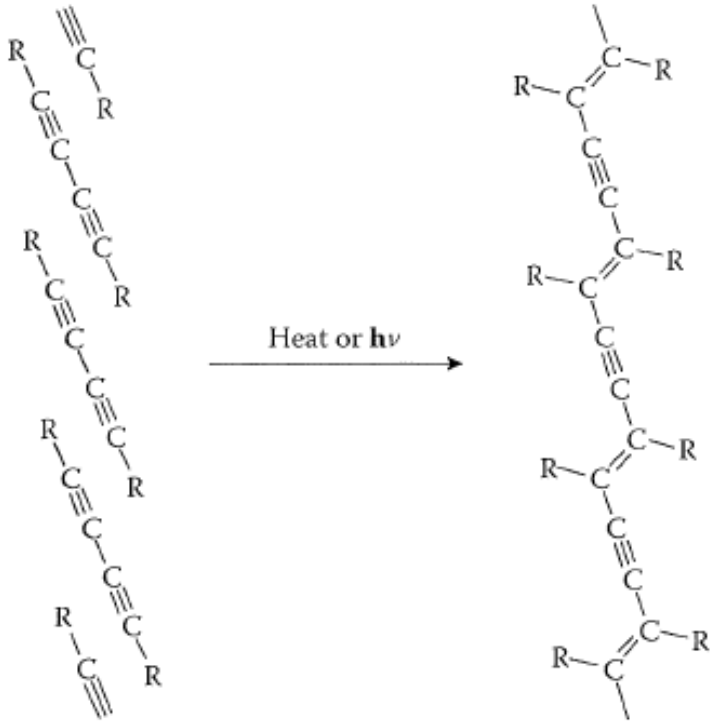
Chapter 8

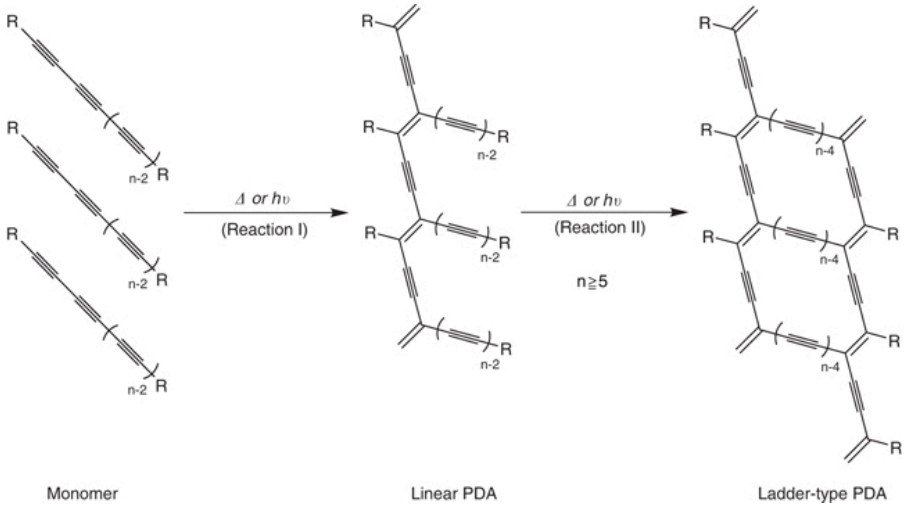
Specialized Methods of Polymer Synthesis

Topochemical solid-state polym'n

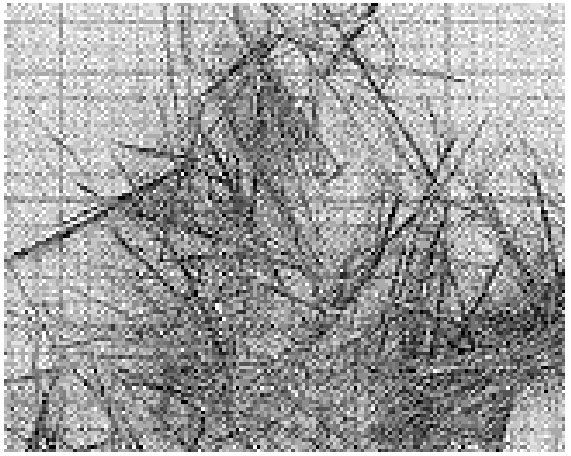
- solid-state polym'n
  - for step or chain monomers/polymers
    - using high energy radiation or heat
    - functional, radical, or ionic
    - between T_g and T_m
  - solid-state polym'n of vinyl or cyclic monomers (by UV or γ-ray)
  - post-polym'n of polyesters and polyamide (by heat)
  - cross-linking of PE (by γ-ray) ~ XPE
- topochemical polym'n
  - monomer crystal to polymer crystal
  - topology kept

