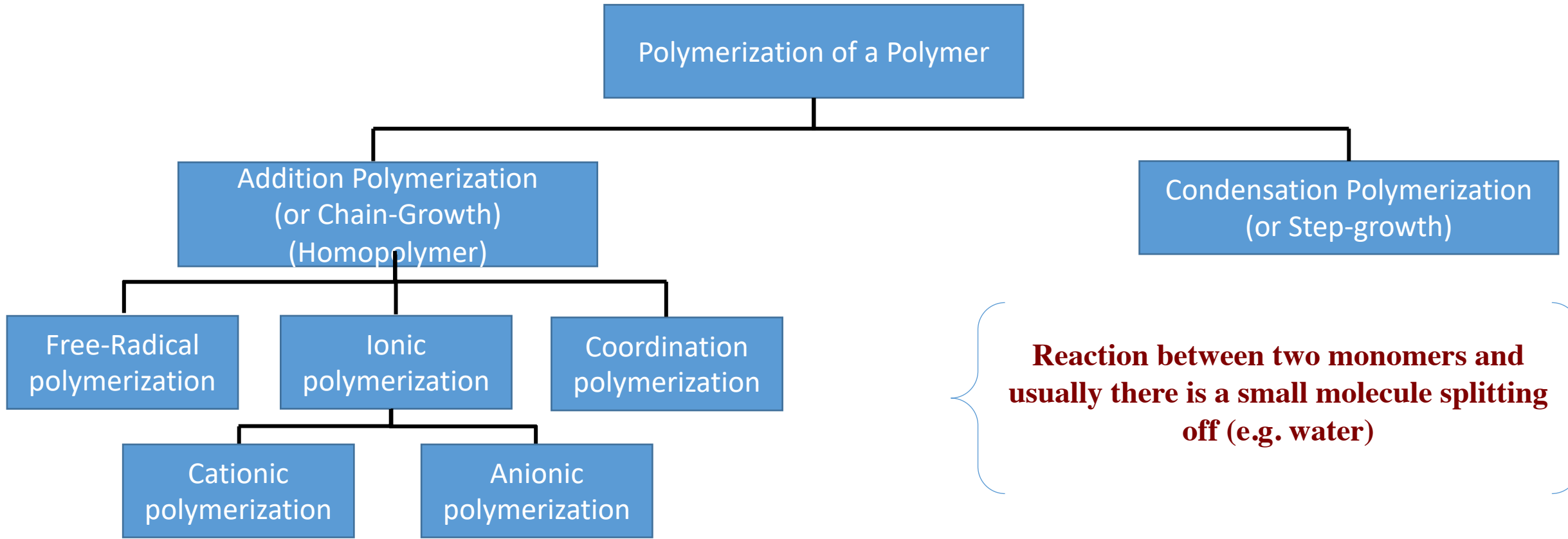# Coordination Polymerization

At the end of this lecture, you should be able to:

- Understand what is the meant by coordination polymerization.
- Understand the role of Ziegler– Natta catalysts in coordination polymerization.
- Understand the mechanism and Kinetic of coordination polymerization.
- Understand what is meant by "Ring opening polymerization".

NOTE: there are some extra- problems at the end of the lecture.

Mustansiriyah University/ Materials Eng. Dept.
Dr Ahmed A. AYASH   **February 2021**

SUMMARY

```
                    ┌─────────────────────────────┐
                    │  Polymerization of a Polymer │
                    └─────────────────────────────┘
```

Addition Polymerization (or Chain-Growth) (Homopolymer)

Condensation Polymerization (or Step-growth)

