5. $[Pt(acac)(py)_2]^+$

   = Acetylacetonatodi(pyridine)platinum(II)

6. $[Os(C_2O_4)_3]^{2-}$

   =Trioxalatoosmate(IV)

7. *fac*-$[Mo(CO)_3(PMe_3)_3]$

   = *fac*-Tricarbonyltris(trimethylphosphine) molybdenum(0)

Problems

1. (i) What is the oxidation number of Fe in $[FeSO_4(gly)(bipy)]$ (**A**)?

  (ii) Give the IUPAC name of (**A**).

  (iii) What is the coordination number of Fe in (**A**)?

  (iv) Determine the Effective Atomic Number (EAN) of Fe in (**A**).
     (Atomic number of Fe is 26)

(v) Write the chemical formula of glycenatodicarbonyldichloridocobalt(III)

2. The substance with the composition $FeCl_3\cdot5NH_3\cdot H_2O$ has a molar conductivity of 430 m²ohm⁻¹mol⁻¹ (*i.e.*, 1:3 electrolyte). Write the molecular formula of it?

3. A neutral mononuclear 16e-complex (**B**) containing a Co(I) center is coordinated only to chloride and CO ligands.

  (i) What is the molecular formula of (**B**)?

  (ii) Comment on the geometry of (**B**) and draw the structure of (**B**).

4. What is the molecular formula of diamminebromidocarbonyloxalatocobalt(III).

5. (i) Give the IUPAC name of $[Co_2(\mu\text{-}Cl)_2(CO)_4]$ (**C**).

  (ii) (**C**) is a symmetrical molecule without a metal-metal bond. Draw the structure of (**C**).

Introduction to Polymer Chemistry

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Polymers play an important role in our day-to-day life. In Greek, poly means "many" and mer means "parts". Polysaccharides, proteins and nucleic acids are the main **bio-polymers/macromolecules**. A large number of industries (*e.g.*, packaging, textile, automobile, paper *etc.*) are based on **synthetic polymers** such as polyethylene (PE), poly(vinylchloride) (PVC), polyesters, nylon, *etc.*, and **natural polymers** such as rubber, cellulose, *etc.* Joseph Priestly discovered "**natural rubber**", a natural **polymer** derived from the **monomer** 1,3-*cis*-isoprene. **Bakelite** was the 1st **synthetic polymer** prepared by Leo Baekeland in 1907 from **phenol** and **HCHO**.
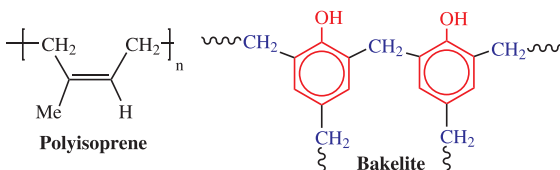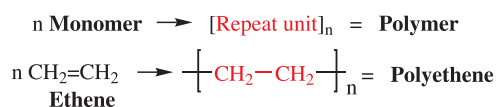

Figure 1: Natural rubber and Bakelite

Polymerization is the process which makes macromolecules by chemically bonding a large number of monomer units, consisting of two or more functional

groups or reactive sites such as acid (-COOH), alcohol (-OH), amino (-NH_2) groups, halide, -SH, -NCO, C=C, C≡C, *etc.*

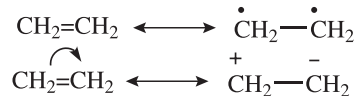Ethene has two reactive sites (two radicals or cation and anion); it produces **linear** polymers.

Figure 2: Reactive sites of ethene

Poly(pent-1-ene) -$[CH_2CHR]_n$- can be considered as a **branched polymer** {R = $(CH_2)_2Me$}. **Hydroxy acids** (*e.g.*, lactic acid, HOCH(Me)COOH) and amino acids (*e.g.*, glycine, H_2NCH_2COOH) are bi-functional monomers, and *via* **condensation**, they produce linear polymers -$[OCH(Me)CO]_n$- / -$[CH(Me)COO]_n$- and -$[HNCH_2CO]_n$- / -$[CH_2CONH]_n$-. 1,3-Diisocyanatobenzene is also a bi-functional

