Supporting material for students registered to subject:

Macromolecular chemistry S112003

Teacher: Jan Merna, Department of Polymers, Institute of Chemical Technology ,Prague

Sources:

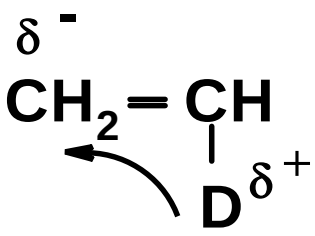
Prokopová I.: Makromolekulární chemie, VŠCHT Praha, 2007. (educational text in Czech)
Merna J.: Polymers Instantly, educational text in English, freely accessible from http://merna.eu/teaching/macromolecular-chemistry/
Encyclopedia of Polymer Science and Technology, J.Wiley Sons, Interscience, Publ., New York, 1964-1991

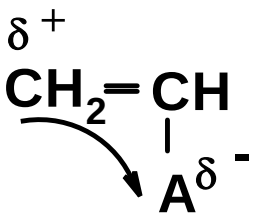
OUTLINE OF THE COURSE:

1. Basic terms, history, nomenclature
2. Structure of macromolecules, molecular weight.
3. Molecular structure and properties of polymers.
4. Polymerizability of low molecular substances.
5. Free radical polymerization - elemental reactions.
6. Kinetics of free radical polymerization.
7. Free radical copolymerization.
8. Ionic polymerization and copolymerization.
9. Ring-opening polymerization.
10. Insertion polymerization, polymerization techniques
11. Step-growth polymerization - characterization, reactivity of monomer functional groups.
12. Polycondensation - mechanism and kinetics, molecular weight distributions.
13. Polyadditions - typical syntheses.
14. Reactions of polymers.

Ionic polymerizations

- Highly selective compared to radical polymn.





cationic polymerization **anionic polymerization**

Initiator:

acid	base
H_2SO_4, H_3PO_4, $HClO_4$	alkaline metals, alkoxides
Lewis acids, e.g.	and hydroxides of alkal. metals,
BF_3, $AlCl_3$, $SnCl_4$, $TiCl_4$, ...	fosphins, amines, n-Bu-Li, ...
+ coinititor (water , alcohol,...)	

Ionic polymerization

Types of growing centers:

ionization

dissociation

polariz. bond | ionic pair contact | Solvent separated ion. pair | Free ions

Media polarity →

Formation of growing center :

1) $R^-X^+ + CH_2=CHR \longrightarrow R-CH_2-\underset{\displaystyle R}{\overset{\displaystyle |}{CH}}-X^+$ electrophilic attack

$H^+X^- + CH_2=CHR \longrightarrow CH_3-\underset{\displaystyle R}{\overset{\displaystyle |}{CH}}-X^-$ nucleophilic attack

Living vs. controlled polymerization

Living polymerization

$R_{tr}^{irr}=0$ $R_{term}=0$

Does not mean any control

Jenkins, A. D.; Kratochvil, P.; Stepto, R. F. T.; Suter, U. W. *Pure Appl. Chem.* **1996**, *68*, 2287.

Controlled polymerization

Kinetically driven:

$R_i >> R_p$

$R_{tr}^{irr} << R_p$ $R_{term} << R_p$

$\Rightarrow$ DISPERSITY=Đ=M_w/M_n->1

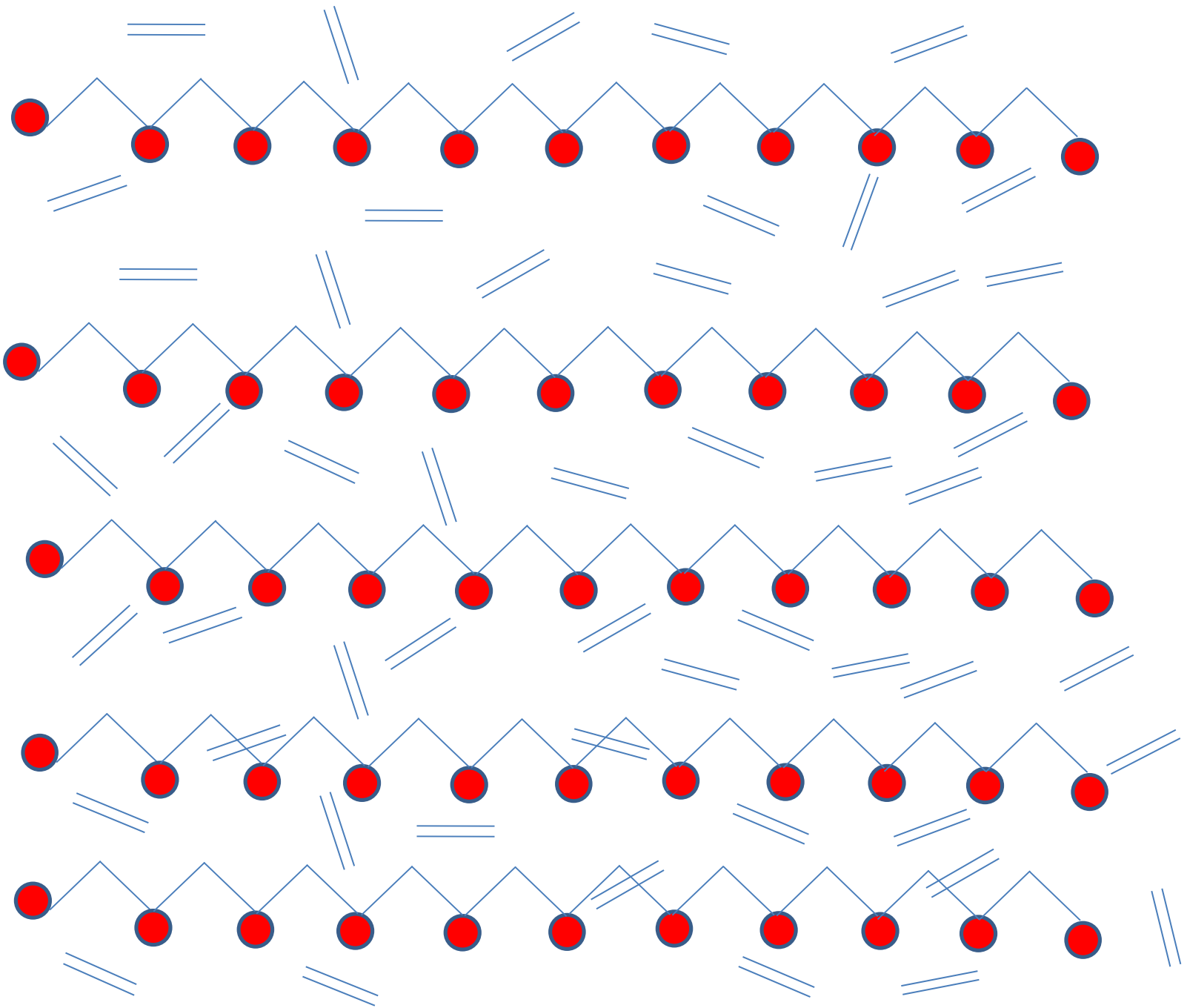
$\Rightarrow$ M_n determined by stechiometry

