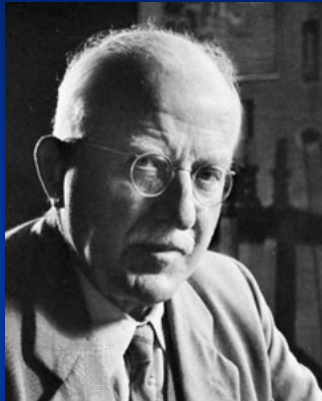


Functional Polymer/1st Semester, 2006

- History of Polymers
- Classification of Polymer
 - By Polymerization Mechanism
 - By Polarity
 - By Polymerization Process
 - By Recycle Ability
 - By Tacticity
- Interaction of Polymer

History of Polymer

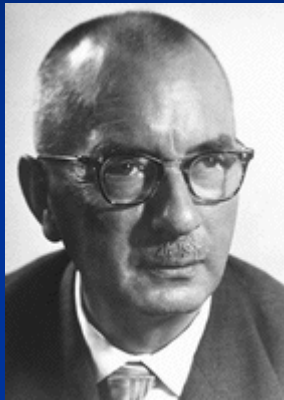


- H. Staudinger (1881–1965)
- 고분자설을 실험적으로 증명
- 천연고무의 수소화 실험
($\text{CH}_2=\text{CH}_3\text{C}-\text{CH}=\text{CH}_2$)
- Polystyrene의 점도가 말단기의 수가 작아짐에 따라 증가함을 실험적으로 증명
- 1953 Noble Prize

