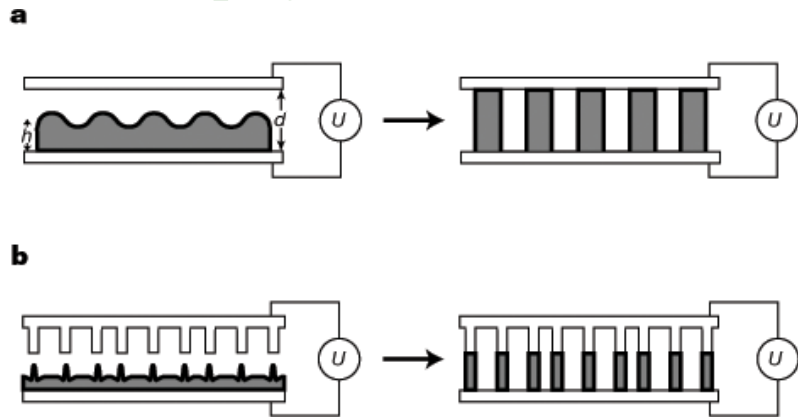


# Chapt. 9 Electrical Properties of Polymers

- The electrical properties are required when polymers are used for cable insulation, for capacitors, for insulation or packaging of electronic devices or as integral parts of electronic devices.
  - **Resistivity:** The resistance (电阻) of most polymer to the flow of direct current is very high.
  - **Dielectric constant and loss factor**
  - **Dielectric strength (介电强度):** Insulators (绝缘体) will not sustain an indefinitely high voltage. As the applied voltage is increased, a point is reached where a catastrophic decrease in resistance takes place, accompanied by a physical breakdown (击穿) of the dielectric.
  - **Ferroelectric polymers (铁电高分子):** Some polymers are permanently polarized when they are subjected to a very strong electric field.
  - **Piezoelectric polymers (压电高分子):** The polymers, such as polyvinylidene fluoride, may generate a net positive charge on one side and a negative charge on the other side when pressure is applied.
  - **Conducting polymers (导电高分子)**

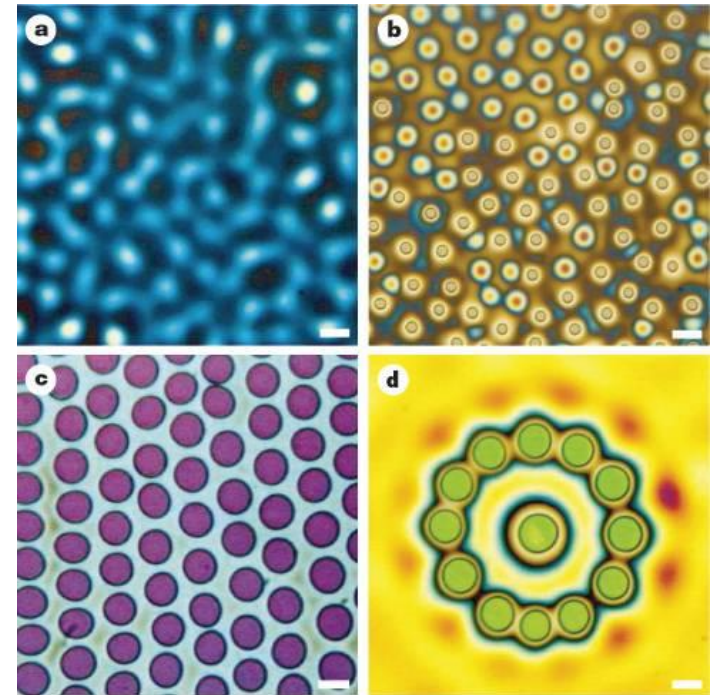
# What can happen when polymers are in electric field - Homopolymer

## ➤ Homopolymer PS



**Figure 1** Schematic representation of the capacitor device. **a**, The electrostatic pressure acting at the polymer (grey)–air interface causes an instability in the film (left). This instability has a well defined wavelength. Eventually, polymer columns span the gap between the two electrodes (right). **b**, If the top electrode is replaced by a topographically structured electrode, the instability occurs first at the locations where the distance between the electrodes is smallest (left). This leads to replication of the electrode pattern (right).

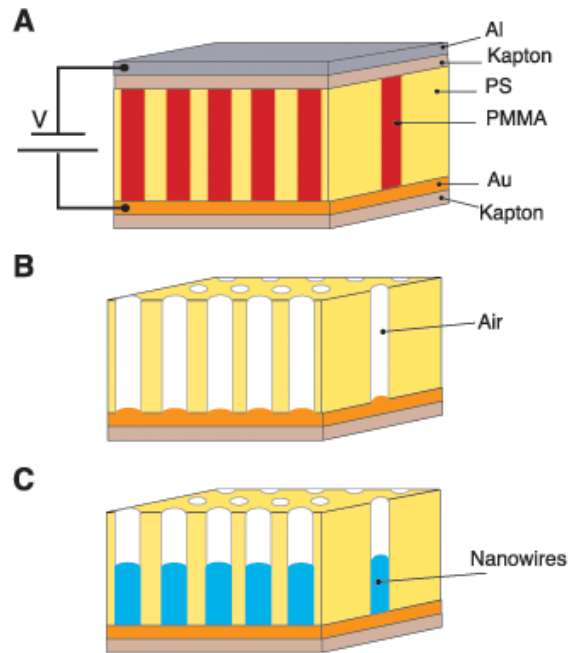
**Figure 2** Optical micrographs of polystyrene films which have been exposed to an electric field. In **a** and **b**, a 93-nm-thick polystyrene film was annealed for 18 h at 170 °C with an applied voltage  $U = 50$  V. As the electrode spacing in **a** was larger than in **b**, corresponding to a lower electric field  $E_p$ , two different stages of the instability were observed, corresponding to Fig. 1a and b. In **c** and **d**, the thickness of the polystyrene film was doubled ( $h = 193$  nm). This leads to a denser packing of the polymer columns and to an enhanced repulsion between the columns. As a result, we observe a more complete



hexagonal order in **c**. In **d** a second-order effect is observed for a nucleated instability (see text). Instead of a hexagonal symmetry which characterizes the nearest neighbours in **c**, a ring of 12 columns lies on a circle with a radius of  $2\lambda$ . The scale bars correspond to 10  $\mu\text{m}$  in **a** and **b** and to 5  $\mu\text{m}$  in **c** and **d**. The colours arise from the interference of light, and correspond to the local thickness of the polymer structures (for example, in **d**, yellow corresponds to a film thickness of  $\sim 200$  nm, green to  $\sim 450$  nm).