Matyjaszewski, K.; Müller, A. H. E. *ACS, Macromolecular Nomenclature Note No. 12*

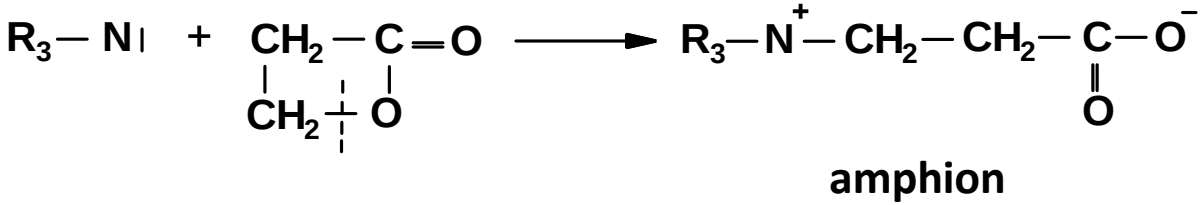
Stepto, RFT et al.
IUPAC Recommendation 2008: Dispersity

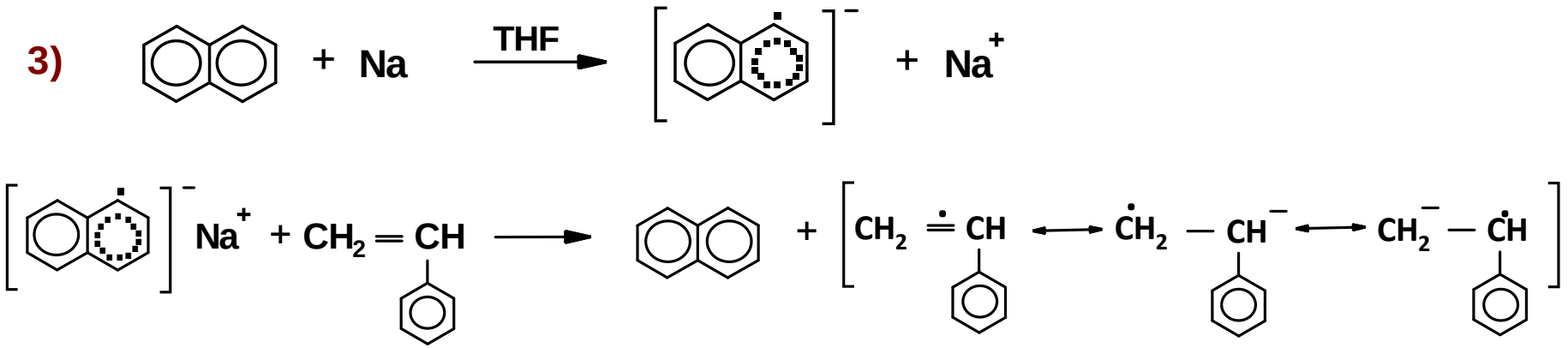
Typical Đ values in controlled polymerization according to mechanism:

ionic	Đ<1.1
radical	Đ<1.1-1.2
coordination	Đ<1.2-1.3

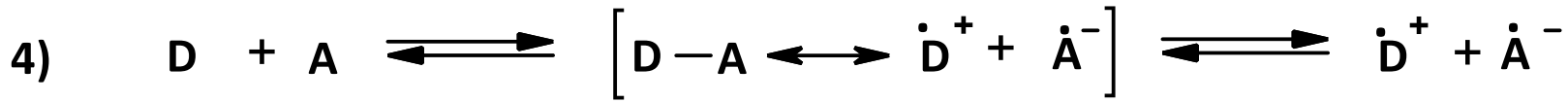


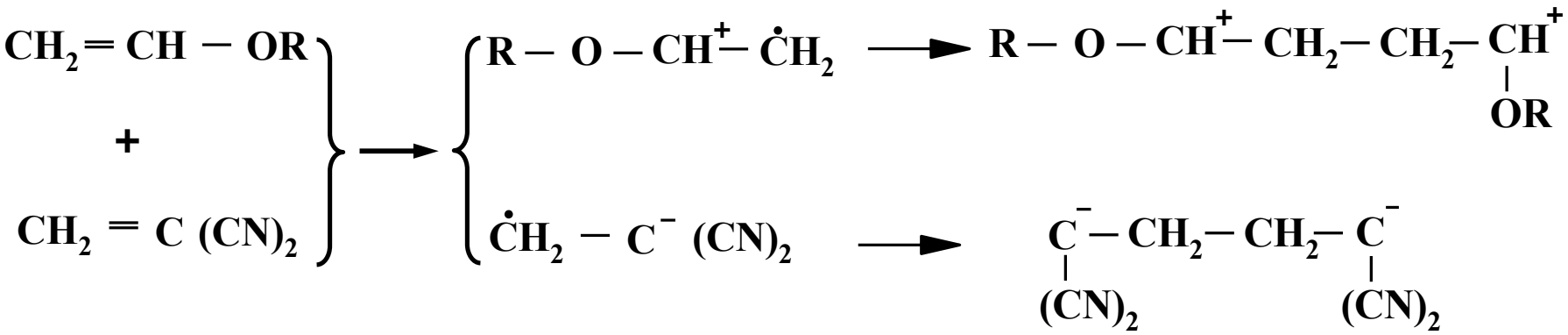
Formation of growing center

2) 

3) 