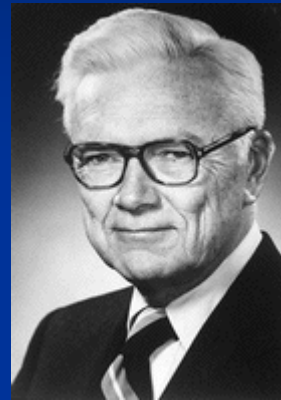


- W.H. Carothers (1896–1937)
- Nylon 최초 합성
- 1937년 Dupont社 상업화

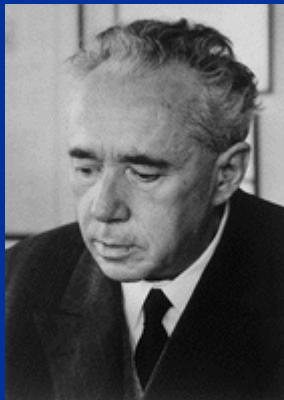
History of Polymer



- K. Ziegler (1898–1973)
- 상압 폴리에틸렌 합성
- 1963년 Noble Prize



- P. J. Flory (1910–1985)
- 고분자 물리화학의 이론 집대성
- 1974년 Noble Prize

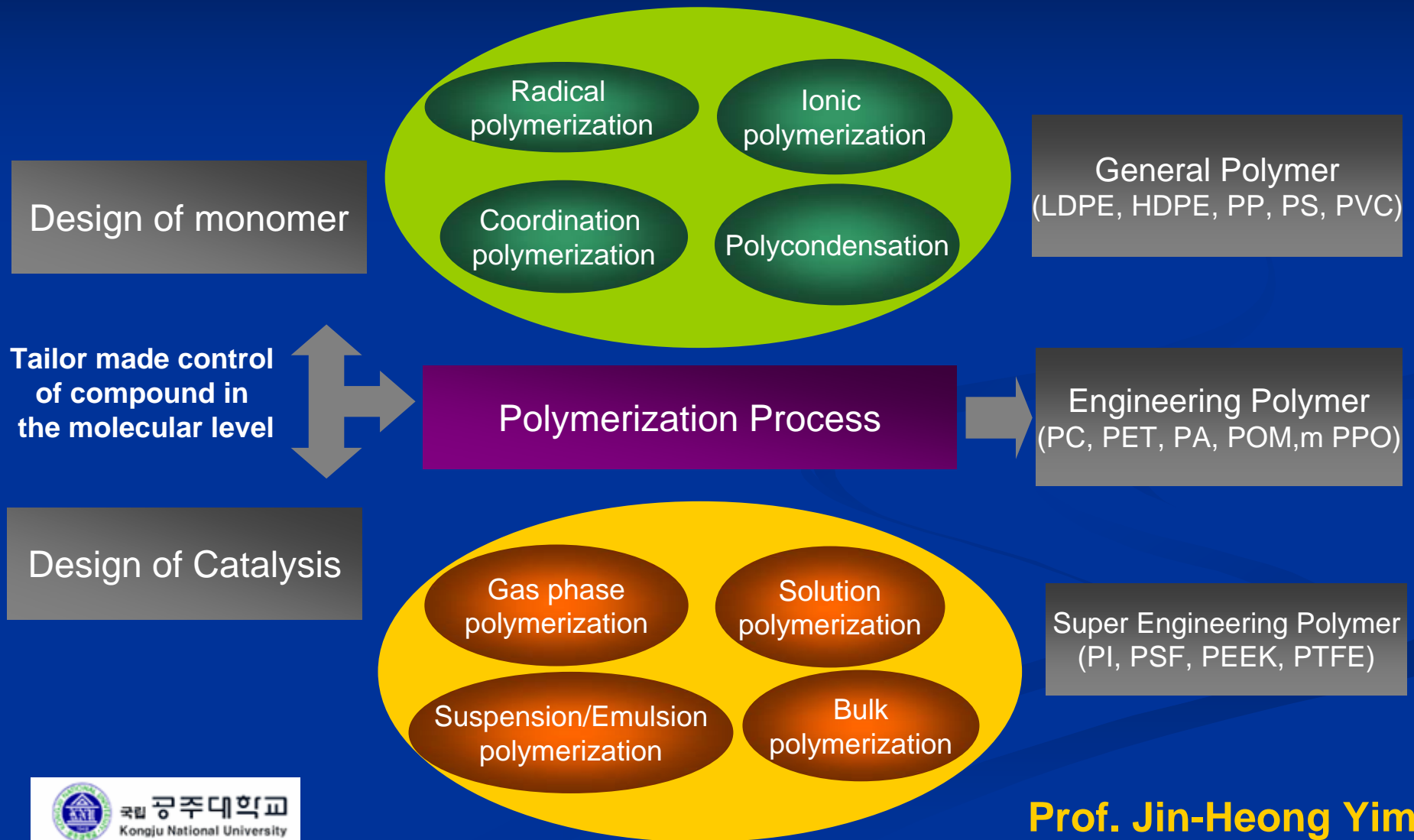


- G. Natta (1903–1979)
- Ziegler 촉매 이용 입체 규칙성을 지닌 폴리프로필렌 합성
- 1963년 Noble Prize



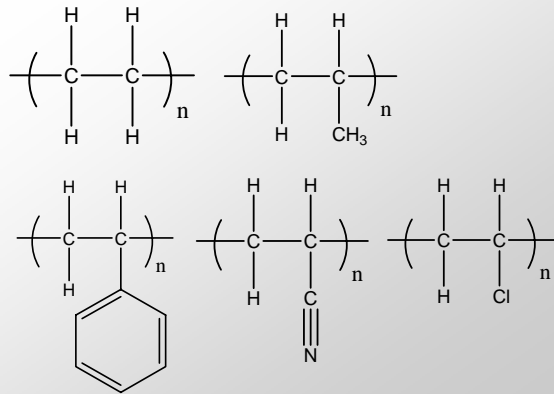
- A. J. Heeger (1936–)
- 반도체/전도성 고분자 발견
- 2000년 Noble Prize
- UCSB 물리학과 교수

