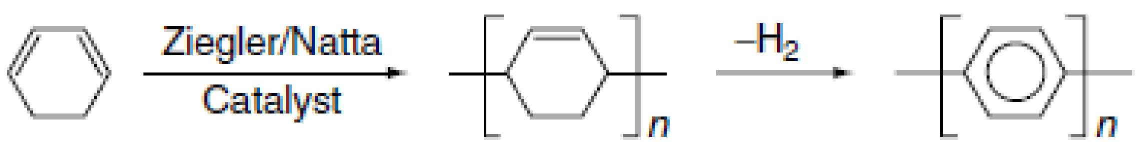
Chapter 5

Polymers in Special Uses

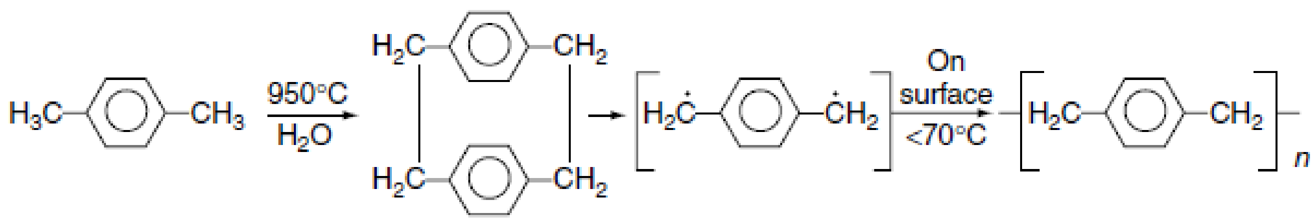
high-Temp, fire-resistant, LCP,
conductive, electroactive, electrolytes, photoresist,
degradable, ionic, hydrogel, membrane polymers
nanocomposites

High temperature polymers

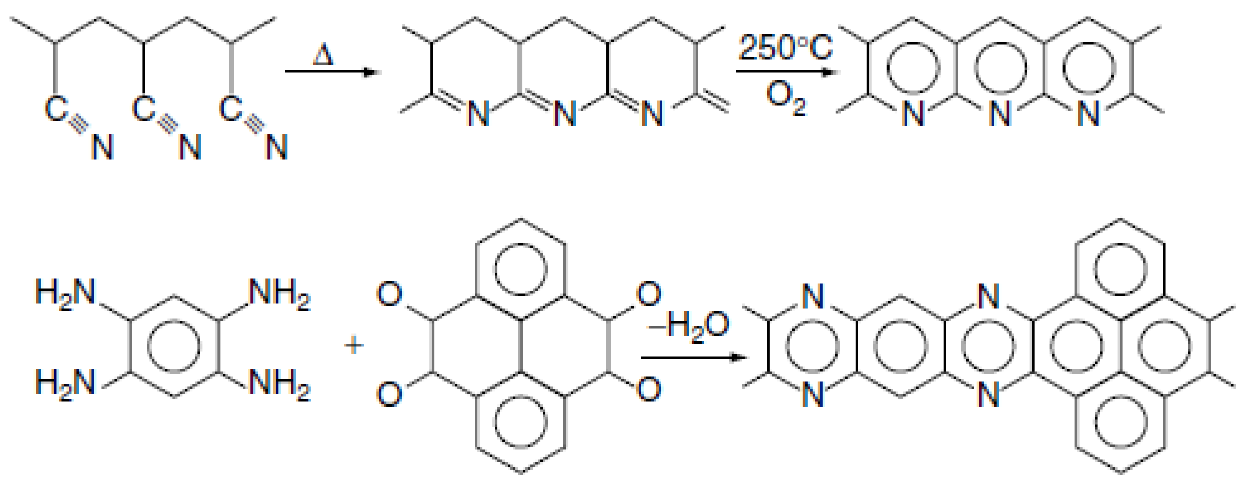
- thermal stability vs heat resistance
  - thermal stability ~ degradation Temp ~ T_5 etc
    - bond strength ~ weakest bond
  - heat resistance ~ use Temp ~ T_g or HDT
    - chain stiffness, intermol interaction
    - MW, X_c, M_c
  - usually, related
- (wholly) aromatic polymers
  - poly(p-phenylene)



- poly(p-xylene)

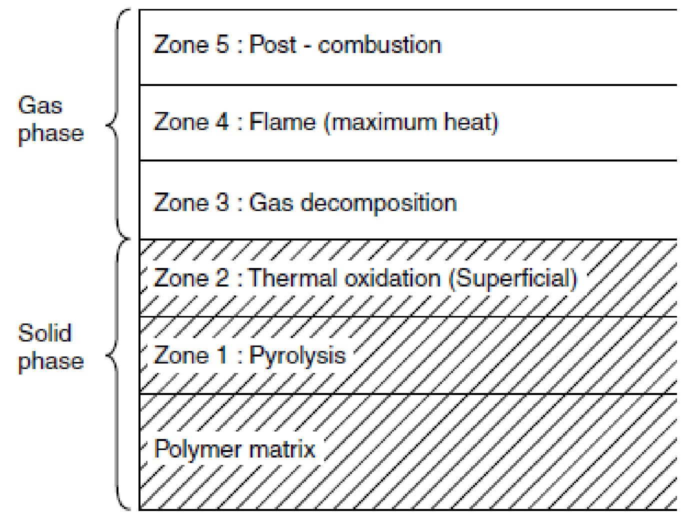


- aramid, PI, PBI, PSF, PEEK, ---
- ladder polymers



Fire-resistant polymers

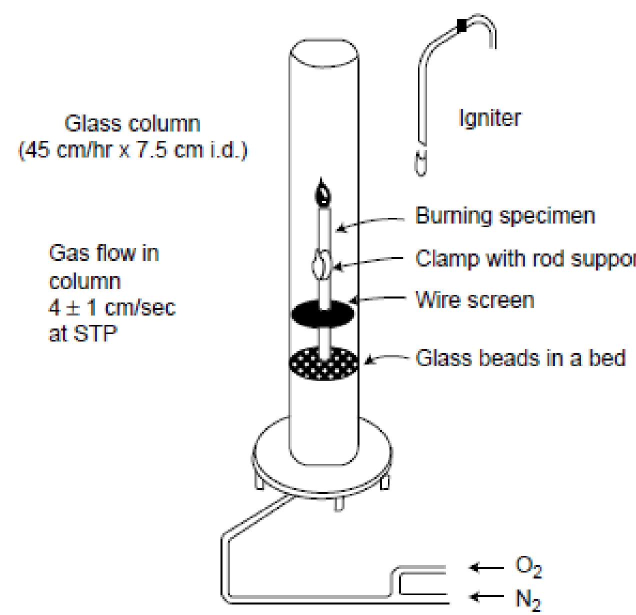
- burning
  - pyrolysis (1) → gas (2,3) + char
  - combustion (4) → heat (5)