- diacetylene





- polymer single crystal
- conjugated ~ electro-optical property



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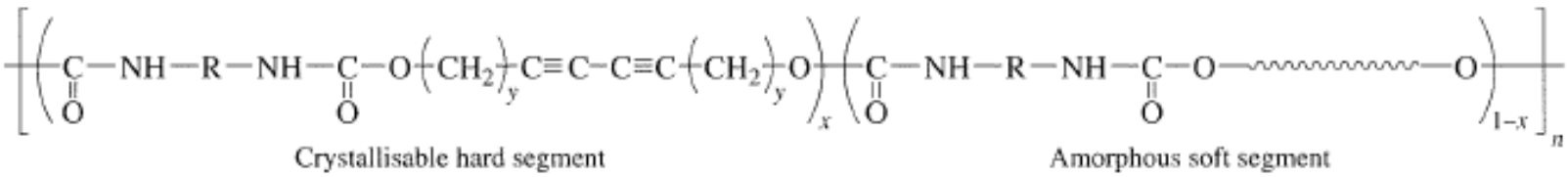
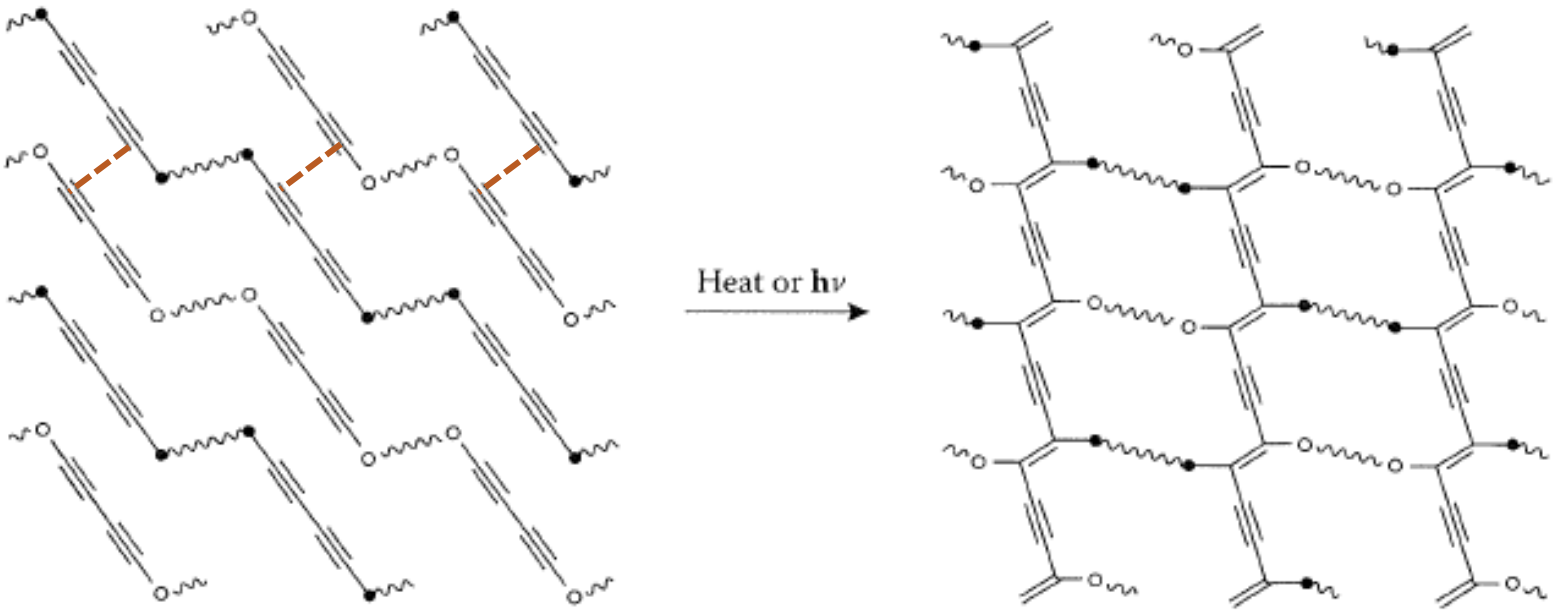
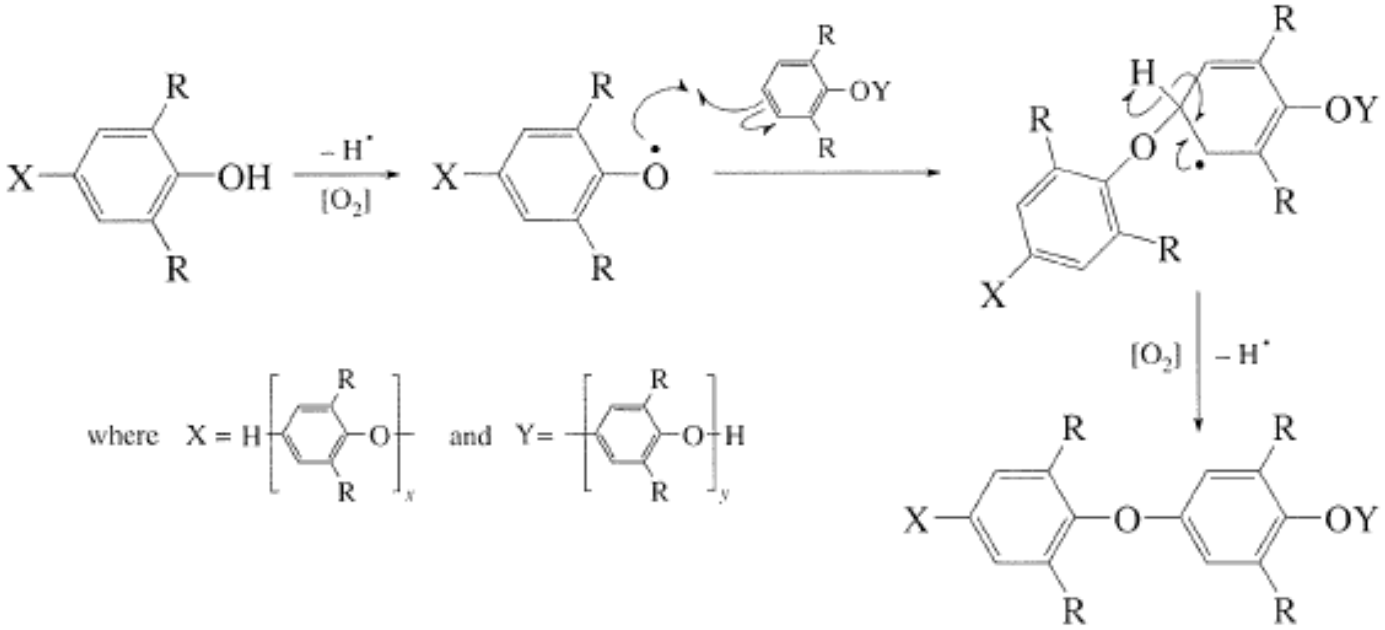
- cross-polym'n