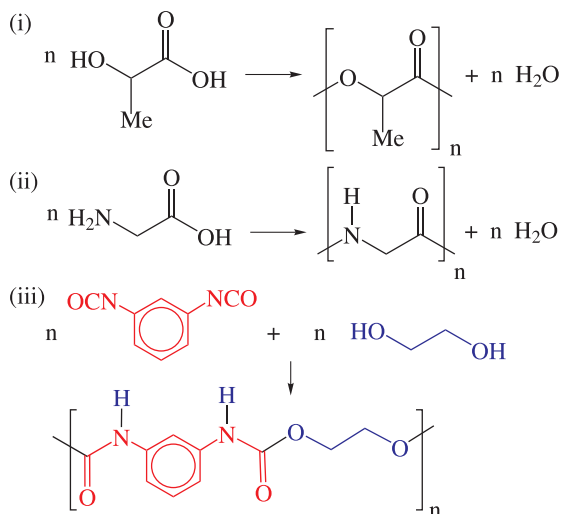monomer which can undergo addition polymerization with diamines or dialcohols as shown in Figure 3.

(i)

(ii)

(iii)

Figure 3: Polymers from hydroxy acids, amino acids and diisocyanates

Phenol can generate **three** active sites (two *ortho* and one *para*). 1,3,5-Triisocyanato-benzene and melamine are tri-functional monomers; they produce **cross-linked** polymers.
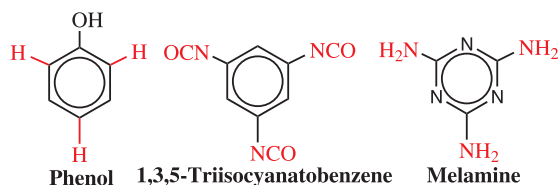
Phenol   **1,3,5-Triisocyanatobenzene**   **Melamine**

Figure 4: Tri-functional monomers

Classification of polymers

Polymers can be categorized by their origin into **organic** and **inorganic** polymers. Inorganic polymers or partially inorganic polymers are linked by covalent bonds, in the absence or near absence of hydrocarbon units in the main backbone. Some examples for such polymers are polysilanes, polyphosphazenes, poly(sulphur-nitride), poly(1,1´-ferrocene-silane), polysiloxanes, *etc.*

Organic polymers can be divided into either **synthetic** (*e.g.*, polyethylene (PE), polyurea, nylon, polystyrene (PS), Teflon, PVC, *etc.*) or **natural** (*e.g.*, cotton, silk, rubber, starch, cellulose, proteins, *etc.*) polymers.

By considering their applications and physical properties, polymers are grouped into **plastics** (become hard at ambient temperatures), **fiber** (strong threads such as nylon), **elastomers** (*e.g.*, rubber) and **adhesives** (*e.g.*, resins).
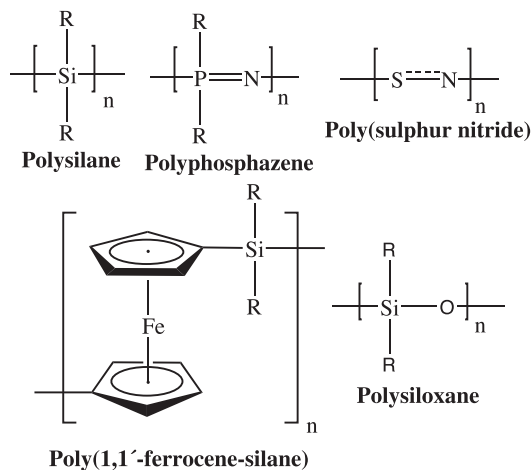
Polysilane   **Polyphosphazene**   **Poly(sulphur nitride)**

Poly(1,1´-ferrocene-silane)

Polysiloxane

Figure 5: Examples for inorganic polymers

Branched and cross-linked polymers such as Bakelite and vulcanized rubber can be molded only once and are called **thermosets**, which cannot be recycled. Tri-functional monomers form irreversible cross-link/3D structures during the curing process. The other type is **thermoplastics** which are mostly linear polymers obtained from bi-functional monomers. They can be recycled and reshaped by heating and cooling (*e.g.* PE, PP, PVC, nylon).