- LOI

$$\mathrm{LOI} = \frac{[O_2]}{[O_2] + [N_2]} \times 100$$

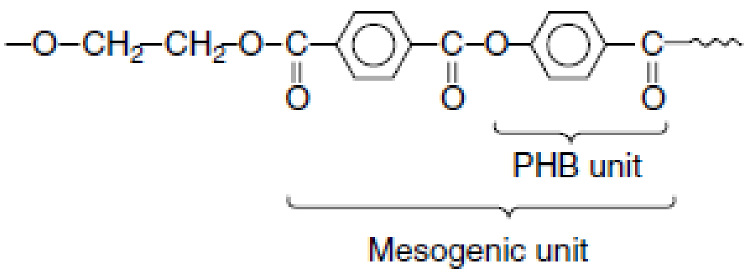
Table 5-2 p597



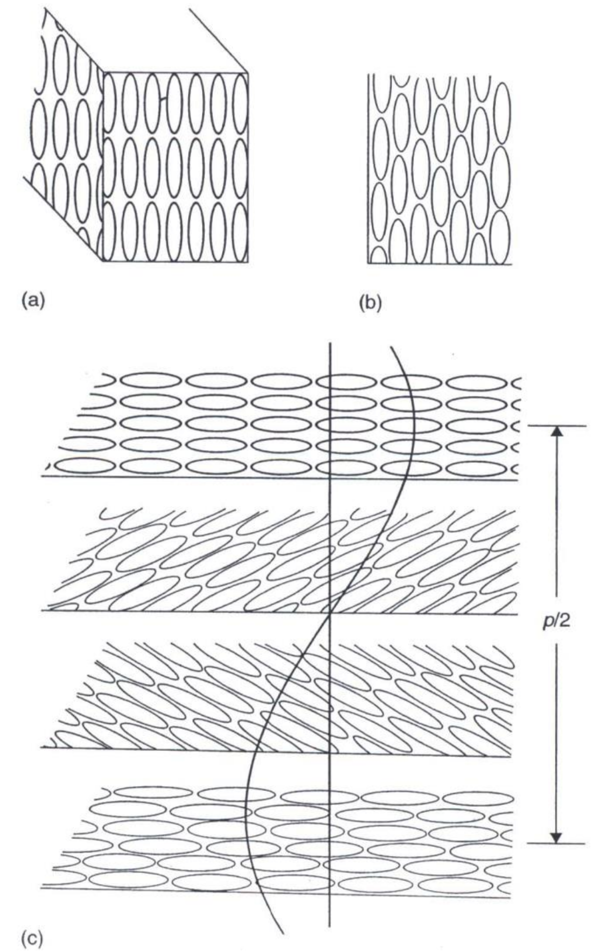
- for fire resistance
  - high thermal stability
  - low H/C ~ ring   also related
  - halogen

LCP

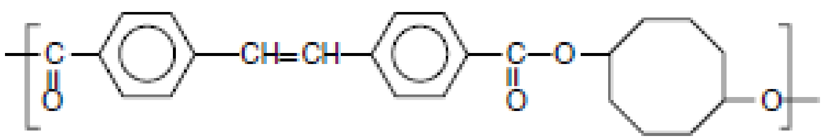
- LC ~ mesophase ~ KL betw KS and IL
- thermotropic, lyotropic
- smectic, nematic, cholesteric (chiral)
- mesogen ~ rod or disc
  - two or more cyclic units



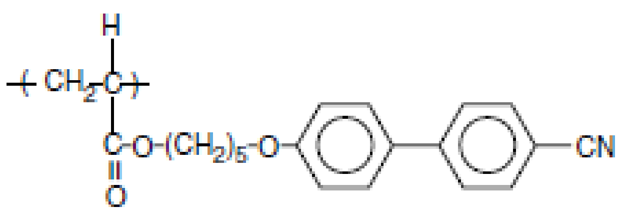
- observation of LC behavior
  - DSC ~ T_{tr}
  - POM ~ texture ~ type
  - XRD ~ type and number of phases



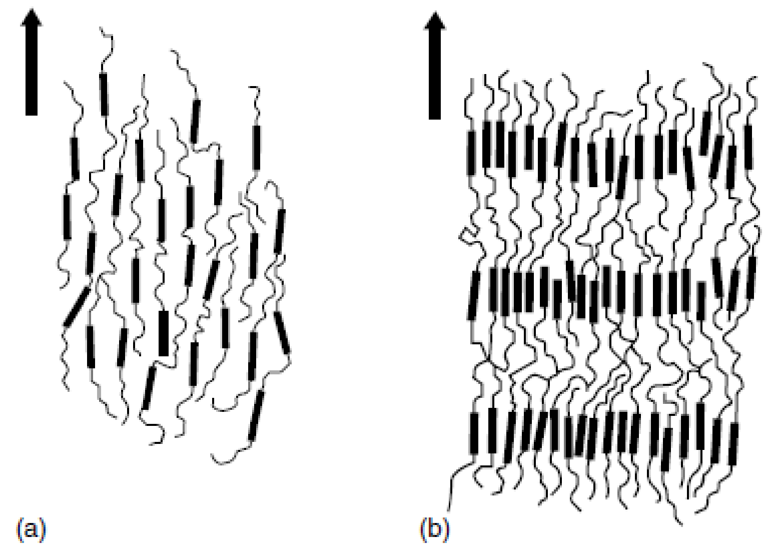
- LCP
  - main-chain LCP
  - side-chain LCP

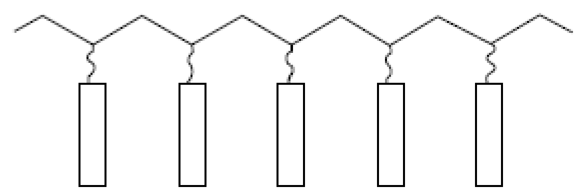


(a) solid (crystal) $\xrightarrow{257^\circ C}$ Smectic $\xrightarrow{282^\circ C}$ nematic $\xrightarrow{295^\circ C}$ isotropic



