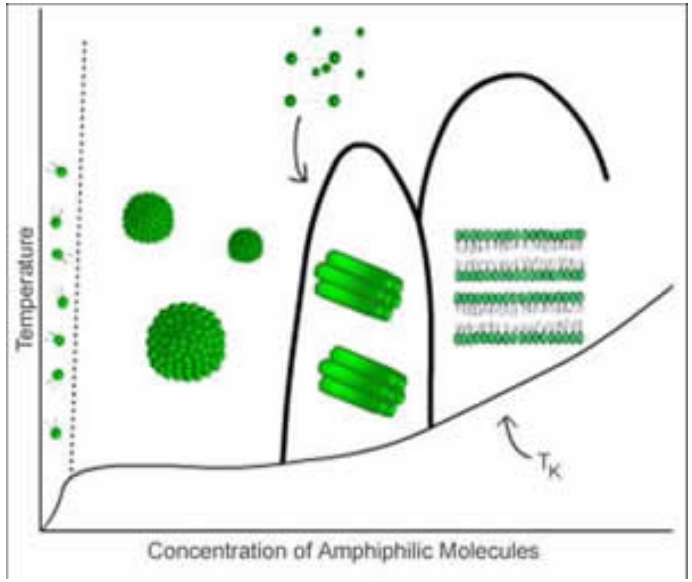
Chapter 7

Liquid Crystalline State

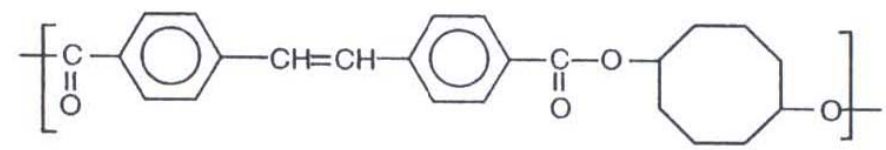
LC State

- LC ~ mesophase ~ order in 1 or 2 dimensions
  - amorphous ~ liquid ~ no order
  - crystalline ~ solid ~ order in 3 dimensions
- mesogen ~ rod or disc 📖Fig 7.2
- mesophase structures 📖Fig 7.1
  - smectic, nematic, cholesteric
  - discotic
- thermotropic LC
- lyotropic LC

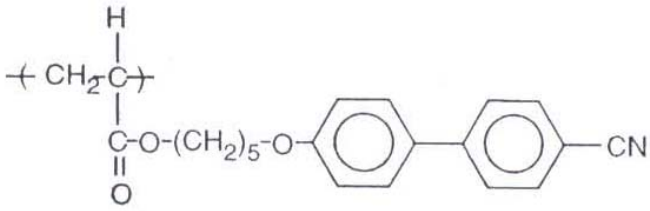


Liquid Crystalline Polymers

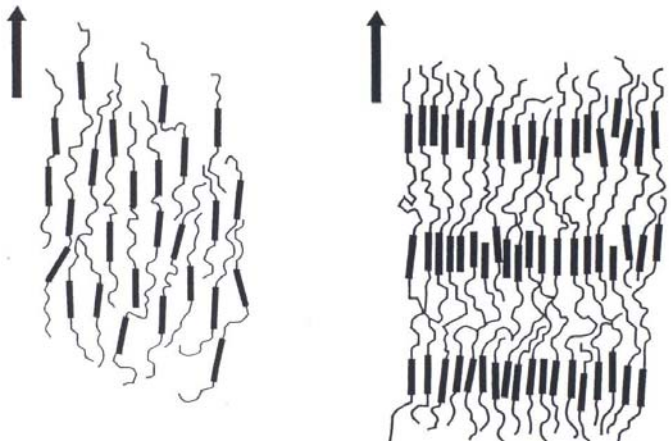
- main-chain LCP
- side-chain LCP

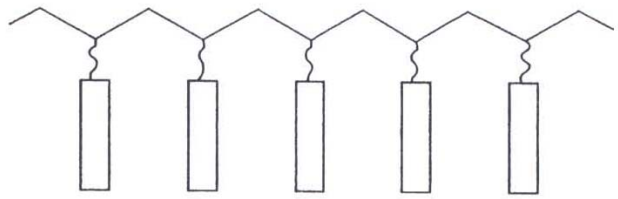


(a) solid (crystal) $\xrightarrow{257^\circ C}$ Smectic $\xrightarrow{282^\circ C}$ nematic $\xrightarrow{295^\circ C}$ isotropic