Formation of growing center

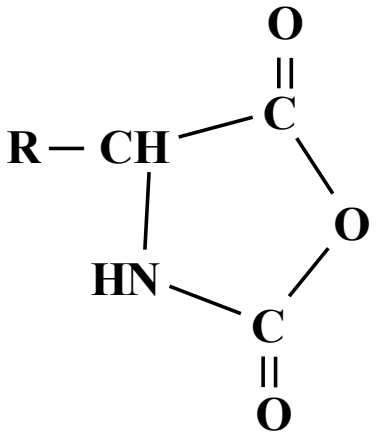




Anionic polymerization

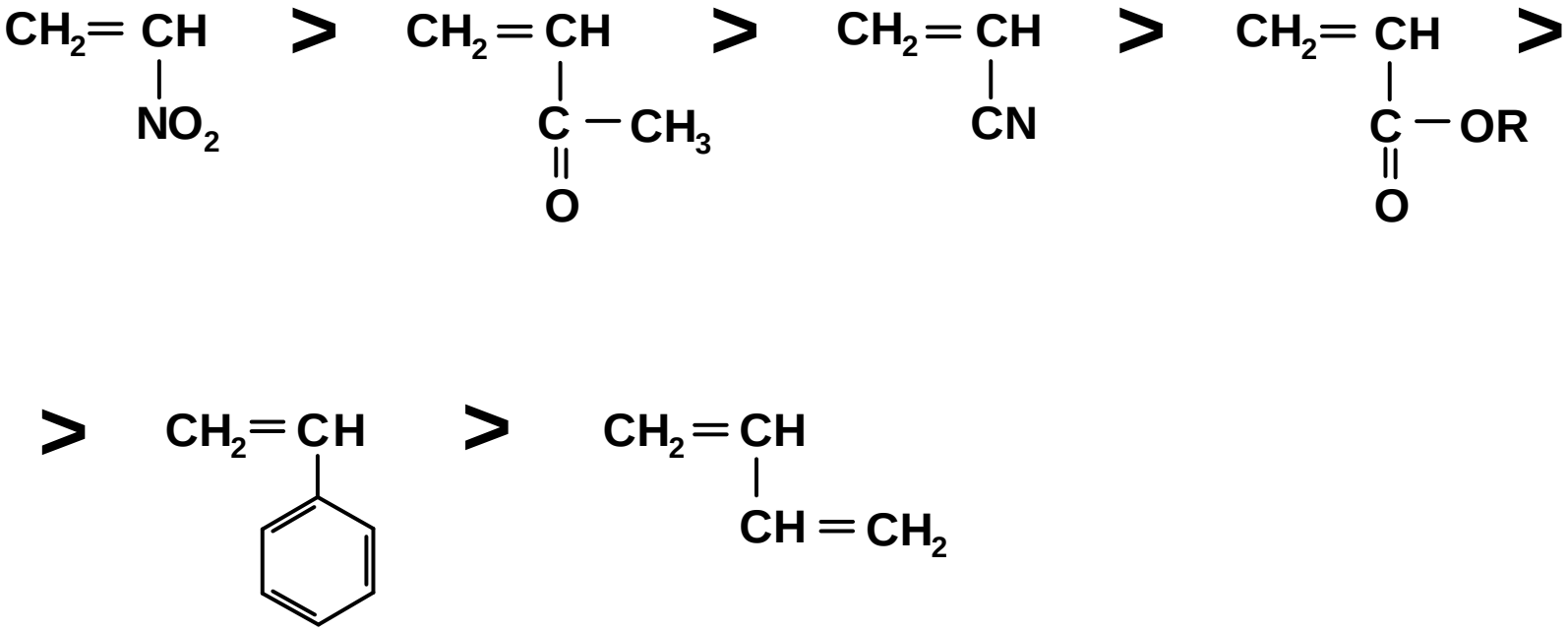
Monomers:

- **Olefin derivatives (subst. -I, -M)**
- **Cyclic monomers**
  - **lactams**
  - **lactones**
  - **oxiranes**
  - **anhydrides of N-carboxylic aminoacids**



- **isocyanates**

Polymerization ability of vinyl monomers

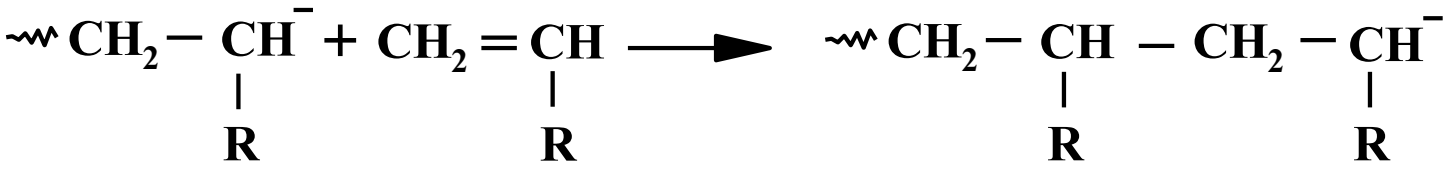


Initiators of anionic polymerization

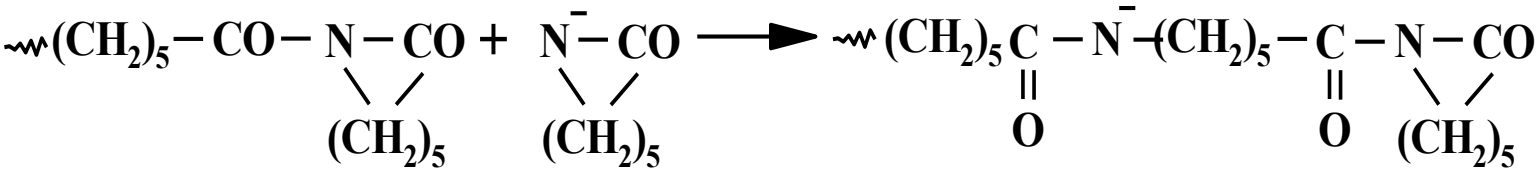
Alkaline metals, alkyl metals, alkoxides, amines, fosphins, alkylmagnesiumbromides, ……

Chain growth

mostly addition of M to macroion:

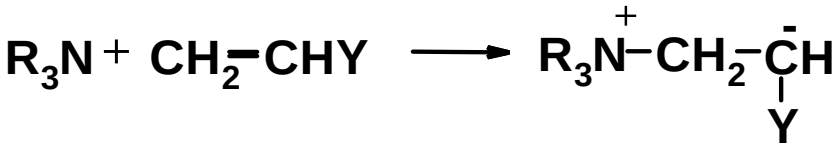


Less often addition of monomer anion on activated chain end (activated monomer mechanism):

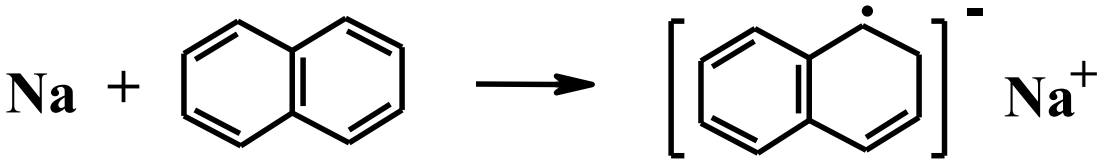


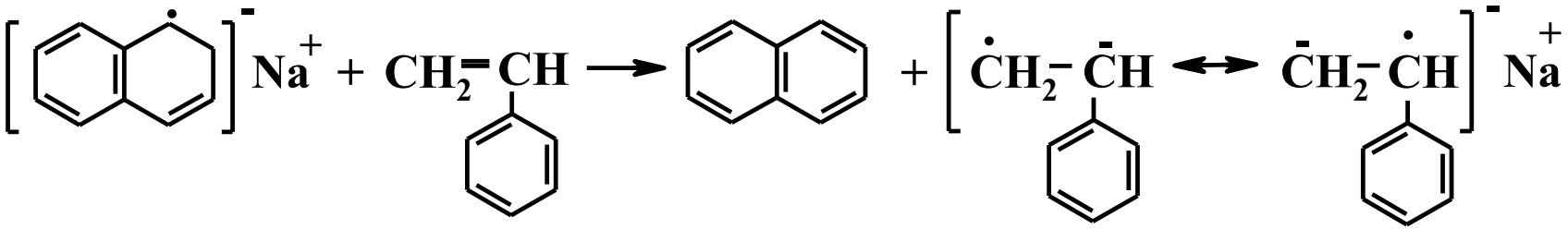
Anionic polymerization

Initiation:



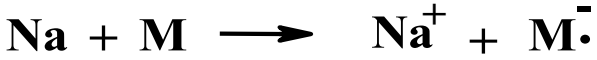
Szwarc catalyst:





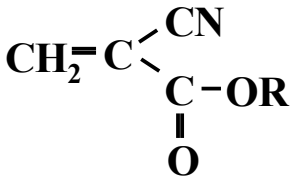
Anionic polymerization - initiation

Alkaline metals:



Monomers with strongly electron-withdrawing substituents

For initiation less nukleofilic (basic) initiators are required :



(Super Glue) **Initiator: water**

Anionic polymerization - growth

Rate of polymerization depends on type of growing center

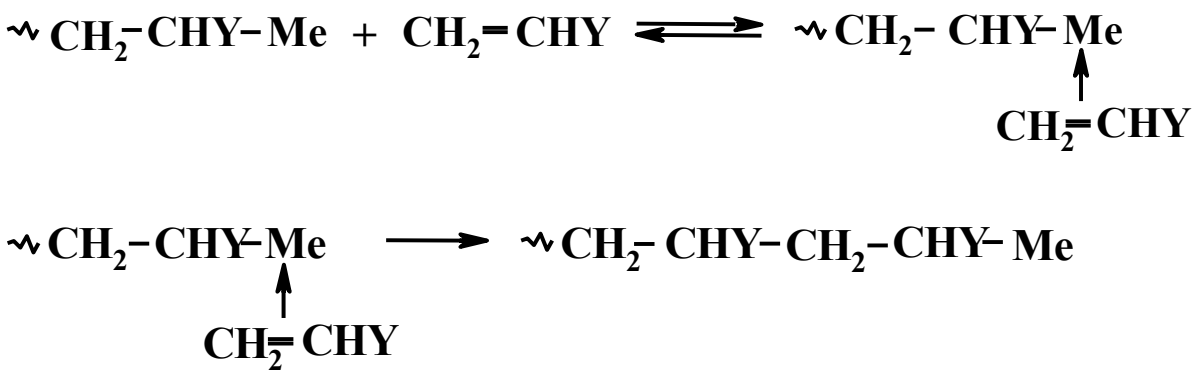
Free ions > ion. pairs solv. separated > ion. pairs contact > polarized bonds

Stechiometric polymerization

- initiator dissociate very fast,
  the only growing centers are free ions

Pseudo-ionic polymerization

(in non-polar media)



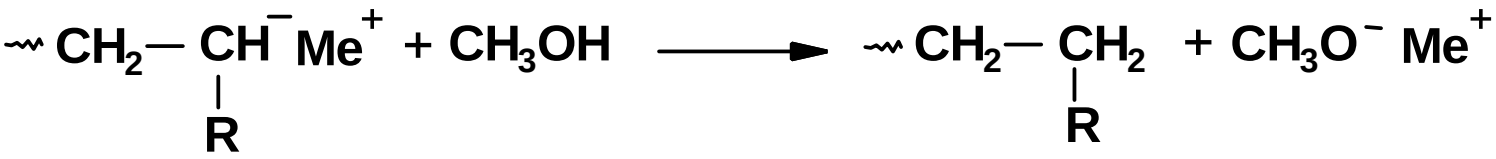
Coordination of monomer always in the same stereo configuration ⇨
tactic polymers

(transition between anionic and coordination polymerization)

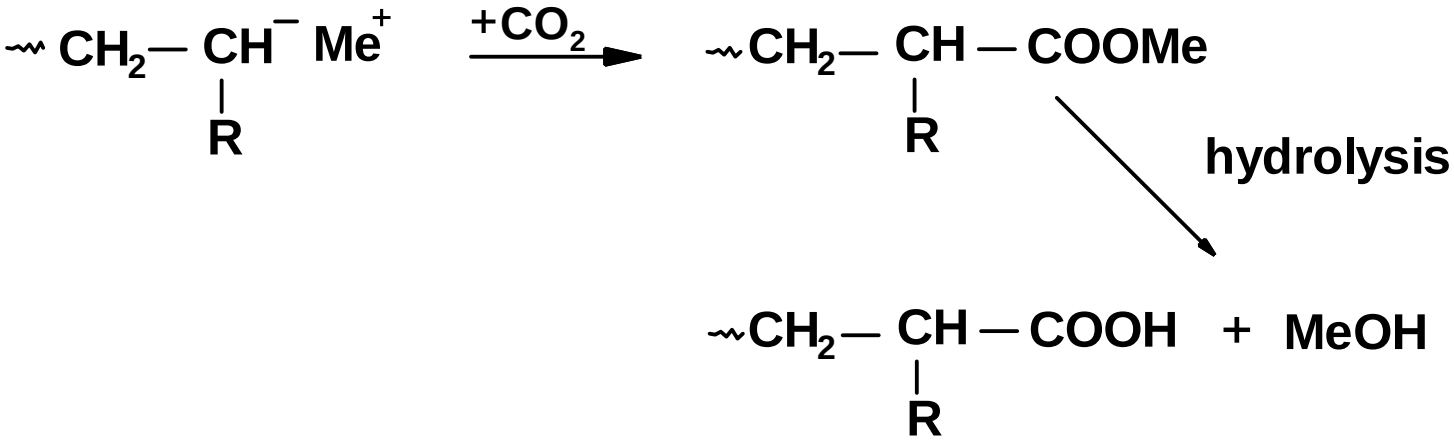
Termination

Me=metal

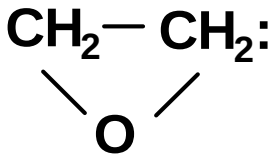
CH_3OH:



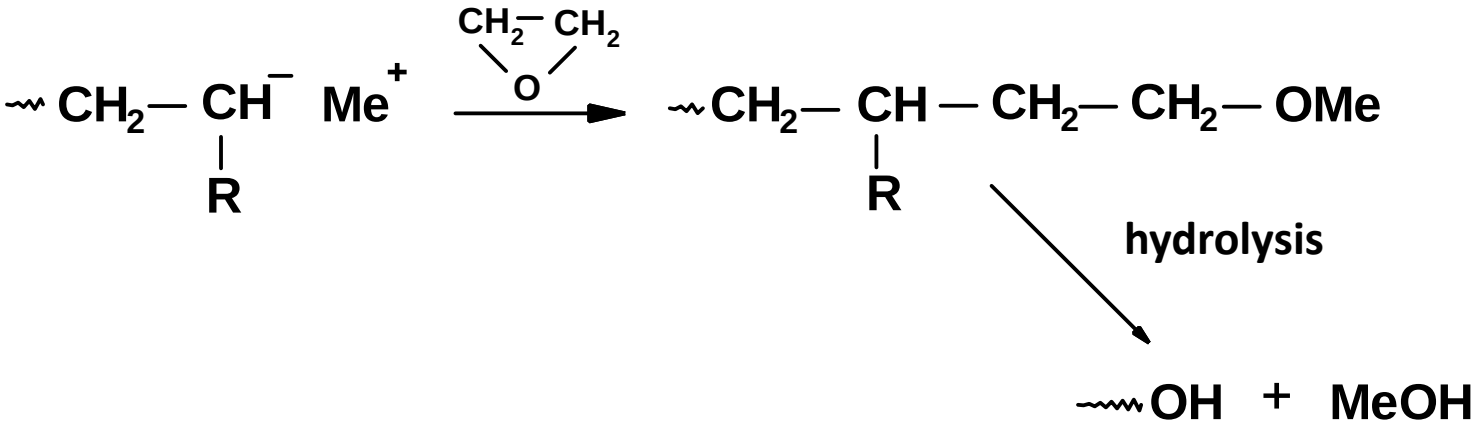
CO_2:



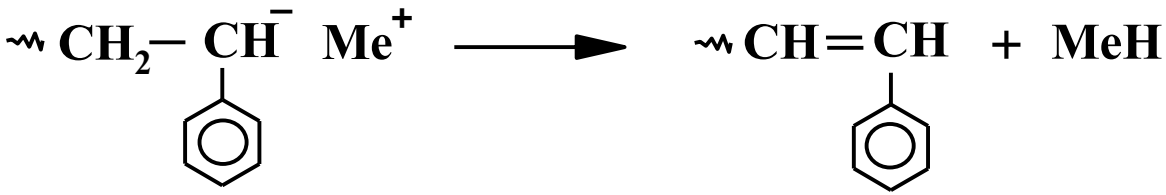
Termination



Me=metal

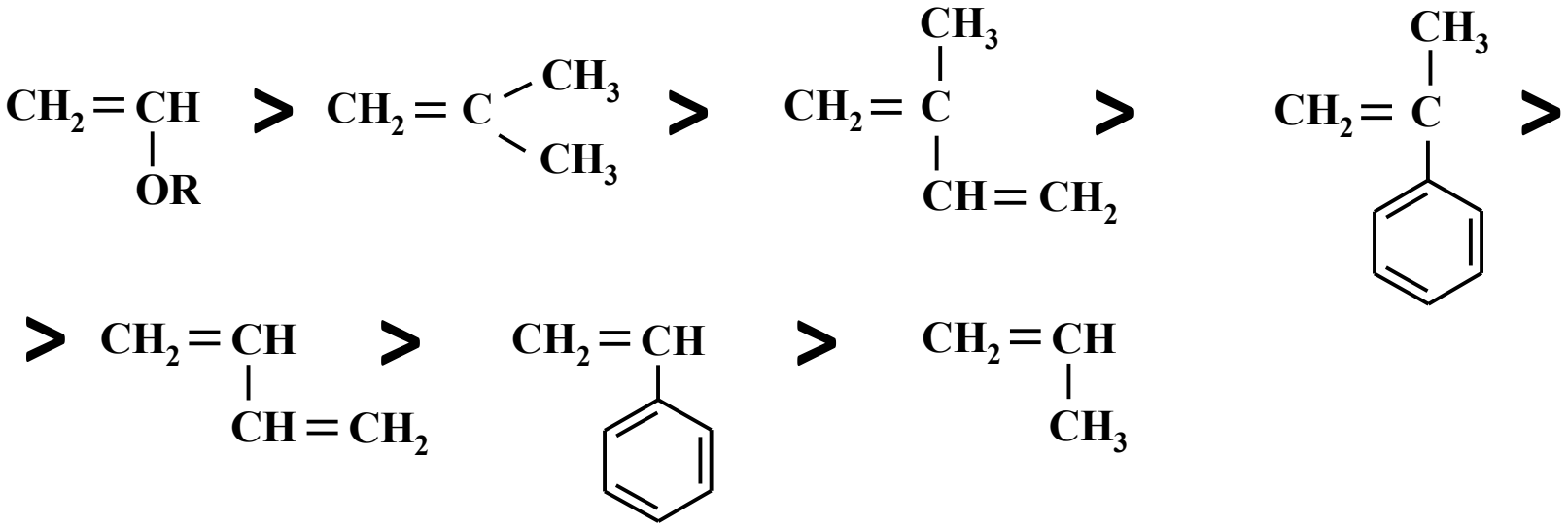


Monomolecular termination:

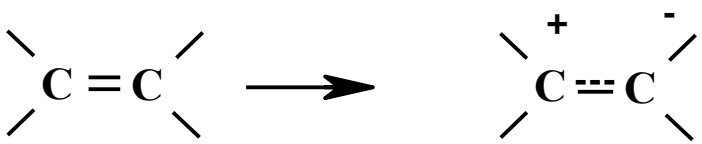


Cationic polymerization

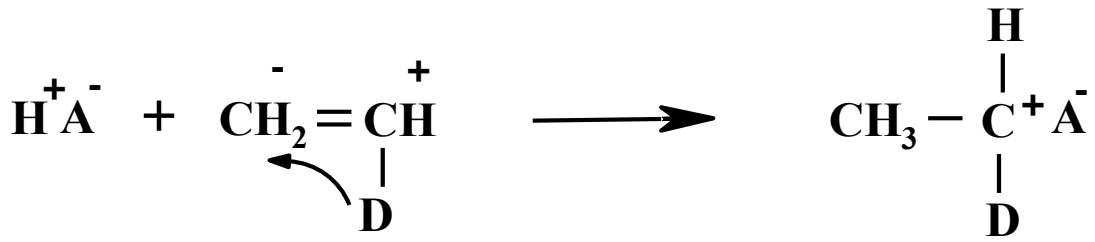
Monomers:



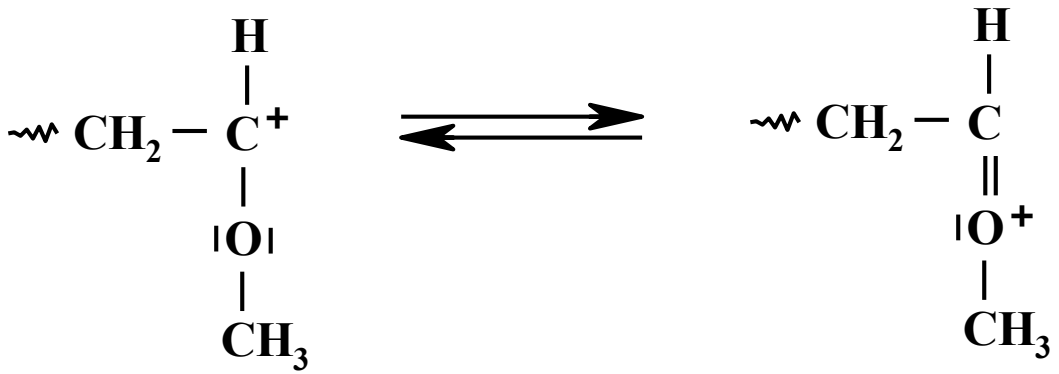
Cyclic ethers – imines
Unsaturated hydrocarbons
Lactams
Lactones
aldehydes



