생유기화학
(Bioorganic Chemistry)

Synthetic Polymer-II
(합성고분자-2)

Soonchunhyang University

Department of Chemical Engineering

Prof. Jungkyun Im

SCH 순천향대학교

순천향대

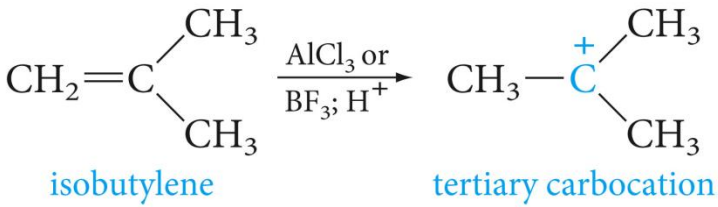
나노화학공학과

임 정 균 교수

3. **Cationic** Chain-Growth Polymerization (양이온성)

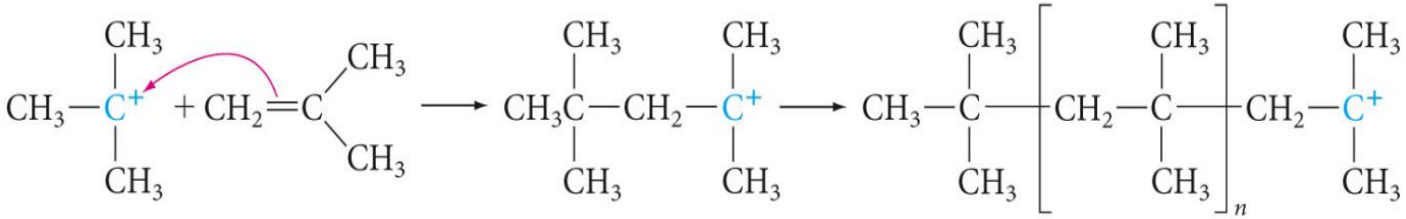
어떠한 vinyl compound들은 cationic intermediate (양이온성 중간체)을 거쳐서 중합반응이 일어난다.

Initiation :



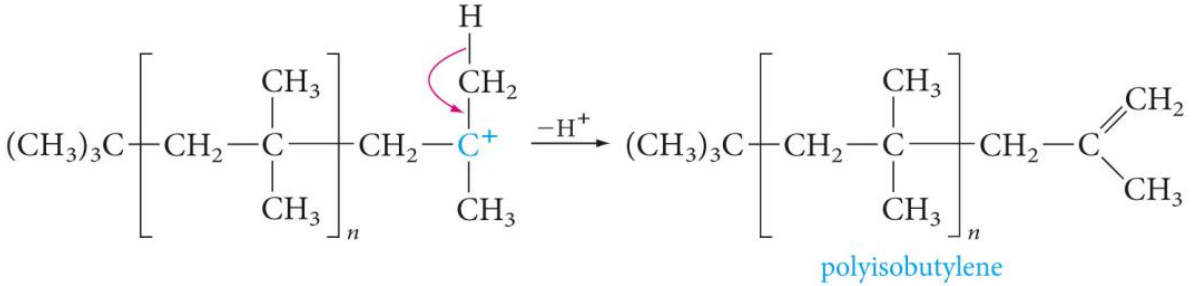
- Friedel-Craft 촉매 사용
- 안정한 3차 carbocation이 생성

Propagation :



- Markovnikov's rule에 따라 첨가반응

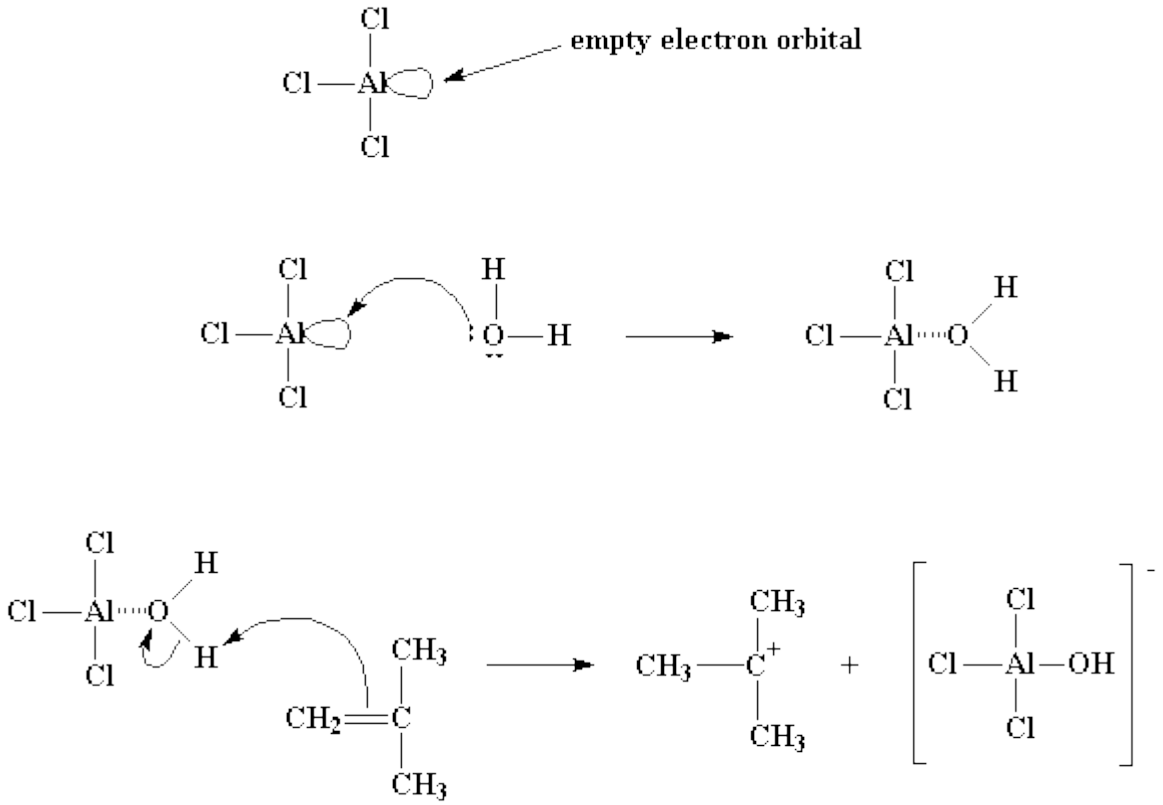
Termination :