Polymerization

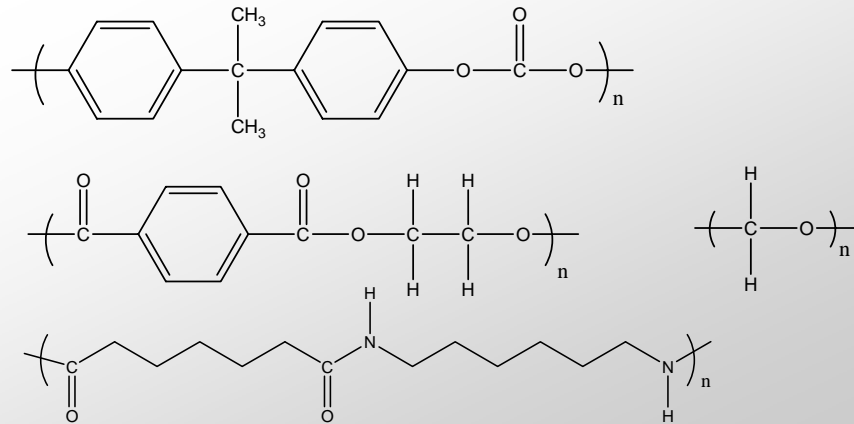


Various Polymers

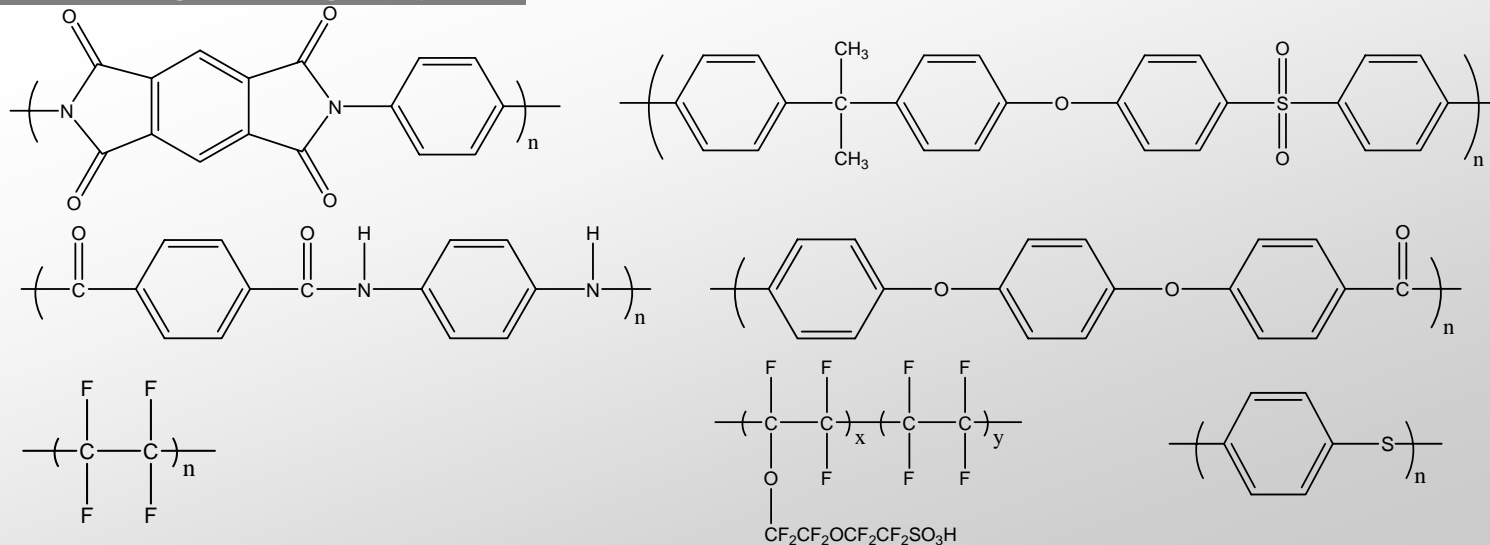
General Polymer



Engineering Polymer



Super Engineering Polymer



Classification by Mechanism

Step Polymerization



Polycondensation

Chain Growth
Polymerization



Radical Polymerization

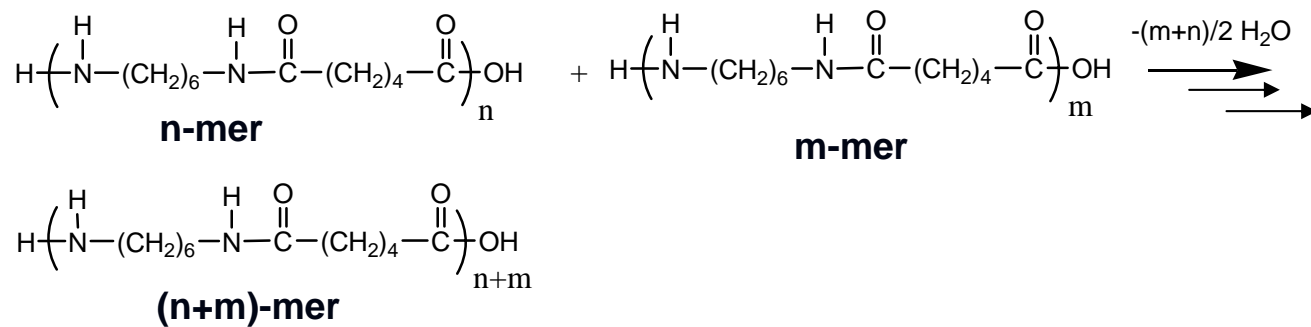
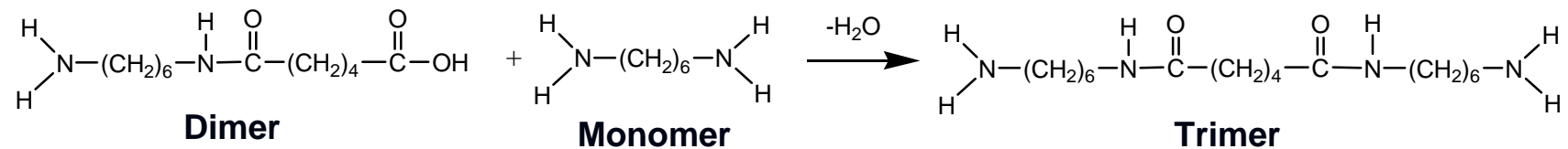
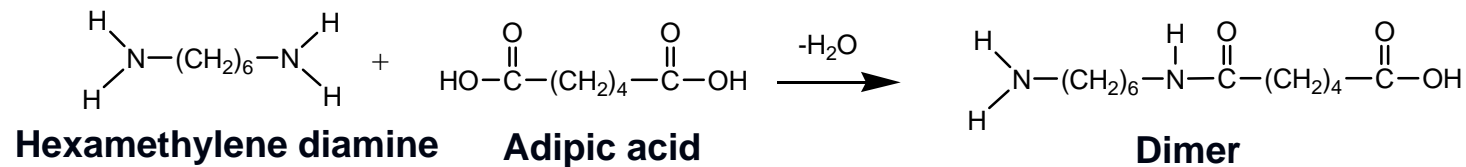
Cationic Polymerization

Anionic Polymerization

Coordination Polymerization

Step Polymerization

Nylon 66 (PA 66)



Chain Growth Polymerization

Radical Polymerization

Cationic Polymerization

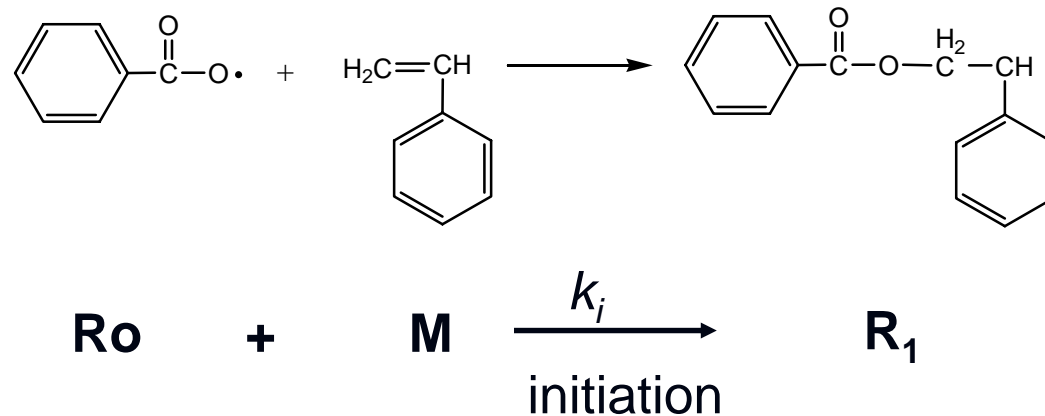
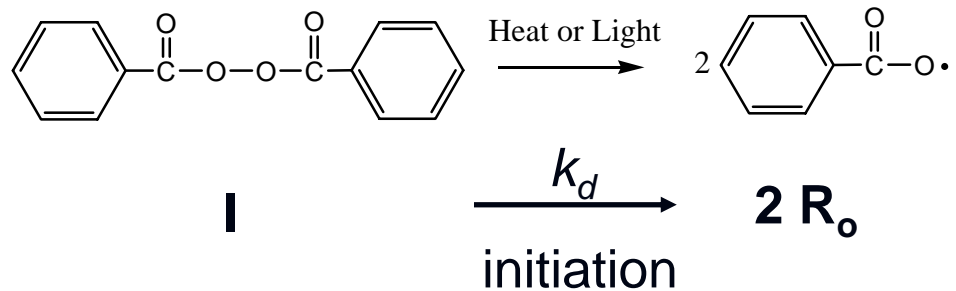
Anionic Polymerization