Initiation of cationic polymerization:



Resonance stabilization of cation:

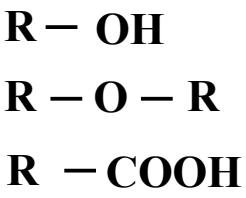


Initiators

A) Proton (Broensted) acids

B) Lewis acids

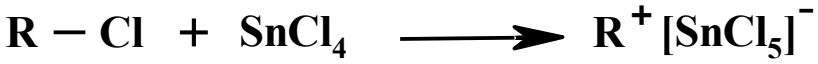
$$BF_3 + H_2O \longrightarrow H^+ [BF_3OH]^-$$



$$R - OH$$

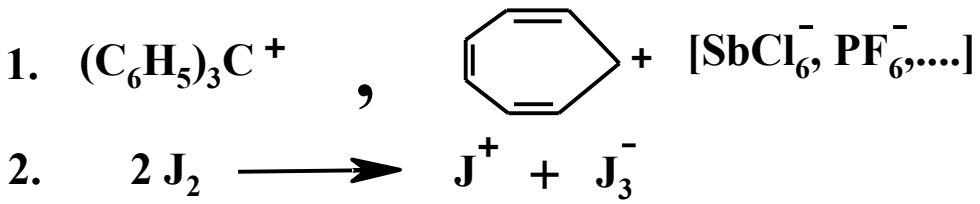
$$R - O - R$$

$$R - COOH$$



$$R - Cl + SnCl_4 \longrightarrow R^+ [SnCl_5]^-$$

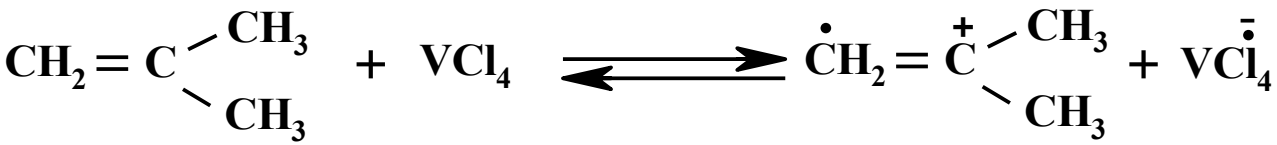
C) Others



1. $(C_6H_5)_3C^+$, $+ [SbCl_6^-, PF_6^-, \ldots]$

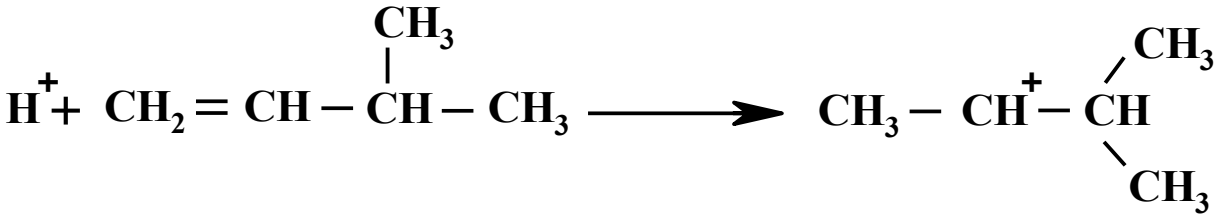
2. $2\,J_2 \longrightarrow J^+ + J_3^-$

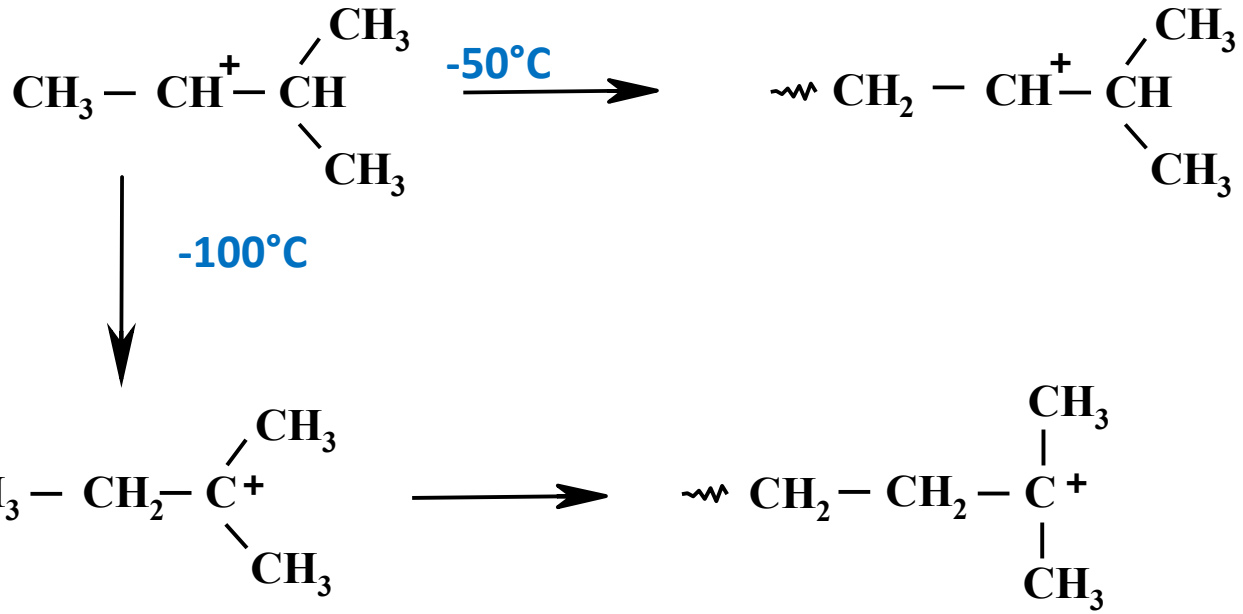
D) Irradiation



$$CH_2 = C(CH_3)(CH_3) + VCl_4 \rightleftharpoons \dot{C}H_2 - \overset{+}{C}(CH_3)(CH_3) + \dot{V}\overset{-}{Cl}_4$$

