  x-mer + y-mer → (x +y)-mer

- In a reaction that leads to **condensation polymers**.

Comparison of Step-Reaction and Chain-Reaction Polymerization

Step Reaction	*Chain Reaction*
Growth occurs throughout reaction between monomers, oligomers, and polymers	Growth occurs by successive addition of monomer units to limited number of growing chains
$\overline{DP}$[a] low to moderate	$\overline{DP}$ can be very high
Monomer consumed rapidly while molecular weight increases slowly	Monomer consumed relatively slowly, but molecular weight increases rapidly
No initiator needed; same reaction mechanism throughout	Initiation and propagation mechanisms different
No termination step; end groups still reactive	Usually chain-terminating step involved
Polymerization rate decreases steadily as functional groups consumed	Polymerizaion rate increases initially as initiator units generated; remains relatively constant until monomer depleted

[a]$\overline{DP}$, *average degree of polymerization.*