- loss of proton

Polyisobutylenes are used as additives in lubricating oil and as adhesives in pressure-sensitive tape and removable paper labels.

Initiator가 aluminum trichloride($AlCl_3$)일 경우 initiation step 과정



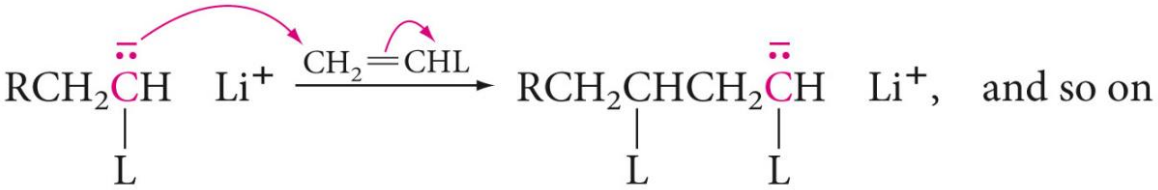
4. **Anionic** Chain-Growth Polymerization (음이온성)

Alkene에 electron-withdrawing group(EWG)이 존재하면 carbanion 중간체가 형성될 수 있다.

Initiation :

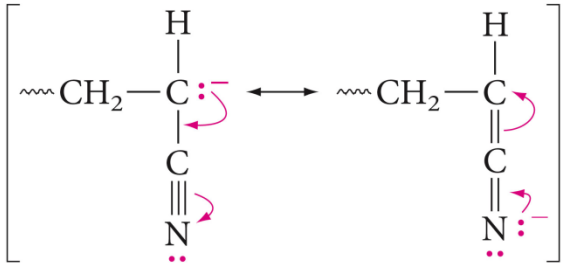
- organometallic(유기금속) compound로 구성된 촉매가 필요하다.
- L은 전자를 잡아당겨 전자의 비편재화(delocalization)를 일으켜 carbanion의 안정화에 기여하고 resonance를 일으킬 수 있다.
- L은 cyano (CN), carbomethoxy (CO_2CH_3), phenyl, and vinyl ($CH=CH_2$)등이 가능하다.

Propagation :



Termination : water 또는 alcohol을 첨가하면 proton source가 되어 protonation에 의하여 반응 종료.

L이 cyano group일 경우



(resonance)

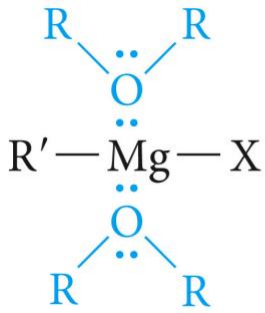
Organometallic Compound

Grignard Reagent

$$R{-}X + Mg \xrightarrow{\text{dry ether}} R{-}MgX$$

a Grignard reagent

Grignard found that when magnesium turnings are stirred with an ether solution of an alkyl or aryl halide, an exothermic reaction occurs. The Mg, which is insoluble in ether, disappears as it reacts with the halide to give solutions of ether-soluble Grignard reagents.

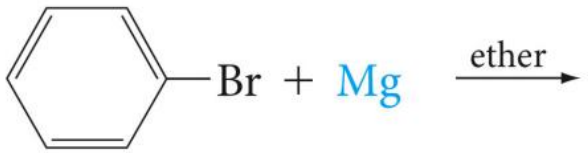


Acting as a Lewis base, ether stabilizes a Grignard reagent.

Ether oxygen helps to stablilize the magnesium through coordination.

$$CH_3{-}I + Mg \xrightarrow{\text{ether}} CH_3MgI$$

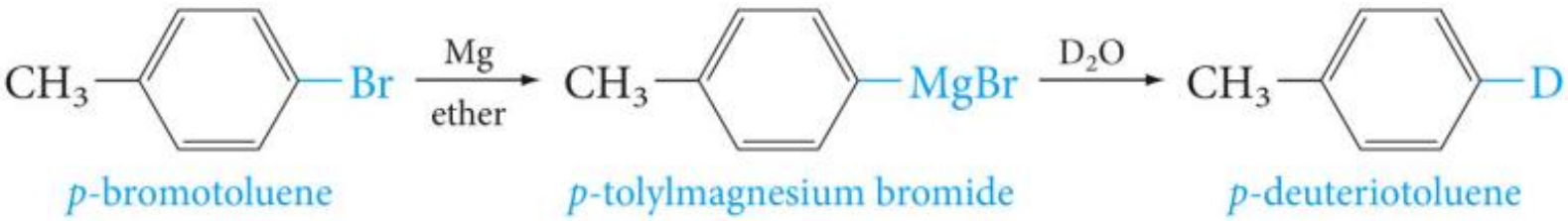
methyl iodide — methylmagnesium iodide



bromobenzene — phenylmagnesium bromide

$\overset{\delta-}{R}—\overset{\delta+}{MgX}$ **Grignard reagent** R이 carbanion처럼 행동한다.

