생유기화학
(Bioorganic Chemistry)

Synthetic Polymer-I
(합성고분자-1)

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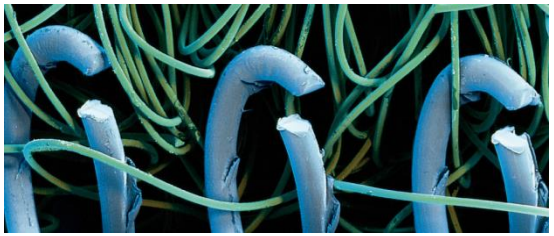
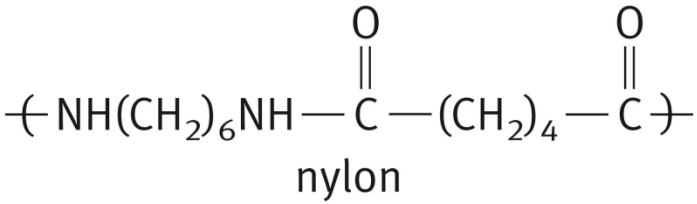
나노화학공학과

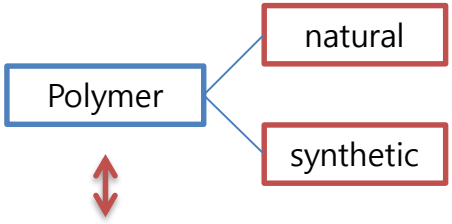
임 정 균 교수



Zippers and shoelaces are made of nylon.



Polymer (macromolecules) : built by repetitive linking of many smaller units called monomers (단량체).



carbohydrate, protein, nucleic acid

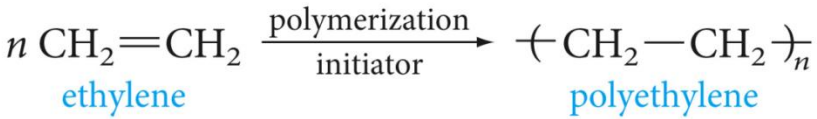
Nylon, Teflon, Styrofoam, polyurethane, polyethylene terephthalate (PET)

(small) molecule

1. Classification of Polymers

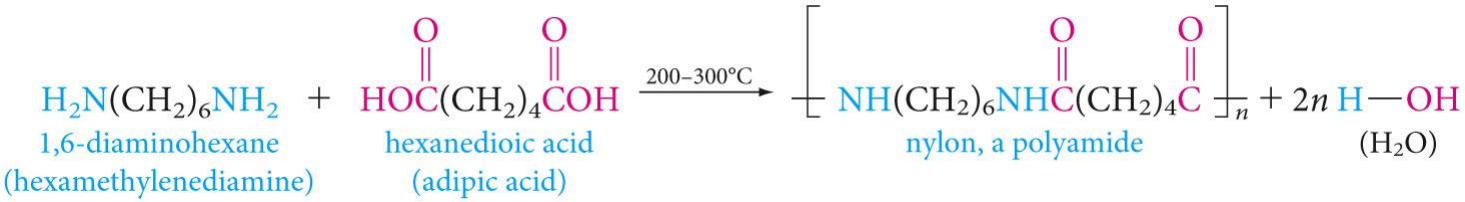
Chain-growth polymer (addition polymer): 연쇄성장 고분자

- **Free-Radical** Chain-Growth Polymerization
- **Cationic** Chain-Growth Polymerization
- **Anionic** Chain-Growth Polymerization



- alkene이 monomer로 작용
- catalyst required for initiation
- polymer는 monomer의 모든 원자들을 포함한다.

Step-growth polymer (condensation polymer) 단계 성장 고분자

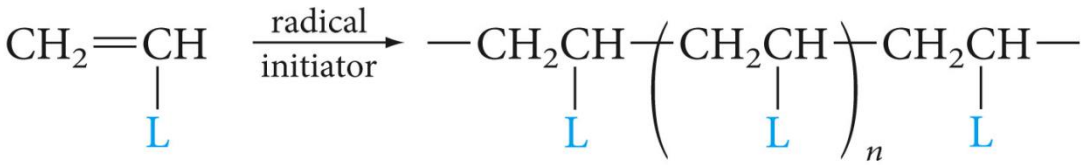


- 두 개의 서로 다른 작용기가 만나서 반응을 일으키고 물과 같은 작은 분자 하나를 내놓을 수 있다.
- 폴리머는 monomer의 모든 원자들을 포함하지 않는다.
- 각 monomer는 다수의 작용기를 갖고 있다.
- Monomers usually appear in alternating order in the polymer chain.