Free-Radical polymerization

Ionic polymerization

Coordination polymerization

Cationic polymerization

Anionic polymerization

Reaction between two monomers and usually there is a small molecule splitting off (e.g. water)
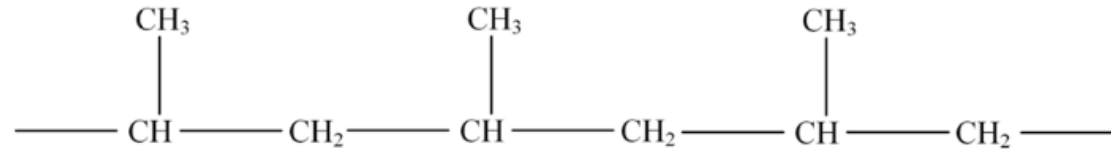
Usually, there is a single monomer and addition process occurs. However, note if there are more than two types of monomer reacting together by addition polymerization , the process is called " copolymerization " and the obtained polymer is called " copolymer ".
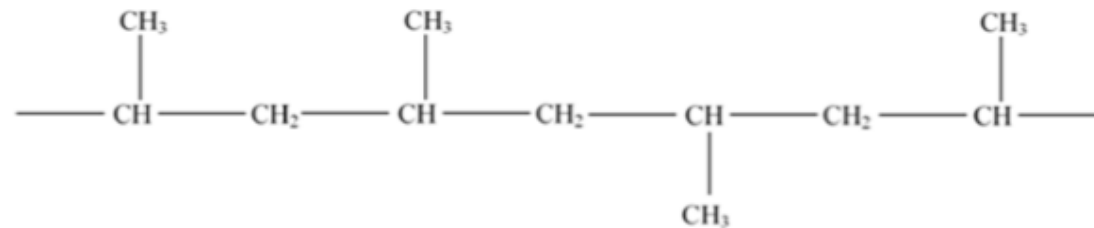
COORDINATION POLYMERIZATION

In the early 1950's a major new polymerization technique was discovered that led to the production of polymers with unusual stereospecific structures. Although there were earlier indications of this type of polymerization (Schildkne'cht 1947), the field actually came into existence with the work of Ziegler (1955) and Natta (1955), who developed new polymerization catalysts with unique stereoregulating powers. Their Nobel Prize addresses (Ziegler 1964; Natta 1965) form excellent introductions to the field.

Syndiotatic Polypropene
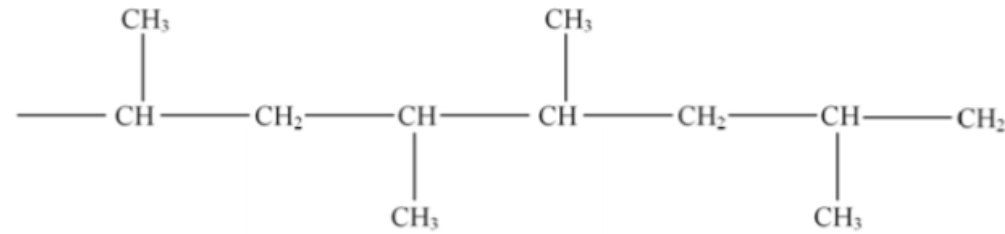
Isotactic Polypropene

Atactic Polypropene

A coordination polymer is an inorganic or organometallic polymer structure containing metal cation centers linked by ligands (atom or group of atoms will formally donate a lone pair of electrons to a metal cation and form a coordination complex via a Lewis acid/ base relationship). More formally a coordination polymer is a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions.

Some Features:

1. Coordination polymerization is far from simple in terms of mechanism, kinetics, or application.

2. The most important catalysts are solids, leading to heterogeneous polymerization systems, but soluble catalyst systems are known. Additional complications to the study of coordination systems arise because the same catalysts, under other conditions, can initiate polymerization by cationic, anionic, or even free-radical mechanisms.

3. Quite often coordination polymerization is carried out using a catalyst in the form of a slurry of small solid particles in an inert medium (*a fluidized-bed* process) or a supported solid catalyst.
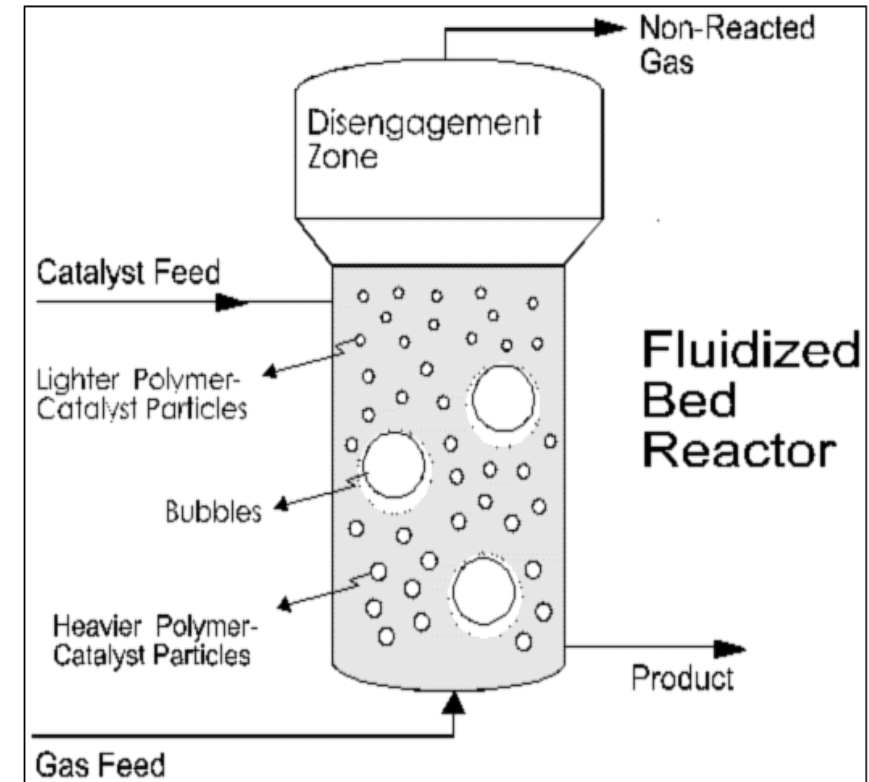
Ziegler– Natta catalysts