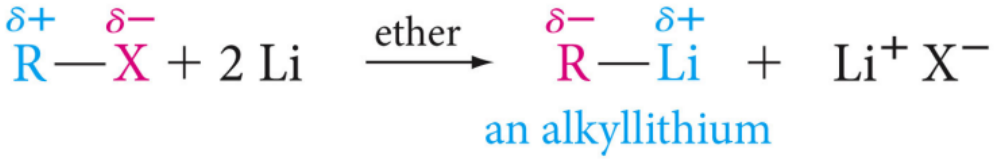
$$\underset{\text{stronger base}}{\overset{\delta-}{R}—MgX} + \underset{\text{stronger acid}}{\overset{\delta+}{H}—OH} \longrightarrow \underset{\text{weaker acid}}{R—H} + \underset{\text{weaker base}}{Mg^{2+}(OH)^{-}X^{-}}$$



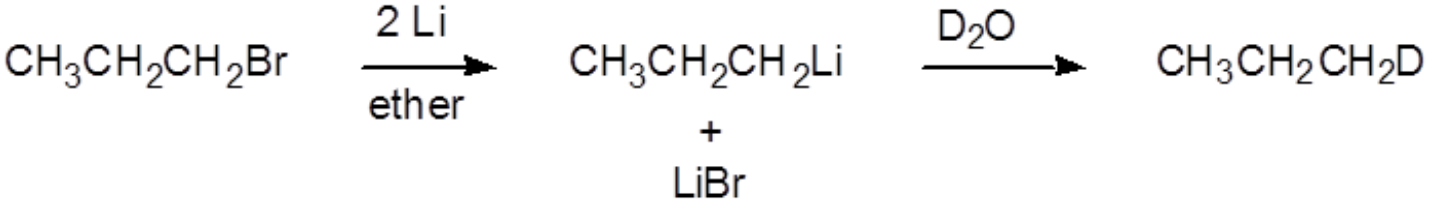
p-bromotoluene *p*-tolylmagnesium bromide *p*-deuteriotoluene

Organometallic Compound

Organolithium compound

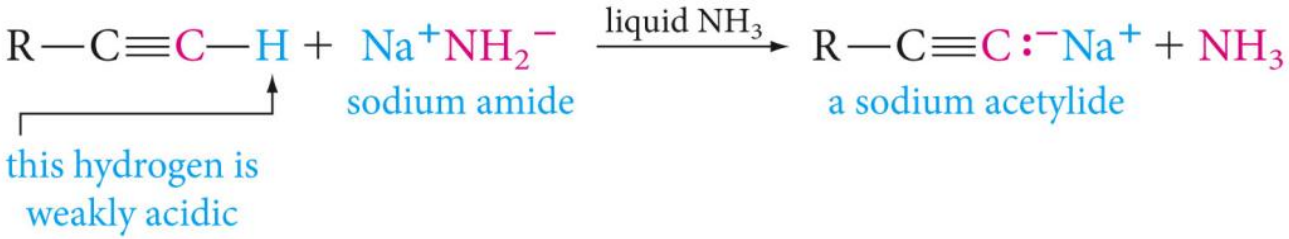


It can be prepared in a manner similar to that for Grignard reagents.

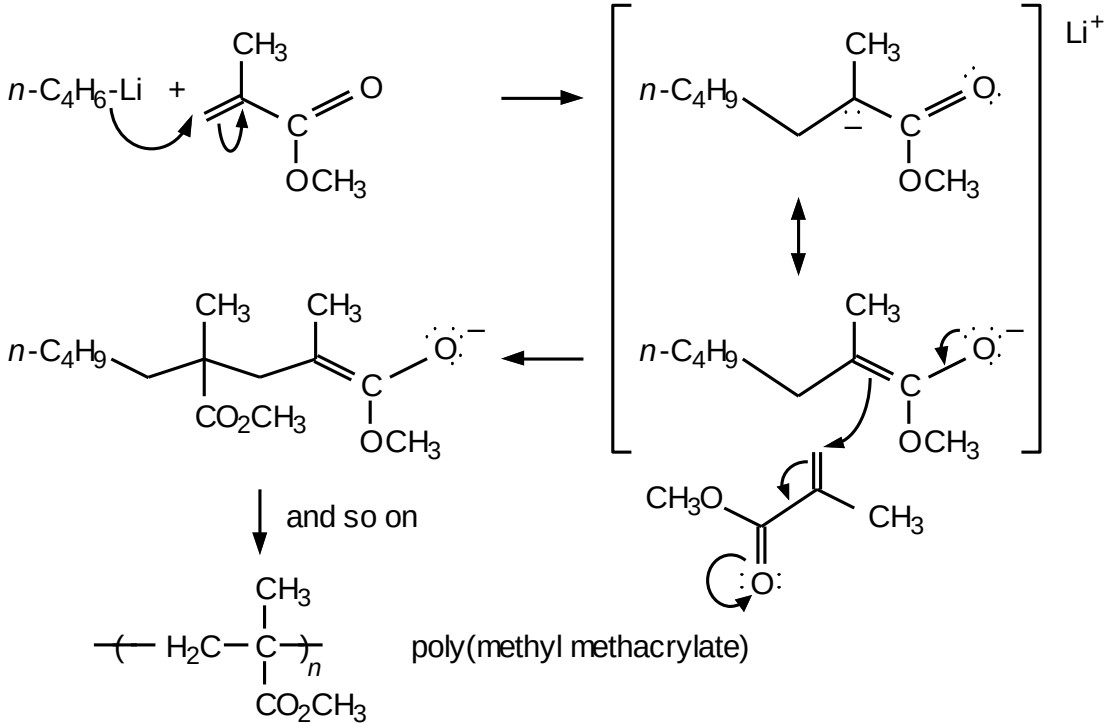


Acetylide

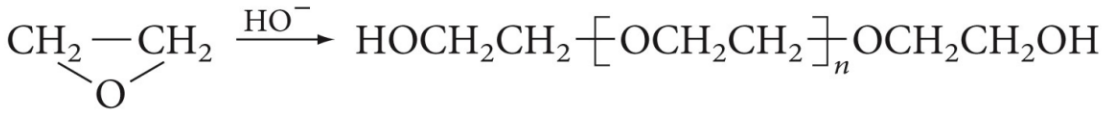
(eq. 3.53)