Coordination Polymerization

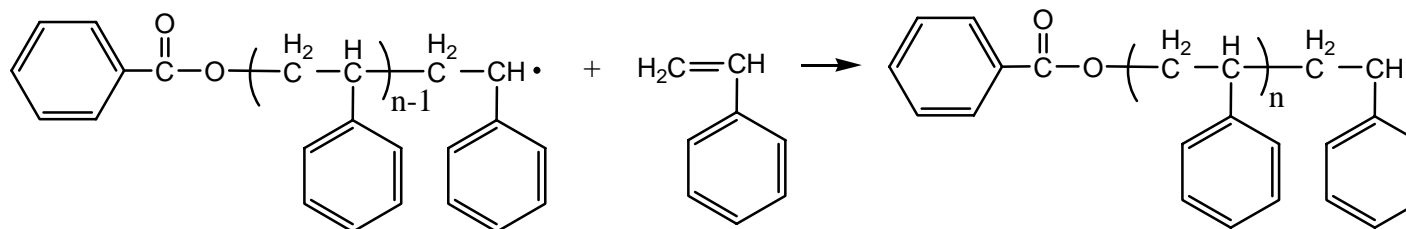
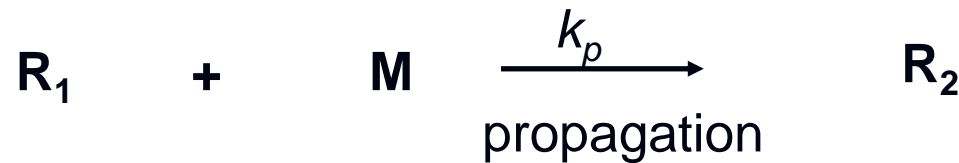
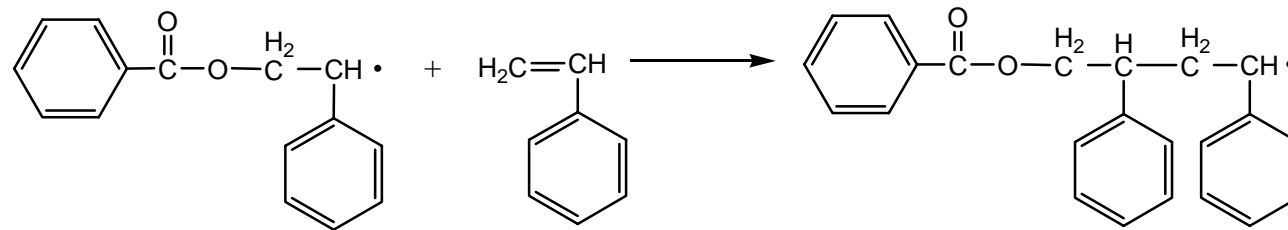
Chain Growth Polymerization

- **Initiation**
 - Generation of active initiator
 - Reaction with monomer to form growing chains
- **Propagation**
 - Chain extension by incremental monomer addition
- **Termination**
 - Conversion of active growing chains to inert polymer
- **Chain Transfer**
 - Transfer of active growing site by terminating one chain and reinitiating a new chain.

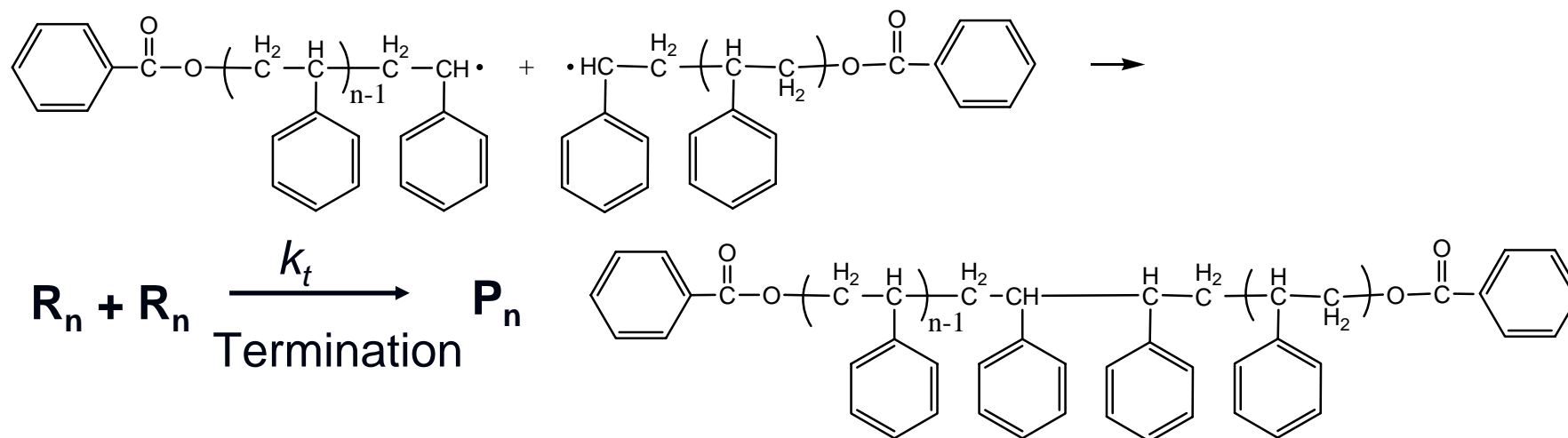
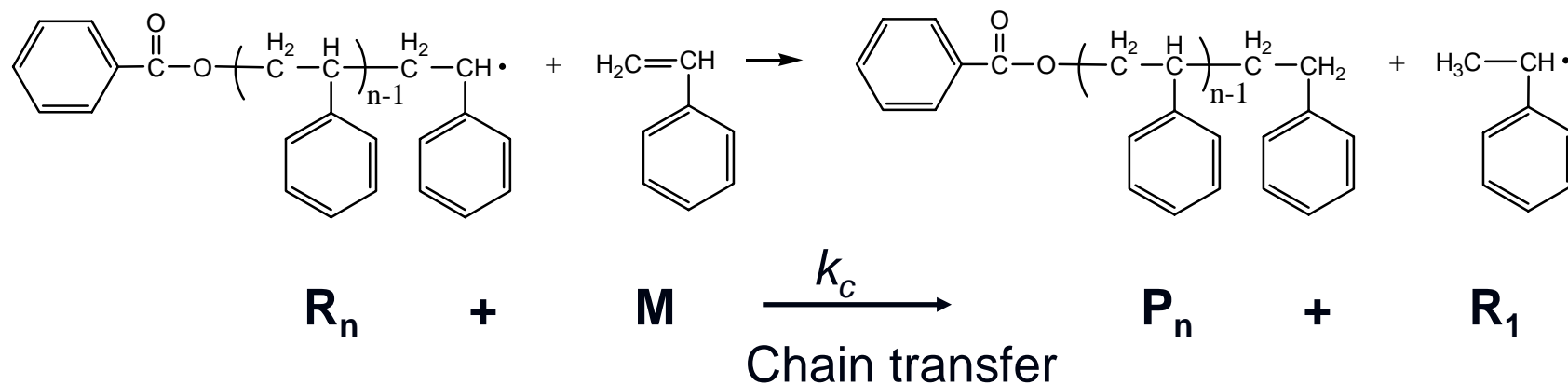
Radical Polymerization