2. **Free-Radical** Chain-Growth Polymerization (자유라디칼)

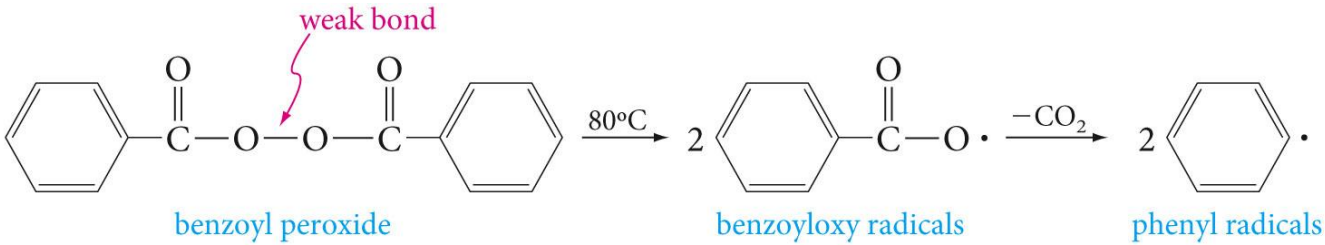
Free radical : an atom, molecule, or ion that has unpaired valence electrons
highly chemically reactive towards other substances
They often dimerize or polymerize if they come in contact with each other.

활성산소도 자유라디칼의 한 종류로서 세포 내에서 많은 원치않는 부반응을 일으켜 세포를 파괴시킬 수 있다.



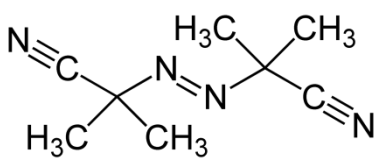
vinyl monomer — vinyl (or chain-growth) polymer

initiator :

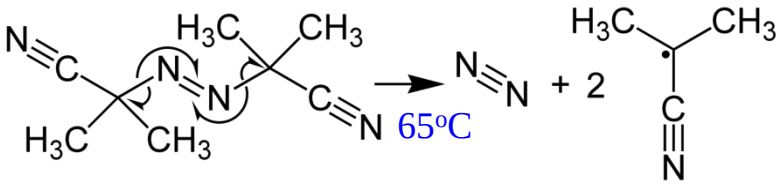


benzoyl peroxide — benzoyloxy radicals — phenyl radicals

explosive



Azobisisobutyronitrile (AIBN)



Reactive Oxygen Species (ROS)