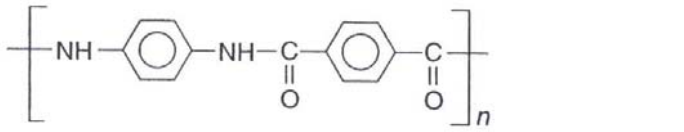
(b) solid (glassy) $\xrightarrow{153^\circ C}$ Smectic $\xrightarrow{200^\circ C}$ nematic $\xrightarrow{203^\circ C}$ isotropic

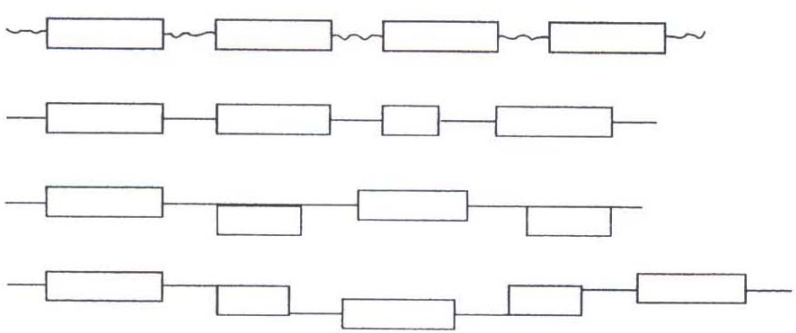




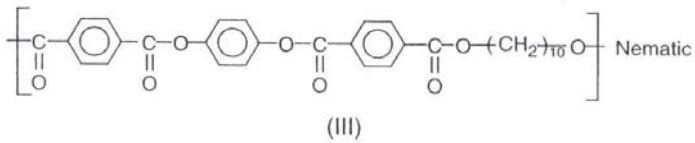
Main-chain LCP

- structure
  - all-mesogen
    - T_m too high
    - lyotropic only
  - modifications

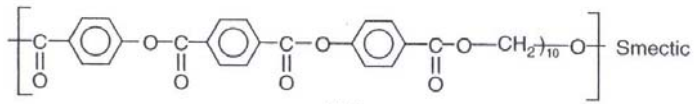




- phase behavior
  - nematic usual
  - smectic
    - LCP with long spacer
    - in some special cases

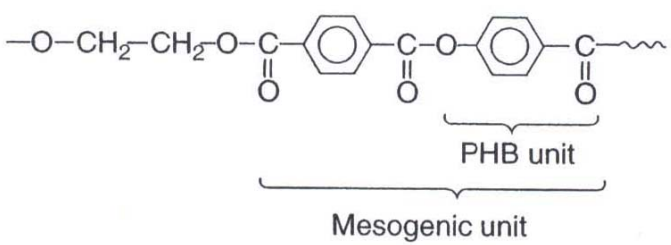


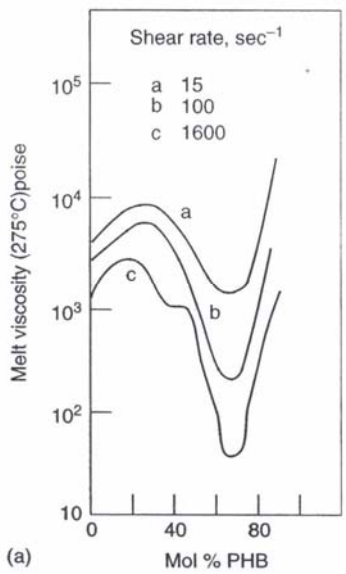
(III)

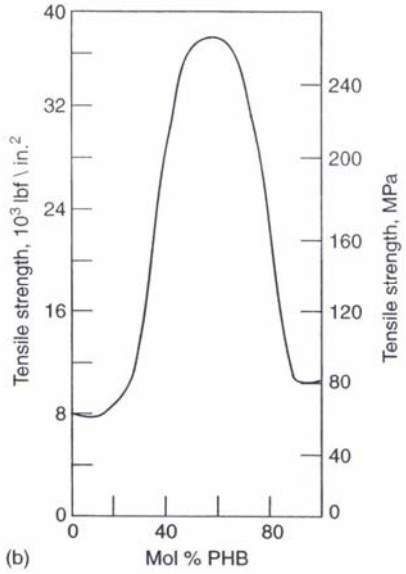


(IV)