Homopolymers have one repeating unit and are produced by polymerizing a single monomer or two parts of a pair. Some polymers have two or more types of monomers with different repeating units; which are called **copolymers**.

The **degree of polymerization** (DP = n) gives an idea about the number of monomer or repeat units present in the polymer.

$$DP = \frac{\text{Molar mass of the polymer}}{\text{Molar mass of the repeat unit}} = \frac{M}{m} = n \text{ (integer)}$$

Thermal stability, heat/fire resistance, conductivity, tensile strength, viscosity, solubility, fluidity, elasticity, molten/melting point, crystallinity/amorphousness, *etc.* are some of the properties of polymers, which depend on their chemical nature/bonding, structure, and size/molar mass.

Methods of polymerization

The three main methods of polymerization are (i) **addition**, (ii) **condensation**, and (iii) **ring-opening** polymerization.
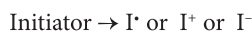
Addition Polymerization

This is also known as chain growth polymerization. Monomers such as **vinyl** (CH_2=CH-R) (R = H, halogens, OMe, CO_2Me, CN), **allyl** compounds (CH_2=CH-CH_2R), and **dienes** (CH_2=CR–CH=CH_2) (R = an organic group) with reactive double bonds undergo **addition** reactions to form polymers (*e.g.*, PE, PS, PVC, polyisoprene *etc.*). The elemental composition of the polymer is similar to the monomer since by-products are not formed.

Mechanisms of addition polymerization

Three mechanisms are possible for addition polymerization depending on the nature of the substituents. They are (a) **free radical**, (b) **cationic** and (c) **anionic** polymerization. Each method is composed of three steps. They are 1) **initiation**, 2) **propagation**, and 3) **termination**.

1. Initiation

The initiator can be a free radical - I•, cationic species - I^+, anionic species- I^- or a metal complex or catalyst.

Initiator → I• or I^+ or I^-

(a) Free radical polymerization using I•

Initiation is achieved by (a) decomposing a labile compound such as **peroxide** or **peracid**, (b) using an **azo-compound**, (c) *via* a redox-reaction and (d) using UV-light. Some examples are given below (I• = RO• or R• or HO• *etc.*).

Cumene hydroperoxide   **Cumyloxy radical**   **Hydoxy radical**

Benzoyl peroxide

Benzoyloxy radical

Phenyl radical

Azobisisobutyronitrile (AIBN)   **Cyanopropyl radical**

(c)
$$HOOH + Fe^{2+} \longrightarrow \, ^{•}OH + HO^- + Fe^{3+}$$
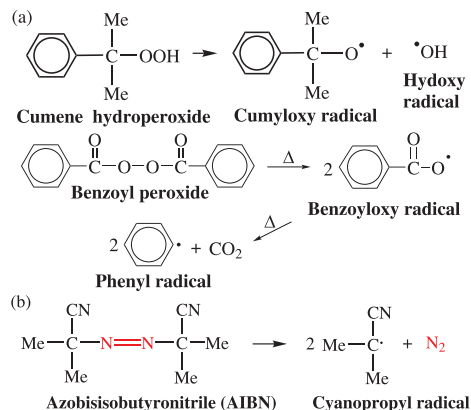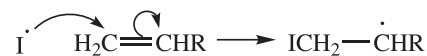$$ROOH + Co^{2+} \longrightarrow RO^{•} + HO^- + Co^{3+}$$

Figure 6: Formation of free radicals

The initiation step for a terminal olefin is as follows.

The stability of the free radical, reaction temperature and solvent determine the rate of initiation.

Modes of addition of free radicals

In free radical polymerization, the addition or coupling of free-radicals can take place in four ways: (**i**) head-to-head, (**ii**) head-to-tail, (**iii**) tail-to-head, and (**iv**) tail-to-tail as shown below.
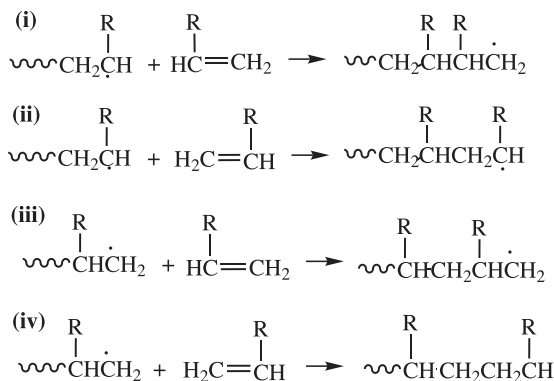
The most favored addition is head-to-tail, which minimize the steric repulsion and produces a stable radical.