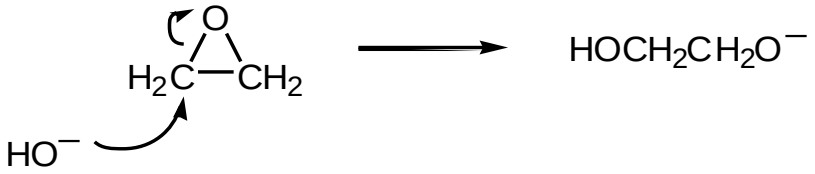
Problem 6. Methyl methacrylate can be polymerized by catalytic amounts of n-butyllithium. Show the intermediate carbanion is resonance-stabilized.

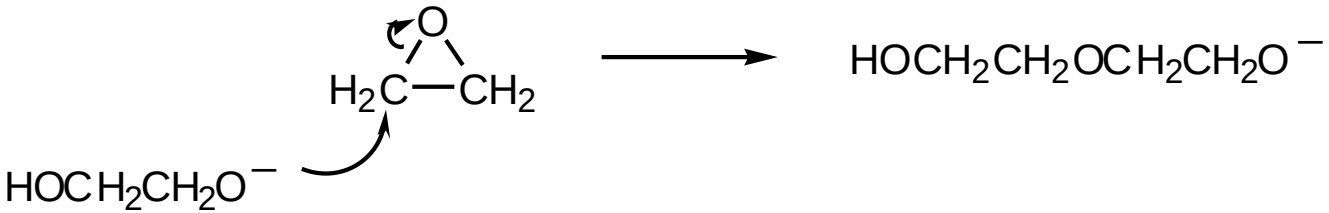


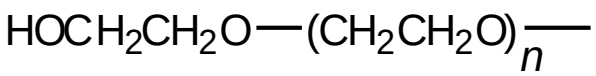
Problem 7. Ethylene oxide can be polymerized by base to give carbowax, a water-soluble wax. Suggest a mechanism for the reaction.



ethylene oxide carbowax





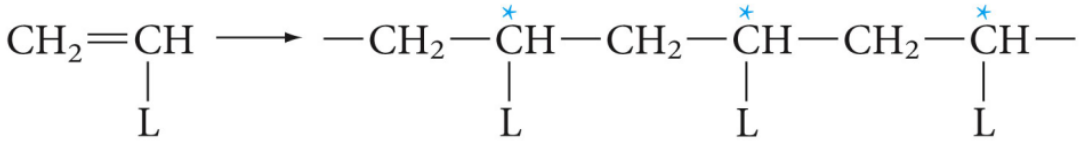


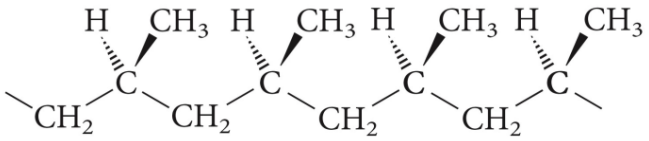
carbowax (PEG, PEO)

5. Stereoregular Polymers; Ziegler-Natta Polymerization

A **Ziegler–Natta catalyst**, named after Karl Ziegler and Giulio Natta, is a catalyst used in the synthesis of polymers of alkenes (olefins). → 촉매를 발견한 공로로 1963 노벨 화학상을 공동 수상

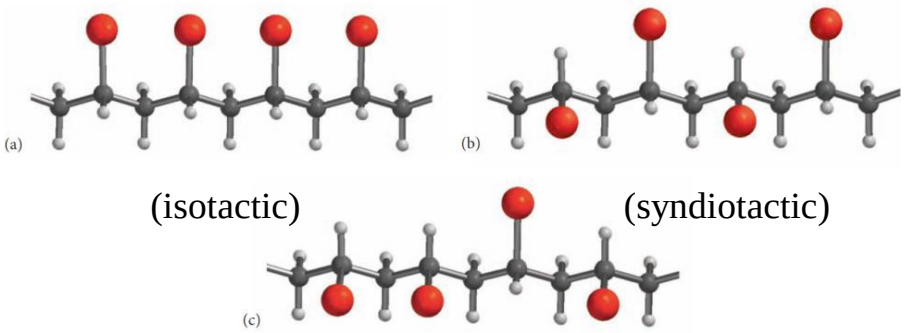
stereocenter





빨강색: L group

- **atactic**: stereocenters have random configurations
- **isotactic**: stereocenters have the same configuration
- **syndiotactic**: stereocenters alternate in configuration



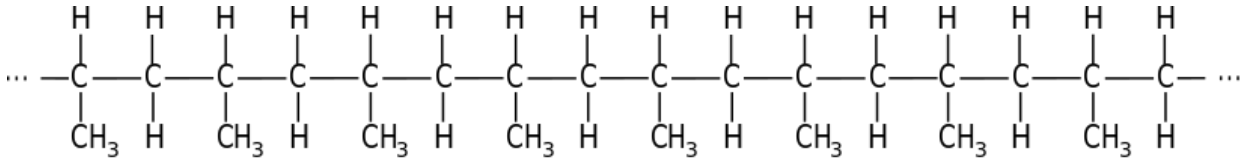
(isotactic) (syndiotactic)