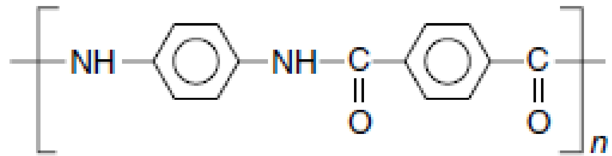
(b) solid (glassy) $\xrightarrow{153^\circ C}$ Smectic $\xrightarrow{200^\circ C}$ nematic $\xrightarrow{203^\circ C}$ isotropic



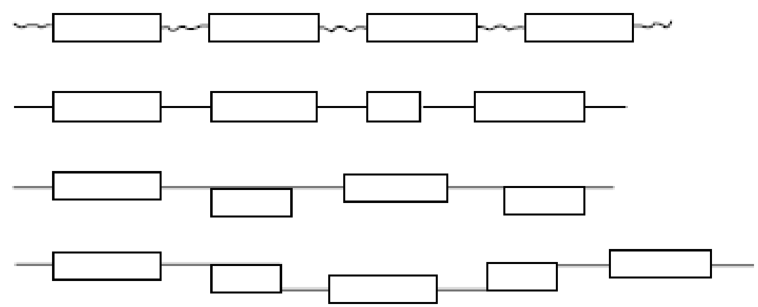


Main-chain LCP

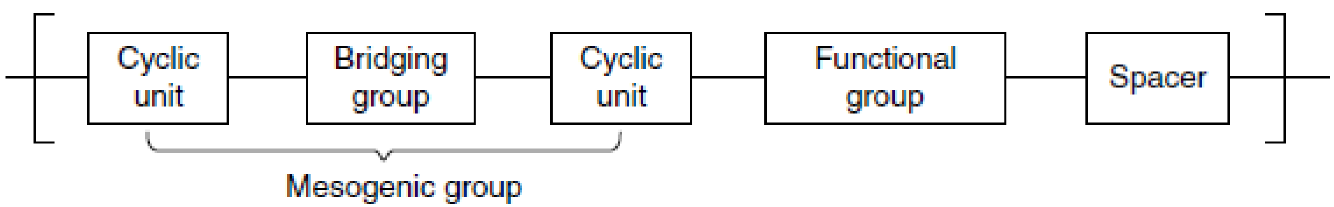
- structure
  - all-mesogen
    - T_m too high
    - lyotropic only



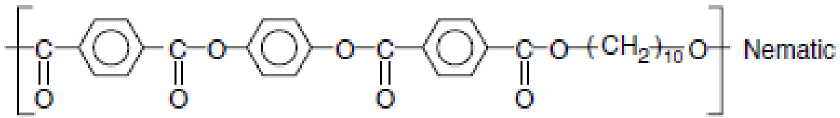
  - modifications ~ spacer



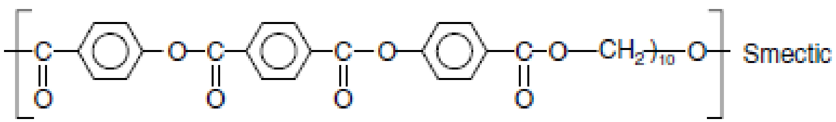
    - general structure Table 5.3



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

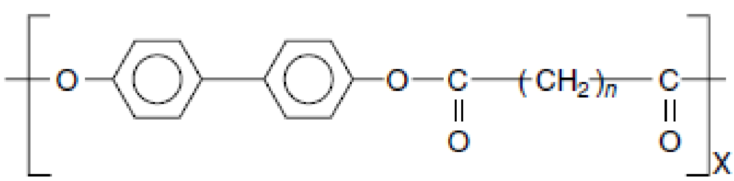


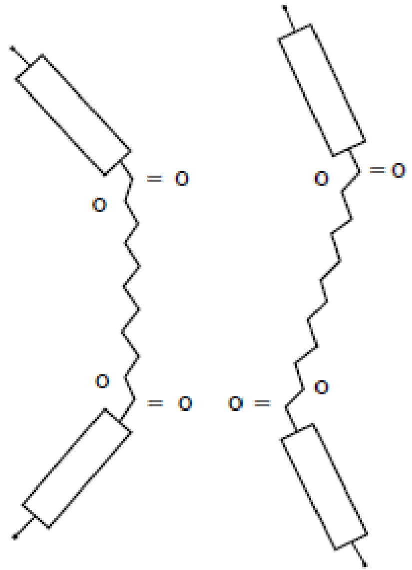
(III)



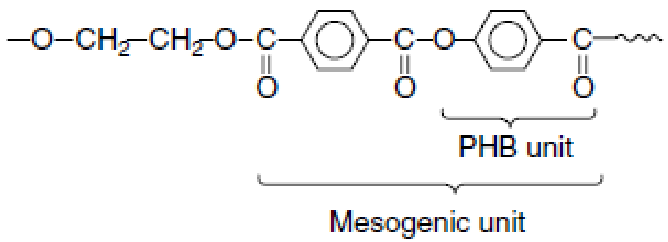
(IV)

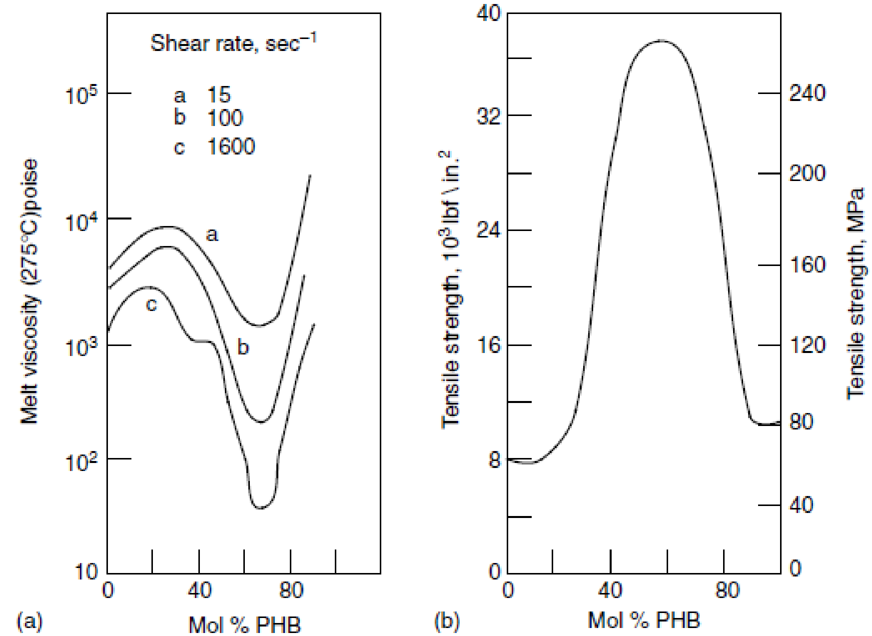
- even-odd effect
  - higher T_m, T_i for even
  - nematic (o)/smectic (e)