(b) Cationic polymerization using I^+

Electrophilic compounds particularly proton donor acids such as HCl, H_2SO_4, $HClO_4$, *etc.* and Lewis acids (*e.g.*, BF_3, $AlCl_3$, $TiCl_3$, $SnCl_4$) can act as cationic initiators as shown below (I^+ = H^+, for example BF_3 reacts with water to produce $H[BF_3(OH)]$).
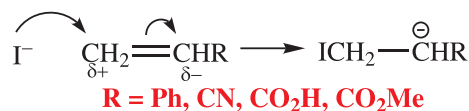
R = H, Me, OMe, Ph *etc*
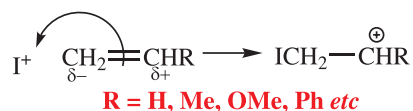
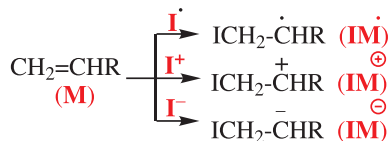The stability of the carbocation determines the

growth of the polymer.

(c) Anionic polymerization using I⁻

In this case, a negative ion attacks the double bond of the monomer. Monomers consist of nitro, cyano, carboxyl, vinyl, and phenyl groups are more likely to produce more stable carbanions via resonance or induction. Triphenylmethyl potassium (Ph$_3$CK), NaH, KNH$_2$, KOH, BuLi, can act as anionic initiators (I⁻ = base, nucleophile, H⁻, R⁻, HO⁻ *etc.*).
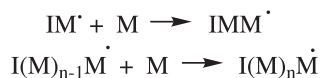
$$I^- \quad CH_2 \overset{\delta+}{=} \underset{\delta-}{CHR} \longrightarrow ICH_2 - \overset{\ominus}{C}HR$$

R = Ph, CN, CO$_2$H, CO$_2$Me

The initiation step of olefin polymerization is abbreviated as shown below.

$$CH_2=CHR \underset{\textbf{(M)}}{} \begin{cases} \overset{\textbf{I}^{\cdot}}{\longrightarrow} & ICH_2\text{-}\overset{\cdot}{C}HR \ \textbf{(IM)} \\ \overset{\textbf{I}^+}{\longrightarrow} & ICH_2\text{-}\overset{+}{C}HR \ \textbf{(IM)} \\ \overset{\textbf{I}^-}{\longrightarrow} & ICH_2\text{-}\overset{-}{C}HR \ \textbf{(IM)} \end{cases}$$
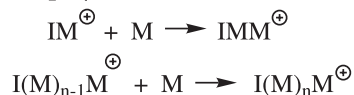
2. Propagation

This step is important to increase the length of the polymer chain.

(a) Free radical polymerization

$$IM^{\cdot} + M \longrightarrow IMM^{\cdot}$$
$$I(M)_{n-1}\overset{\cdot}{M} + M \longrightarrow I(M)_n\overset{\cdot}{M}$$

(b) Cationic polymerization

$$IM^{\oplus} + M \longrightarrow IMM^{\oplus}$$
$$I(M)_{n-1}\overset{\oplus}{M} + M \longrightarrow I(M)_n M^{\oplus}$$

(c) Anionic polymerization

$$IM^{\ominus} + M \longrightarrow IMM^{\ominus}$$
$$I(M)_{n-1}\overset{\ominus}{M} + M \longrightarrow I(M)_n M^{\ominus}$$
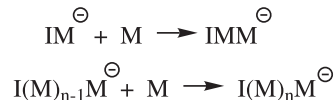
3. Termination

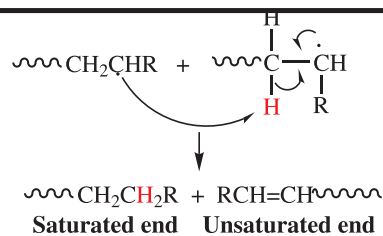**(a) Free radical polymerization**

Polymer radicals can be ceased or quenched in several ways.

