Chapter. 22

Relationship between Macromolecular Structure and Properties

Influence by the macromolecular skeleton

1. **Polymer backbone maintains linearity of molecules;**
   flexibility, strength, and high viscosity can be generated.

2. **Side groups determine the solubility, crystallinity, surface chemistry ……..**

The aliphatic C-C bond

1. flexible; low barrier to tortion of the C-C bond
Ex) PE, PP, polyisobutylene, poly(methyl vinylether),….

2. Weak points; thermooxidative cleavage from the free radical cleavage.

The aliphatic C=C bond

Could be stiffer than C-C because rotation is not possible. But cis-polypentenamer has very low glass transition temperature (Tg) (-114 ^{o}C)

Tg for PE (-125 ^{o}C ~ -20 ^{o}C)

cis-polypentenamer
Tg -114 ^{o}C

Natural rubber
Poly(cis-1,4-isoprene)
Tg -70 ^{o}C

Poly(acetylene)

Tg ?

Double bonds are easily attacked by ozone and oxygen (under UV or visible light); easily oxidized

Aromatic rings and aromatic ladder structures as skeletal units

Rigid and extended chain structures
High Tg, thermally chemically stable!

The etheric carbon-oxygen bond

Flexible unit

Ether linkage is stable to hydrolysis and thermooxidation

Poly(ethylene oxide) is soluble in water; biomedical application

The ester bond

Aliphatic ester; easily hydrolyzed
biomedical application
(DDS)

Aromatic ester; chemically stable
with crystalline structures

타이어코드는 자동차 타이어에 들어가는 섬유 및 강선 소재로 타이어의 내구성, 주행성, 안정성을 보강해 주어 타이어의 안전과 성능에 지대한 영향을 미치는 핵심 소재입니다.

고분자를 이용한 약물 전달 체계

The anhydride linkage

Unstable to moisture; drug delievery

The amide linkage

Chain stiffening

Moderately sensitive to hydrolysis; other constituent determines the property

The urethane linkage

Moderately sensitive to hydrolysis; other constituent determines the property

The siloxane linkage

Very flexible unit
Si-O-Si bond can vary from 120^{o} to 140^{o}
Very low Tg; PDMS Tg = -123 ^{o}C

Siloxane bond is more stable to thermooxidative attack than C-O bond
Siloxane polymer is hydrophobic, high oxygen permeation

Influence of side groups

Hydrogen as a side group; C-H in the polymer

Hydrophobic, soluble in nonpolar solvent, sensitive to free radical attack, relatively insensitive to chemical reactions.

Si-H and P-H groups are reactive

Low glass transition, high crystallinity (symmetric structure)

Alkyl groups as side units

Methyl groups

PP; tacticity determines the crystallinity
ex) atactic; gum

polyisobutylene; suprisingly more flexible than PP due to the increased free volume (back bone has more rooms to move)

Ethyl, propyl, butyl …..; increase the free volume (more flexible)

Aryl side groups

Phenyl rings are hydrophobic, rigid, and relatively bulky.

Tg (°C)	**~ 100**	**~ 0**	**~ -100**

Tg is lower

Mesogenic side groups

Liquid crystals (액정)

Liquid crystallane polymers (액정고분자)

액정이란?

Example of a compound that shows no liquid crystal phase

Ice Cube

Solid crystalline water
3 degrees of order

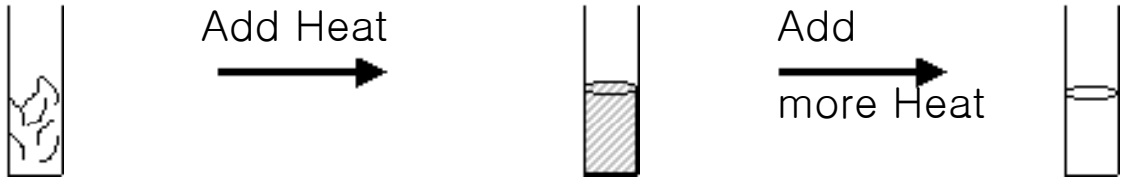
Water

Liquid water
0 degrees of order

Steam

Gaseous water
0 degrees of order

Example of a compound that shows liquid crystal phases



Crystals of a solid
organic compound

3 degrees of order

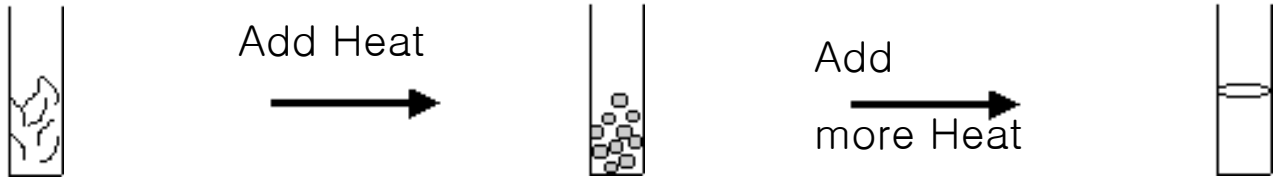
Nematic liquid
crystal phase

1 degree of order

Isotropic liquid

0 degrees of order

액정 구조및 상변화



Crystals of a solid organic compound

3 degrees of order

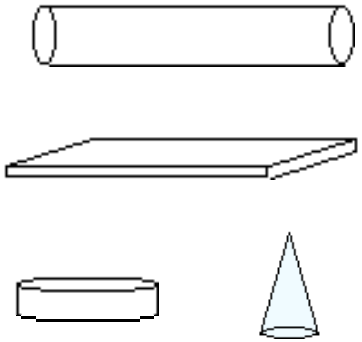
Smetic liquid crystal phase

2 degree of order

Isotropic liquid

0 degrees of order

Liquid crystalline phases most often occur in compounds that have a shape that favors parallel packing:



Rods

Disks

Disks/cones

Stacks of these form columns

액정의 상

Nematic

Smectic

Liquid Crystal Phases

액정물질의 전기장에서의 거동

Applications

LCD Notebook

LCD TV

Plastic Display

Fluorine as a side group unit ; fluoropolymer

Fluorine confers are extremly hydrophobicity and water insolubility.