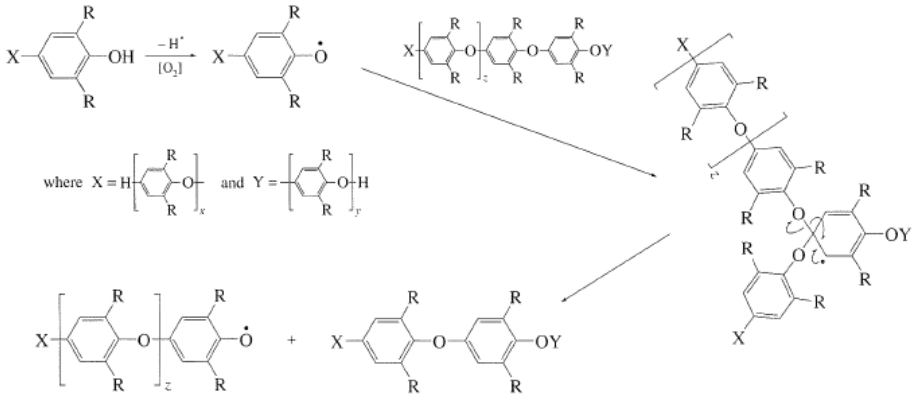
Polym'n by oxidative coupling

- polym'n of phenols

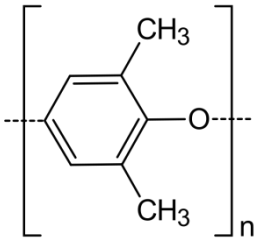


- bubbling O_2 through solution of phenol and CuCl (cat)
- oxidation-coupling of phenols with any MM
- a step polym'n

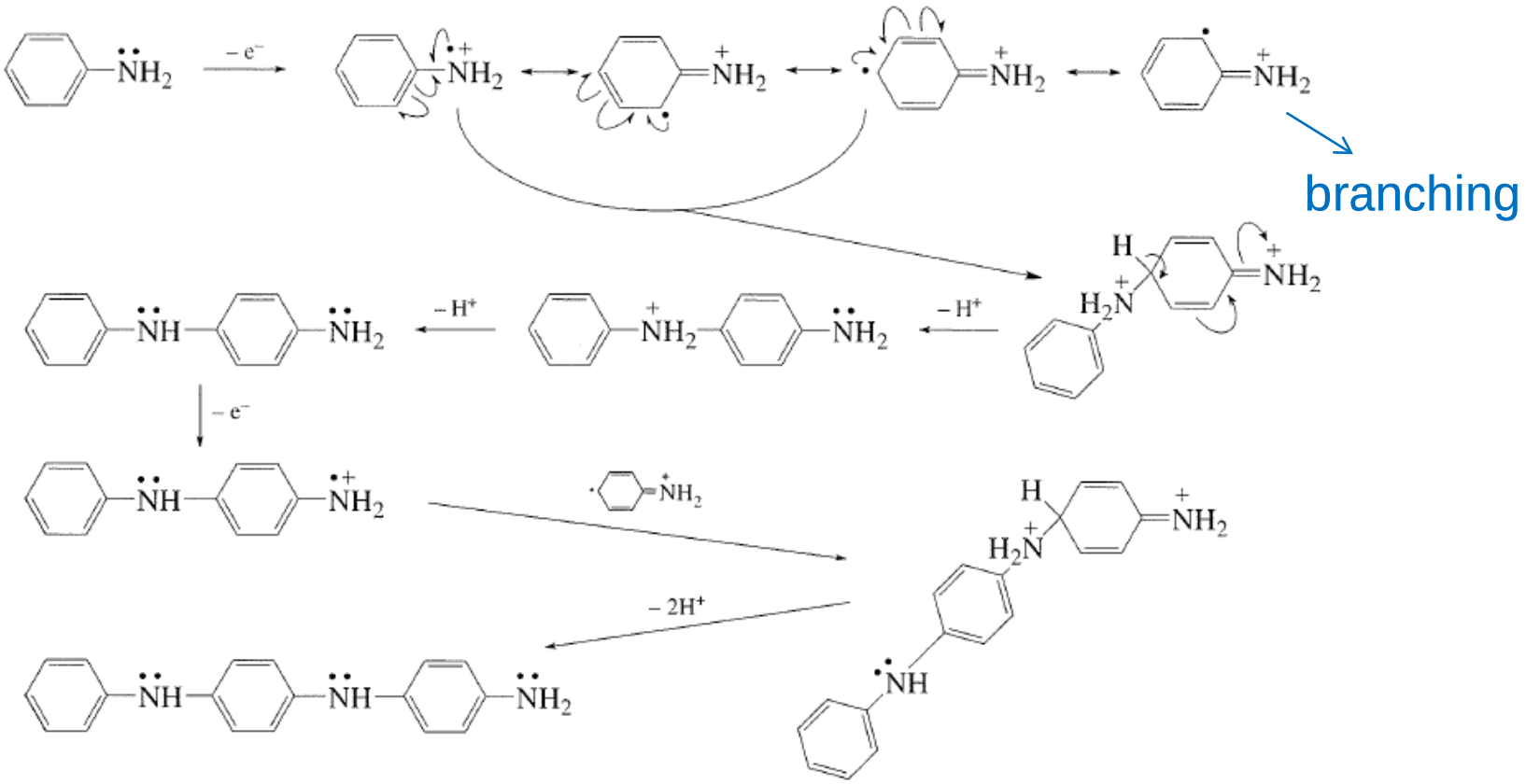
- polym'n of phenols (cont'd)
  - interchange rxn