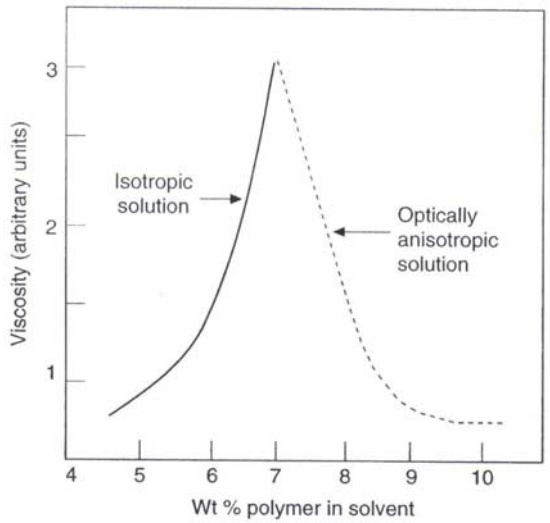
- viscosity
  - thermotropic







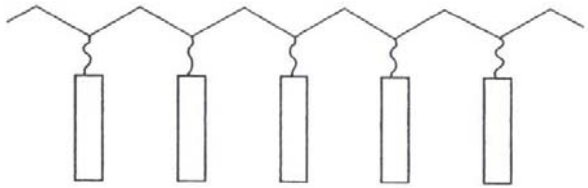
  - lyotropic



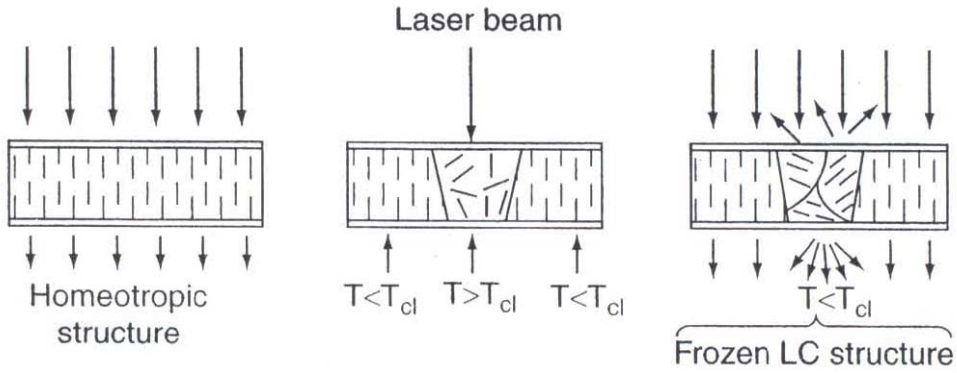
- properties
  - high thermomechanical property
    - stiff and self-reinforcing
  - processability
    - low viscosity ~ precision product
    - low ΔH_c and time for Xtallization ~ low cycle time
- applications
  - fiber
  - electronics parts

Side-chain LCP

- structure



- phases ~ nematic, smectic, cholesteric (chiral)
- applications
  - not for display
  - optical storage



Properties of Polymers

Properties of Polymers

- Material properties
  - 화학적 성질
    - » stability, solubility, permeability, flammability
  - 전기적성질
  - 광학적 성질
  - 열적성질
  - 기계적 성질
- Processing properties
- Product properties ~ product design

❖ There are no bad materials, but only bad articles.

❖ *Structure-property relationship*

✓ Properties are determined by chemical and physical structures.