(atactic)

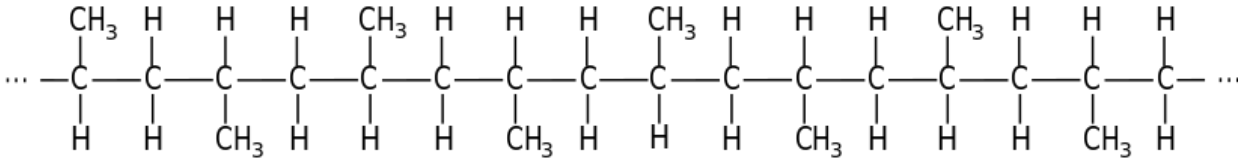
같은 monomer로 출발을 했지만 서로 다른 physical properties를 갖고 있다.

Isotactic and syndiotactic polymer는 crystalline 이고, atactic polymer는 amorphous이다.
Isotactic and syndiotactic polymer는 stereoregular하고, atatctic polymer는 stereorandom하다.

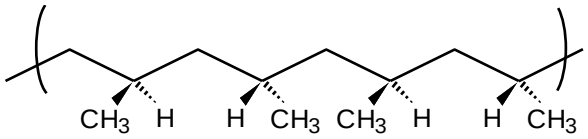
Polypropylene



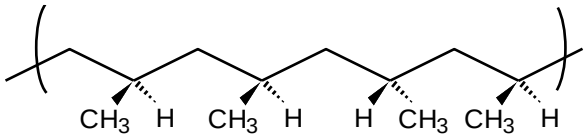
(isotactic)



(syndiotactic)

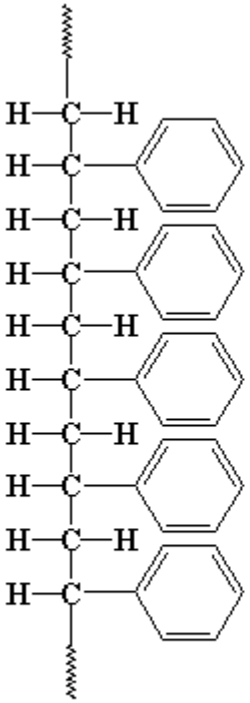


(syndiotactic)

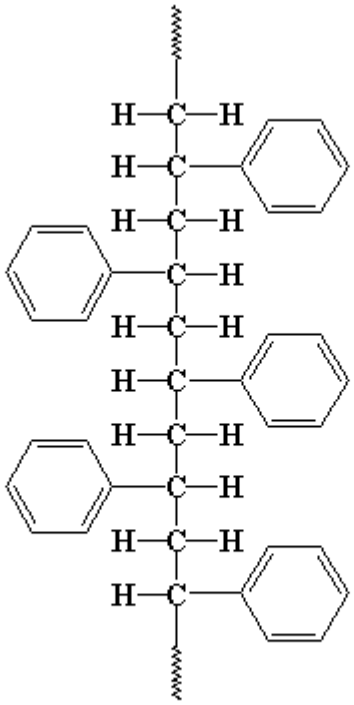


(isotactic)

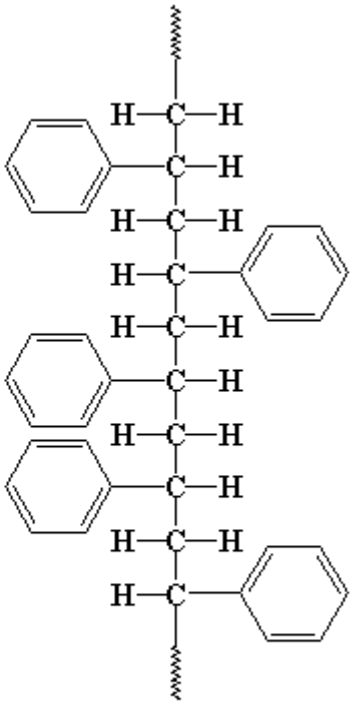
Polystyrene



이소멱틱



신디오멱틱



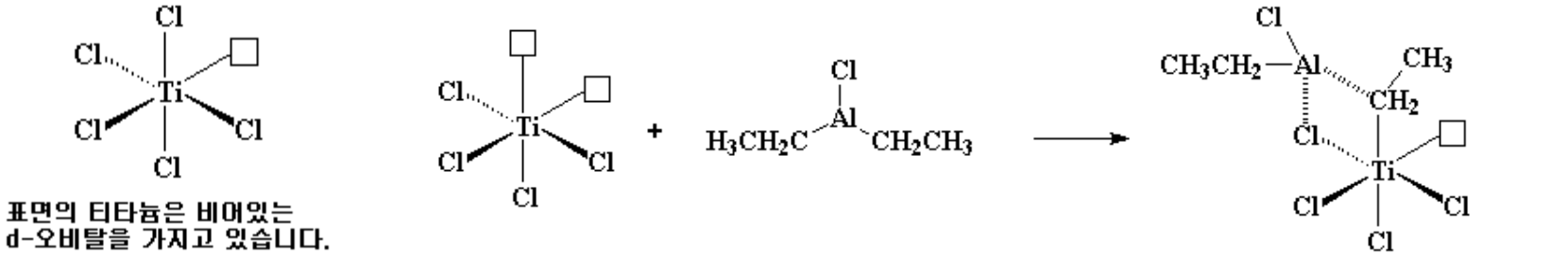
어멱틱

Polymer	T_g atactic	T_g isotactic	T_g syndiotactic
PP	–20 °C	0 °C	–8 °C
PMMA	100 °C	130 °C	120 °C

어떤 고분자 규칙적인 배열을 거진 원자로 되어 있으면 함께 규칙적인 모양으로 쌓여 결정과 섬유로 된다.
어택틱 폴리스티렌과 같이 규칙성이 없으면 결정으로 성장할 수 없다.
분자는 자기와 비슷한 모양으로 생긴 고분자와 규칙적으로 배열될 수 있기 때문이다.
(예: 공과 공이나 상자와 상자를 공간내에 쌓기는 쉬우나 공과 상자를 함께 쌓기는 어렵다.)