  - R = CH_3 ~ polyphenylene oxide (PPO)
    - an engineering plastic
    - usually as blends ~ mPPO
      - with PS ~ Noryl®
      - with nylon ~ Noryl GTX

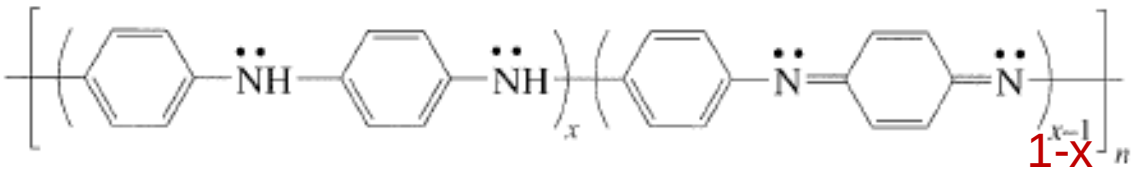


- polyaniline (PANi)
  - chemical or electrochemical oxidation/coupling

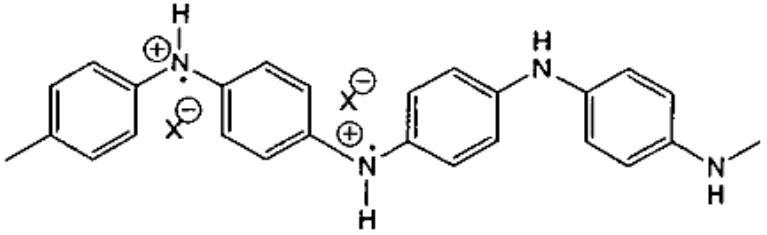


    - a step polym'n

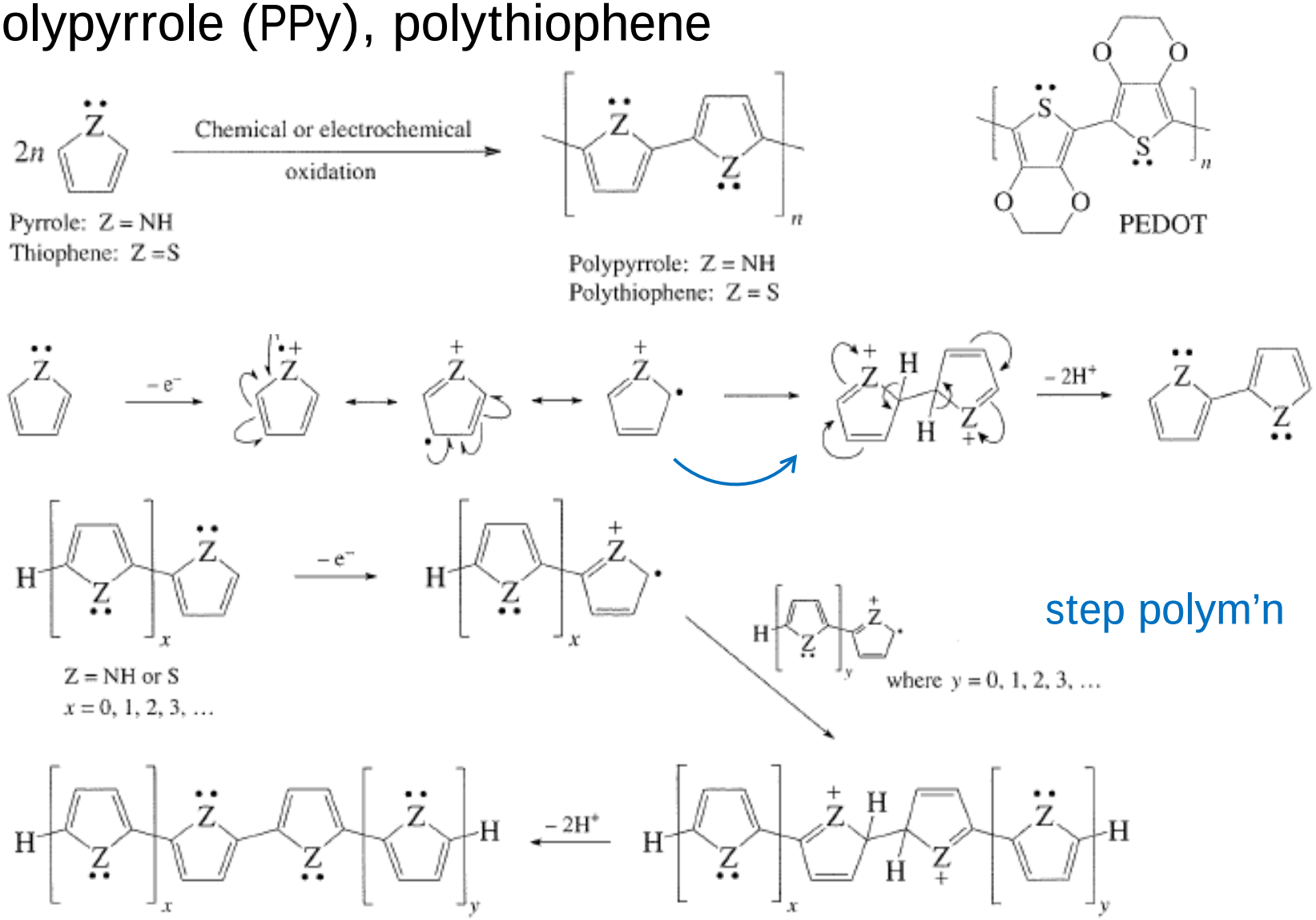
- PANi (cont'd)