The Ziegler-Natta or, often, Ziegler catalysts have the remarkable property of polymerizing a wide variety of monomers to linear and stereoregular polymers. Ethylene is polymerized to a highly linear chain, in contrast to the products of radical polymerization. Polypropylene may be made in either the isotactic or syndiotactic form, but higher or-olefins yield only isotactic polymers. Dienes such as butadiene may be polymerized to products that are almost exclusively cis-1,4, trans-1,4, depending on choice of catalyst and conditions. Many other examples exist.
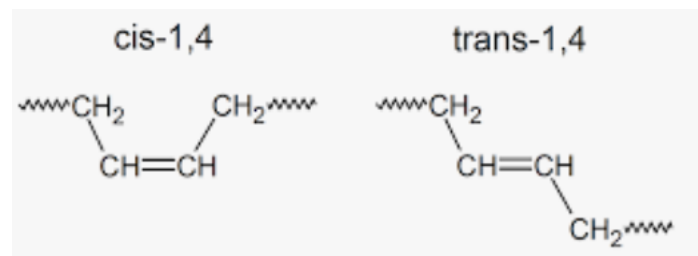

The metals that are more frequently found as components of Ziegler– Natta catalysts are some light elements of groups I–III of the periodic table (e.g., Li, Mg, Al), present as organometallic compounds and halides, or other derivatives of transition metals of groups IV–VIII (e.g., Ti, V, Cr, Mo, Co, and Ni).
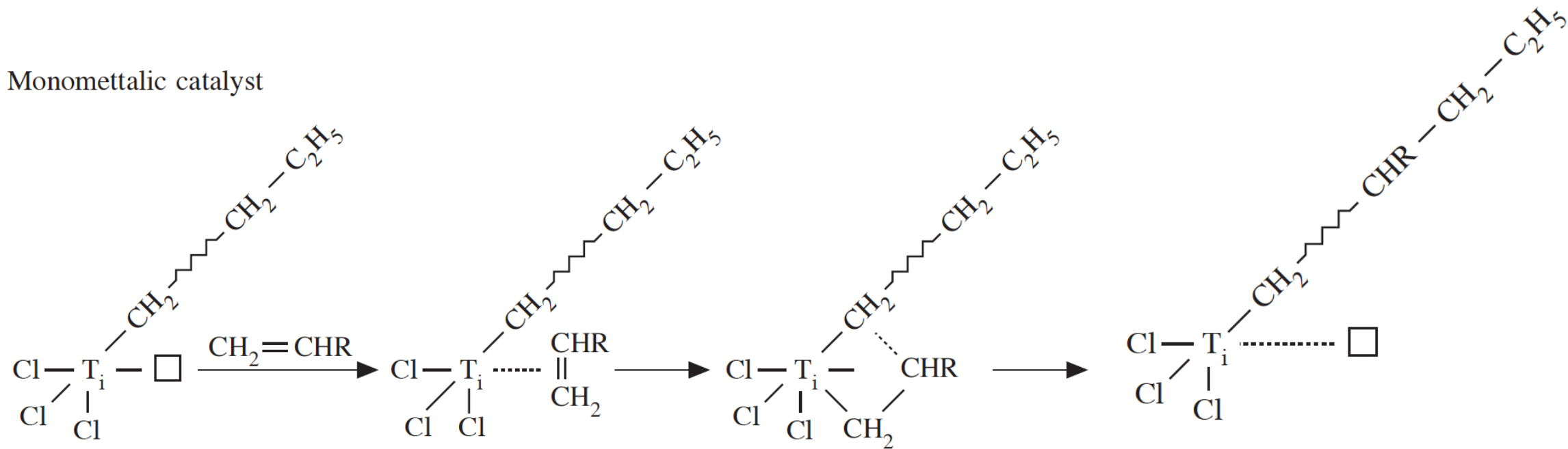
List of common Ziegler-Natta catalysts