(i) By combining of two radicals

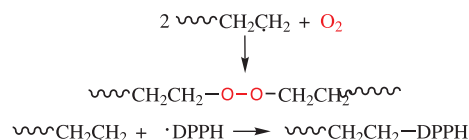$$I \backsim M^{\cdot} + \overset{\cdot}{M} \backsim I \longrightarrow I \backsim M\text{-}M \backsim I$$

(ii) By disproportionation

$$\text{CH}_2\text{CHR} + \quad \backsim\text{C}\overset{H}{\underset{H}{|}}\text{CH}R$$

$$\downarrow$$

$$\backsim CH_2CH_2R + RCH=CH\backsim$$
Saturated end   Unsaturated end

(iii) By chain/H atom transfer

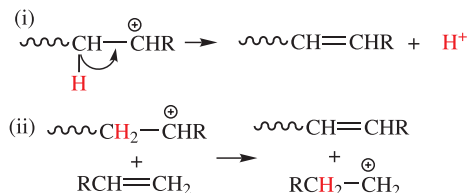$$\backsim M^{\cdot} + \text{Solvent-H} \longrightarrow \backsim MH + \text{Solvent}^{\cdot}$$

(iv) By inhibition

Dioxygen and inhibitors or radical scavengers such as diphenyl picryl hydrazine (·DPPH) can stop the polymerization process.

$$2 \backsim CH_2CH_2 + O_2$$
$$\downarrow$$
$$\backsim CH_2CH_2-O-O-CH_2CH_2\backsim$$
$$\backsim CH_2CH_2 + \cdot DPPH \longrightarrow \backsim CH_2CH_2-DPPH$$

(b) Cationic polymerization

In cationic polymerization, termination can occur by (i) rearrangement or (ii) H atom transfer reaction with a monomer.

(i)
$$\backsim CH - \overset{\oplus}{C}HR \longrightarrow \backsim CH = CHR + H^+$$
$$\underset{H}{}$$

(ii)
$$\backsim CH_2 - \overset{\oplus}{C}HR \quad \backsim CH = CHR$$
$$+ \qquad\qquad \longrightarrow \quad + $$
$$RCH = CH_2 \qquad\quad RCH_2 - \overset{\oplus}{C}H_2$$

(c) Anionic polymerization

The termination step of the anionic polymerization differs from the other methods since it gives living polymers. This means that the **carbanion** of the last monomer of the polymer chain-end remains potentially active. If one adds more monomers again to the polymer solution, it will continue to grow, provided that there are no more impurities/inhibitors.

Condensation polymerization

The polymers are built-up *via* step-wise reactions which occur between functional groups of the monomers; H$_2$O and HCl are produced as by-products. The rate of the reaction is slow compared to that of chain polymerization. The 3 main reaction types are: 1, polycondensation, 2. polyaddition and 3. ring-opening polymerization (ROP).

Both polycondensation and polyaddition reactions occur between monomers with two functional groups.

1. Polycondensation reaction

Polyamides $-[HN(CH_2)_xNHCO(CH_2)_yCO]_n-$ are prepared by condensing diamines $H_2N(CH_2)_xNH_2$ and dicarboxylic acids $HO_2C(CH_2)_yCO_2H$.

n $HO_2C-Z-CO_2H$ + n $H_2N-Z'-NH_2$

Polyamide

Z and Z' = organic fragments + $(2n-1)$ H_2O
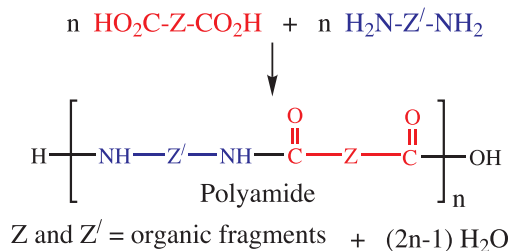
Figure 7: Synthesis of polyamides

Polyesters are prepared in a similar way. Condensation reaction between bisphenol-A and diphenyl carbonate or phosgene ($COCl_2$) produces polycarbonates.