● = unpaired electrons

oxygen
O_2

Peroxide
O_2^{-2}

Hydroxyl ion
OH^-

Superoxide anion
$O_2^{\bullet-}$

Hydroxyl radical
•OH

생체 내 활성산소의 종류와
발생하는 경로들

여기에 stress도 포함

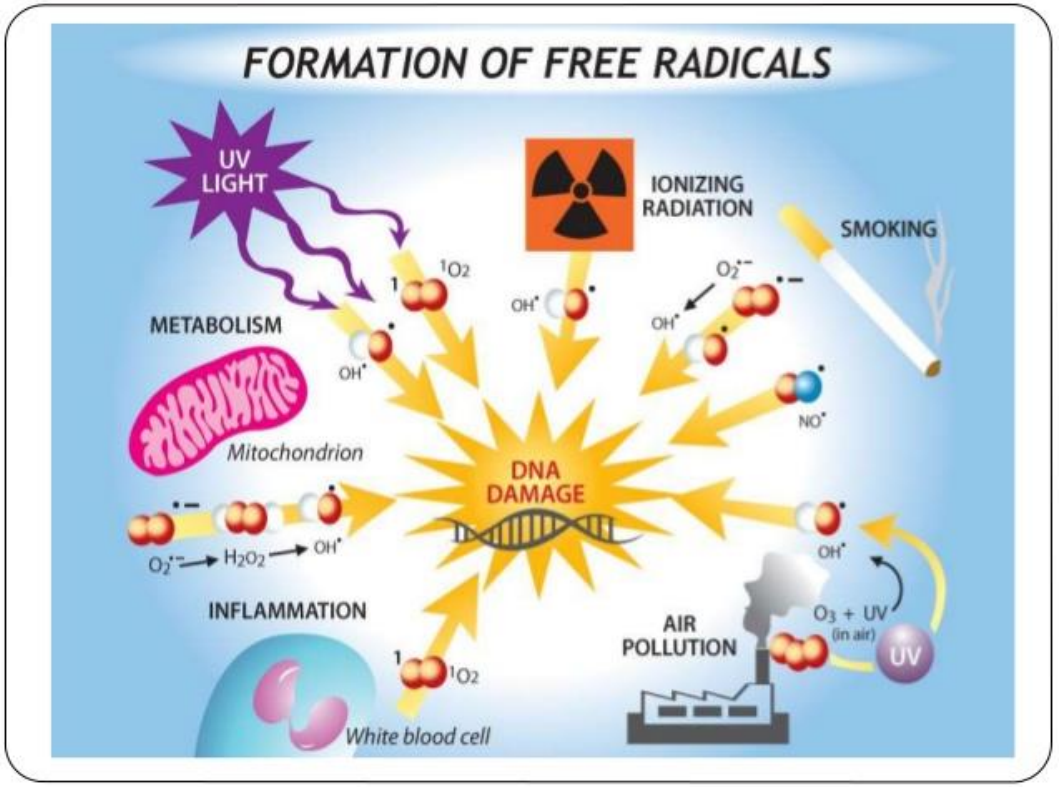


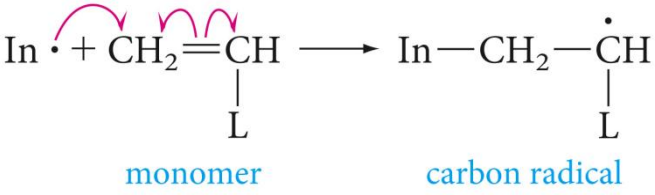
Table 14.1 Some Commercial Chain-Growth (Vinyl) Polymers Prepared by Free-Radical Polymerization

Monomer name	Formula	Polymer	Uses
ethylene (ethene)	$CH_2{=}CH_2$	polyethylene (PE)	sheets and films, blow-molded bottles, injection-molded toys and housewares, wire and cable coverings, shipping containers
propylene (propene)	$CH_2{=}CHCH_3$	polypropylene (PP)	fiber products such as indoor–outdoor carpeting, car and truck parts, packaging, toys, housewares
styrene	$CH_2{=}CH$–C$_6$H$_5$	polystyrene (PS)	packaging and containers (Styrofoam), toys, recreational equipment, appliance parts, disposable food containers and utensils, insulation
acrylonitrile (propenenitrile)	$CH_2{=}CHCN$	polyacrylonitrile (Orlon, Acrilan) (PAN)	sweaters and other clothing
vinyl acetate (ethenyl ethanoate)	$CH_2{=}CH{-}OCCH_3$ (O)	polyvinyl acetate (PVA, PVAc), polyvinylalcohol(PVA)와 혼동X	adhesives, latex paints
methyl methacrylate (methyl 2-methylpropenoate)	$CH_2{=}C(CH_3){-}COCH_3$ (O)	polymethyl methacrylate (Plexiglas, Lucite) (PMMA)	objects that must be clear, transparent, and tough (간판, 가로등, 자동차등) a lightweight or shatter-resistant alternative to glass.
vinyl chloride (chloroethene)	$CH_2{=}CHCl$	polyvinyl chloride (PVC)	plastic pipe and pipe fittings, films and sheets, floor tile, coatings
tetrafluoroethylene (tetrafluoroethene)	$CF_2{=}CF_2$	polytetrafluoroethylene (Teflon) (PTFE)	coatings for utensils, electric insulators (hydrophobic, non-reactive(내화학성 우수), 절연성, 마찰계수가 어떠한 고체보다 낮음, 들러붙지 않음, PTFE에 대한 용매가 없음)

In 1941, Dow Chemical invented a Styrofoam process. In 1954, non-stick pans under the brandname Tefal.

In · : initiator radical

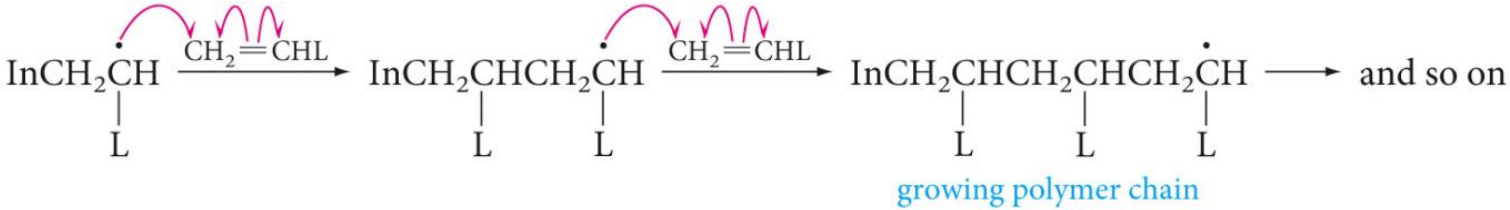
Initiation step:



Initiator adds to the least substituted carbon.
Why? (two reasons)

1. less hindered
2. L stabilizes carbon radical

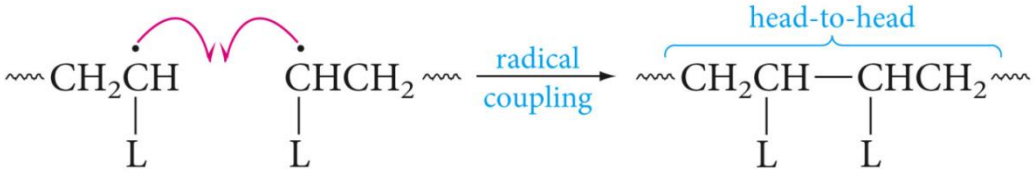
Propagation step:



Linkage in head to tail manner, 수천개~ 수만개의 monomer의 polymerization

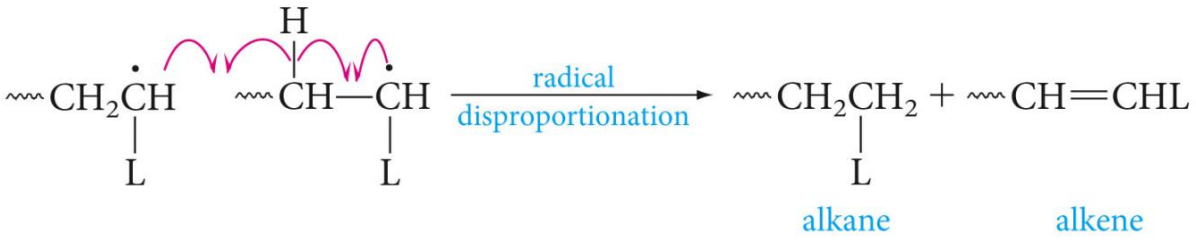
Termination step:

(radical coupling)



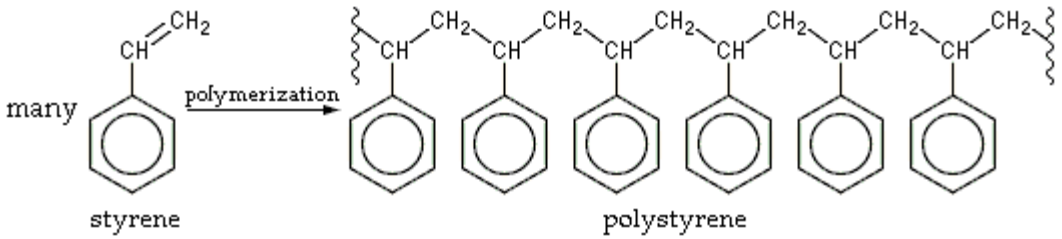
모두 라디칼 소멸

(radical disproportionation)



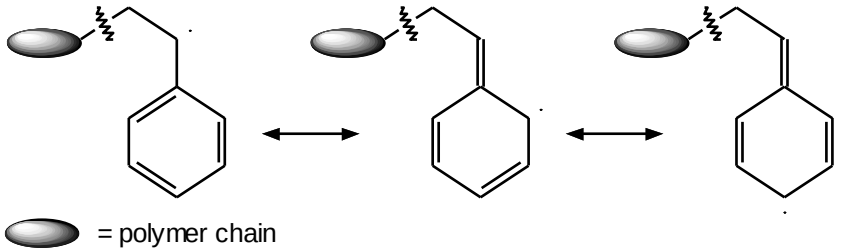
(수소 한 개가 붙으면서 alkene이 형성)

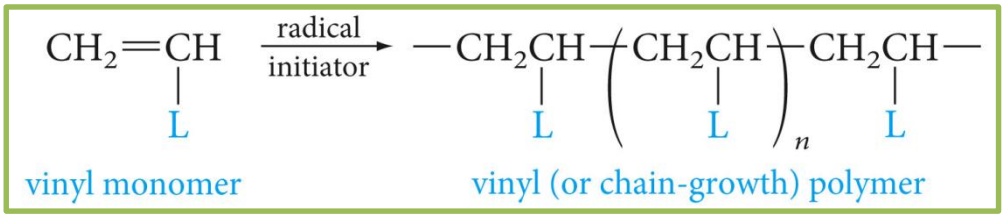
The extent of the chain propagation reaction depends on several factors, some of which are the reaction conditions (temperature, pressure, solvent, concentration of monomer, catalyst, for example); the nature of the monomer, especially the substituent L; and the rates of competing reactions, which may terminate the chain.



Problem 1. In PS, draw the intermediate radical, and show how it is stabilized through resonance.

The odd electron can be delocalized to the ortho and para carbons of the phenyl group.