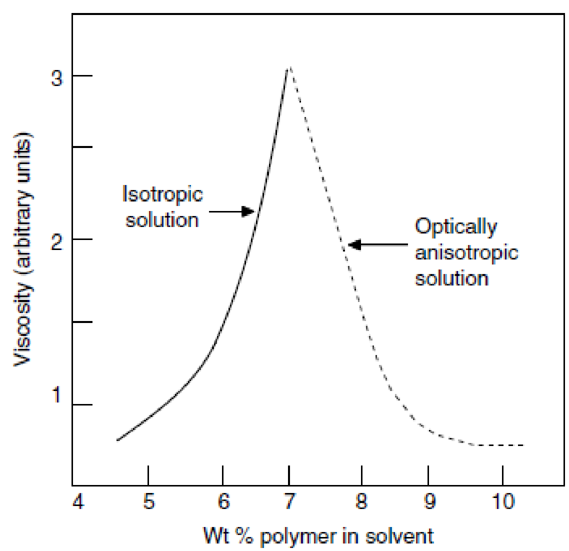


- viscosity
  - thermotropic





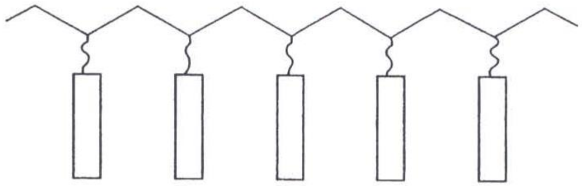
  - lyotropic

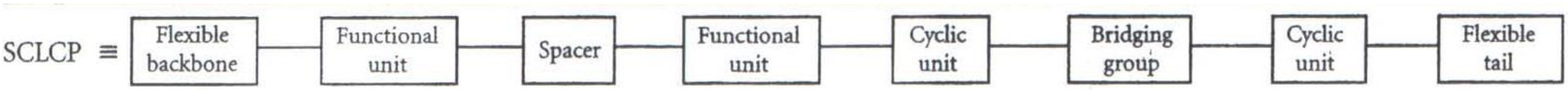


- properties
  - high thermomechanical property
    - stiff and self-reinforcing
  - processability
    - low viscosity ~ precision product
    - low ΔH_c and time for Xtallization ~ low cycle time
    - can be highly-filled
- applications
  - fiber
  - (precision) electronics parts
  - PCB replacing epoxy

Side-chain LCP

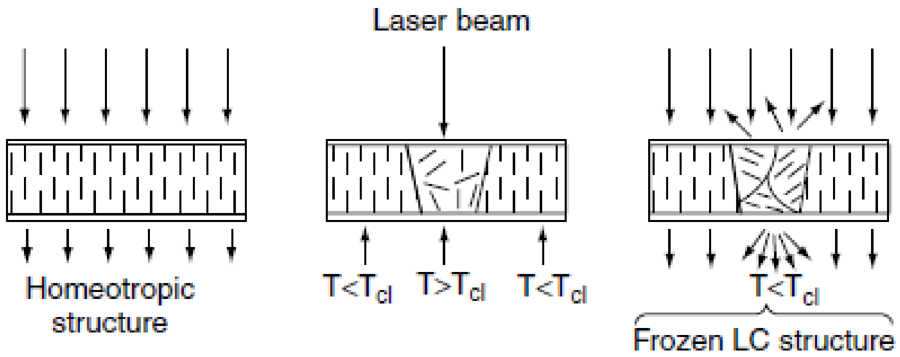
- structure
  - Table 5.4 and 5.5





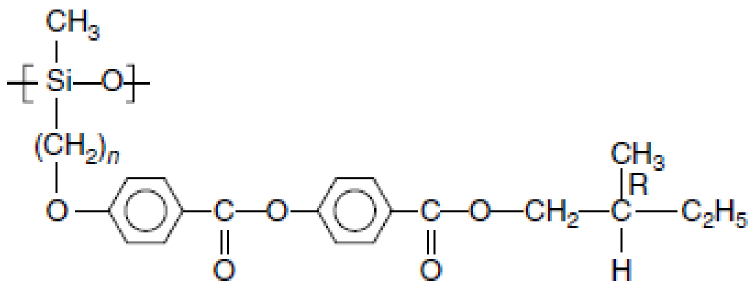
- phases ~ nematic, smectic, cholesteric (chiral)
- applications
  - alignment
    - homogeneous vs homeotropic

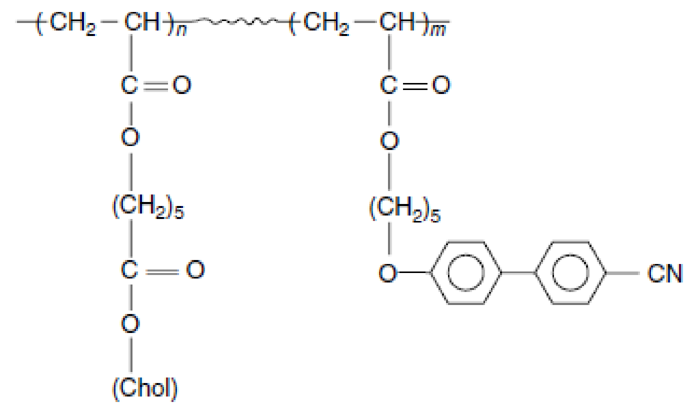
  - not for display
  - optical storage



Cholesteric LCP

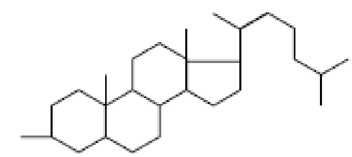
- contains chiral center



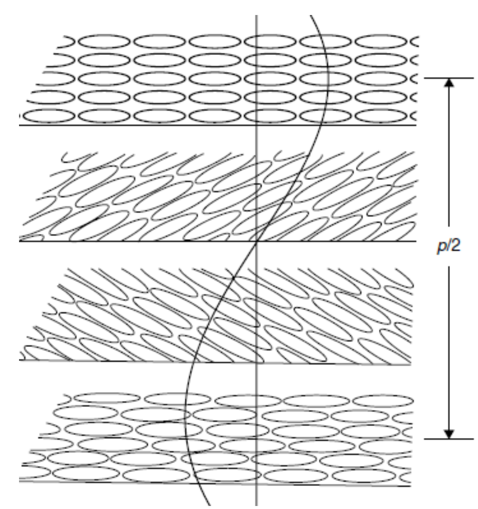


$$\lambda_R = np$$

Chol =



% Chol	T_g (°C)	T_i (°C)	λ_R (nm)
34	10	32	850
40	10	39	660
55	13	40	555
65	13	65	500