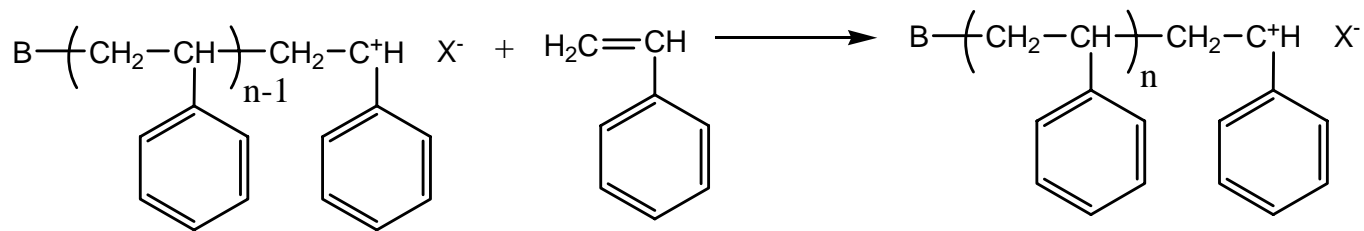
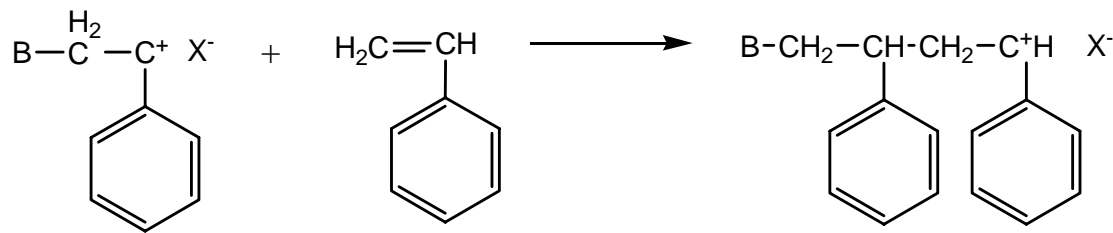
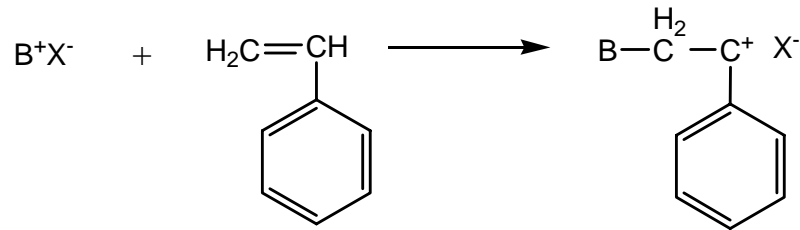
Radical Polymerization



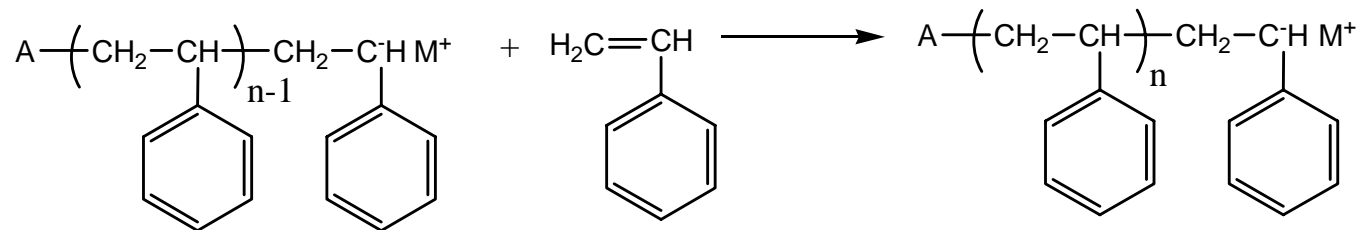
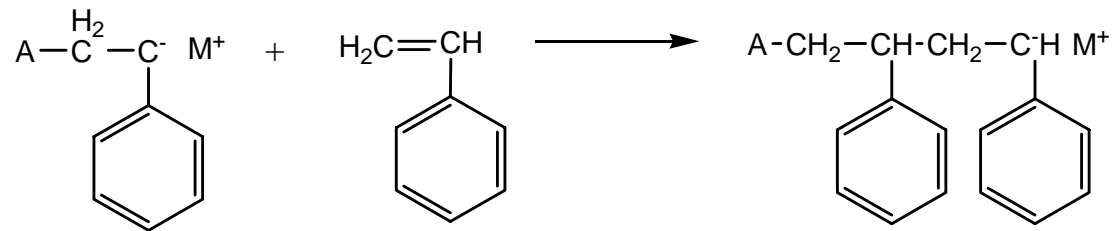
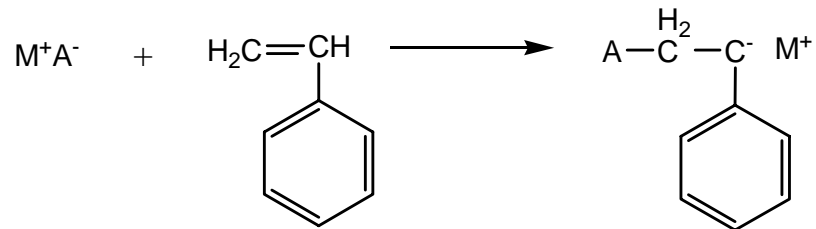
Radical Polymerization