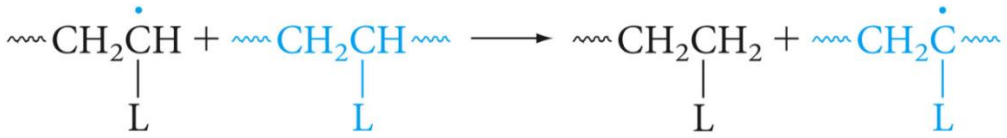




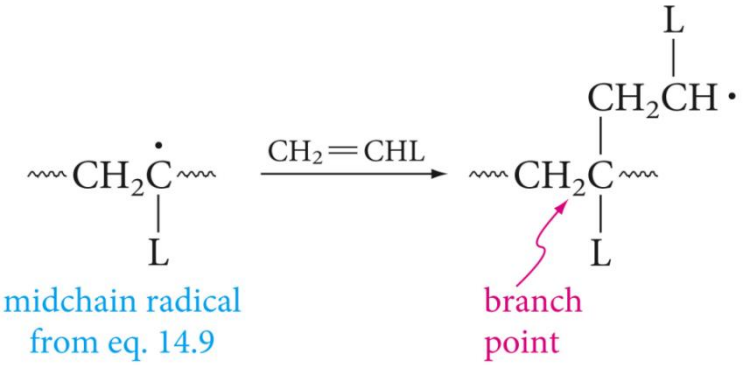
linear polymer only

How about branched chains?

Chain-transfer reaction (라디칼이 있던 폴리머는 라디칼 소멸, 새로운 물질에 라디칼 생성)



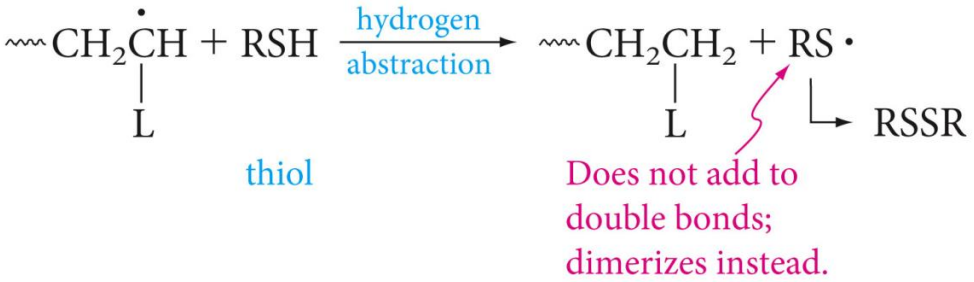
- 성장하고 있는 고분자가 다른 고분자 사슬의 수소원자를 잡아간다. (말단이 아님)
- 이 때 성장은 멈추지만, 수소가 떨어져나간 고분자는 새로운 라디칼이 형성된다.



- 새로운 propagation step이 일어나는데 branch(곁사슬)가 형성된다.
- 고분자 합성단계에서 두 가지 경쟁 반응: 1. chain propagating step, 2. chain-transfer step.
- Monomer의 종류, solvent, 압력, 농도, 온도 등에 따라서 두 가지 경쟁 반응의 우위가 달라진다.

- Radical addition이 매우 빠를 경우, polymer는 linear 해질 것이다.
- Radical addition 반응이 느릴 경우, chain-transfer reaction의 가능성이 높아서 branch가 많아질 것이다.
- 예를 들어 chain-transfer reaction이 radical addition의 1/10 속도라면, 10개의 monomer들이 linear하게 합성이 될 때 1개의 branch가 형성될 것이다.

다른 Chain-transfer reaction의 예 (폴리머의 분자량 또는 사슬 길이 조절)



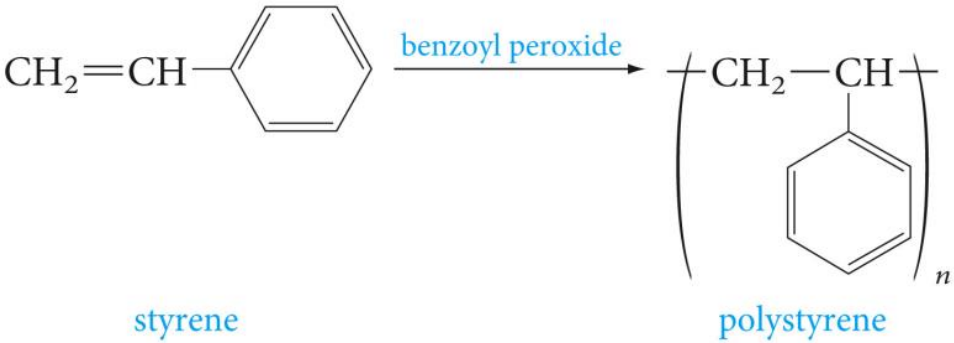
RS · 은 reactive하지 않아서 polymerization하지 않고 disulfide가 된다.

Thiol이 chain terminator가 된다. Polymerization도 중 thiol을 addition하면 된다.

Chain-transfer reactions can be used to control the molecular weight of a polymer.

Therefore, thiols are chain terminators, and when added to a polymerization reaction mixture in small amounts, they limit the polymer chain length.