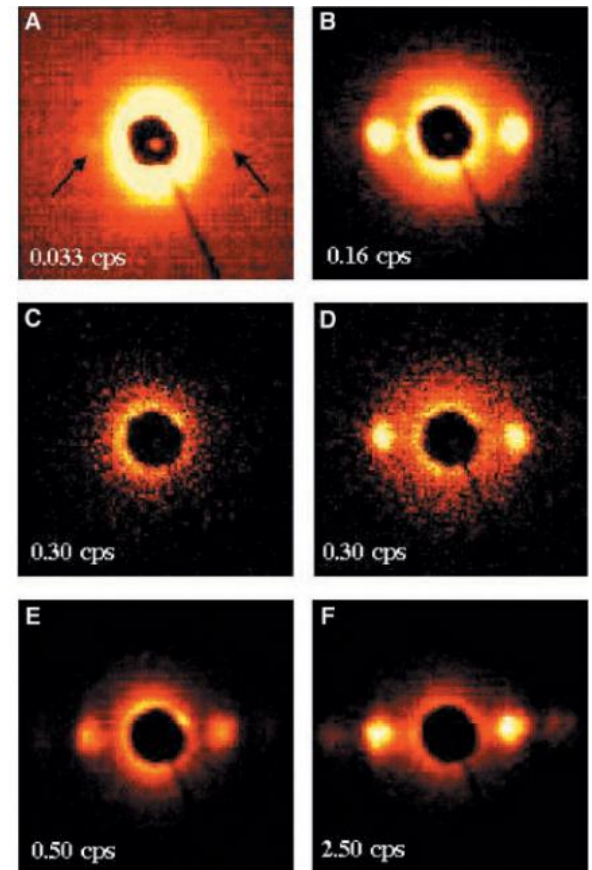
# What can happen when polymers are in electric field – Diblock Copolymer

## ➤ Diblock copolymer PS-*b*-PMMA



**Fig. 1.** A schematic representation of high-density nanowire fabrication in a polymer matrix. (A) An asymmetric diblock copolymer annealed above the glass transition temperature of the copolymer between two electrodes under an applied electric field, forming a hexagonal array of cylinders oriented normal to the film surface. (B) After removal of the minor component, a nanoporous film is formed. (C) By electrodeposition, nanowires can be grown in the porous template, forming an array of nanowires in a polymer matrix.

**Fig. 2.** Small-angle x-ray scattering patterns taken at different steps during the process of nanowire fabrication. All measurements were made at an angle of incidence at 45°. (A) Sample oriented in the electric field. Two weak equatorial reflections (indicated by arrows) show the alignment of the cylindrical microdomains oriented in the electric field normal to the surface. (B) Because of the increased contrast after pore formation the scattering intensity is strongly enhanced, whereas the position of the peaks is unchanged. (C) A water-methanol mixture wets the interior of the pores; because of contrast matching, the scattering pattern disappears. (D) Water alone does not wet the interior of the pores; the scattering pattern remains unchanged. (E and F) Scattering pattern obtained from the same sample before (E) and after (F) electroplating with Co. Because of the high electron density of Co the intensity increases strongly. Again, the peak positions remain unchanged. Higher order reflections can be seen, indicating the highly ordered structure of the nanowire array. Note that the difference between (B) and (E) arises from the change in scale.

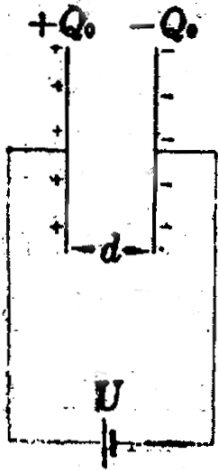


Thurn-Albrecht T.; etc. *Science* **2000**, *290*, 2126.

# Polarization and Dielectric Constant

➤ **Dielectric constant ( $\epsilon$ , 介电常数):** the ratio of the capacities ( $C$ , 电容) of a parallel plate condenser (平行板电容器) measured with and without the dielectric material placed between the plates.

➤ **Parallel condenser without dielectric material**



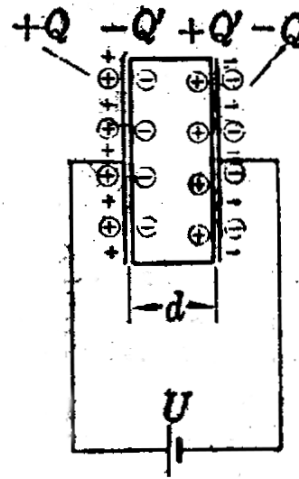
$$C_0 \equiv \frac{Q_0}{U} = \epsilon_0 \frac{S}{d}$$

$C_0$ : capacitance of the capacitor in vacuum.

$\epsilon_0$ : permittivity of free space (真空电容率).

$S$ : area of the plate

➤ **Parallel condenser with dielectric material**



The dielectric is polarized (极化) when field is applied.

$$C \equiv \frac{Q}{U} = \frac{Q_0 + Q'}{U} = \epsilon \epsilon_0 \frac{S}{d}$$

$$\epsilon = \frac{C}{C_0}$$

# Polarization and Dielectric Constant

- Polarization ( $P$ , 极化强度) and dielectric displacement vector ( $D$ , 电位移矢量)

$$E = \frac{U}{d} \quad P = \frac{Q'}{S} \quad \longrightarrow \quad P = \varepsilon_0 (\varepsilon - 1) E, \quad D \equiv \varepsilon_0 E + P = \varepsilon_0 \varepsilon E$$

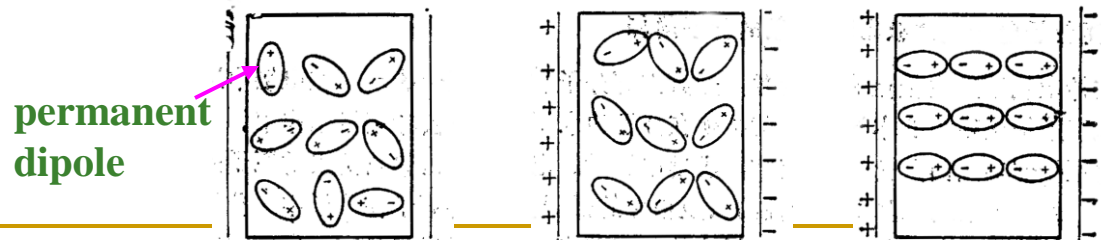
When a constant field  $E_0$  is switched on at zero time, one finds in general a time dependent polarization  $P(t)$ , set up of an instantaneous part  $P_u$  and a retarded part  $P_{or}$ .

$$P(t) = P_u + P_{or}(t), \quad P(t) = \varepsilon_0 (\varepsilon(t) - 1) \cdot E_0, \quad P(t) = \varepsilon_0 (\varepsilon_u - 1) E_0 + \varepsilon_0 \Delta \varepsilon(t) E_0$$

- $P_u$  is due to the shift of the electron clouds and the deformation of the molecular skeletons which occur within times corresponding to frequencies in the UV- and IR-range respectively.

- $P_{or}$  arises for polar molecular fluids and originates from the orientation of the permanent dipoles.