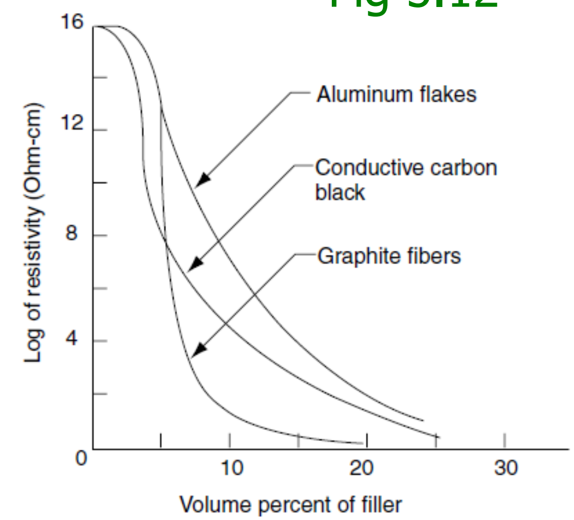


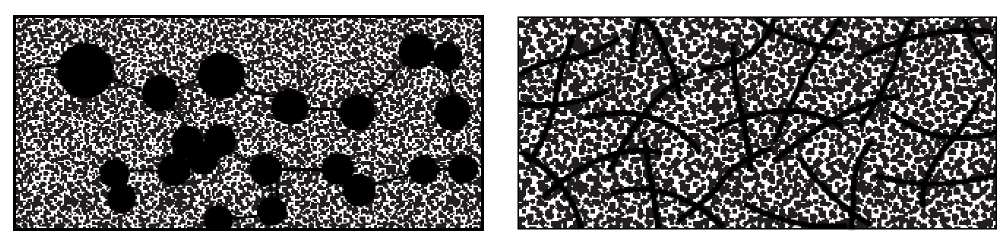
- (monochromatic) optical film

Filled conductive polymers

- conductive [conducting] polymers
  - filled conductive polymers
  - inherently conductive polymers
- conductive plastics
  - dispersing conductive materials
    - Al, Fe, C, GF
    - not Cu (oxidize)
  - for electrical a/o thermal conductivity
    - metalloplastic = high electrical (< 1 ohm cm) and thermal (> 10 times normal) conductivity
  - fiber (of high AR) more effective than particle

Fig 5.12





same vol%

Fig 5.13

  - if only for thermal conductivity, continuous phase <u>not</u> necessary
    - electrical insulator with high thermal conductivity possible
    - high thermal conductivity to shorten cycle time
- conductive coating
  - brushing, plating, in-mold, ---
  - for some EMI shielding
- conductive rubber
  - silicone/carbon black popular
  - connector, electrode, tire (leak off static electricity)

- EMI shielding
  - shielding effect, $\alpha(dB) = 20 \log_{10}(E_b/E_a)$ Table 5.8
    - 99% shielding = α of 40 dB
  - steel fiber ~ most effective shielding
    - only 1 vol% → α = 50 dB ≈ 1 (ohm cm)$^{-1}$ = 1 S/cm
  - carbon black ~ most cost effective
    - amorphous C ~ .01; graphite fiber ~ 300 S/cm
    - need higher conc'n than metals
    - disadvantage ~ color, low IS
    - sandwich molding

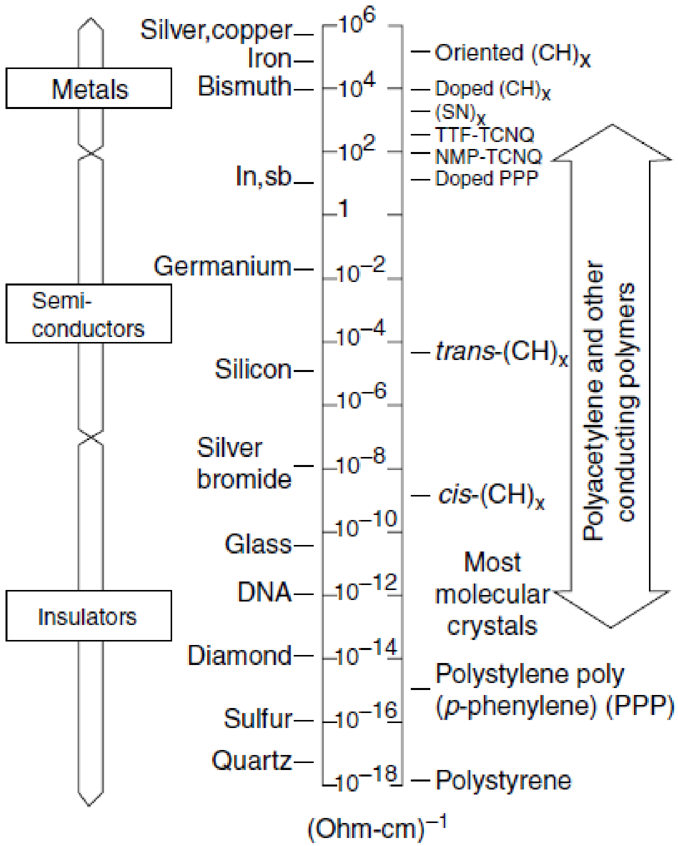
- stealth material

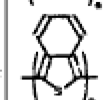
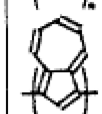
  radar absorbent materials [RAM]

  - radar stealth = no reflection + deflecting radar
  - no reflection by
    - absorbing radar ~ materials w/ high ε'' and μ'' at 3-30 GHz
      - ε = permittivity [dielectric constant]
      - μ = (magnetic) permeability
    - blacking-out net reflection ~ reflection by coat and metal cancels each other
  - ferrite dispersed in binder [painting polymer]