Free radical chain growth polymerization은 매우 빨리 일어나기 때문에 1000개 이상의 monomer들이 사슬을 이루는데 1초 이내에도 가능하다.



PS의 평균 분자량은 1~3 백만이 될 수 있다. (n = 10,000~30,000)

Polystyrene popcorn used in packaging

Amorphous (무정형): 고분자 사슬들이 불규칙하게 배열, Chains are not regularly aligned, as in crystal.

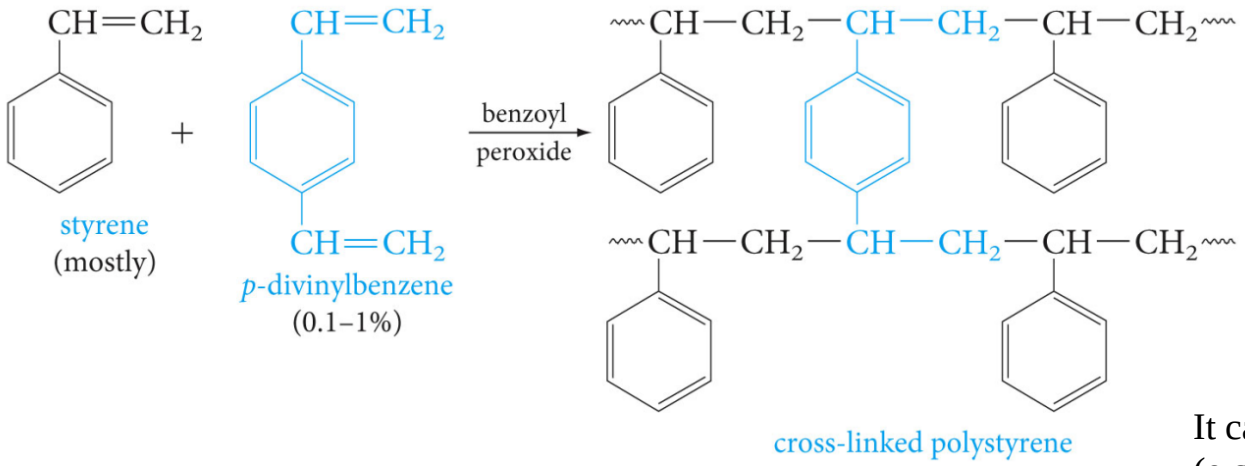
Thermoplastic (열가소성): polymers can be reshaped by melting and heating, 녹일수 있는 적절한 용매가 있음.

Thermosetting (열경화성): 열을 가해도 녹지 않는다. 높은 온도에서 비가역성 분해가 일어남

Cross linking (가교결합): 폴리머가 단단하게 강하게 만들어진다. 가교가 없는 경우 일반적으로 열가소성이다.

PS is an amorphous, thermoplastic polymer.

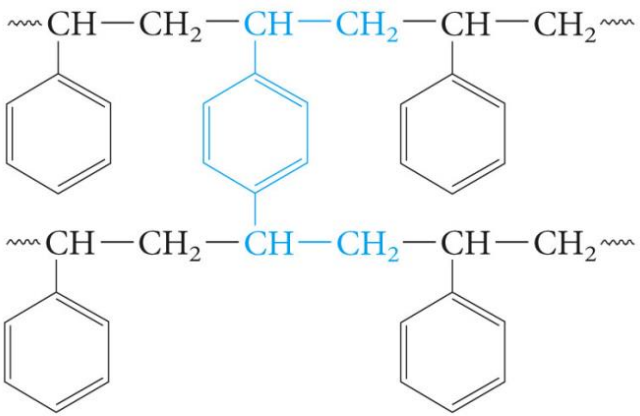
Styrofoam: 가공과정에서 pentane과 같은 저분자량의 탄화수소를 첨가하면 만들어진다. 폴리머가 가열될 때 pentane이 증발하면서 폴리머를 발포시키고 폴리머 표면 내외에 기포가 생겨난다.



합성시 소량의 *p*-divinylbenzene을 첨가하면 cross linking 현상이 일어난다.

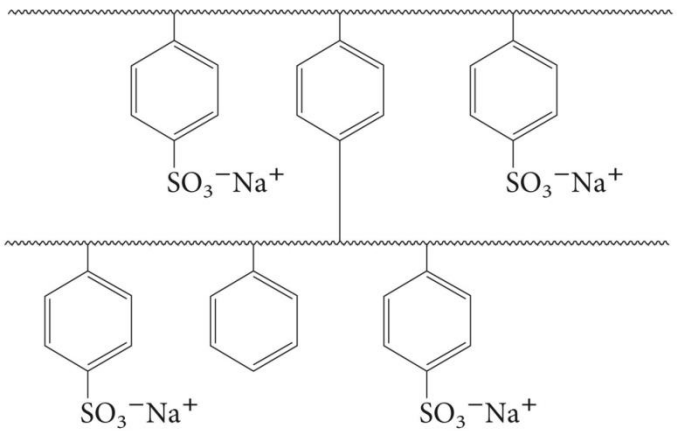
합성된 고분자는 매우 단단하고 유기용매에도 덜 녹는다.