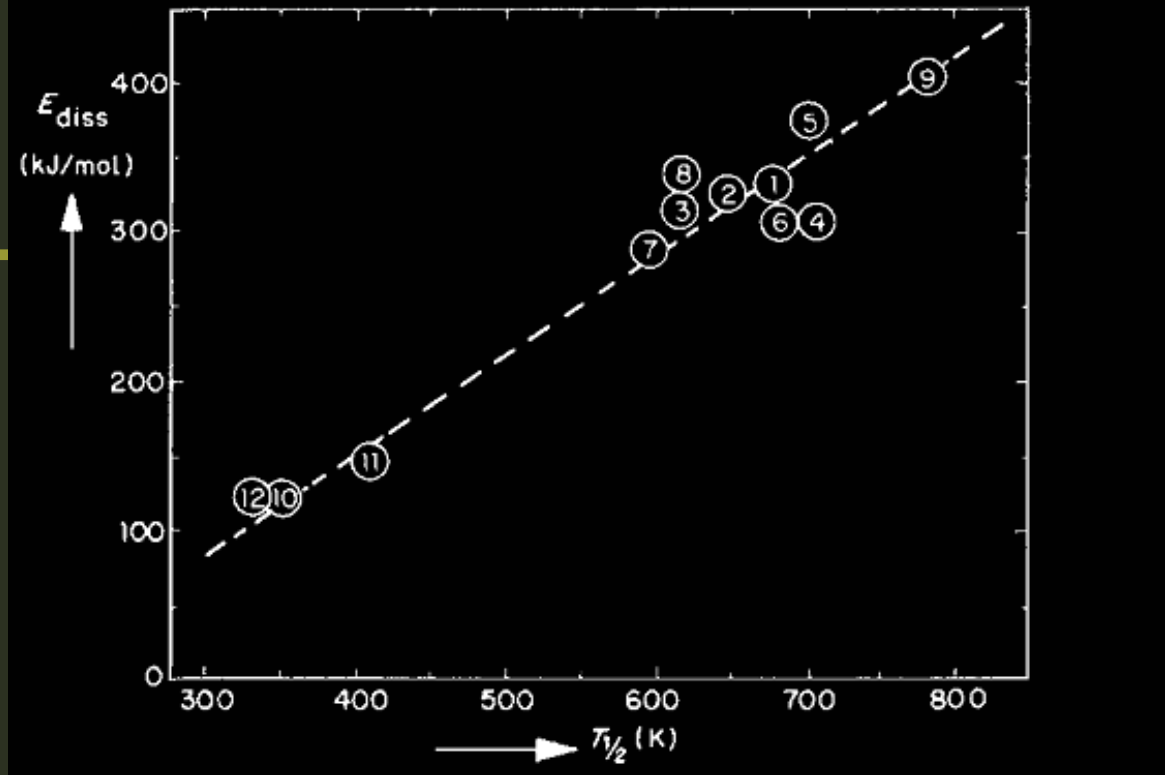
Stability

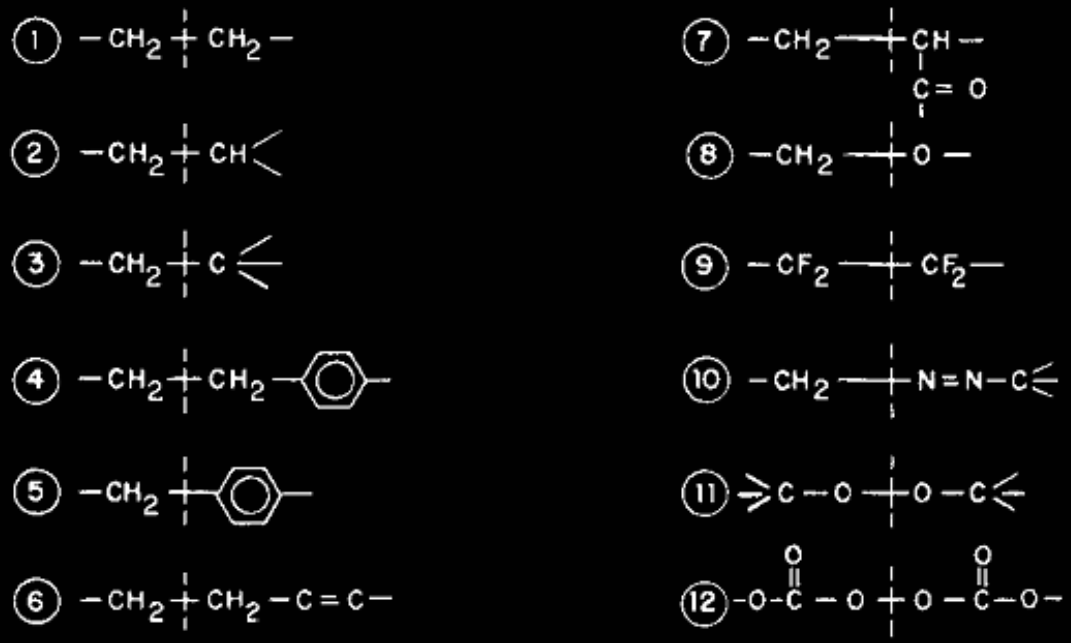
- to heat
  - depends on the dissociation energy of the weakest bond
  - Measurement – thermal gravitational analysis (TGA)
- to light (UV)
  - 300 nm ≈ 400 kJ/mol
  - depends on absorption wavelength
- to oxidation
  - thermal and photochemical
  - Indication ~ yellowing
- to hydrolysis
  - depends on constituent groups