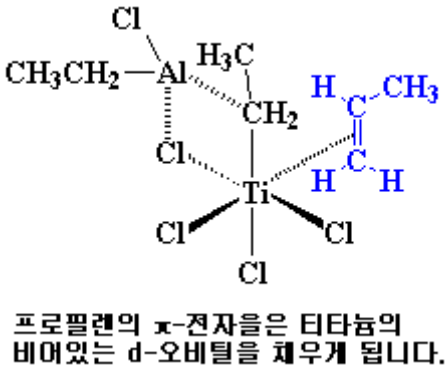
Ziegler and Natta of mixed organometallic catalysts that produce stereoregular polymers was a landmark in polymer chemistry.

One such catalyst system is a mixture of **triethylaluminum** (or other trialkylaluminums) and **titanium tetrachloride**.



이 $Al(C_2H_5)_2Cl$는 하나의 에틸그룹을 불안정한 티타늄에게 전해주고 그 과정에서 하나의 염소원자를 취한다.

이중결합의 pi 전자들이 d orbital을 채운다.



What is glass transition temperature (Tg, 유리전이온도) ?

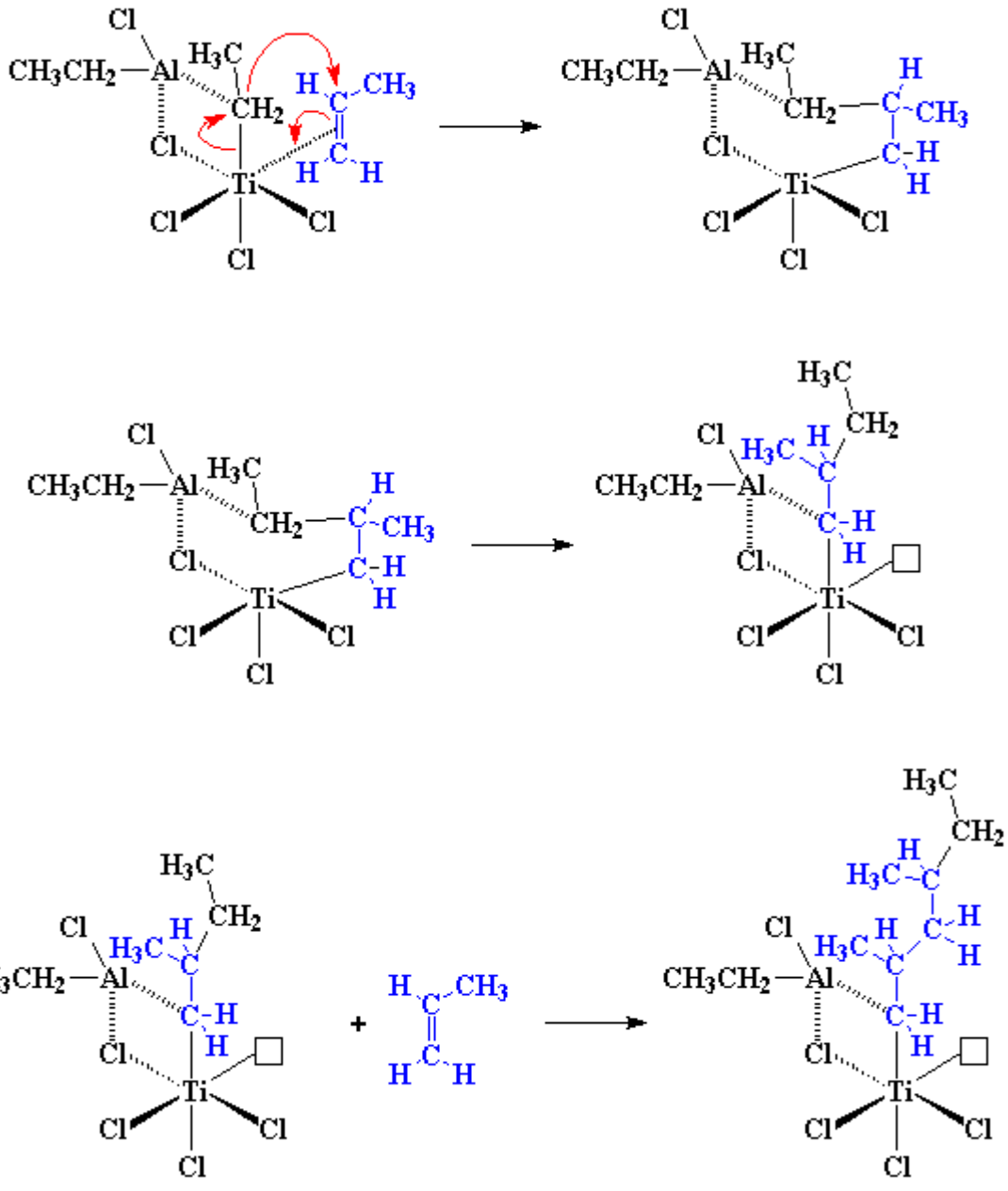
The **glass-transition temperature** T_g of a material characterizes the range of temperatures over which this glass transition occurs. It is always lower than the melting temperature, T_m, of the crystalline state of the material, if one exists.