- obtained as solution, colloid, fiber, film
- (oxidation) states
  - x = 1 ~ leucoemeraldine ~ fully reduced [all-amine]
  - x= 0 ~ pernigraniline ~ fully oxidized [all-imine]
  - x = 0.5 ~ emeraldine (base)
- conducting by doping [+ HX]
  - emeraldine base to emeraldine salt



- polypyrrole (PPy), polythiophene

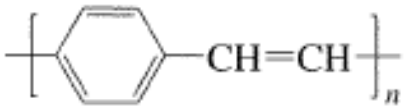


step polym'n

Precursor route to intractable polymers

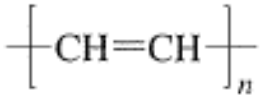
poly(1,4-phenylene)

PPP



poly(1,4-phenylene vinylene)

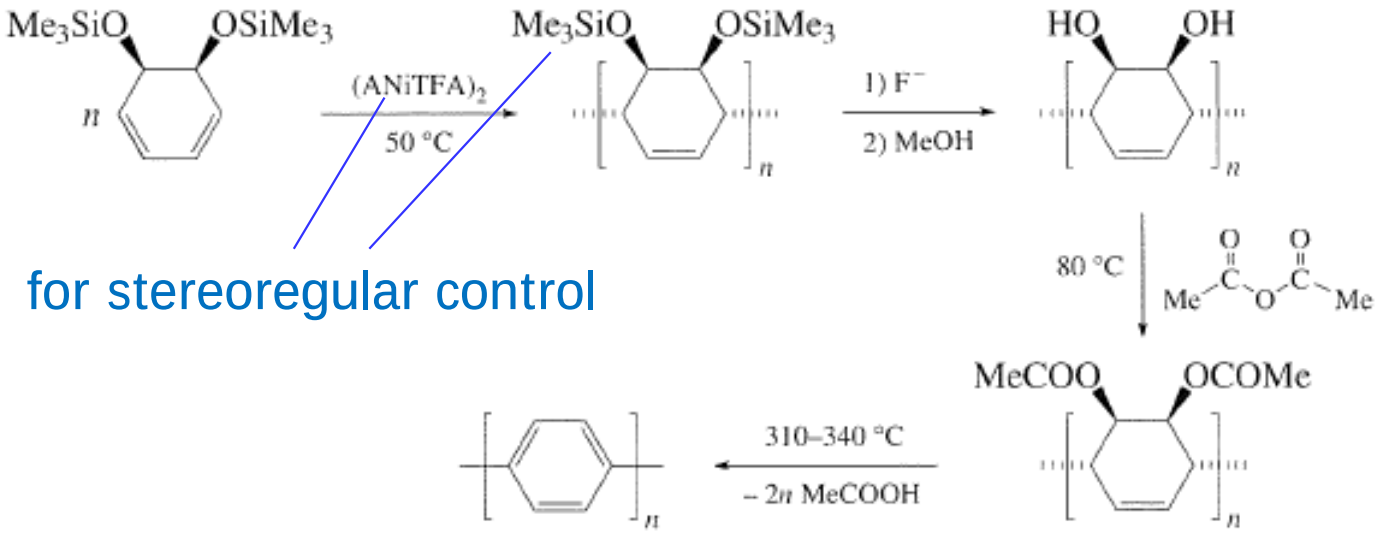
PPV



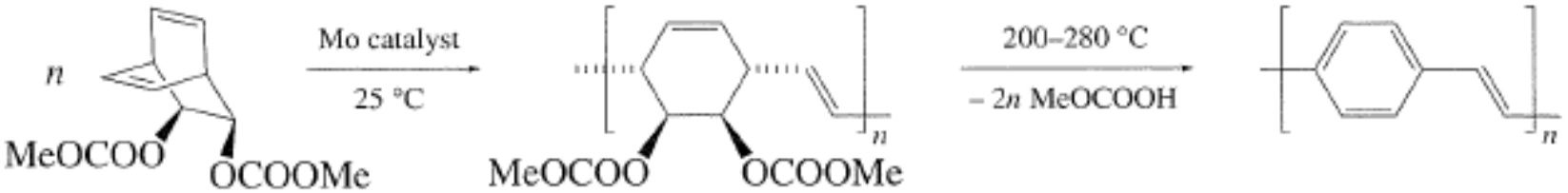
polyacetylene

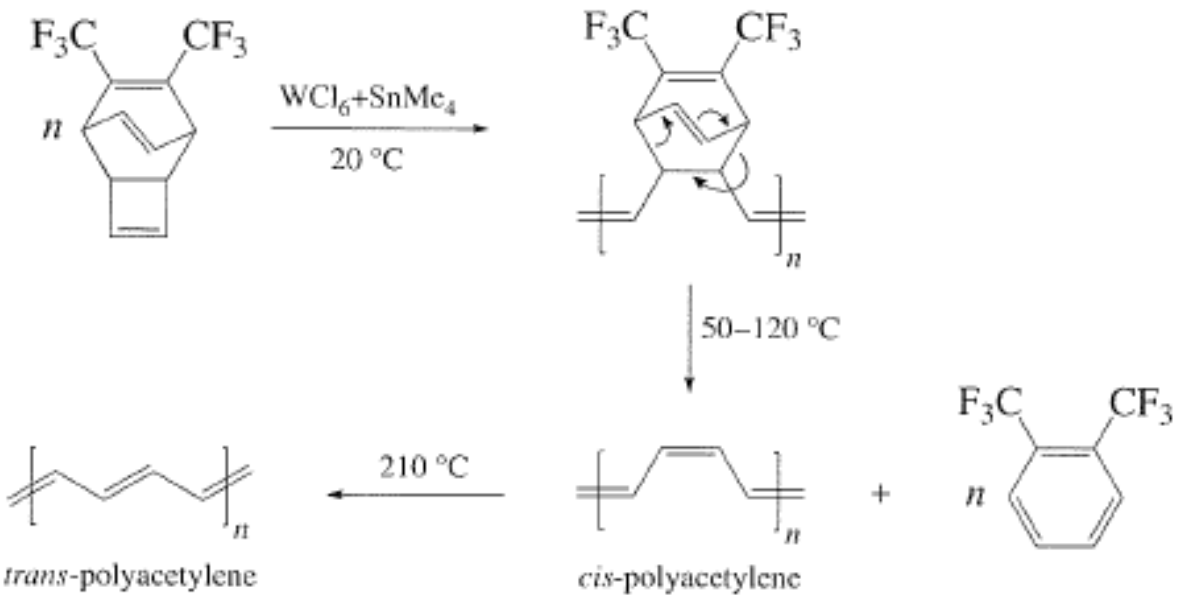
also conducting polymers

- intractable ~ degrade before melting
  - precursor → formed (film, fiber) → polym'n *in situ*