- Orientational polarization (取向极化)



$$P = N \alpha E_l$$

Without field

With field

With strong field



# Relation between Dielectric Constant and Molecular Polarizability

## Clausius-Mosotti Equation:

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{\tilde{N}\alpha}{3\epsilon_0}$$

**nonpolar molecule**

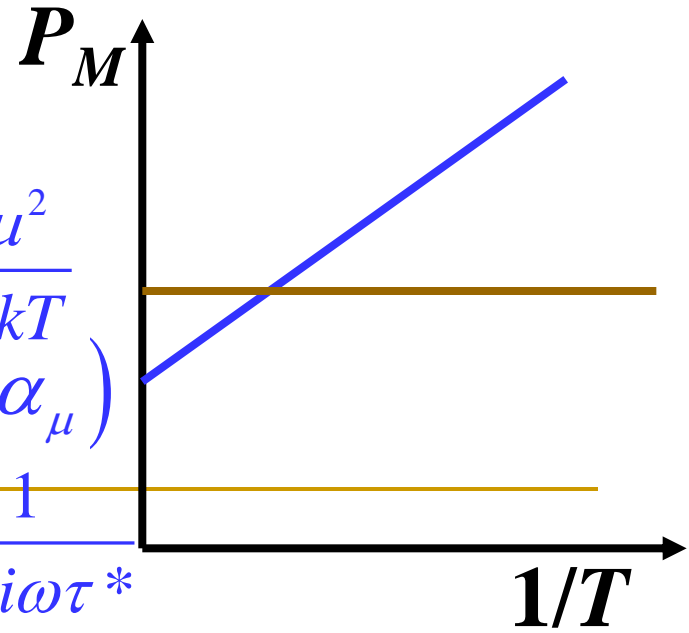
$$P_M = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{\tilde{N}}{3\epsilon_0} (\alpha_e + \alpha_a)$$

**polar molecule**

$$P_M = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{\tilde{N}}{3\epsilon_0} (\alpha_e + \alpha_a + \alpha_\mu)$$

$$\alpha_\mu = \frac{\mu^2}{3kT}$$

$$\alpha_\mu^* = \alpha_\mu \frac{1}{1 + i\omega\tau^*}$$



# Dielectric Relaxation and Loss

- Reorientation of dipoles on a change in the electric field is known as dielectric relaxation.

The strategy of its measurement and its formal description are completely analogous to mechanical relaxation.

$$U = U_0 \exp(i\omega t) \longrightarrow I(t) = i\omega I_0 \exp(i\omega t)$$

- Time dependent polarization with a possible phase-lag of  $\varphi$ :

$$P(t) = P_0 \exp[i(\omega t - \varphi)]$$

- Complex dielectric function:

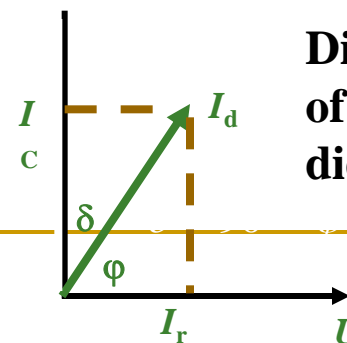
$$\varepsilon^*(\omega) = \underbrace{\varepsilon'(\omega)}_{\text{“real” part}} - i \underbrace{\varepsilon''(\omega)}_{\text{“imaginary” part}}$$

$$I_d = C \frac{dU}{dt} = \varepsilon^* C_0 \frac{dU}{dt} = i\omega \varepsilon^* C_0 U$$

$$I_d = i\omega(\varepsilon' - i\varepsilon'')C_0 U = \underbrace{i\omega\varepsilon' C_0 U}_{I_C} + \underbrace{\omega\varepsilon'' C_0 U}_{I_r}$$

$I_C$ : “pure capacitance” (纯电容)

$I_r$ : “pure resistance” (纯电阻)



Dielectric loss angle: measure of the power dissipation in the dielectric

$$\tan \delta = \frac{I_r}{I_C} = \frac{\varepsilon''}{\varepsilon'}$$

# Complex dielectric constant & Complex Viscosity

$$\gamma = \gamma_0 \sin(\omega t) \quad \sigma(t) = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta$$



$$\dot{\gamma} = \frac{d\gamma}{dt} = \gamma_0 \omega \cos(\omega t)$$



asynchronism



synchronization

Viscosity of  
asynchronism part

Viscosity of  
synchronization part

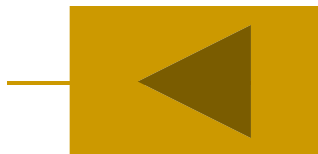
$$\eta'' = \left( \frac{\sigma_0}{\gamma_0 \omega} \right) \cos \delta \quad \eta' = \left( \frac{\sigma_0}{\gamma_0 \omega} \right) \sin \delta$$

$$E' = \left( \frac{\sigma_0}{\gamma_0} \right) \cos \delta \quad \downarrow$$

$$\downarrow E'' = \left( \frac{\sigma_0}{\gamma_0} \right) \sin \delta$$

$$\eta'' = \frac{E'}{\omega}$$

$$\eta' = \frac{E''}{\omega}$$





# mechanics loss & electric loss

The imaginary part of complex viscosity  $\eta$ :  $\eta = \eta' + i\eta''$

$$\sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta = (i\eta' + \eta'')\omega\gamma$$

$$\dot{\gamma} = \frac{d\gamma}{dt} = \gamma_0 \omega \cos(\omega t)$$

“pure  
viscosity”

“pure  
elastic  
modulus”

The real part of dielectric constant  $\varepsilon$ :  $\varepsilon = \varepsilon' + i\varepsilon''$

$$I_d = (i\varepsilon' + \varepsilon'')\omega C_0 U$$

“pure  
capacitanc  
e” (纯电容)

“pure  
resistance”  
(纯电阻)

# Dielectric Relaxation and Loss

## ➤ Single-time relaxation process (Debye-process)

- For a single characteristic time  $\tau$  is included for the relaxation, the dielectric constant is  $\epsilon_s$  at  $\omega\tau = 0$ , and  $\epsilon_\infty$  at  $\omega\tau \rightarrow \infty$ .

$$\frac{\epsilon^* - 1}{\epsilon^* + 2} \frac{M}{\rho} = \frac{\tilde{N}}{3\epsilon_0} \left( \alpha_e + \alpha_a + \frac{\alpha_\mu}{1 + i\omega\tau} \right)$$

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau}$$

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{1 + \omega^2\tau^2} + i \frac{\omega\tau\Delta\epsilon}{1 + \omega^2\tau^2}$$

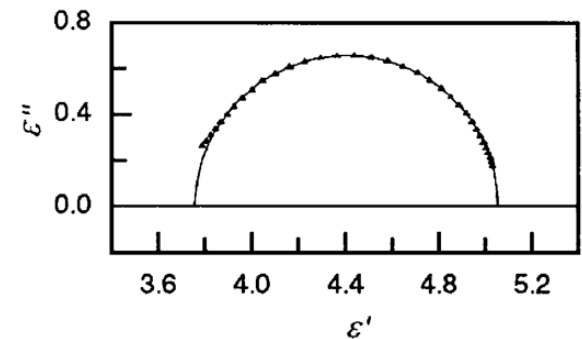
relaxation strength:  
 $\Delta\epsilon = \epsilon_s - \epsilon_\infty$

## ➤ Cole-Cole plot

$$\left[ \epsilon' - \left( \epsilon_\infty + \frac{\Delta\epsilon}{2} \right) \right]^2 + (\epsilon'')^2 = \left[ \frac{2\epsilon' - 2\epsilon_\infty - \Delta\epsilon}{2} \right]^2 + (\epsilon'')^2$$

$$= \left[ \frac{2\Delta\epsilon - \Delta\epsilon(1 + \omega^2\tau^2)}{2(1 + \omega^2\tau^2)} \right]^2 + \frac{\Delta\epsilon^2\omega^2\tau^2}{(1 + \omega^2\tau^2)^2}$$