Inherently conductive polymers

- polymers with π-conjugation
  - insulating/semi-conducting
  - doped ~ semi- to conducting



Polymer	Structure	Doping materials	Approximate conductivity (S/cm)
Polyacetylene	$(CH)_n$	I_2, Br_2, Li, Na, AsF_5	10,000[a]
Polypyrrole		BF_4^-, ClO_4^-, tosylate[b]	500~7500
Polythiophene		BF_4^-, ClO_4^-, tosylate[b], $FeCl_4^-$	1000
Poly(3-alkylthiophene)		BF_4^-, ClO_4^-, $FeCl_4^-$	1000~10,000[a]
Polyphenylene sulfide		AsF_5	500
Polyphenylene-vinylene		AsF_5	10,000[a]
Polythienylene-vinylene		AsF_5	2700[a]
Polyphenylene		AsF_5, Li, K	1000
Polyisothianaphthene		BF_4^-, ClO_4^-	50
Polyazulene		BF_4^-, ClO_4^-	1
Polyfuran		BF_4^-, ClO_4^-	100
Polyaniline		HCl	200[a]

[a] Conductivity of oriented polymer. [b] p-Toluenesulfonate.

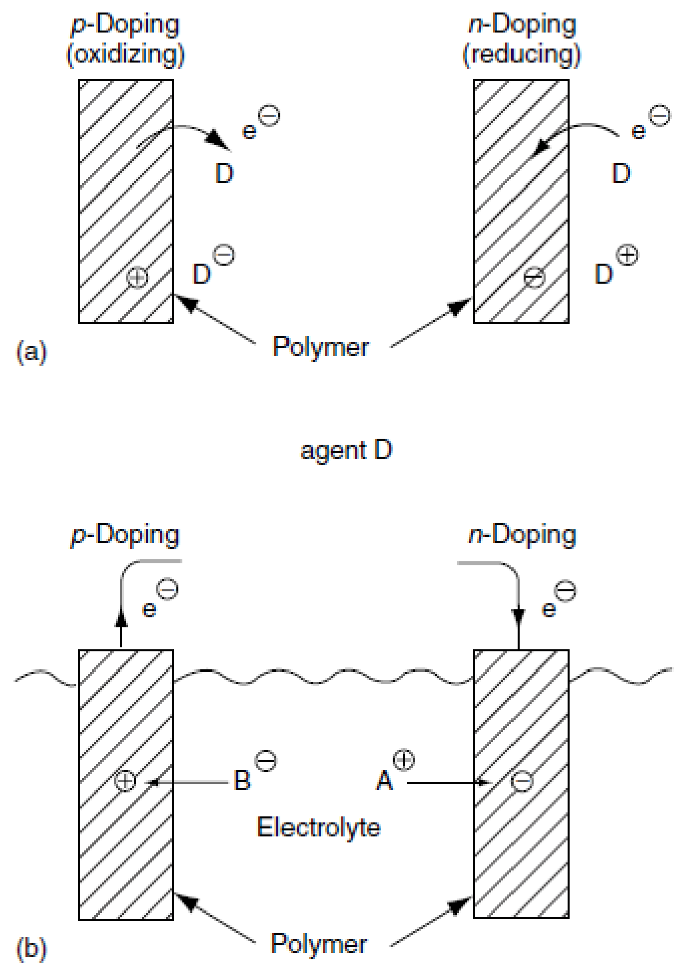
- doping process
  - chemical
  - electrochemical
  - ion implantation
  - photochemical
- p/n-doping
  - p-doping ~ oxidation

    $$\text{Polymer} + \text{X} = (\text{Polymer})^{n+} + \text{X}^{n-}$$

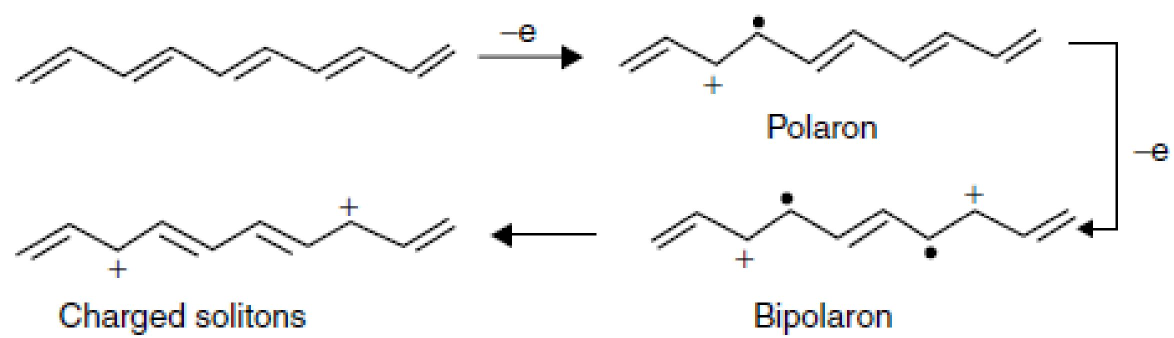
    - Br_2, I_2, AsF_5, $HClO_4$, --
    - for most conducting polymers
  - n-doping ~ reduction