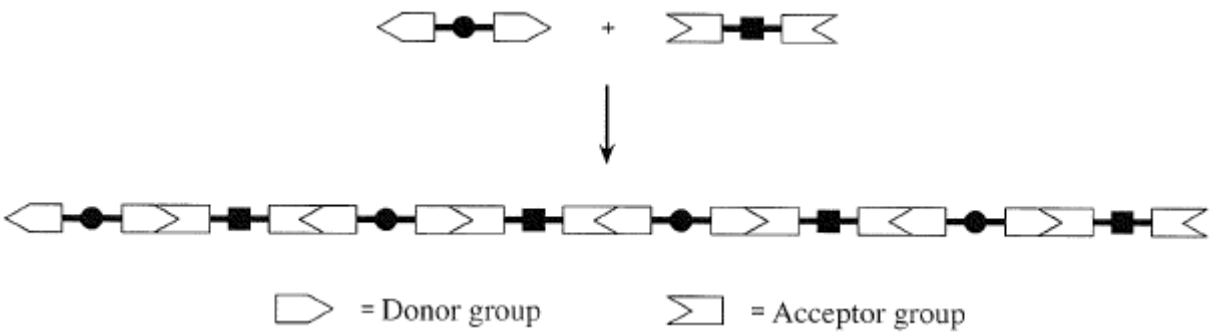
for stereoregular control


n
MeOCOO
OCOOMe
Mo catalyst
25 °C
MeOCOO
OCOOMe
n
200–280 °C
– 2n MeOCOOH
n

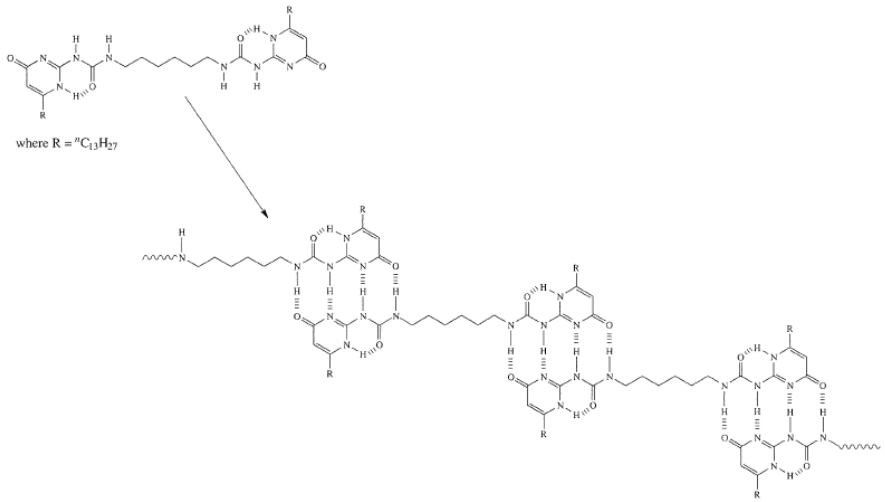

F3C
CF3
n
WCl6+SnMe4
20 °C
F3C
CF3
n
50–120 °C
210 °C
n
trans-polyacetylene
n
cis-polyacetylene
+
F3C
CF3
n

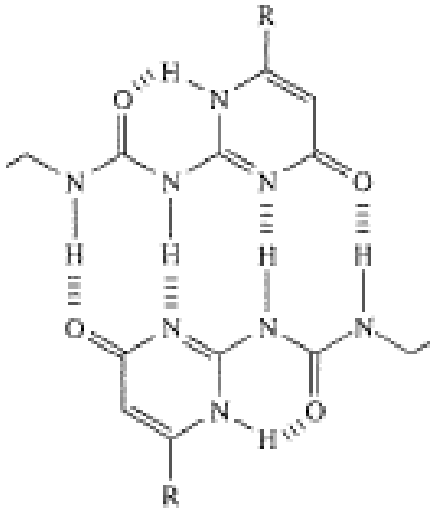
Supramolecular polym'n