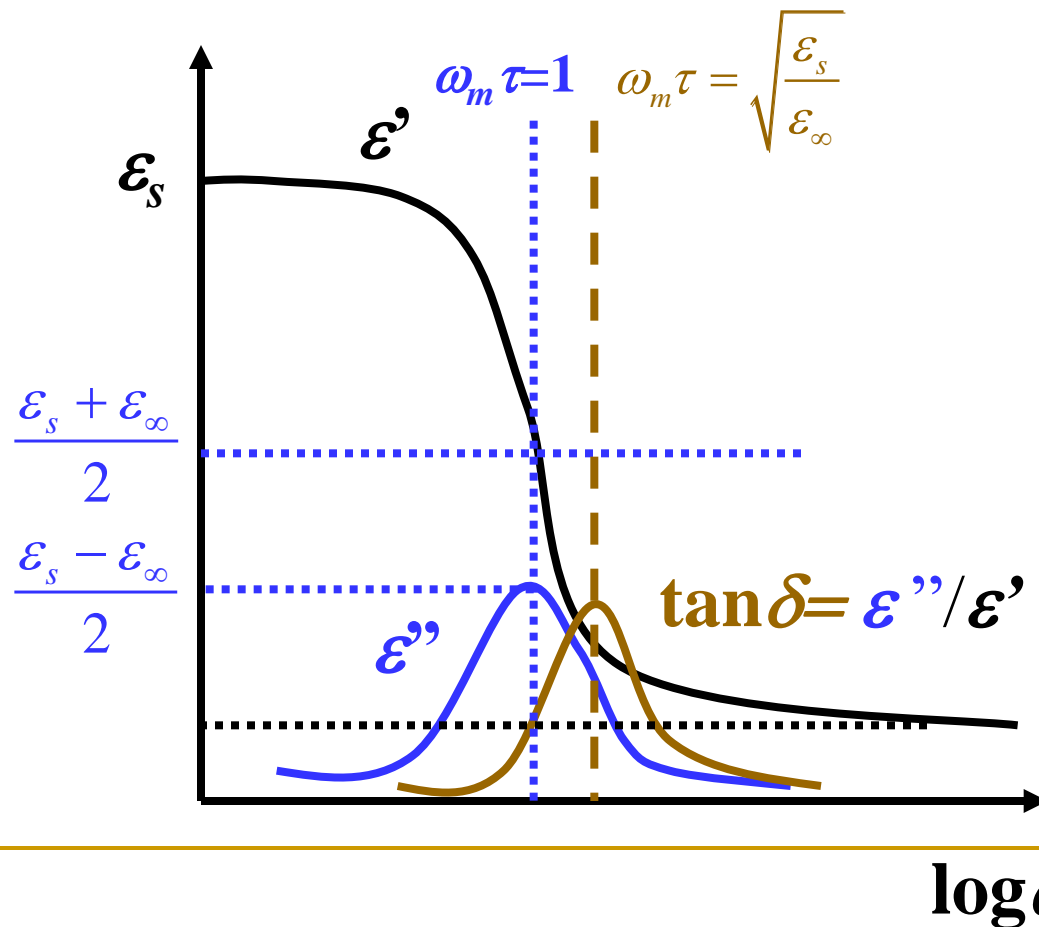
$$= \frac{\Delta\epsilon^2(1 + \omega^2\tau^2)^2}{4(1 + \omega^2\tau^2)^2} = \frac{\Delta\epsilon^2}{4}$$



**Cole-Cole plot of dielectric data obtained for a dipole carrying rod-like molecule ( $C_6C_3$ ) of low molar mass.**  
 (Seiberle, H.; etc. *Macromolecules* **1990**, *23*, 2008.)

How to get  $\varepsilon'$  and  $\varepsilon''$ ,  $\varepsilon_s$  and  $\varepsilon_\infty$

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \omega^2\tau^2} + i \frac{\omega\tau\Delta\varepsilon}{1 + \omega^2\tau^2}$$



$$\tan \delta_m = \frac{\varepsilon_s - \varepsilon_\infty}{2} \sqrt{\frac{1}{\varepsilon_s \varepsilon_\infty}}$$

# Dielectric Relaxation and Loss

➤ Deviations from the single-time relaxation process : Multiple relaxation modes in polymers

➤ Cole-Cole equation

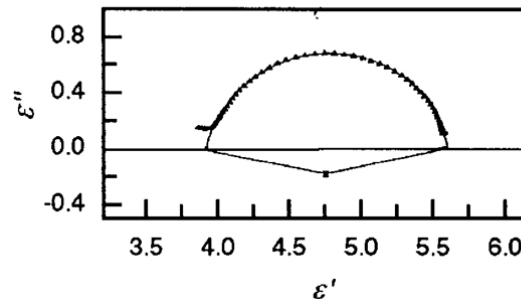
$$\varepsilon^* = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{1 + (i\omega\tau_0)^{\beta}}$$

➤ Cole-Davidson equation

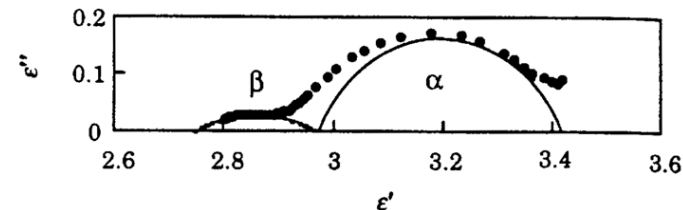
$$\varepsilon^* = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{(1 + i\omega\tau_0)^{\gamma}}$$

➤ Havriliak-Negami equation

$$\varepsilon^* = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{(1 + (i\omega\tau_0)^{\beta})^{\gamma}}$$



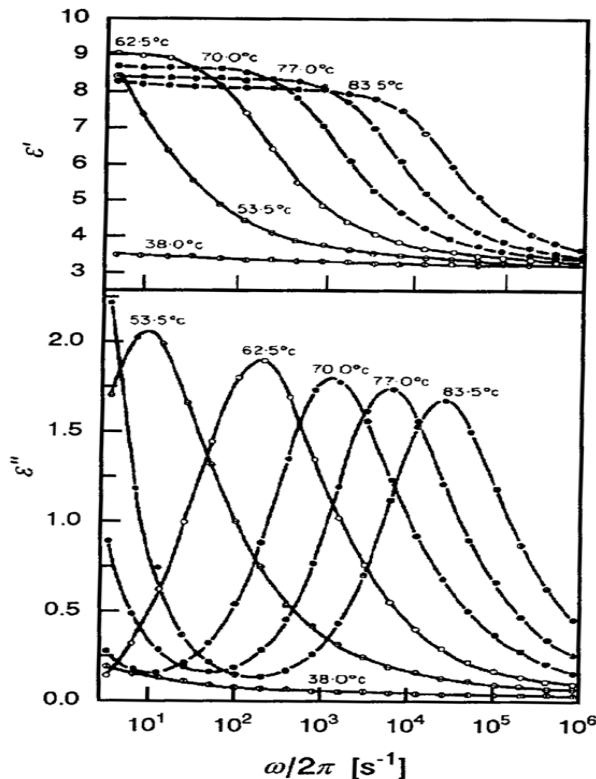
Cole-Cole plot of a polysiloxane with rod-like molecules of  $C_6C_3$  as side-groups. The data is fitted by Cole-Davidson equation. (Seiberle, H.; etc. *Macromolecules* **1990**, *23*, 2008.)