Synthesis and application of fluorinated polymers

Fluorinated polymers

Advantages

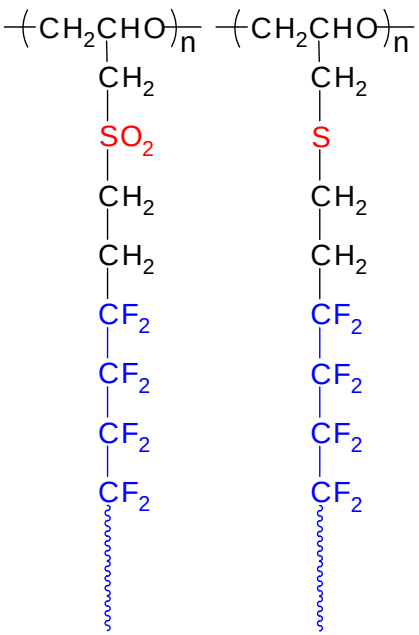
- **Excellent thermal stability**
- **High chemical resistance**
- **Low refractive index**
- **Low dielectric constant**
- **Low surface energy**
- **Soluble in supercritical CO_2**

Surface coating

Electronics

Biomaterial

Environmentally friendly process



Supercritical CO_2

-"Greener" alternative to organic solvents
- Non-toxic, Nonflammable, Relatively Inert
- Low critical conditions ; Tc = 31.1ºC, Pc =72.8atm
- Low cost

Ionic liquid

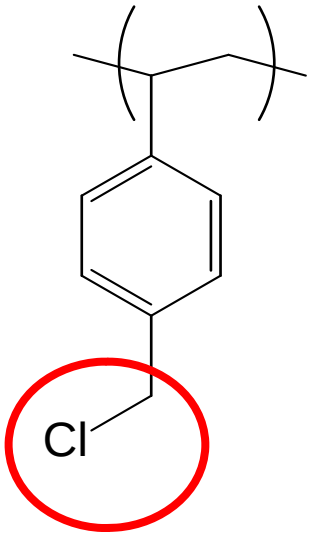
- Salts that are liquid at low temperature
- 'Green' alternative to volatile molecular organic solvents
- We have successfully synthesized fluorinated polymer by chemical modification **in ionic liquids**

Antifouling Materials

Chlorine as a side group unit

Chlorinated polymers are generally resistant to chemical attacks.
Ex) PVC, poly(vinyledene chloride)

Benzyl chloride unit in the side chains are used for modification



The cyano side group

Cyano group is a polar and hydrophilic group.

Decreasing the solubility in nonpolar solvent, while increasing the solubility in polar solvent (DMF, DMSO, DMAc…)

Tg's
PAN ; 85 ^{o}C
PP; ~ 0 ^{o}C
PS; 100 ^{o}C

The hydroxy side group

Hydroxy group; polar, hydrophilic, water soluble

Both are very good barrier polymer

The amide side groups

Very soluble in water
T_g is high (153 ~200 ^oC)

Alkyl ether side groups

Poly(methylvinyl ether); soluble in water at RT, solubilty ↓, temp↑ (why?)
Tg = -31 ^oC

Tg for ethyl, propyl, butyl side groups; -42, -49, -55 ^oC (why?)

The ester side groups

Ester is polar but not hydrophilic much; Soluble in polar solvent, while not soluble in water

For 35 (esters of poly(acrylic acid)) and
36 (esters of poly(methacrylic acid)

If R is small (methyl and ethyl), they are relativey polar
R becomes longer, polarity decrease ! (The same is tru for 37)

Tg of atactic PMMA (36) 105 ^{o}C,
Tg of poly(vinyl acetate) (37) ~30 ^{o}C

The carboxylic acid side groups

Water soluble
Non soluble in HC solvent

poly(acrylic acid) **poly(methacrylic acid)**

Structural influence on solide state properties

Flexibility

T_g and T_m depend on the chain flexibility.
Flexible chain can have a large entropy of melting.
$T_m = \Delta H_m / \Delta S_m$, then flexible polymer can have low T_m
Flexible chains can maintain their long range motion until very low temperature upon cooling, therefore flexible polymer can have low T_g

Stiffness

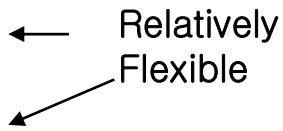
Stiff portion in the collagen, such as proline (PRO) or hydroxyproline (HPRO)) can be made

Collagen is the main protein of connective tissue in animals and the most abundant protein in mammals, [1] making up about 25% of the total protein content.

Intermolecular interaction

$T_m \propto \Delta H_m$

Nonpolar chains < polar chains < hydrogen-bonded chains



Random and block copolymers

How scientists design new polymers and polymer materials

Home work !