Chapter. 7

Reactions of Synthetic Polymers

Reactions in the Main Chain

Reactions in the Side Chains

Surface Reactions

Reactions in the Main Chain

Reasons for interest in main-chain reaction

1. Polymer properties can be changed

2. Understanding of skeletal cleavage reactions;
   then design of stable polymers are possible

3. The choice materials for photoresists;

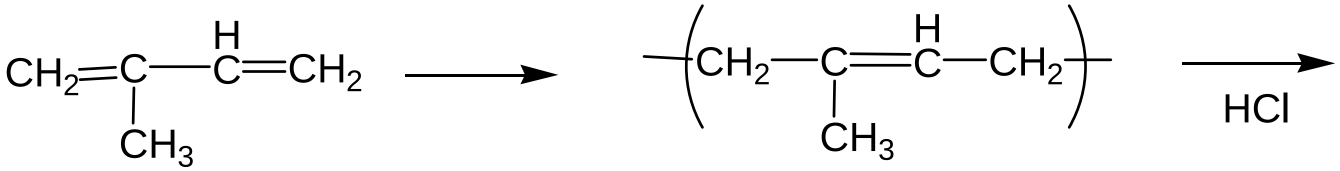
Addition reactions

Production of nonflammable rubber;

Natural rubber or polybutadiene is dissolved in CCl_4*, then* Cl_2 *gas is bubbled (very complex reaction; addition, substitution crystallization)*

Addition of Cl_2 **to polybutadiene;**

Addition of HCl to polyisoprene; produces rubber hydrochloride



$$CH_2{=}\underset{CH_3}{C}{-}\overset{H}{C}{=}CH_2 \longrightarrow \left(CH_2{-}\underset{CH_3}{C}{=}\overset{H}{C}{-}CH_2 \right) \xrightarrow[HCl]{}$$

Reactions that generate skeletal Unsaturation

Metathesis

$$\mathrm{RCH{=}CHR} \quad + \quad \mathrm{R'CH{=}CHR'} \longrightarrow \mathrm{2RCH{=}CHR'}$$

Hydrolytic chain cleavage; *Hydrolysis*

Enzymatic degradation of synthetic polymers

Aliphatic polyesters, polyanhydrides;
biological breakdown !

Polyamides, fluorinated polymers, PE, PP,
PC….; resistant to biological attack
Until now !

고분자의 공해문제 및 이를 극복하는 방법

1. 고분자 제조공정 개발: 고분자 자체는 인체에 무해함
2. 지구상에 영원히 공해물질?
   a. 생분해성 고분자를 이용
   b. **고분자를 분해하는 미생물의 개발**

⇒ 생분해성 고분자의 제조방법
a. 화학적합성 방법
b. 미생물은 신진대사과정 중 배출하는 고분자

⇒ 생분해성 고분자의 응용
일반고분자(가격?), 수술용 실, 약물전달 체계, 조직공학

Oxidation reactions

At room temperature without light; oxidation is very slow
Higher temp. or UV irradiation; faster oxidation
ex) appreciable decomposition of PE for 2 years outdoor

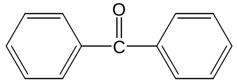
Oxidation of polymers;
increasing brittleness, deterioration of mechanical strength, yellowing in color

Oxidative degradation; through free-radical rxn

Chain cleavage by (2) and (8)

Backbiting

PS is susceptible to photodegradarion.
Polybutadiene and polyisoprene are easily attacked by ozone or oxygen



benzophenone

Additives to retard the degradarion
Substituted benzophenone; UV absorber
Phenolic compounds; radical chain terminator
Carbon black; UV screening and chain terminator

Epoxidation of polymers;

High-Temp. degradation reactions

The reasons for thermal instability of organic polymers

1. Polymerization-depolymerization equilibrium (chap. 10)
2. C-C bond dissociation energy
3. C-C bond chemical stability (oxidatively unstable)
4. Structural abnormality (branch points are weak)
5. Terminal site is more reactive (depolymerization can be initiated)
6. Unzipping process (long chain materials)

Common thermal decomposition mechanism

1. Polymerization-depolymerization of vinyl monomers
2. Random chain fragmentation through chain cleavage
3. Degradation initiated by side group structure (ex. PVC, poly(vinylacetate))

1. Polymerization-depolymerization of vinyl monomers;

PMMA, poly(α-methyl styrene) and PTFT undergo 100% conversion to the corresponding monomer

Ex) PMMA;

at 220 °C half of the polymer unzip (polymers terminted by unsaturated groups; terminated by disproportionation)

at 350 °C all the polymers decomposed

Ex) PS;

at 350 °C polymers decomposed to monomer, dimer, trimer, tetramer in 40:10:8:1 ratio; back biting

2. Random chain fragmentation through chain cleavage for PE, PP, polyamide, and polyesters

Ex) PE and PP; totally random decomposition

Polyamide; initiated by homolytic cleavage of –NH-CH_2-
water (hydrolysis of amide) and CO_2 also liberated
branch formation

Polyester; decomposition between 300 °C and 550 °C yields CO_2, acetaldehyde, terephthalic acid, water, methane, acetylene

Reactions involving the Side Groups

Reasons for the side chain reaction

1. Polymer properties (bulk & solution) can be changed

2. To develop grafting and x-linking reaction

3. Attachment of active groups (catalytically or biologically)

4. Surface modification

Lower reactivity of polymer side group reaction

1. Sterically inhibited due to the randomly coiled polymer chains
2. Neighboring group polar or steric effect

Hydrolysis of side-group structures

Hydrolysis of the ester or amide in the polymer side chain; uncharged groups remain !