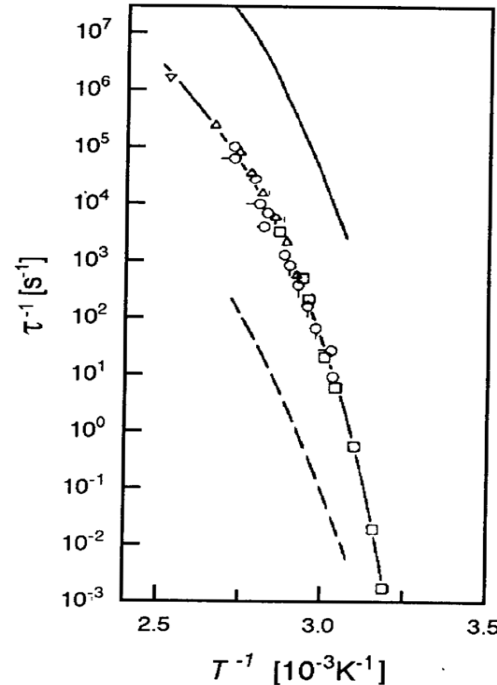
Cole-Cole plot showing two dielectric relaxation processes a and b for a hyper-branched polyester measured at 260 K. The lines are obtained by fitting the Havriliak-Negami equation to experimental data. Malmstrom, E.; etc. *Polymer Bulletin* **1994**, *32*, 679.)

# Dielectric Thermal Analysis (DETA)

## ➤ Dielectric $\alpha$ -process



Dielectric  $\alpha$ -process in poly(vinylacetate) (PVA). (Ishida, Y.; etc. *Kolloid Z.* 1962, 180, 108.)



Frequency-temperature locations of the dielectric loss maxima (*open symbols*) of PVA, compared to the maxima of  $G''$  (*continuous line*) and  $J''$  (*broken line*) observed in mechanical experiments. (McCrum, N. G.; etc. *Anelastic and Dielectric Effects in Polymeric Solids* Wiley & Sons, 1967, p. 305.)

➤ The dielectric  $\alpha$ -process originates from the same group of process as the mechanical  $\alpha$ -process (usually the glass-rubber transition).

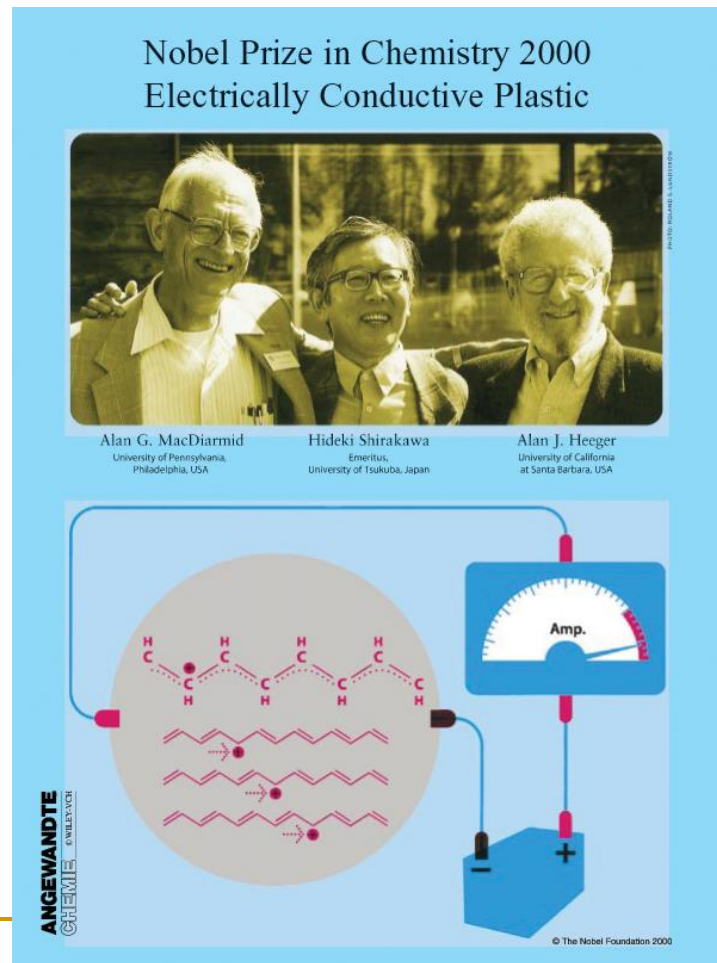
# Conductivities of Polymers

## ➤ The Nobel Prize in Chemistry, 2000: Conductive polymers

“The choice is motivated by the important scientific position that the field has achieved and the consequences in terms of practical applications and of interdisciplinary development between chemistry and physics.”

— The Royal Swedish  
Academy of Sciences

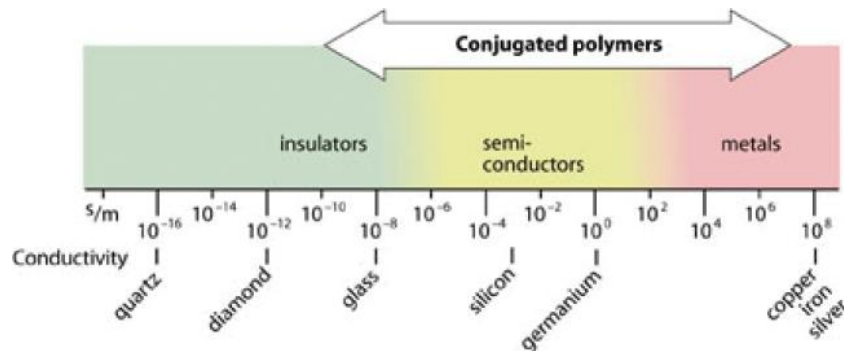
➤ The Three Nobel Prize Laureates:  
Prof. Alan J. Heeger  
Prof. Alan G. MacDiarmid  
Prof. Hideki Shirakawa





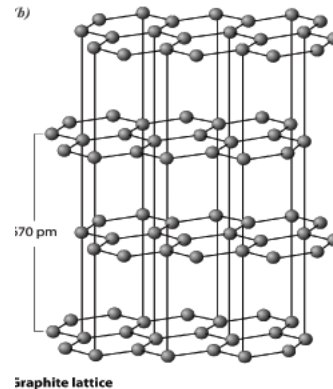
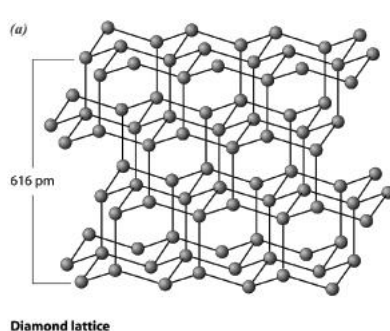
# Conductive Polymers

## ➤ Conductivity of conductive polymers

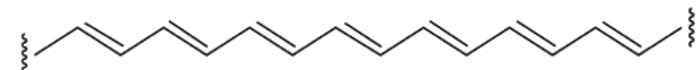


Conductivity of conductive polymers compared to those of other materials, from quartz (insulator) to copper (conductor). Polymers may also have conductivities corresponding to those of semiconductors.