- weatherability (내후성)

E_{diss} ~ bond dissociation energy

$T_{1/2}$ ~ half weight at 30 min





Permeability

📖 *Chapter 4 (pp172-180)*

- In membranes ~ semi-permeable
- In packaging ~ barrier property

- Diffusion-Solution model
  - absorption-diffusion-desorption 📖Fig 4.18
  - $P = D\,S$
  - Diffusivity
    - » T_g of polymer 📖Table 4.5 & Fig 4.19
    - » size of gas 📖Table 4.5-6 & Fig 4.19
  - Solubility
    - » bp of gas
    - » polarity of gas and polymer
- Permeability vs Selectivity 📖Fig 4.20

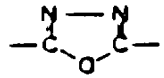
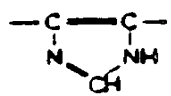
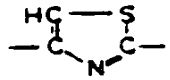
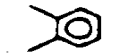
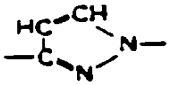
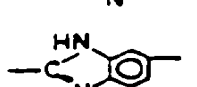
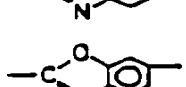
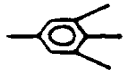
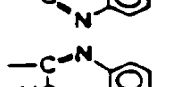
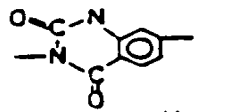
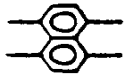
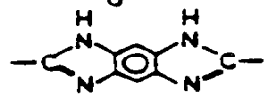
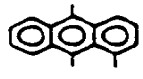
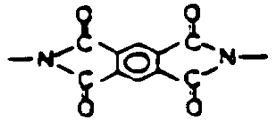
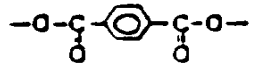
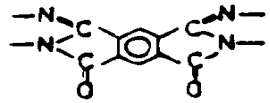
Gas	*P*	*D*	*S*
N_2 (=1)	1	1	1
CO	1.2	1.1	1.1
CH_4	3.4	0.7	4.9
O_2	3.8	1.7	2.2
He	15	60	0.25
H_2	22.5	30	0.75
CO_2	24	1	24
H_2O	(550)	5	–

Flammability (↔ Flame retardancy)

- Burning: 2 step process
  - Pyrolysis (decompose) → ‘char’ + gas – Q_1
  - Combustion (ignite & inflame) → combustion product + Q_2

- For flame retardation
  - lower gas (Q_2)
  - higher ‘char yield’
    - » lower H/C
  - inhibiting gas
    - » halogen, phosphorus
  - endothermic degradation (with releasing H_2O)
    - » inorganic flame retardants like $Mg(OH)_2$, $Al(OH)_3$

Group contribution to 'char yield'

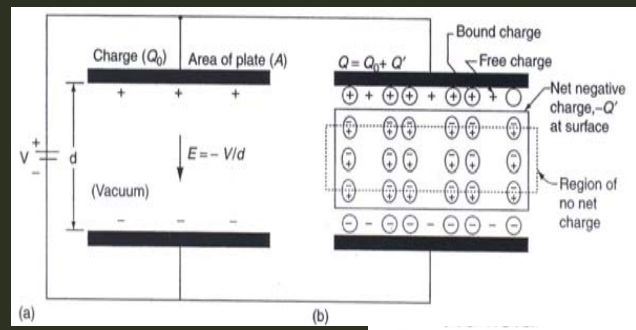
GROUP	CFT in C-equiv.	GROUP	CFT in C-equiv.
ALIPHATIC GROUPS		**HETEROCYCLIC GROUPS**	
—CHOH—	1/3		1
ALL OTHER *)	0		
AROMATIC GROUPS			3 1/2
	1		3 1/2
	2		3 1/2
	3		7
	4		7
	6		9
	6		11
	10		10
	14		12
	1 1/4		10
CORRECTIONS DUE TO DISPROPORTIONING (H-SHIFT): GROUPS DIRECTLY CONNECTED TO AROMATIC NUCLEUS			15
$>CH_2$ and $>CH-CH_2-$	-1		
$-CH_3$	-1 1/2		
$>C(CH_3)_2$	-3		
$-CH(CH_3)_2$	-4		