| Organometallic Compound	Transition-Metal Salt
Triethyl aluminum	Titanium tetrachloride
Diethyl aluminum chloride	Vanadium trichloride
Diethyl aluminum chloride	Triacetyl acetone vanadium
Diethyl aluminum chloride	Triacetyl acetone chromium
Diethyl aluminum chloride	Cobalt chloride–pyridine complex
Butyl lithium	Titanium tetrachloride
Butyl magnesium iodide	Titanium trichloride
Ethyl aluminum dichloride	Dichlorodicyclopentadienyl titanium

1. Mechanisms

A typical example is the product(s) of the reaction between triethylaluminum and titanium tetrachloride. The composition of the product is not well defined but is believed to be either an alkylated metal halide (monometallic I) or a bimetallic complex involving a bridge between the two metals (II).
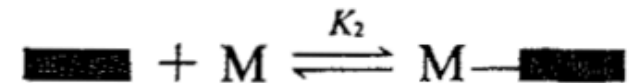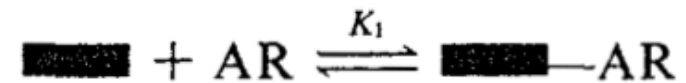
Monomettalic catalyst
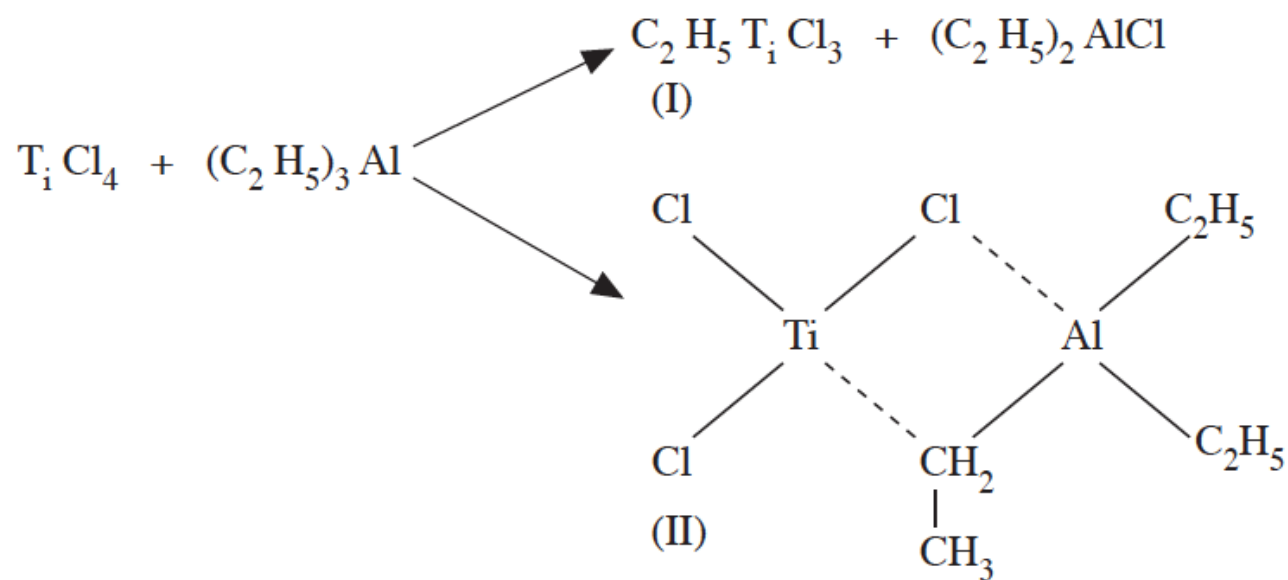
Bimetallic catalyst
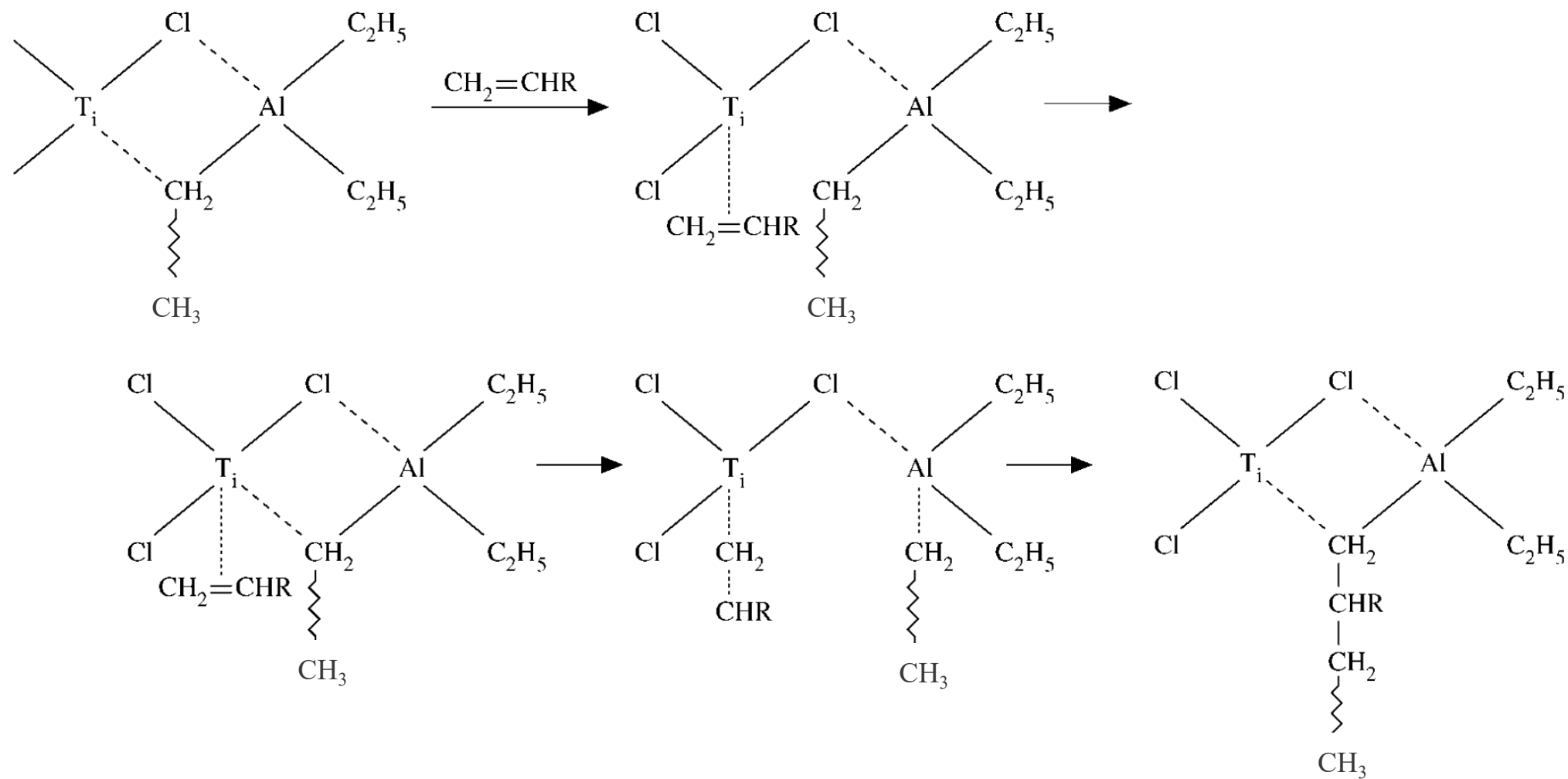
2. Kinetic

Considering here the important but complex case of heterogeneous polymerization, we denote the surface of the transition-metal compound by a heavy bar ▬, the metal alkyl by AR, and the monomer by M. The following reactions me pertinent:

Adsorption of AR from solution to form the active site, and of M from solution,

$$▬ + AR \underset{\longleftarrow}{\overset{K_1}{\longrightarrow}} ▬\!-\!AR$$

$$▬ + M \underset{\longleftarrow}{\overset{K_2}{\longrightarrow}} M\!-\!▬$$

Initiation,

$$M\!-\!▬\!-\!AR \xrightarrow{k_i} ▬\!-\!A\!-\!M\!-\!R$$

Propagation,

$$M\text{---}\blacksquare\text{---}A\text{---}M_x\text{---}R \xrightarrow{k_p} \blacksquare\text{---}A\text{---}M_{x+1}\text{---}R$$
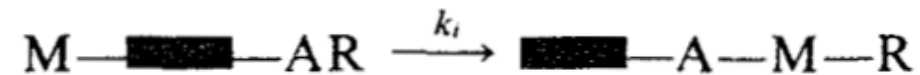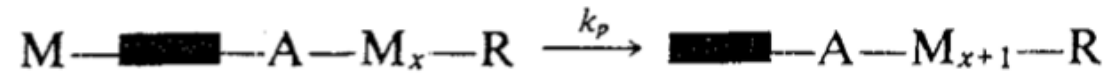
Transfer with monomer,

$$M\text{---}\blacksquare\text{---}A\text{---}M_x\text{---}R \xrightarrow{k_{tr}} \blacksquare\text{---}A\text{---}M\text{---}R + M_x$$
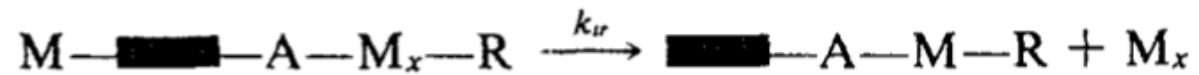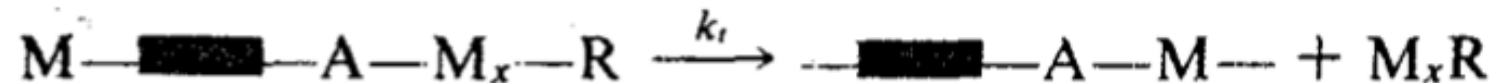
where M_x is polymer.

Other transfer reactions are possible. Termination of the kinetic chain can occur by several reactions, an example being that with monomer to form an inactive site:

$$M\text{---}\blacksquare\text{---}A\text{---}M_x\text{---}R \xrightarrow{k_t} \text{---}\blacksquare\text{---}A\text{---}M\text{---} + M_xR$$

the fractions of the available surface covered by AR and M, θ_A and θ_M, are given by

$$\theta_A = \frac{K_1[AR]}{1 + K_1[AR] + K_2[M]}$$

$$\theta_M = \frac{K_2[M]}{1 + K_1[AR] + K_2[M]}$$

The overall rate is given by

$$\frac{-d[M]}{dt} = (k_p + k_{tr})\theta_M[C^*]$$

where $[C^*]$ is the concentration of growing chains. Assuming that $[C^*]$ reaches the steady state, we can equate the equations for initiation and termination:

$$k_i\theta_A\theta_M = k_t[C^*]\theta_M$$

from which, by elimination of $[C^*]$, we obtain

$$-\frac{d[M]}{dt} = \frac{(k_p + k_{tr})k_i}{k_t} \frac{K_1K_2[AR][M]}{(1 + K_1[AR] + K_2[M])^2}$$

RING-OPENING POLYMERIZATION

Polymers may be prepared by routes involving ring opening, which must be classed stoichiometrically as addition, since no small molecule is split off in the reaction. Some typical examples are given in Table below. The polymerization of these compounds has some aspects of both **chain and step polymerization** as far as kinetics and mechanism are concerned. It resembles chain polymerization in that it proceeds by the addition of monomer to growing chain molecules. However, the chain-initiating and subsequent addition steps may be similar and proceed at similar rates; if so, these are not chain reactions in the kinetic sense. As in stepwise polymerization, the polymer molecules continue to increase in molecular weight throughout the reaction.