Cationic Polymerization

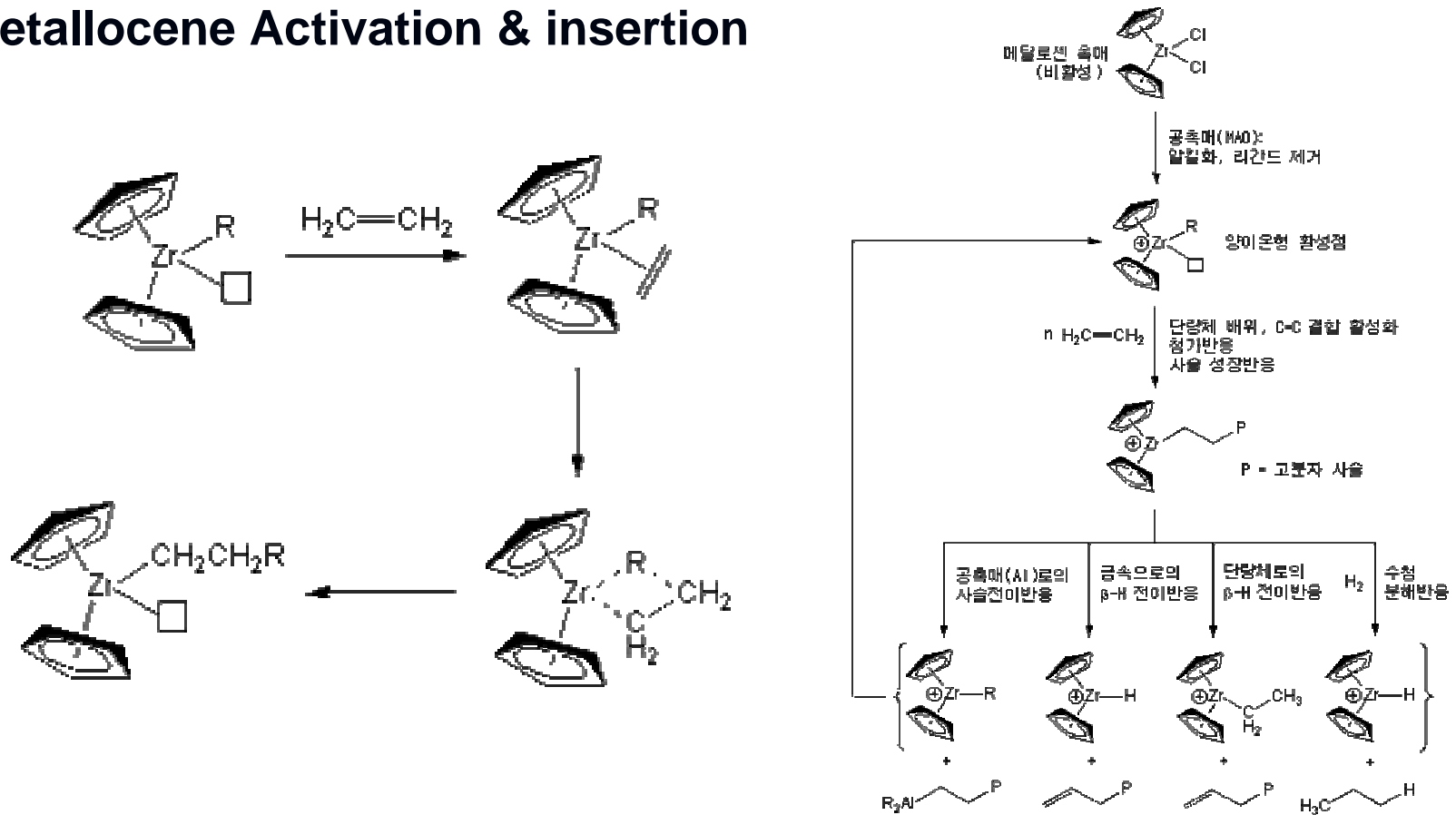


Anionic Polymerization



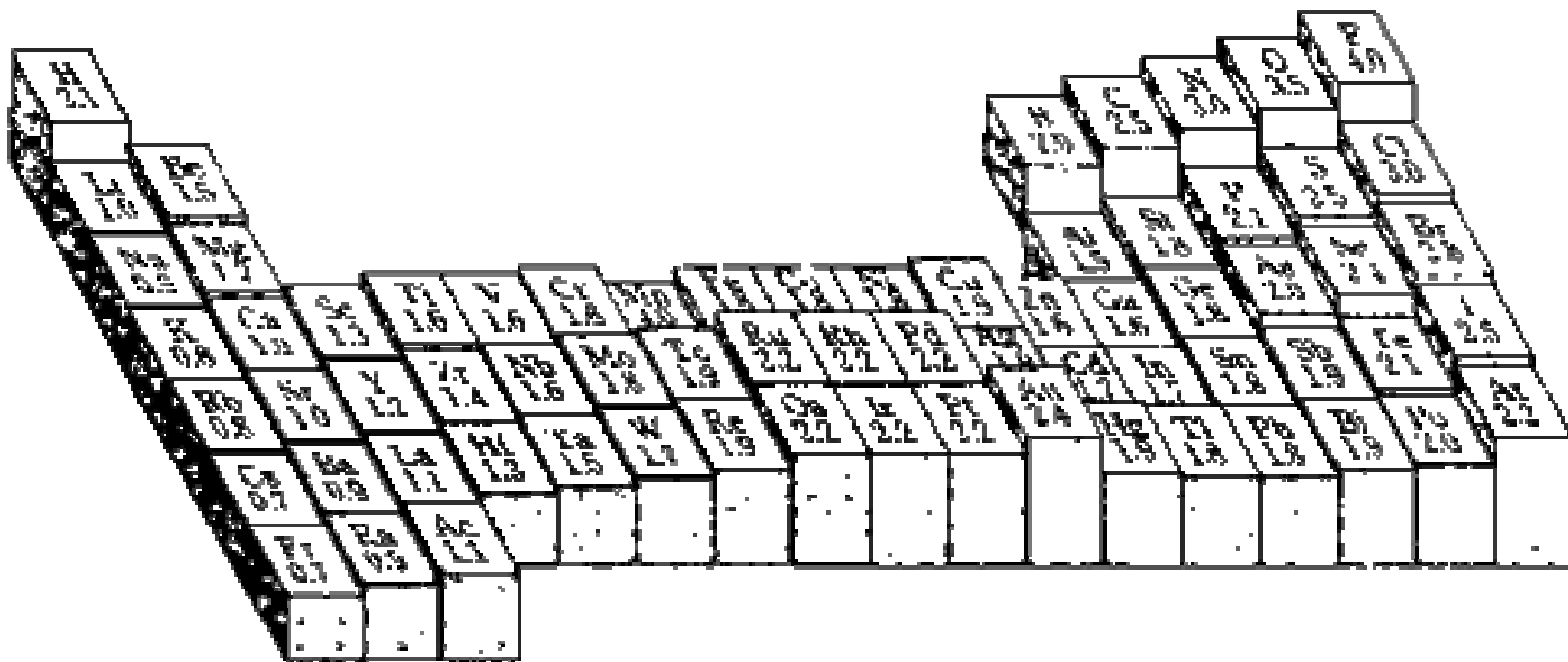
Coordination Polymerization

Metallocene Activation & insertion

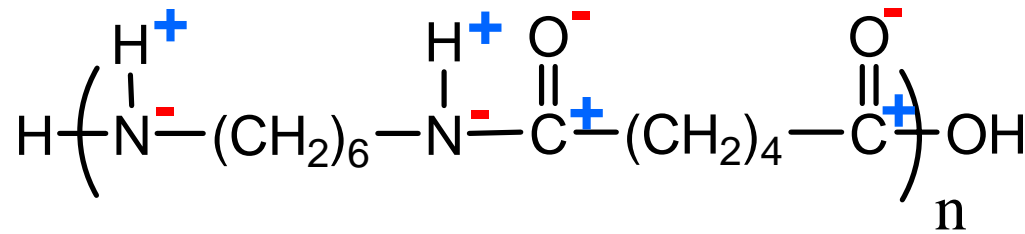


Classification by Polarity

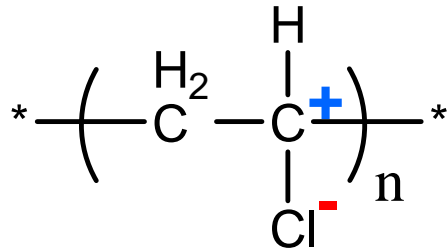
전기음성도의 정의: 공유 결합에서 전자쌍을 끌어 당기는 힘의 크기



Polar Polymer

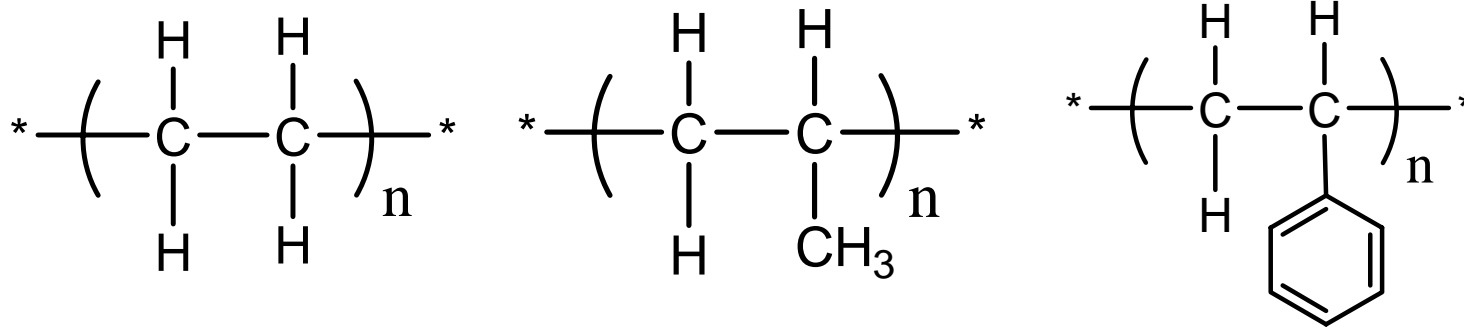


H: 2.2, N: 3.0
C: 2.5, O: 3.4

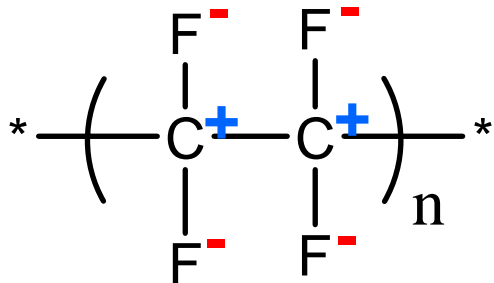


C: 2.5, Cl: 3.2

Nonpolar Polymer



H: 2.2, C: 2.5



C: 2.5, F: 4.0

By Process

| Method | Advantages | Disadvantages |
|---------------------------|---|---|
| Bulk (Neat) | Simple equipment Rapid reaction Pure polymer isolated | Heat buildup Gel effect Branched or crosslinked product |
| Solution | Good mixing Ready for application | Lower mol. Wt. Low R_{poly} Solvent Recovery |
| Suspension (Pearl) | Low viscosity Direct bead formation | Removal of additives |
| Emulsion | High R_{poly} Low Temperatures High Mol. Wt. High surface area latex | Removal of additives Coagulation needed Latex stability |

By Recycle Ability

- **Thermoplastic:**
 - polymers that flow when heated
 - easily reshaped and recycled