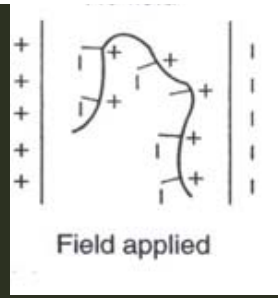
*) NO HALOGEN GROUPS INCLUDED

N.B. SYSTEM IS NOT VALID FOR HALOGEN-CONTAINING POLYMERS

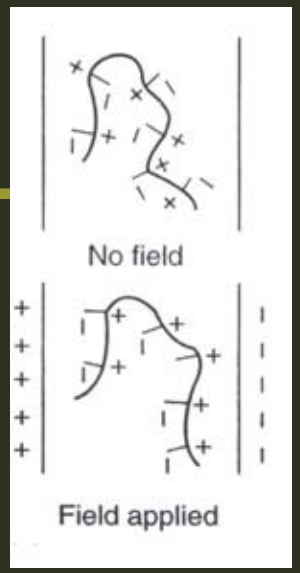
Electrical properties 1

- At high electric field
  - electrical failure, treeing
  - arc resistance
  - No direct relation to chemical structure
- At low electrical field
  - Polymers are insulators
    - » resistivity ~ 10^8–10^{20} Ωcm
  - dielectric constant, $\varepsilon = C / C_{vac}$
  - $\varepsilon \propto$ polarization ~ refractive index
    - » Non-polar polymers, $\varepsilon = n^2$ (electronic polarization only)
    - » polar polymers, $\varepsilon > n^2$ (electronic + dipole polarization)
  - ε related to chemical structure
    - ≈ $\varepsilon = \delta / 7.0$

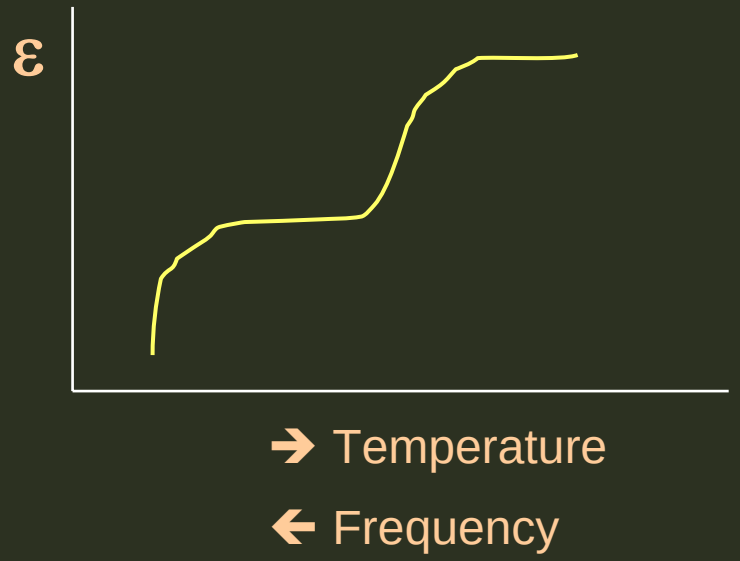




Electrical properties 2



- Frequency dependent ε
  - high ε at low freq and/or at high temp
  - low ε at high freq and/or at low temp
  - dielectric relaxation



- Types of dipole
  - main-chain dipole
    - » better insulator at high frequency
  - side-chain dipole
- conducting polymers
  - resistivity ~ 10^3–10^8 Ωcm (semiconductors)
- piezo-/pyro-/photo-electric polymers

Optical properties 1

- Light upon interaction with polymer
  - reflected ~ gloss ~ surface roughness
  - absorbed ~ color ~ chromophore
  - refracted, scattered, transmitted ~ clarity
    - » transparent < 30% haze < translucent < opaque
      - haze ~ fraction of light 2.5º deviated by scattering

- Opaque by heterogeneity (different *n*) larger than λ of visible light (340 nm)
  - impurity
  - 2nd phase
  - crystallite

Optical properties 2

- For a semicrystalline polymer to be transparent
  - small crystallites
  - $\rho_{crystal} \approx \rho_{amorphous}$
  - biaxial orientation
- refractive index
  - lenses
  - optical fiber
- Non-linear optical behavior