It can be rigidified through cross-linking.
(e.g. 요구르트 용기, 씨디케이스)



cross-linked polystyrene

sulfonation

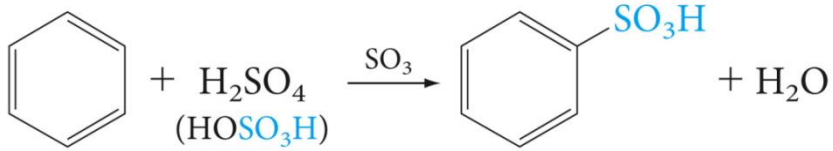


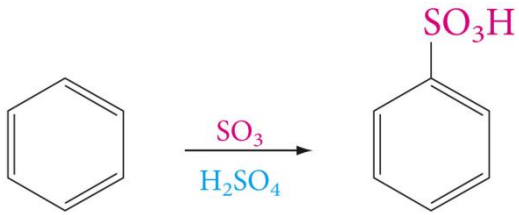
schematic structure of an ion-exchange resin

ion-exchange resin(이온 교환 수지)

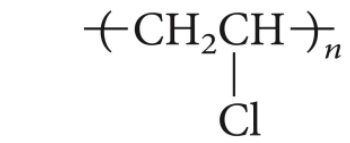
Ca^{2+}, Mg^{2+}이온등을 가지는 경수를 Na^{+}이온들로 교체해준다.

Aromatic ring의 Sulfonation 반응



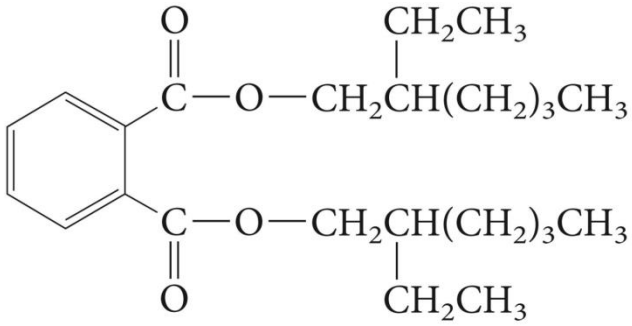


benzenesulfonic acid



polyvinyl chloride (PVC)

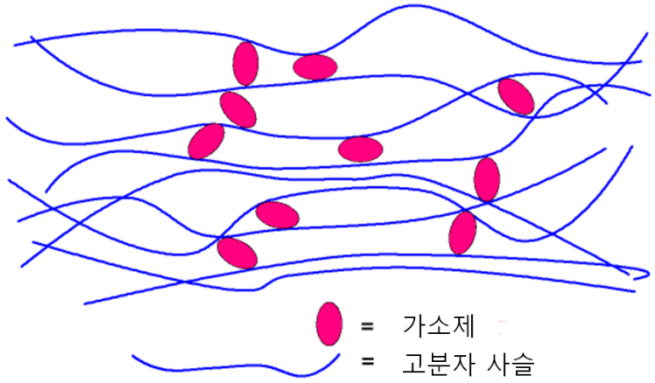
- PVC는 head-to-tail구조이며 매우 딱딱한 폴리머.
- plasticizer를 첨가하면 부드럽게(soft) 만들 수 있다.
- 이 때 plasticizer는 polymer 사슬들 사이에서 윤활제(lubricant) 역할을 한다.
- PVC의 T_g를 많이 낮추는 역할을 한다.



bis-2-ethylhexyl phthalate
(a plasticizer)

Plasticizer (가소제):

- 폴리머 사슬들 사이로 들어가 윤활제 역할을 하여 단단한 폴리머를 부드럽게 만들 수 있다. (분자 수준에서 spacer 역할)
- 딱딱한 플라스틱에 유연성 및 탄성을 주어 성형하기 쉽도록 하는 등 제품으로서의 특성을 갖출 수 있도록 첨가되는 물질을 말한다.
- 그러나 플라스틱 본체와 결합되지 않고 떠 있는 상태로 존재하기 때문에 작은 충격에도 용출되기 쉽다.



- 플라스틱은 긴 끈 같은 분자가 모여서 된 것으로, 분자 사이에 서로 끌어당기는 힘이 강할수록 딱딱해짐.
- 이때 분자 사이에 가소제가 끼어들면 플라스틱 분자 사이의 직접 끌어당기는 힘이 약해져 잘 휘게 된다.