- polyassociation of donor and acceptor

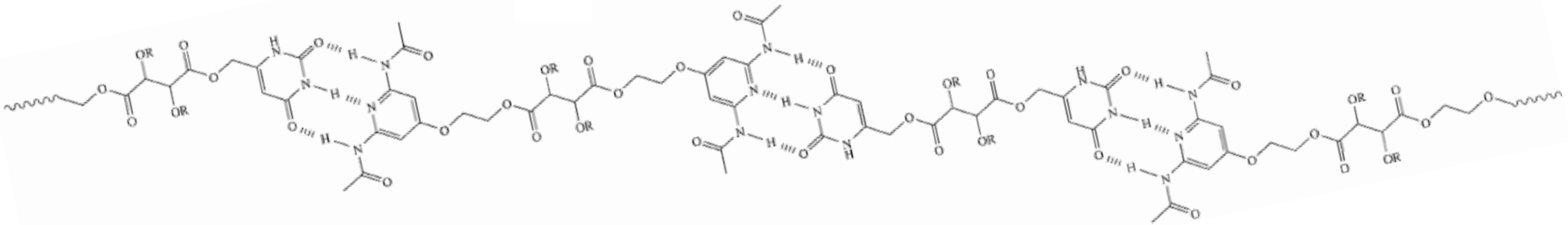


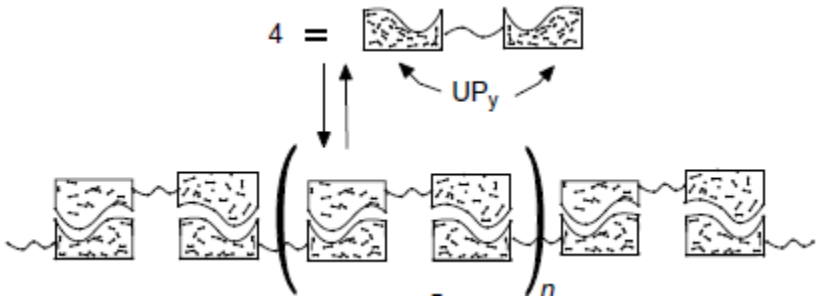
- usually by multiple hydrogen bonding Table 8.1

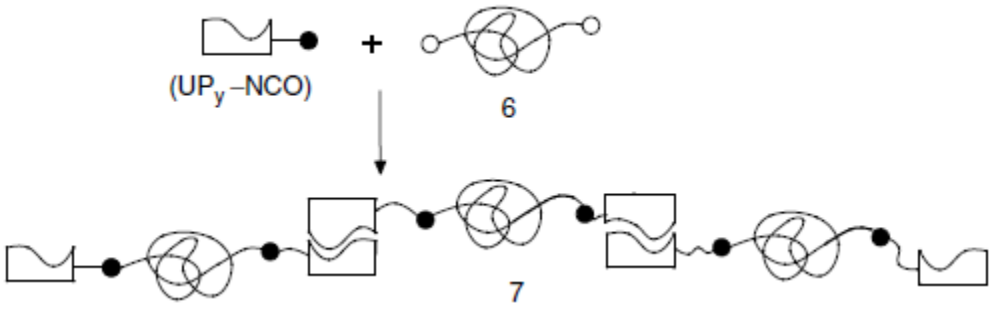




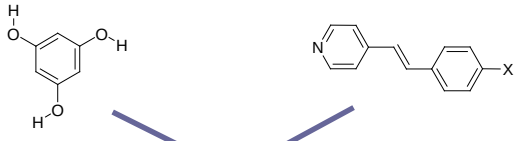
- forms stable yet reversible chain
- high mechanical property and good processability