The negatively charged groups retard the ^{-}OH groups

In some cases, the charged carboxylate ion can accelerates the rate of hydrolysis

Geometric factor !

Isotactic PMMA undergoes the hydrolysis more rapidly than the syndiotactic and atactic PMMAs.

The preparation of poly(vinyl alcohol).

Direct polymerization is not possible!

Although the product is unchared, still 100% conversion is very difficult!

Polymer-supported organic reactions

The advantages of using a reagent, catalyst, or substrate attached to an insoluble polymer support

1.The purification

Centrifuge and filtering can be used

2. Recovering and recycle is easy

3. Automation process is possible (separation the reagent from the product is easy)

Two aspects

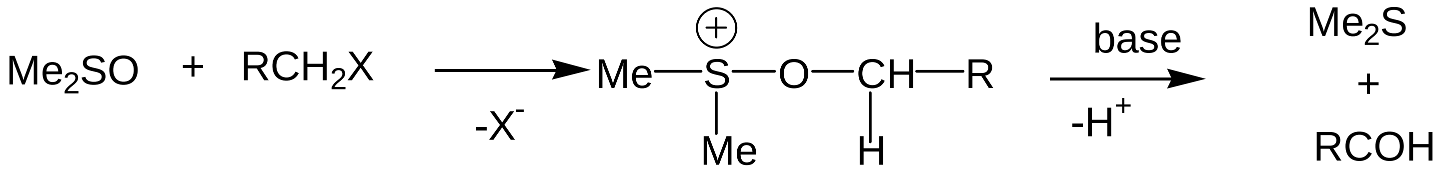
1. **The binding of the reagent, catalyst, or substrate to a polymer.**
2. **The reaction of the polymer-supported materials**

Chloromethylation of polystyrene (linear or x-likned)

The x-liked one can be a polymer support (ex. bead)

Thioether unit; the reaction with KSR

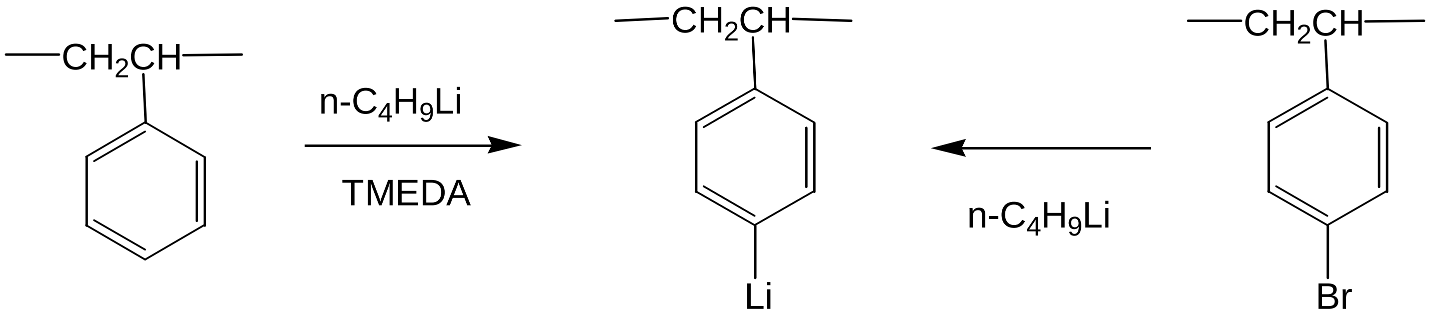
Aldehyde: the reaction with DMSO in base



$$Me_2SO + RCH_2X \xrightarrow[-X^-]{} Me-\overset{\oplus}{\underset{Me}{S}}-O-\underset{H}{CH}-R \xrightarrow[-H^+]{base} Me_2S + RCOH$$

Reactions based on lithiopolystyrene derivatives

Preparation of lithiopolystyrene



Reactions of lithiopolystyrene

Polymer-bound transition metal

Applications in the heterogeneous catalysts; easy recovery (cost effective)

Use phosphine ligand bound to x-liked polystyrene beads

Graft Polymer Formation

How?

1. **Free radical initiator abstract a hydrogen from polymer chains**
2. **Through chain transfer of propagating chain with polymer chain**
3. **Irradiation of UV, gamma ray, electron beam, x-ray to the polymer**
4. **Polymer mixtures are mechanically stirred with heating**

X-linking reaction

1. **Heating the polymer having aliphatic side groups with radical initiator such as benzoyl peroxide**
2. **Introduction of unsaturated aliphatic side groups to the polymer, then free radical initiation.**
   Ex) rubber x-linking
3. **Use functional groups**
   ex) polymers with hydroxy end groups are reacted with multi functional compounds such as tri-isocyanated

Photolithography using polymer side chain reactions

See p 117 Figure 5.1 (lithography process)

Positive resist; PVA is soluble alcohol or base solution (washing solvent)

Surface reactions of polymers

Bulk property; flexibility, strength, rigidity ………
Surface property; resistance to corrosive reagent,
solvents fuels, sunlight, oxidation……

Surface fluorination

To produce hydrophobic surface;

biomedical compatibility, oxidation resistance, solvent or fuel resistance

Surface nitration and sulfonation

immobilizatio of enzyme

Surface oxidation

To produce hydrophilic surface;

Ex) oxidation of PE surface with chromic acid to produce
carboxylic acid surface.
adehesion, metal binding characteristics can be imparted

Other systems