Type	Example
Lactone	$O(CH_2)_xCO \longrightarrow$ $-[O(CH_2)_xCO-]_y$
Lactam	$HN(CH_2)_xCO \longrightarrow$ $-[HN(CH_2)_xCO-]_y$
Cyclic ether	$-(CH_2)_xO- \longrightarrow$ $-[(CH_2)_xO-]_y$
Cyclic anhydride	$CO(CH_2)_xCO \longrightarrow$ $-[CO(CH_2)_xCOO-]_y$ (with $-O-$)
N-Carboxyanhydride	$COCHRNHCO \longrightarrow$ $-[COCHRNH-]_y + CO_2$ (with $-O-$)

Extra – Problems

Q1 The following data were obtained by Arnett[*] for the polymerization of methyl methacrylate in benzene at 77°C with azo-*bis*-isobutyronitrile initiator. Assuming that the initiator efficiency is independent of monomer concentration, are the data consistent with the model for the rate of polymerization by free-radical mechanism?

[M] (kmol/m³)	[I] (mol/m³)	−d[M]/dt (mol/m³ · sec)
9.04	0.235	0.193
8.63	0.206	0.170
7.19	0.255	0.165
6.13	0.228	0.129
4.96	0.313	0.122
4.75	0.192	0.0937
4.22	0.230	0.0867
4.17	0.581	0.130
3.26	0.245	0.0715
2.07	0.211	0.415

[*] J. Am. Chem. Soc. 74, 2027 (1952)

$$R_p = k_p \left(\frac{fk_d}{k_t} \right)^{1/2} [I]^{1/2} [M]$$

Since f is independent of monomer concentration,

[M]	$[I]^{1/2}$	$R_p/[I]^{1/2}[M]$
9.04	0.485	0.044
8.63	0.454	0.043
7.19	0.0505	0.045
6.13	0.478	0.044
4.96	0.560	0.044
4.75	0.438	0.045
4.22	0.480	0.043
4.17	0.162	0.041
3.26	0.495	0.044
2.07	0.459	0.044

Since $R_p/[I]^{1/2}[M]$ is constant, data are consistent with rate of polymerization by free-radical mechanism.

Q2 A steady-state free-radical styrene polymerization process is being controlled such that the rate of polymerization is constant at 1.79 g of monomer/ml-min. The initiator concentration is 6.6×10^{-6} mol/ml.

a. What must be done to maintain the constant rate of polymerization?
b. If the rate constant for the first-order decomposition of the initiator, k_d, is 3.25×10^{-4} min^{-1}, what is the rate of free radical generation per second per milliliter? What is X_n?
c. What percentage of the original initiator concentration remains after a reaction time of 3 h?

Sol:

a.
$$R_p = k_p \left(\frac{fk_d}{k_t} \right)^{1/2} [I]^{1/2} [M]$$

Assuming f is independent of [M] to keep R_p constant, [I] and [M] must be kept constant.

b. If the rate constant for the first-order decomposition of the initiator, k_d, is 3.25×10^{-4} min^{-1}, what is the rate of free radical generation per second per milliliter? What is X_n?

Sol:

$$\frac{d[M\cdot]}{dt} = 2fk_d[I]$$

$$= 2k_d[I] \text{ assume } f = 1$$

$$k_d = 3.25 \times 10^{-4} \text{ min}^{-1}$$

$$= 5.42 \times 10^{-6} \text{ s}^{-1}$$

$$I = 6.6 \times 10^{-6} \text{ mol/ml}$$

$$R_i = \frac{d[M\cdot]}{dt} = 2(5.42 \times 10^{-6} \text{ s}^{-1})(6.6 \times 10^{-6} \text{ mol/ml})$$

$$= 7.5 \times 10^{-11} \text{ mol/ml} - \text{s}$$

$$\overline{X}_n = \frac{R_p}{R_i}$$

$$R_p = 1.79 \times 10^{-3} \text{ g/ml} - \text{min}$$

$$= \frac{1.79}{104} \times 10^{-3} \text{ mol/ml} - \text{min}$$

$$= 1.72 \times 10^{-5} \text{ mol/ml} - \text{min}$$

$$\overline{X}_n = \frac{1.72 \times 10^{-5} \text{ mol/ml} - \text{min}}{4.29 \times 10^{-9} \text{ mol/ml} - \text{min}}$$

$$= 4.01 \times 10^3$$

c. What percentage of the original initiator concentration remains after a reaction time of 3 h?

Sol:

$$\frac{-d[I]}{dt} = f k_d [I]$$

$$\frac{-d[I]}{[I]} = k_d \, dt; \ f = 1$$

$$[I] = e^{-k_d t}$$

$$= e^{-\left(3.25 \times 10^{-4} \times 60 \times 3\right)}$$

$$= 94.3\%$$