 - due to presence of long chains with limited or no crosslinks
 - polyethylene, polyvinylchloride

By Recycle Ability

- **Thermosetting:**
 - decomposed when heated
 - can not be reformed or recycled
 - presence of extensive crosslinks between long chains
 - epoxy and polyesters

By Recycle Ability

- **Elastomers:**

- intermediate between thermoplastic and thermosetting polymers
- some crosslinking
- can undergo extensive elastic deformation
- natural rubber, silicone

Structural Characteristics

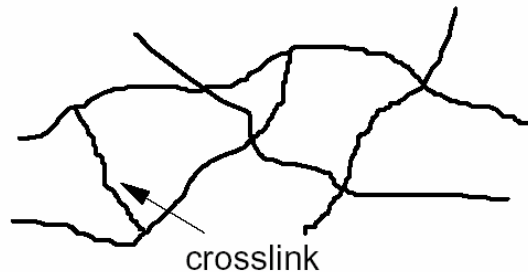
Structural characteristics – Closely related to material properties



linear (uninterrupted straight chain)



branched (occasional branches off longer chain)



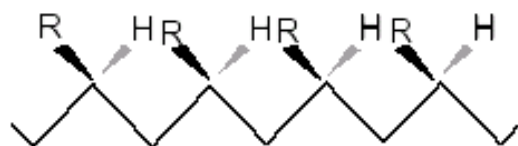
networked (many interconnected linear chains; one giant molecule)

By Tacticity

- Polymers can be either amorphous or semi-crystalline
- Tacticity, i.e. arrangements of substituents around the backbone, determines the degree of crystallinity
- Atactic polymers are amorphous
- Isotactic and syndiotactic may crystallize
- Crystallinity depends on:
 - size of side groups (smaller, \uparrow crystallinity)
 - regularity of chain
- Increased crystallinity enhances mechanical properties