## ➤ The key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer.



**all-cis-polyacetylene**  
(copper coloured)



**all-trans-polyacetylene**  
(silver coloured)

— **Diamond:** contains only  $\sigma$  bond

— **Graphite:** Mobile  $\pi$  electrons in the plane of the graphite rings

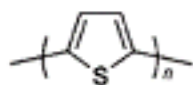
# Conductive Polymers

## ➤ Some examples

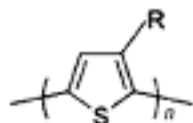
Polyacetylene  
(PA)



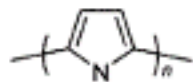
Polythiophene  
(PT)



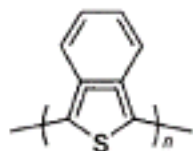
Poly (3-alkyl)  
thiophene  
(P3AT)  
(R=methyl, butyl, etc.)



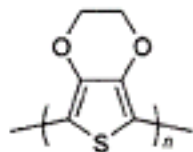
Polypyrrole  
(PPy)



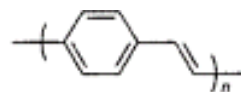
Poly  
isothianaphthene  
(PITN)



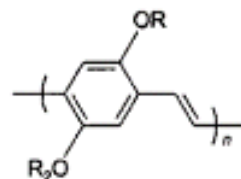
Polyethylene  
dioxythiophene  
(PEDOT)



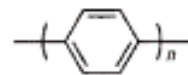
Polyparaphenylene  
vinylene  
(PPV)



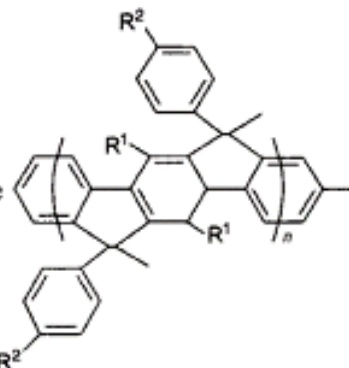
Poly (2,5 dialkoxy)  
paraphenylene  
vinylene  
(e.g. MEH-PPV)



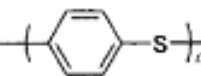
Polyparaphenylene  
(PPP)



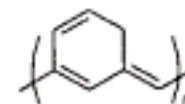
Ladder-type  
polyparaphenylene  
(LPPP)



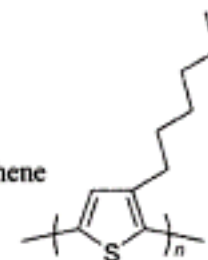
Polyparaphenylene  
sulphide  
(PPS)



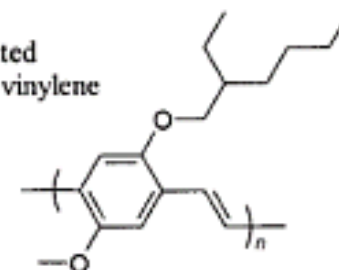
Polyheptadiyne  
(PHT)



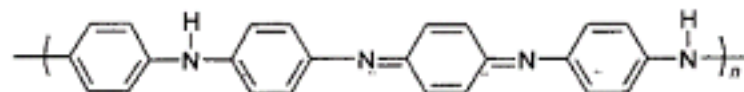
Poly (3-hexyl) thiophene  
(P3HT)



Alkoxy-substituted  
poly *para*-phenylene vinylene  
(MEH-PPV)

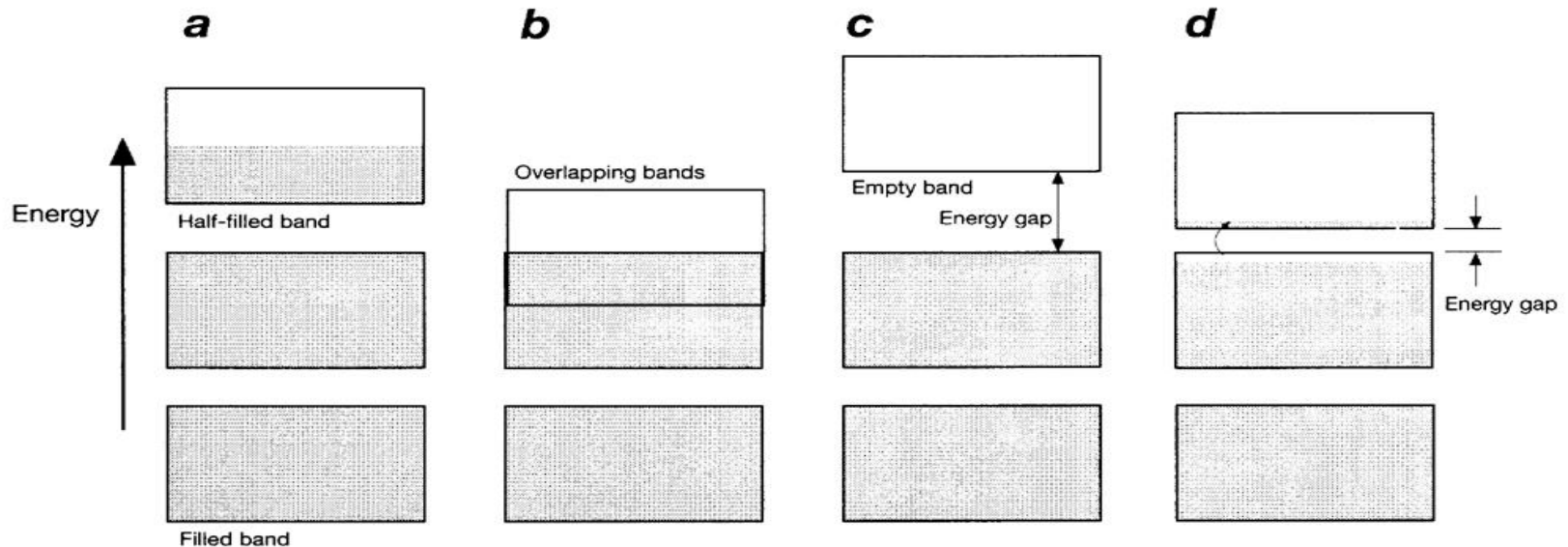


Polyaniline, PANI



# What Makes a Material Conductive?

➤ Valence Band (价带), conduction band (导带) and band gap (能隙)

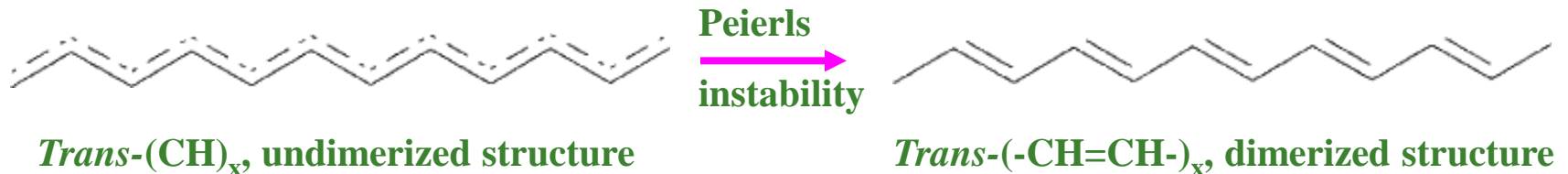


In a metal, the electronic band of highest energy is incompletely filled by electrons, and so these electrons are mobile (*a*). Some elements, such as the alkaline earth metals, are rendered metallic by the overlap of a filled and an empty band (*b*). In an insulator such as diamond, the uppermost occupied band is full, and the next empty band is separated by an energy gap (*c*). In a semiconductor such as silicon, the highest occupied band is again full, but the energy gap between this and the lowest unoccupied band is small enough for the electrons to jump up to it by acquiring thermal energy. These “conduction” electrons are then free to act as mobile carriers of electrical charge (*d*).