    $$\text{Polymer} + \text{M} = (\text{Polymer})^{n-} + \text{M}^{n+}$$

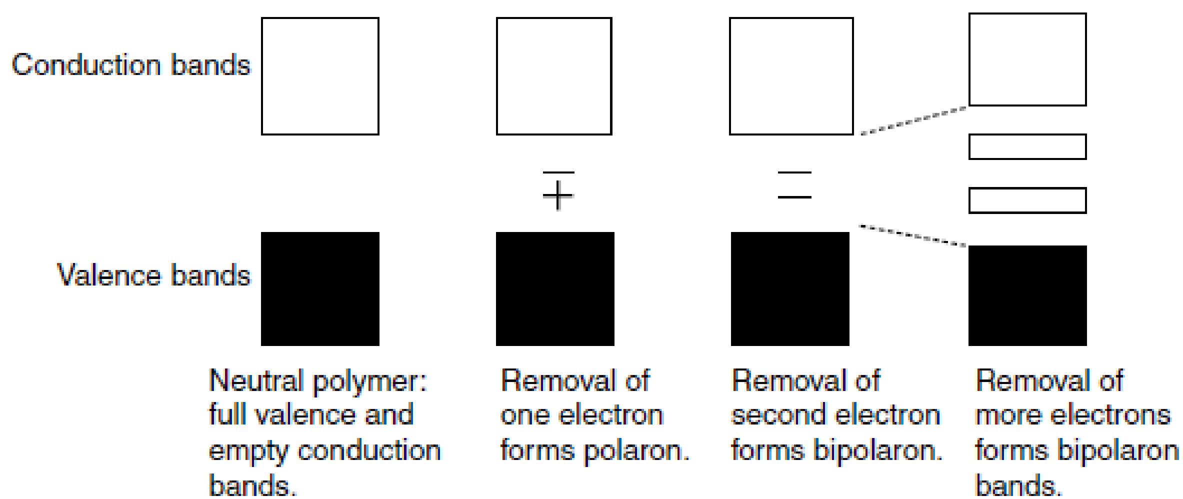
    - metals



- conducting

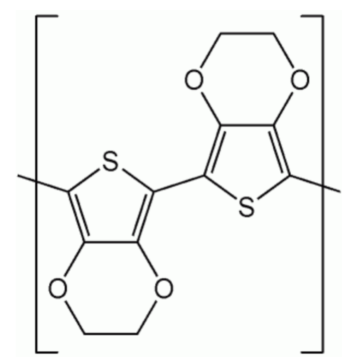


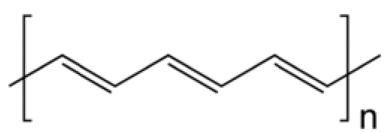
–e
Polaron
–e
Charged solitons
Bipolaron

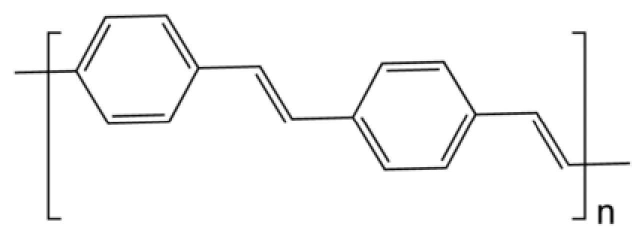


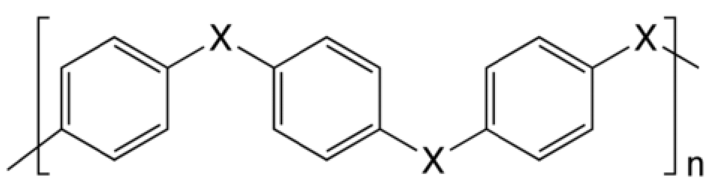
Conduction bands
Valence bands
Neutral polymer: full valence and empty conduction bands.
Removal of one electron forms polaron.
Removal of second electron forms bipolaron.
Removal of more electrons forms bipolaron bands.

- CPs
  - polyacetylene
  - PPP, PPV
  - PPS
  - PPy, PT, PEDOT, PANI
  - modified
  - blend/composite

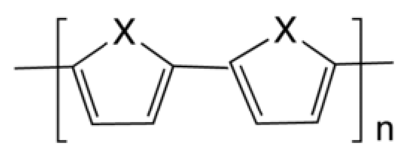








(X = NH/N, S)

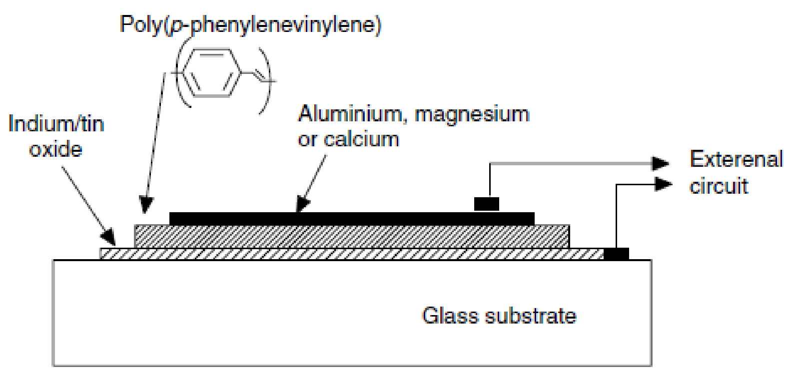


(X = NH, S)

- applications
  - rechargeable battery [secondary battery]

    cf> lithium secondary batteries
    - LIB ~ Li M oxide/liquid electrolyte/carbon
    - LIPB ~ Li M oxide/polymer electrolyte/carbon
    - LPB ~ Li M oxide/polymer electrolyte/Li metal
    - CP as electrode(s) ~ light wt, easy to process, but low energy and charge/discharge efficiency
      - Fig 5.23-25 and Table 5.11
  - electrochromic device [ECD]
    - color change doped/undoped
    - all-solid, low power consumption, wide viewing angle
    - slow response (doping-undoping)
    - display, smart window

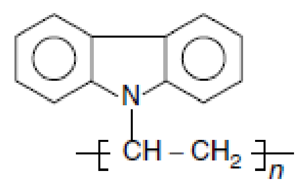
- sensors
  - change in conductivity by chemical, pH, humidity, biomolecule
    - e.g., nucleophiles cause decrease in conductivity
  - by interaction betw dopant and environment
- LED



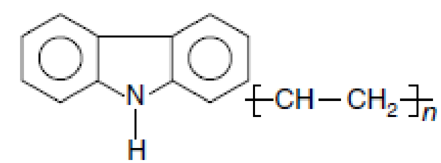
- electrostatic discharge
- solar cell, etc

Photoconductive polymers

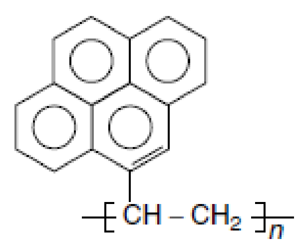
- photoconduction ~ change in the electrical conductivity by absorbing radiation
- polymers with large aromatic side group
  - helical conformation with parallel side group
- PVCz with TNF popular
  - TNF for modulating (360 to 550 nm)
- xerography
  - coated on the drum
  - uniformly charged
  - selectively discharged
  - attract toner and printing



(VII)



(VIII)