2. Polyaddition reaction

Polyaddition of diamines to diisocyanates gives polyurethanes.

n $O=C=N-Z-N=C=O$ + n $H_2N-Z'-NH_2$

Polyurethane
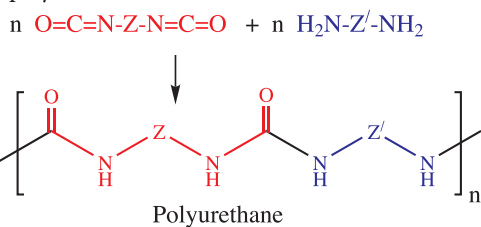
Z and Z' = organic fragments

Figure 8: Synthesis of polyurethane

3. Ring-opening polymerization

The third method of polymer preparation involves a ring-opening polymerization (ROP) of cyclic monomers. Monomers having ring structures can be opened up to form polymers under favorable conditions. This type of polymerization can be achieved by thermally, photochemically (*e.g.*, trioxane) or using specific catalyst systems.
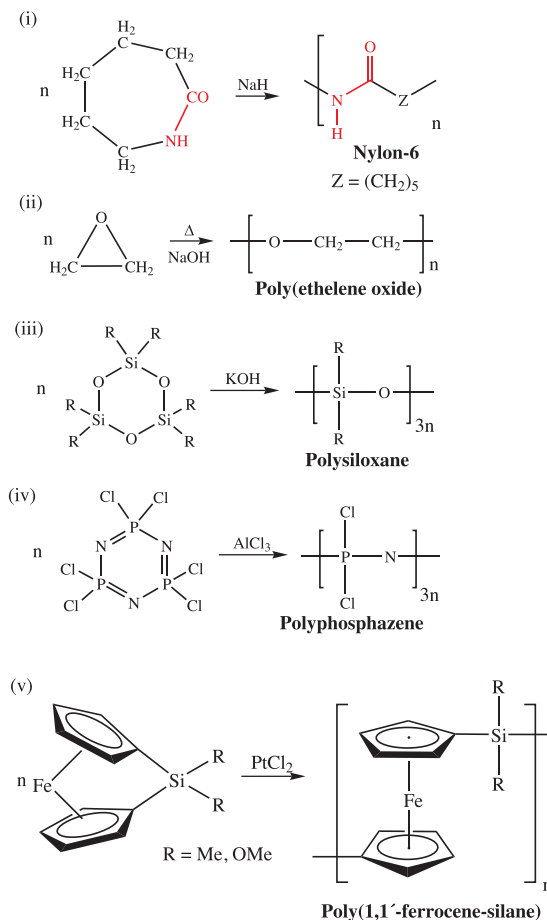
(i)

Nylon-6

$Z = (CH_2)_5$

(ii)

Poly(ethelene oxide)

(iii)

Polysiloxane

(iv)

Polyphosphazene

(v)

$R = Me, OMe$

Poly(1,1'-ferrocene-silane)

Figure 9: Some examples for ROP

Cyclic amides (lactams) and epoxides can easily be polymerized. It is important to note that all cyclic organic compounds cannot be converted into linear chains. Some examples of inorganic polymers include $-[SiR_2O]_n-$, $-[PCl_2=N]_n-$ and $-[(C_5H_4)Fe(C_5H_4SiR_2]_n-$.

Coordination polymerization

Coordination polymerization uses organometallic compounds as initiators. Some examples include Ziegler-Natta catalyst ($TiCl_3$/$AlEt_3$), Cp_2MCl_2/$(MeAlO)_3$, (M = Ti, Zr, Hf; Cp = cyclopentadienyl), Schrock catalysts, Grubbs catalysts, *etc*.