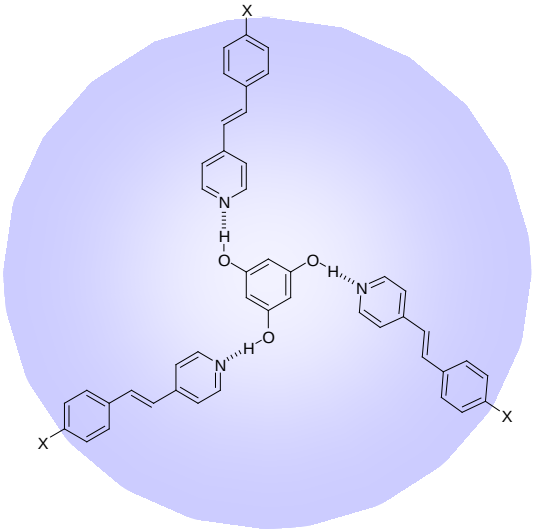




Self-assembled Discotic Liquid Crystals



" Self-assembly via H-Bonding "



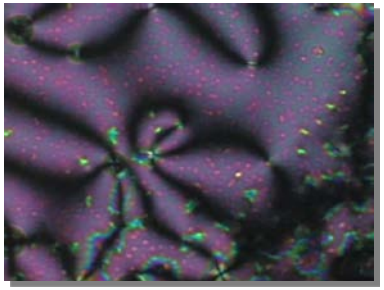
X = $-O(CH_2)_{n-1}CH_3$

Self-assembled Disk

Molecular ordering

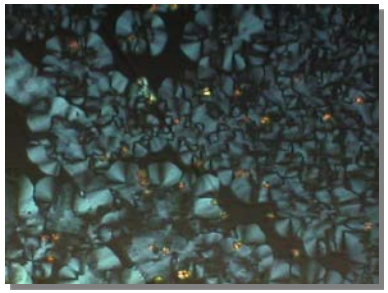
Liquid Crystalline Structures

Short alkyl chain



Nematic columnar (N_c)

Long alkyl chain

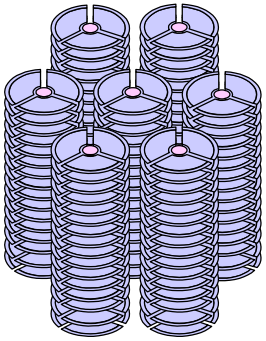


Hexagonal columnar (Col_h)

Dynamic charge transport materials

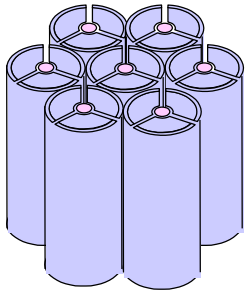
Nanoporous Materials using DLC Template

polymerization

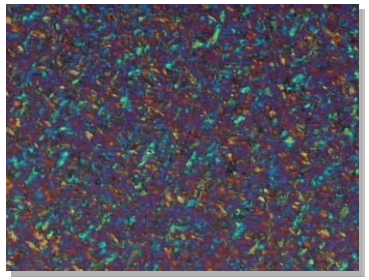


Assembled Structures

UV



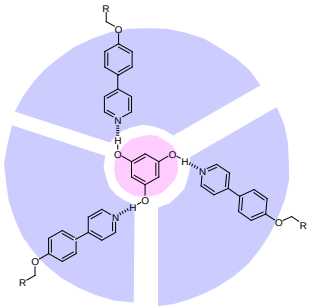
POM



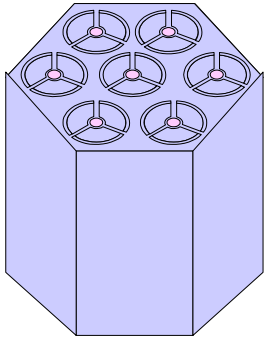
- Columnar direction
- Fixation of columnar order

Discotic LC polymer

UV

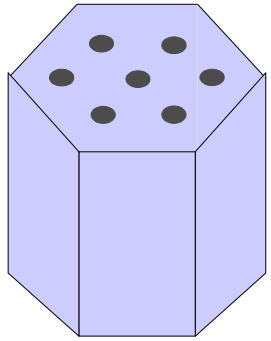


Disk



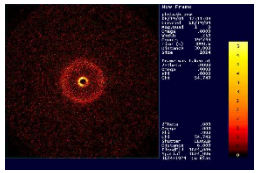
removal

Base

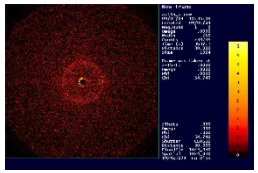


Nanoporous polymer

SAXS



SAXS



- Columnar structure maintained.