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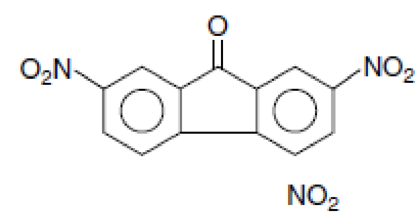
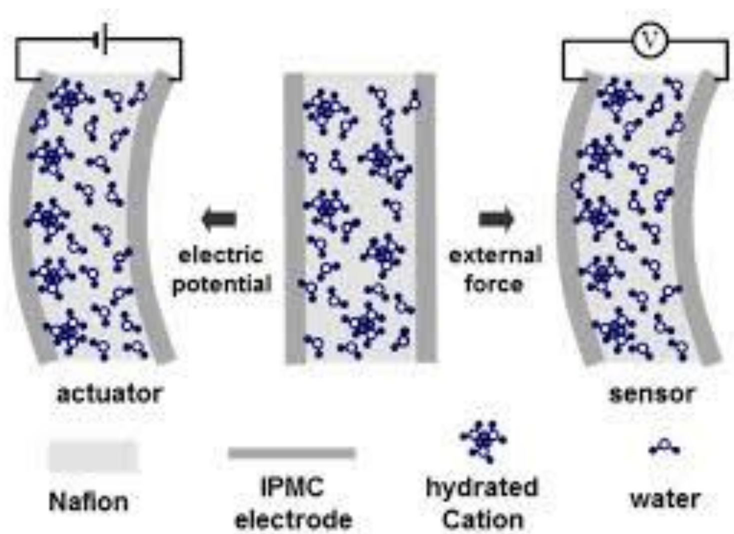


(X)

Electroactive polymers [EAP]

- change in size a/o shape by electric field
- polymer actuator/sensor
- ionic, electronic

- ionic EAP
  - ionic polymer-metal composites [IPMC]
    - cation/solvent moves to cathode



- ionic EAP (cont'd)
  - ionic polymer gel
    - crosslinked ionomer
    - electric field → H^+ moves in/out → actuation
  - CNT
    - polymer supported ionic liquid center
    - CNT as electrode
    - ions moves cathode/anode
  - conductive polymers
    - CP/insulating bilayer
    - actuation by counter ion in/out

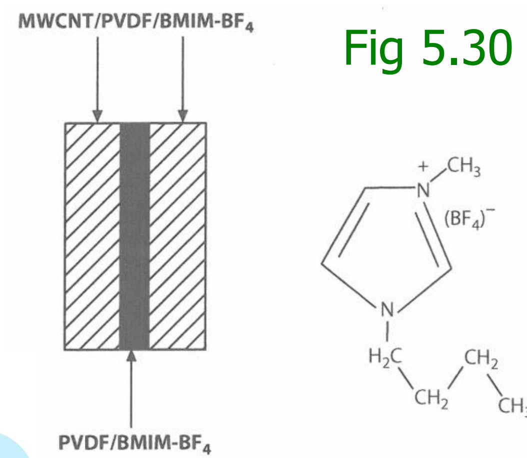
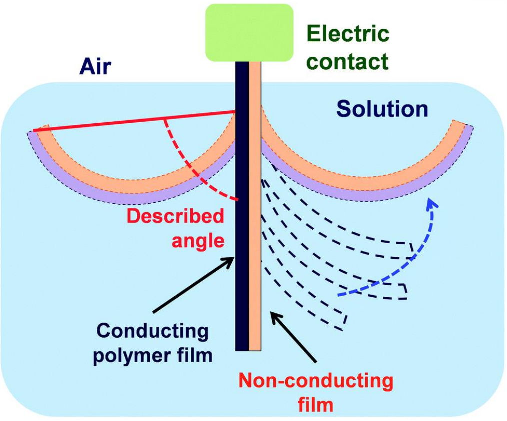


Fig 5.30



- electronic EAP
  - ferroelectric polymers
    - PVDF, odd # PA, and copolymers
    - ferro-paraelectric transition at Curie Temp → change in lattice parameter → actuation
  - polymer electrets
    - porous PP, fluoro, PET electret [electric magnet]
    - converse of piezoelectric = change in thickness by voltage
  - electrostrictive polymers
    - PVDF-based or LC polymers
    - polymer (nano)crystals
    - align by electric field
    - main- or side-chain

ferro/para/diamagnetic
ferro/para/dielectric
permanent/temporary/small

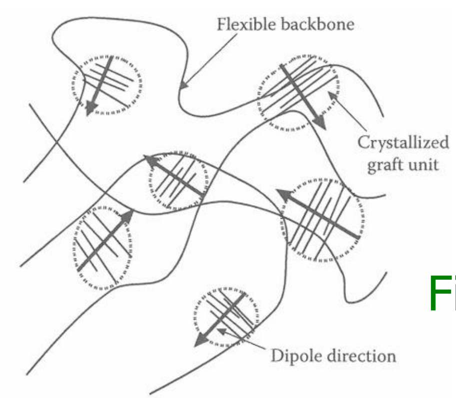


Fig 5.32

- electronic EAP (cont'd)
  - dielectric elastomers
    - flexible electrodes (like CB)
      - attraction betw electrodes
      - repulsion on electrodes
    - PDMS, PU, acrylates
    - large strain, force; high V

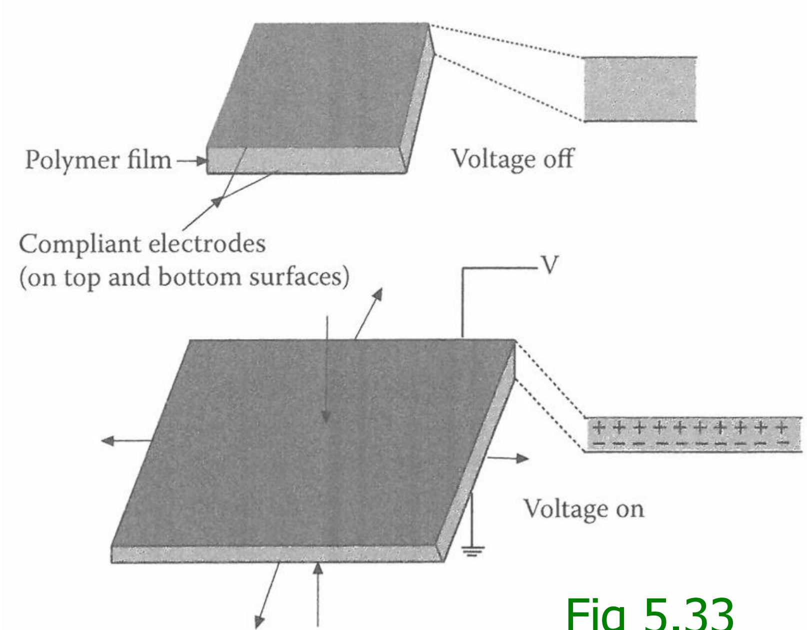


Fig 5.33