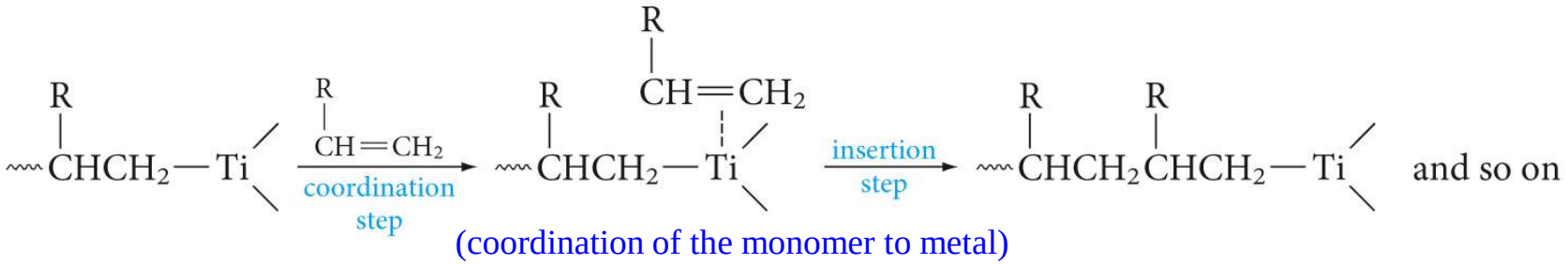
What is glass transition ?

The **glass–liquid transition** or **glass transition** for short is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle "glassy" state into a molten or rubber-like state, as the temperature is increased. An amorphous solid that exhibits a glass transition is called a glass.

Hard plastics like polystyrene and poly(methyl methacrylate) are used well below their glass transition temperatures, that is in their glassy state. Their T_g values are well above room temperature, both at around 100 °C (212 °F). Rubber elastomers like polyisoprene and polyisobutylene are used above their T_g, that is, in the rubbery state, where they are soft and flexible.