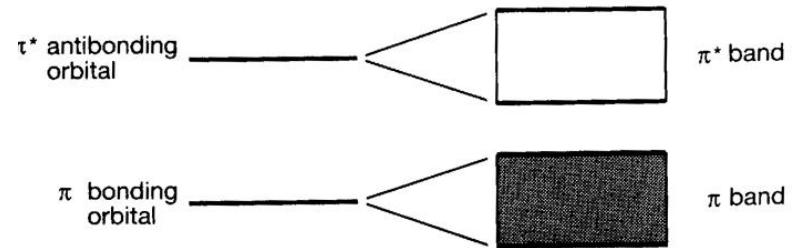
# Polyacetylene

## ➤ Pure Polyacetylene is a semiconductor

- **Peierls instability:** A regular array of molecules with a linear, chain-like structure can lower its energy by distorting so as to make the distances between successive molecules alternate between long and short.

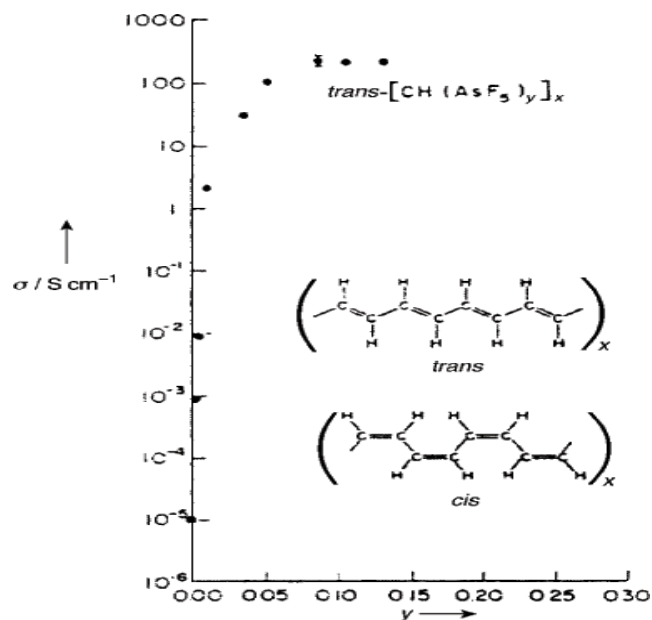


- The  $\pi$  band of  $(CH)_x$  is split into two sub-bands, a full occupied  $\pi$  band (the valence band in semiconductor terminology) and an empty  $\pi^*$  band (the conduction band), each with a wide bandwidth ( $\sim 5$  eV) and significant dispersion.

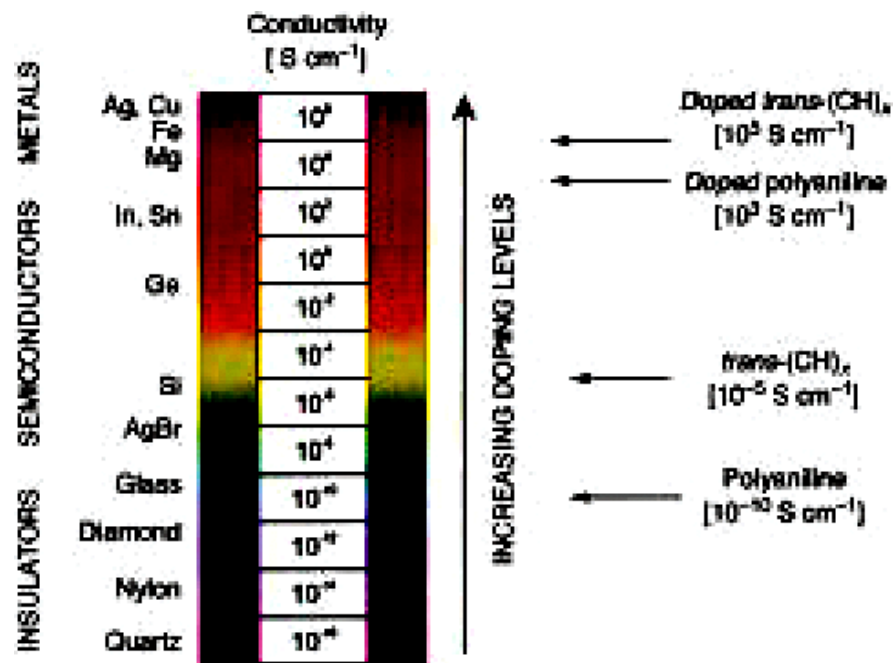


# The Concept of Doping (掺杂)

- Conjugated organic polymers are either electrical insulators or semiconductors. Increases in electrical conductivity of many orders of magnitude can be obtained by doping.



Electrical conductivity of *trans*-(CH)<sub>x</sub> as a function of (AsF<sub>5</sub>) dopant concentration. The *trans* and *cis* structure are shown in the inset.



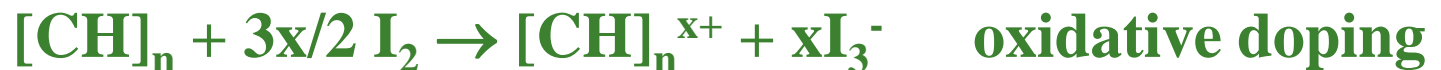
Conductivity of electronic polymers. Conductivity increases with increased doping.

# The Concept of Doping

## ➤ *p*-type and *n*-type doping

➤ While the addition of a donor or an acceptor molecule to the polymer is called “doping”, the reaction that takes place is actually a redox reaction (氧化还原反应).

➤ *p*-type doping: removal of electrons from the valence band by the oxidizing agent, leaving the polymer with a positive charge.



➤ *n*-type doping: donation of an electron to the empty conduction band by a reducing agent.