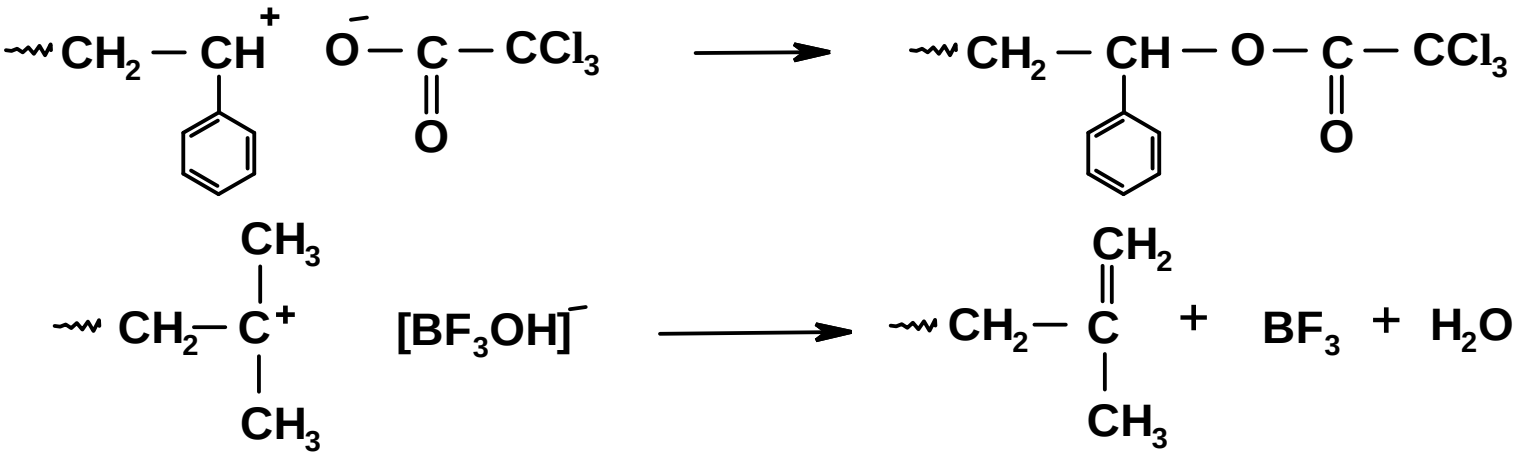
Izomerization polymerization



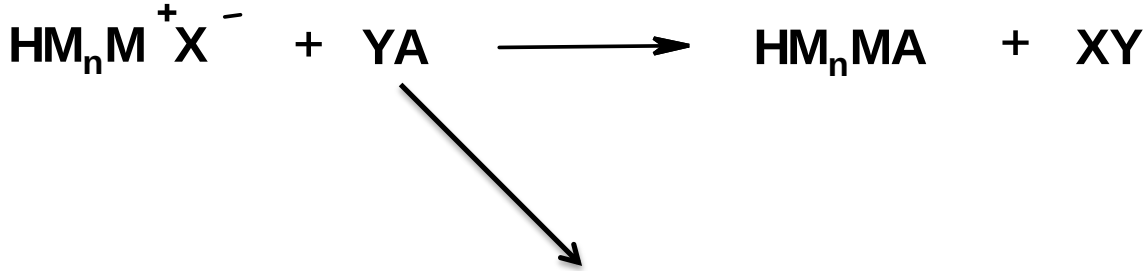


Termination and transfer

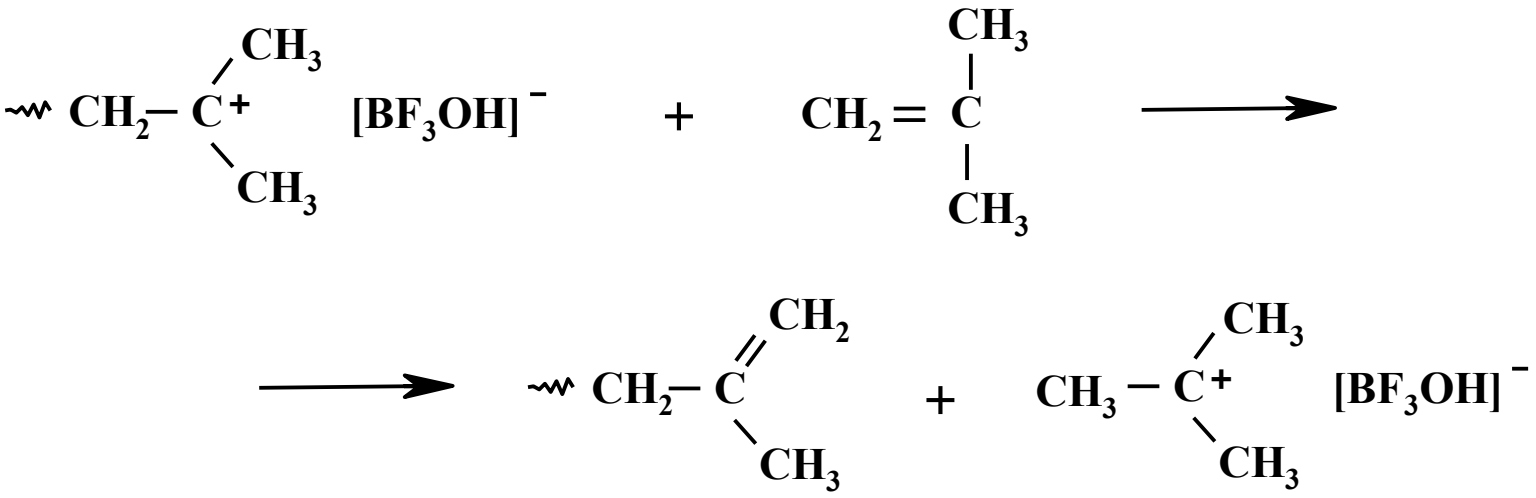
A) Termination with stopping of kinetic chain growth