In ironing, a fabric is heated through the glass-rubber transition

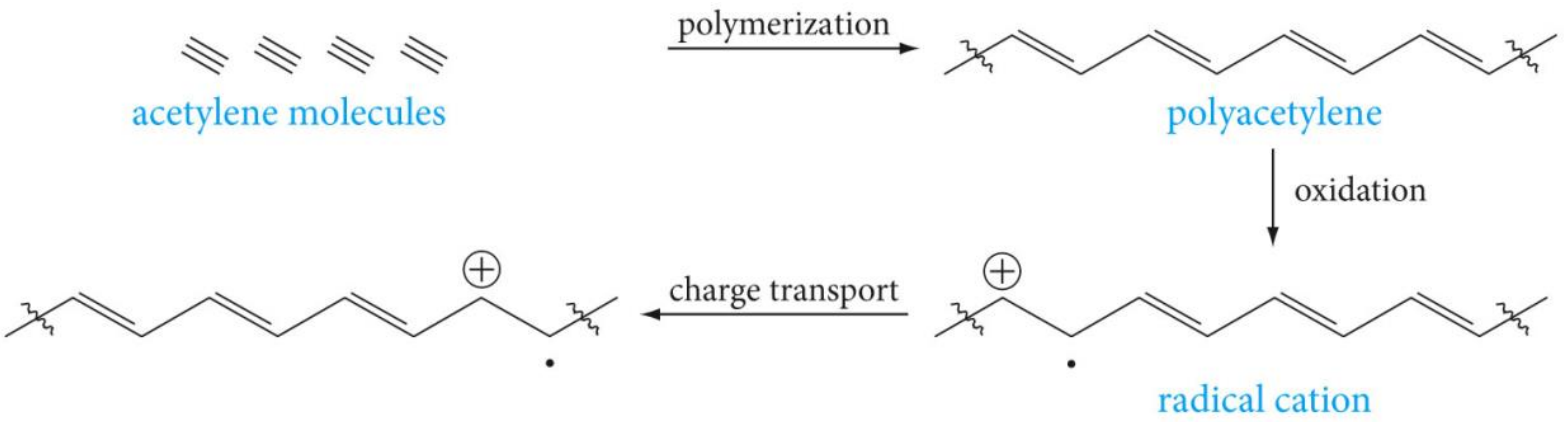


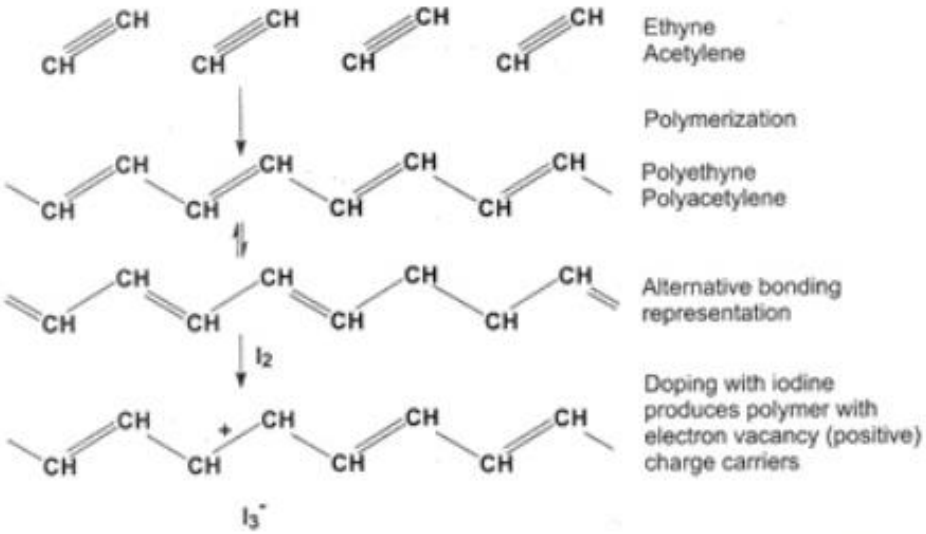


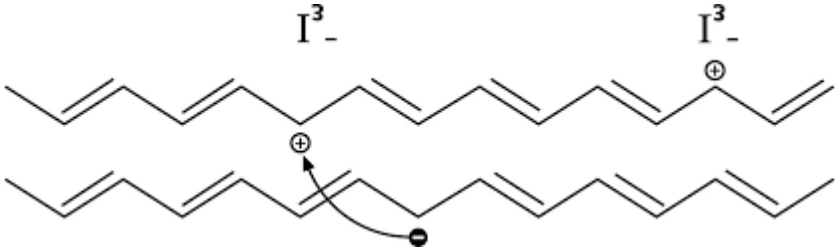
(coordination of the monomer to metal)

- 가지가 많이 달린 폴리프로필렌은 자유라디칼 과정으로 만들어지는 반면에, 지글러-나타 촉매로 만든 폴리프로필렌은 선형구조를 하고 있다.
- 선형의 폴리프로필렌은 가지가 달린 고분자보다 결정성이 더 우수하고, 밀도가 더 크며, 인장 강도(tensile strength)도 더 크고, 경도(hardness) 또한 더 크다.
- 이 고분자는 세탁물 표백제와 세제를 담는 용기, 혼합용 사발, 냉장고 용기, 그리고 장난감과 같이 주형을 떠서 만드는 가정용품, 그리고 사출 성형으로 만드는 플라스틱 관이나 도관 등을 만드는데 이용한다.
- Coordination and insertion occur in a stereoregular manner and can be controlled to give either an isotatic or a syndiotatic polymer.

폴리아세틸렌 (polyacetylene) and conducting polymer







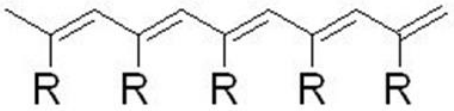
Substituent Effects:

Solubility

Conductivity

doped with I_2

> 10 S/cm



R = Me, Br, Cl ..... etc.

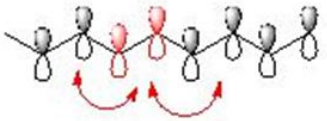
doped with I_2; < 0.001 S/cm

Steric hindrance effect of substituent is very important

Because,

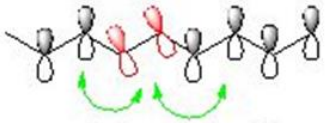
- R group destroy the coplanarity of the conjugation system
- Reduce electron mobility of intrachain and interchain

Coplanarity is the key for gaining high conductivity



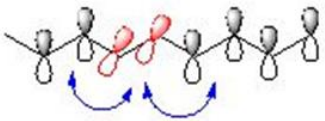
full overlaping

- Coplanarity gives best overlaping between π orbitals



partial overlaping

- Distortion from coplanarity reduces the electron mobility



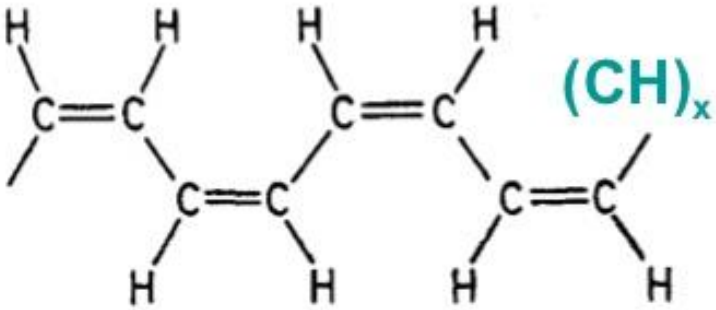
no overlaping

- 90^0 distortion lead to conjugation defects

In the beginning…

H. Shirakawa, A.G. MacDiarmid, and A. J. Heeger first reported polymer conduction from oxidized ("doped") **polyacetylene**

J. Chem. Soc., Chem. Commun. ***1977***, *578.*



$\sigma = 10^{-9}$ S/cm (insulator)

↓

$\sigma = 38$ S/cm (conducting plastic)

↓

2000 Nobel prize in Chemistry

Alan McDiarmid dances the Mauri's 'Haka' during the 'Nobel' ceremony in Stockholm, 2000

- 1986, Organic photovoltaic cell OPV (Ching W Tang, Kodak)
- 1986, Orgaic field-effect transistor OFET (H Koezuka, Mitsubishi)
- 1987, Organic light-emitting diode OLED (Ching W Tang, Kodak)

Conducting organic polymer는 실리콘과 같은 metal을 대체할 수 있는 물질이다.

Iodine으로 doping할 경우 organic polymer의 전도성이 증가한다. (Iodine은 산화제로서 polyacetylene을 radical cation으로 만든다.)

The charge can move along the polyacetylene chain and also be transferred from one polyacetylene chain to another.

Organic polymers are lightweight and strong yet flexible.

이러한 전도성 고분자의 발견으로 2000년에 Shirakawa, MacDiarmid, Heeger가 공동으로 노벨 화학상을 수상하였다.