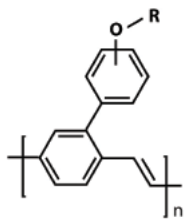




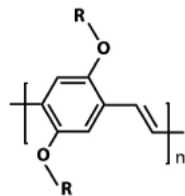
# Electroluminescent (电致发光) Polymers

## ➤ Polymer light-emitting diode (发光二极管)

Conjugated polymers

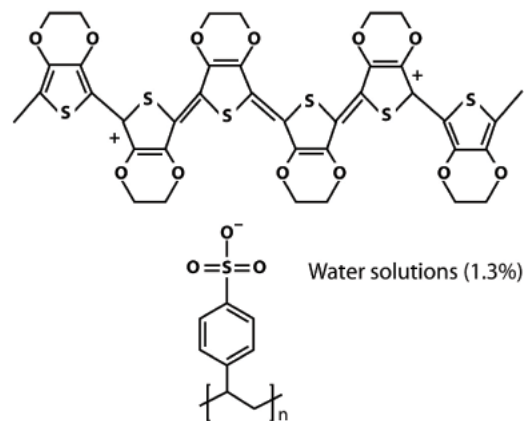


Green emission



Orange-Red emission

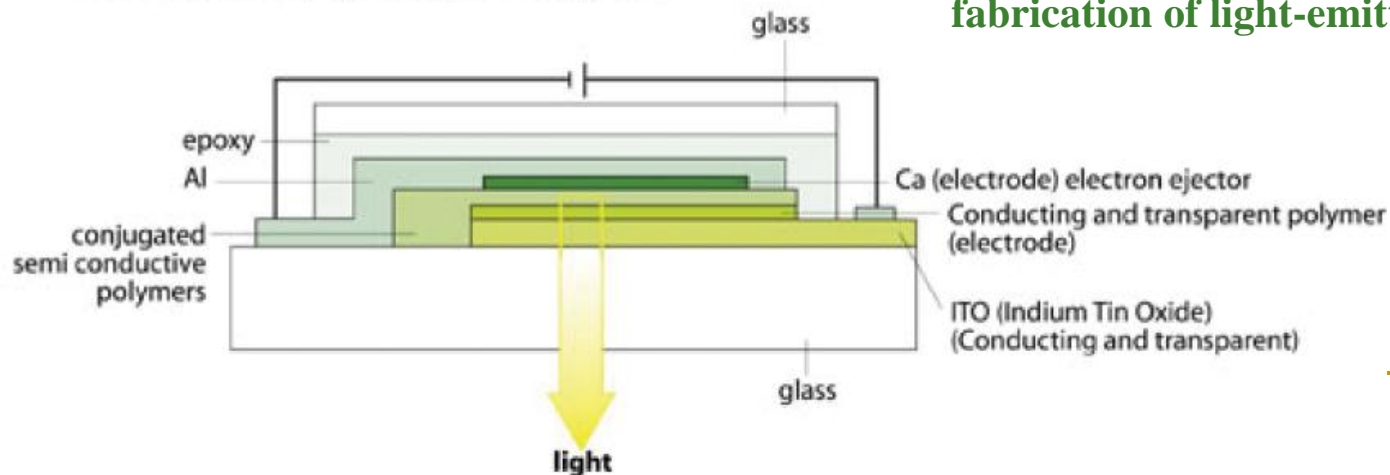
PEDOT-PSS



Water solutions (1.3%)

## Semiconductor polymer with different emission colors

A cross section of polymer light-emitting diode

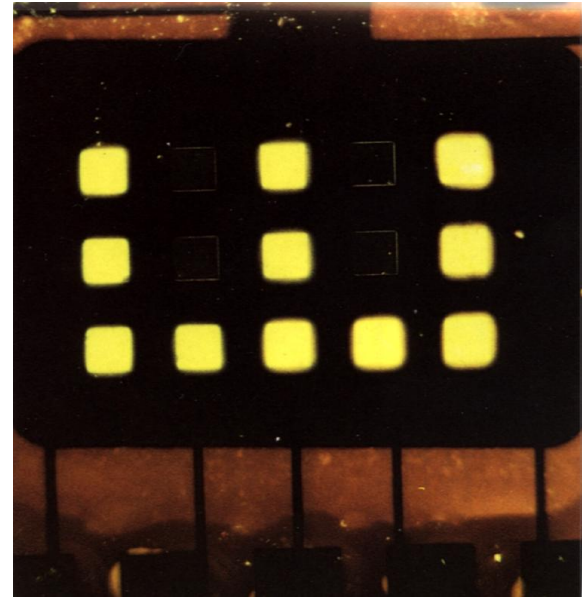


## Conductive electron polymer used for fabrication of light-emitting diodes

# Electroluminescent Polymers

## ➤ Polymer light-emitting diode (发光二极管)

- The electrons can be injected into the conduction band, and the holes can be created by removing electrons from the valence band. The electrons and holes can move along the polymer backbone, but when one encounters the other they stick close together forming a bound pair. In a process called recombination, the electron eventually falls down into the hole in the valence band, annihilating the pair of charge carriers. Therefore, the electron loses energy, which is radiated away in the form of light.



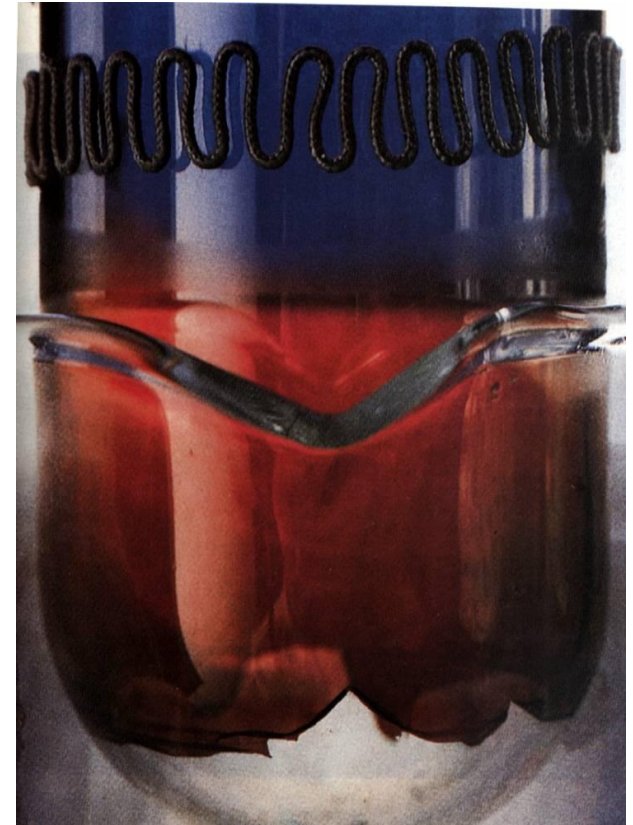
Plastic light-emitting diodes have been made from the polymer poly(paraphenylene vinylene) (PPV), which luminesces when electrons and holes are injected into it. The first polymer LEDs shone with yellow light, but tinkering with the chemical makeup of the polymer can change the color of the emitting light; red, orange, green and blue polymer LEDs have now also been made.

# Conductive Polymers

## ➤ Many applications are possible

For example:

- polymer battery
- electromagnetic shielding of computers
- “electrochromic” display
- transistors (晶体管)
- chemical sensors
- superconductivity
- laser
- artificial nerves (人造神经)
- .....



Polyacetylene changes color with temperature. The lower, red part of the film shown here is kept cool by immersion in dry ice. The upper part of the film has turned blue on being warmed by a heating element. It may be used for temperature measurement.