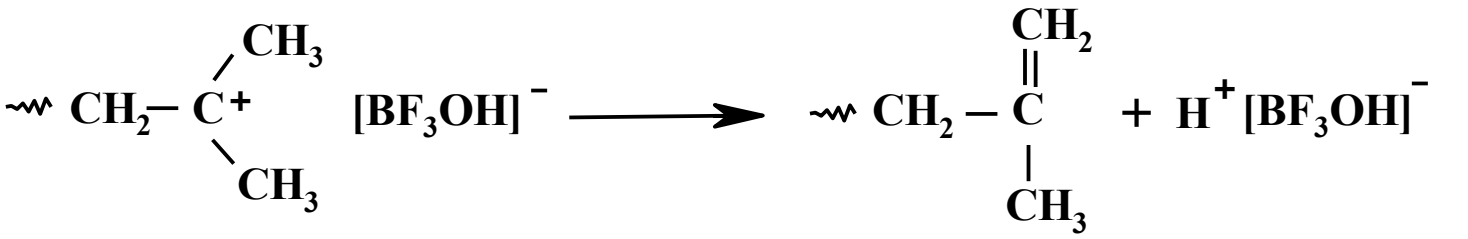
generally



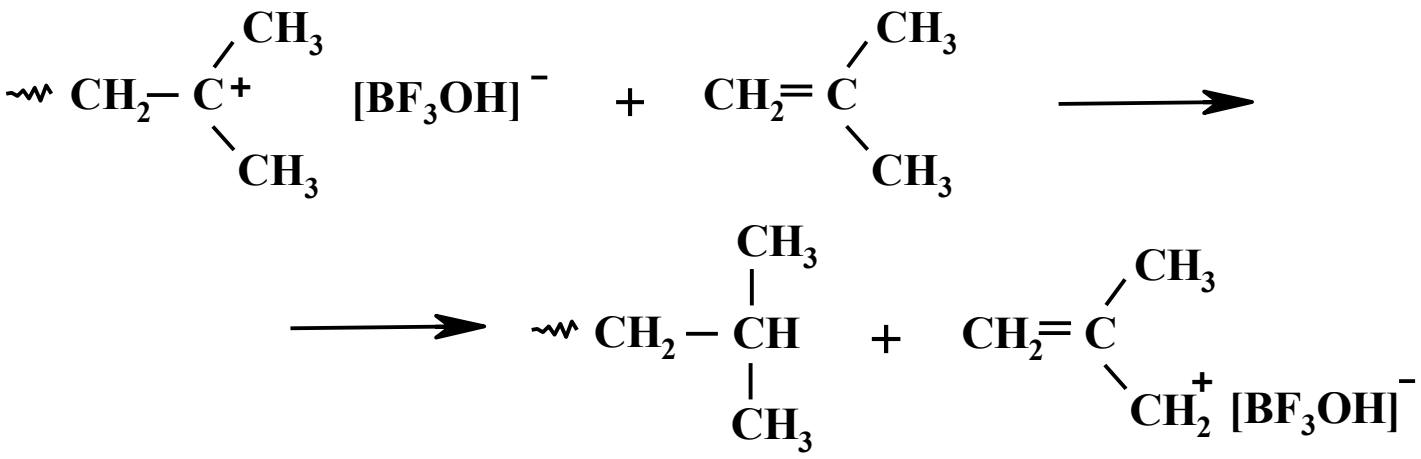
B) Termination without stopping of kinetic chain growth



Transfer to monomer

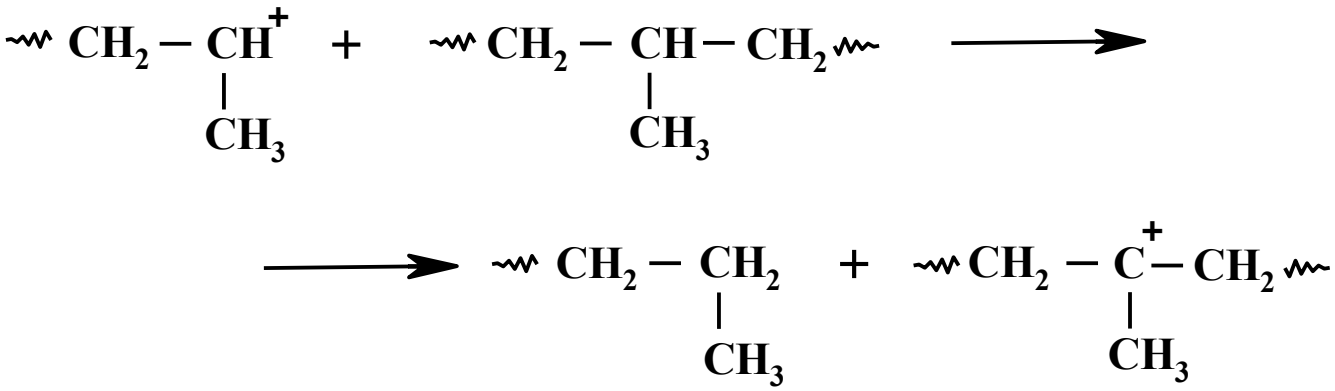


Elimination of catalytic complex



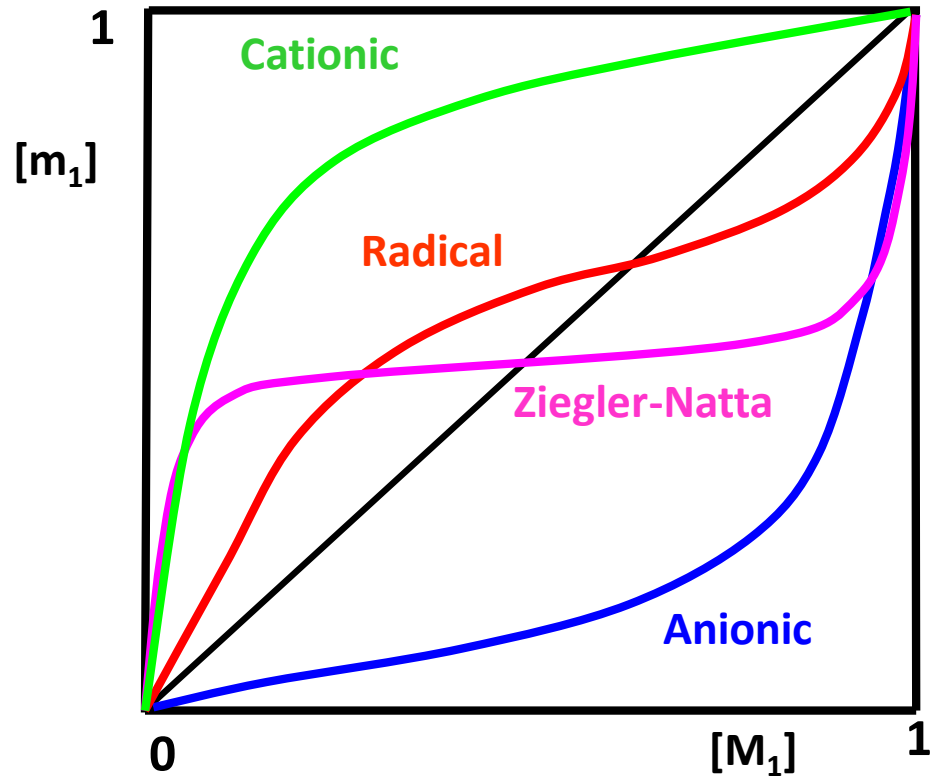
Elimination of hydrido ion from monomer

PP- branching



Ionic copolymerization

Requirements to comonomers, order of addition, block copolymers, SBS , SIS



Copolymerization of styrene (M_1) and methylmethacrylate (M_2) at various copolymerization conditions

Exercises:

1. Combine the following monomers with suitable initiators:

Monomers:

a) vinylidencyanide (1,1-dicyanoethylene)
b) acrylonitrile
c) Styrene

Initiators:

1) potassium amide
2) potassium alkoxide
3) ethylalcohol

2. Which of the following monomers can polymerize by cationic mechanism? :