By Tacticity

Stereochemistry of Linkages



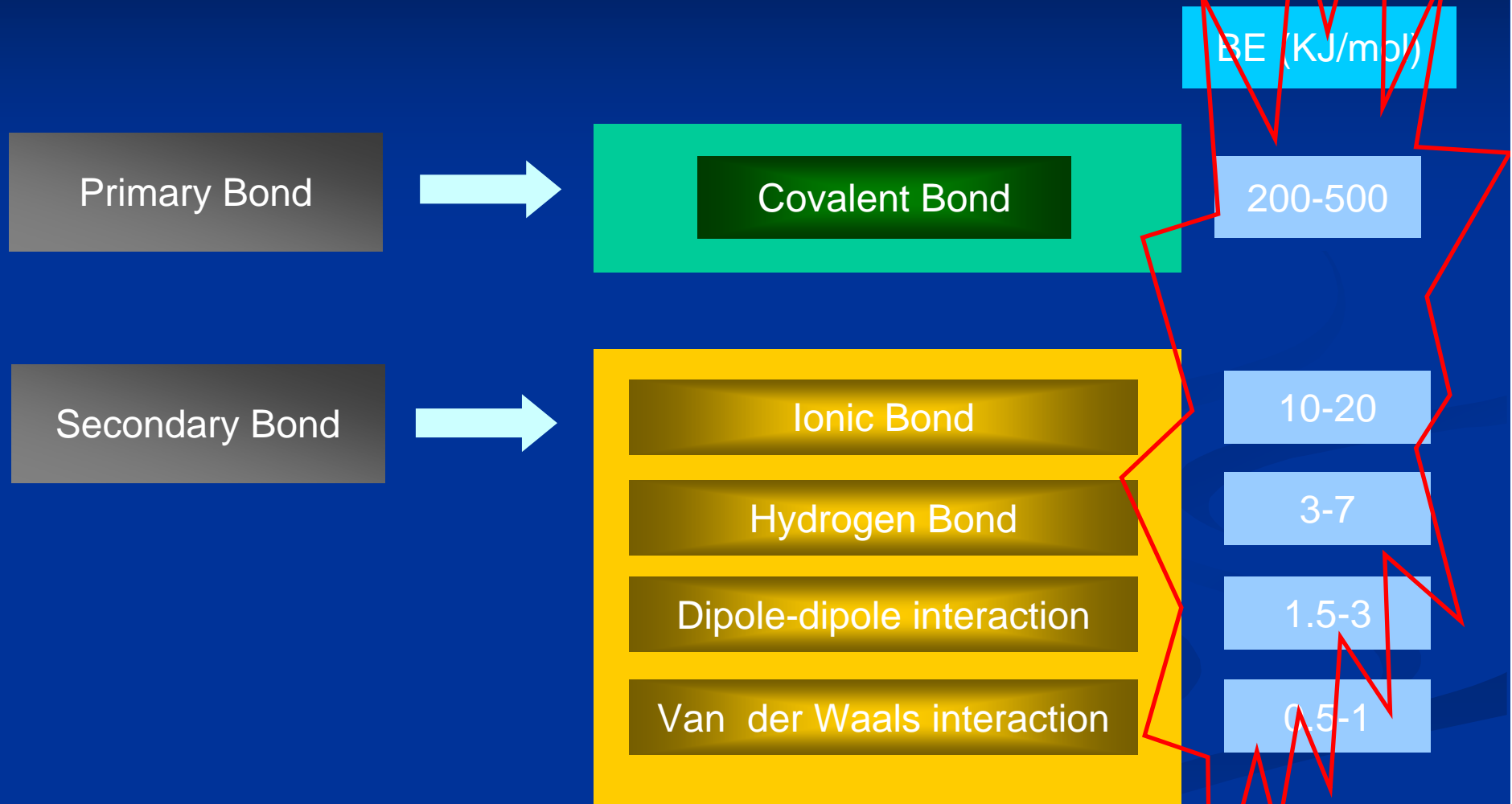
ISOTACTIC – R groups on same side of backbone



SYNDIOTACTIC – R groups on alternating sides of backbone

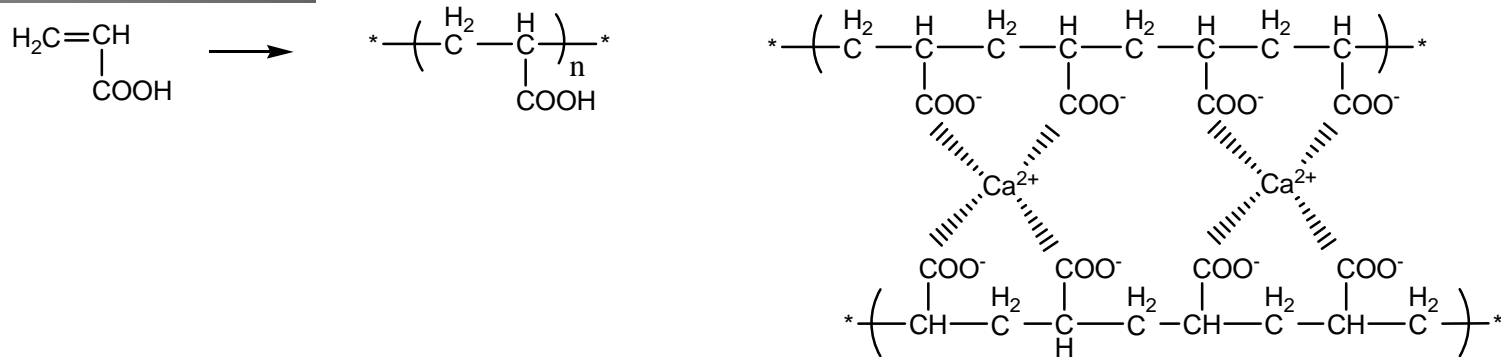
ATACTIC — Random (most common)

Interaction of Polymer

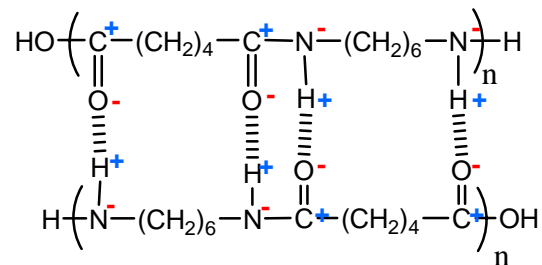


Interaction of Polymer

Ionic Bond



Hydrogen Bond



Dipole-dipole interaction