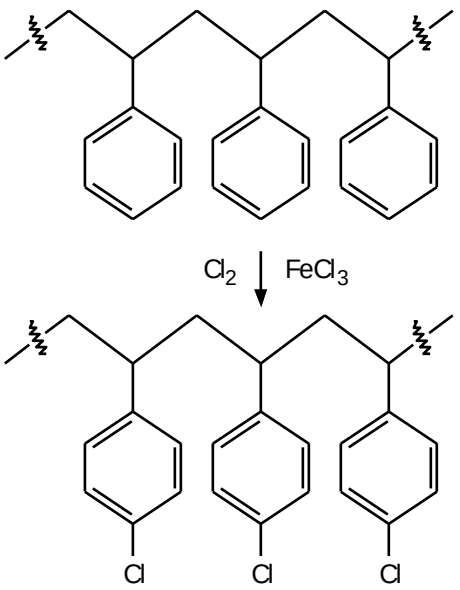
PVC는 바닥 타일, 비닐 제품(인조가죽), 플라스틱 파이프, squeeze bottle등을 만드는데 사용한다.

Problem 5 Using a three-monomer segment, write an equation for

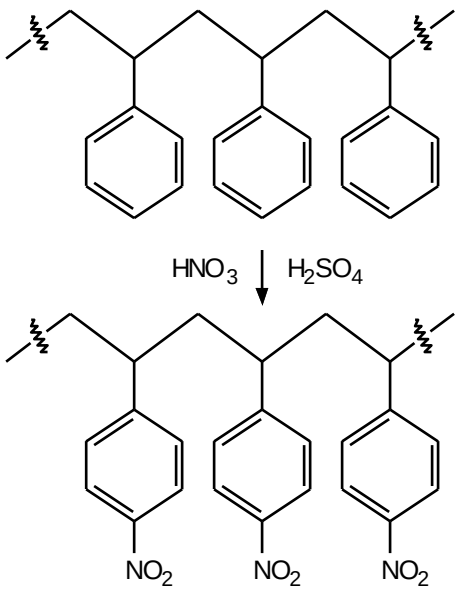
a. the reaction of polystyrene with $Cl_2 + FeCl_3$

b. the reaction of polystyrene with $HNO_3 + H_2SO_4$

a.

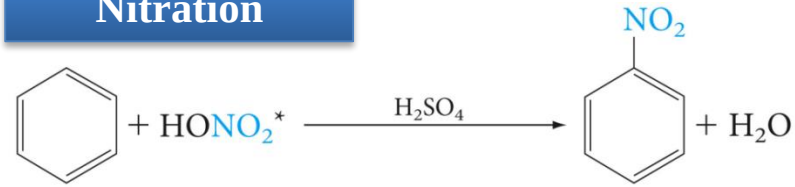


b.

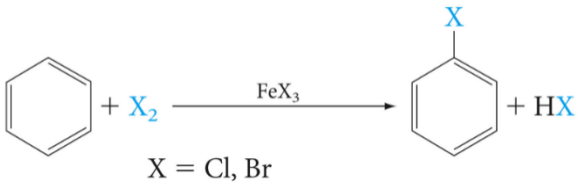


Electrophilic Aromatic Substitution

Nitration

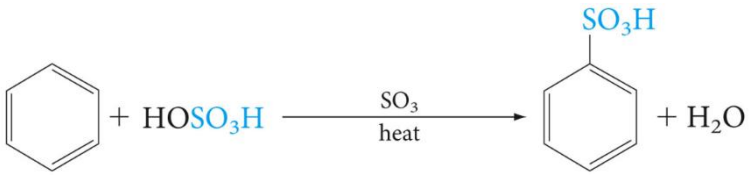


Halogenation

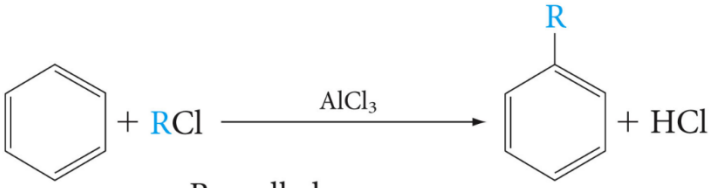


X = Cl, Br

Sulfonation

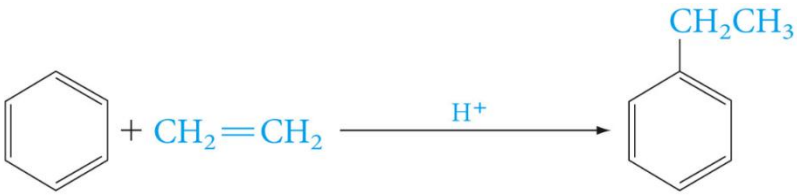


Alkylation (Friedel-Crafts)



R = alkyl group

Alkylation



Acylation (Friedel-Crafts)