First-generation Grubbs catalyst

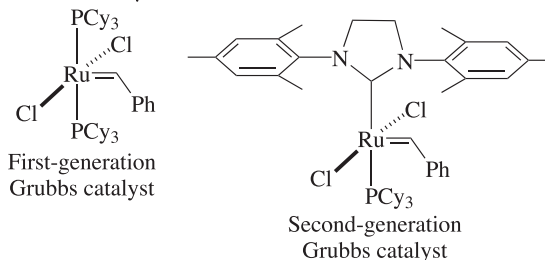Second-generation Grubbs catalyst

Figure 10: 1st and 2nd generations of Grubbs catalysts

Copolymers

Generally homopolymers are produced by addition and ring-opening polymerization of a single monomer. Polycondensation of two bi-functional molecules also results in homopolymers, which are consisting of one type of repeat unit, for example, nylon-4,6 -$[(HN(CH_2)_4NHCO(CH_2)_4CO]_n$- can be considered as a homopolymer made from $H_2NCH_2CH_2CH_2CH_2NH_2$ and adipic acid, $HO_2C(CH_2)_4CO_2H$.

Addition polymerization of two or more monomers (*e.g.*, olefins) in different ratios yields copolymers. SBR is a copolymer -$[(CH_2CH=CHCH_2)_x(CH_2CHPh)_y]$- made by polymerizing a mixture of styrene (25%) and butadiene (75%), (SBR = Styrene Butadiene Rubber = synthetic rubber). The copolymers are classified into 4 types: (**i**) random, (**ii**) block, (**iii**) alternate, and (**iv**) graft as shown in Figure 11.
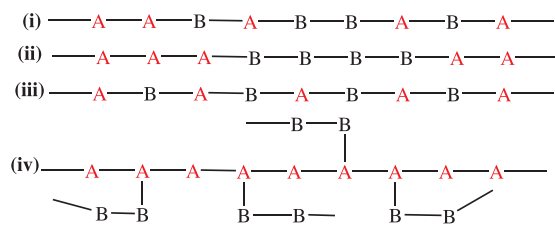

Figure 11: Types of copolymers

In a random copolymer, the monomers (**A** and **B**) are arranged in a random manner. The polymer -$[(CH_2CH_2)_n(CH_2CHPh)_m]$- is a block copolymer made from ethene and styrene; **m** and **n** are integers. The polymer $[CH_2CH_2CH_2CHPh]_n$- is an alternate copolymer made from ethene and styrene. The polymer -$[HN(CO)NHCH_2]$- can be considered as an alternate copolymer made from urea and HCHO. Joining of styrene and maleic anhydride gives an alternate copolymer. Alternate copolymers have one type of repeating unit. The monomer **B** is grafted on to an existing polymer -$(A)_n$-, prepared from monomer **A**. For example, acrylonitrile can be grafted on to polystyrene. Methyl methacrylate can also be grafted on to natural rubber.

Student Corner

Metathesis and Polymerization of Olefins

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Metathesis of simple salts is a double replacement reaction as shown below.

$$AX + BY \rightarrow AY + BX$$

In Greek, "Metathesis" is known as the change of position or transposition. **Olefin metathesis** (OM) is the catalytic **scission** and **regeneration** of C=C bonds as shown in Figure 1. This is a **reversible** process and the reverse reaction is called "**cross metathesis**" of olefins.
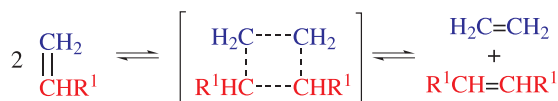

Figure 1: Metathesis of olefins

Ethene is a volatile molecule, thus, metathesis of a terminal olefin $R^1CH=CH_2$ produces a quantitative amount of $R^1CH=CHR^1$. Using this procedure tetra-substituted alkenes such as $R_2C=CR_2$ are obtained in good yields.
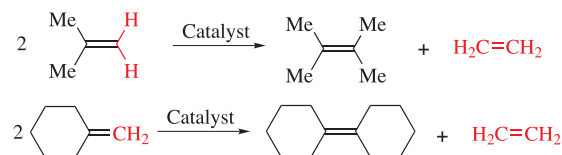

Figure 2: Synthesis of tetra-substituted alkenes

Catalysts for olefin metathesis

Olefin metathesis is normally catalyzed by homogeneous catalysts. Homogeneous catalysis refers to reactions