Special polymers

1. Polymer electrolytes
2. Conjugated polymers and organic electronics

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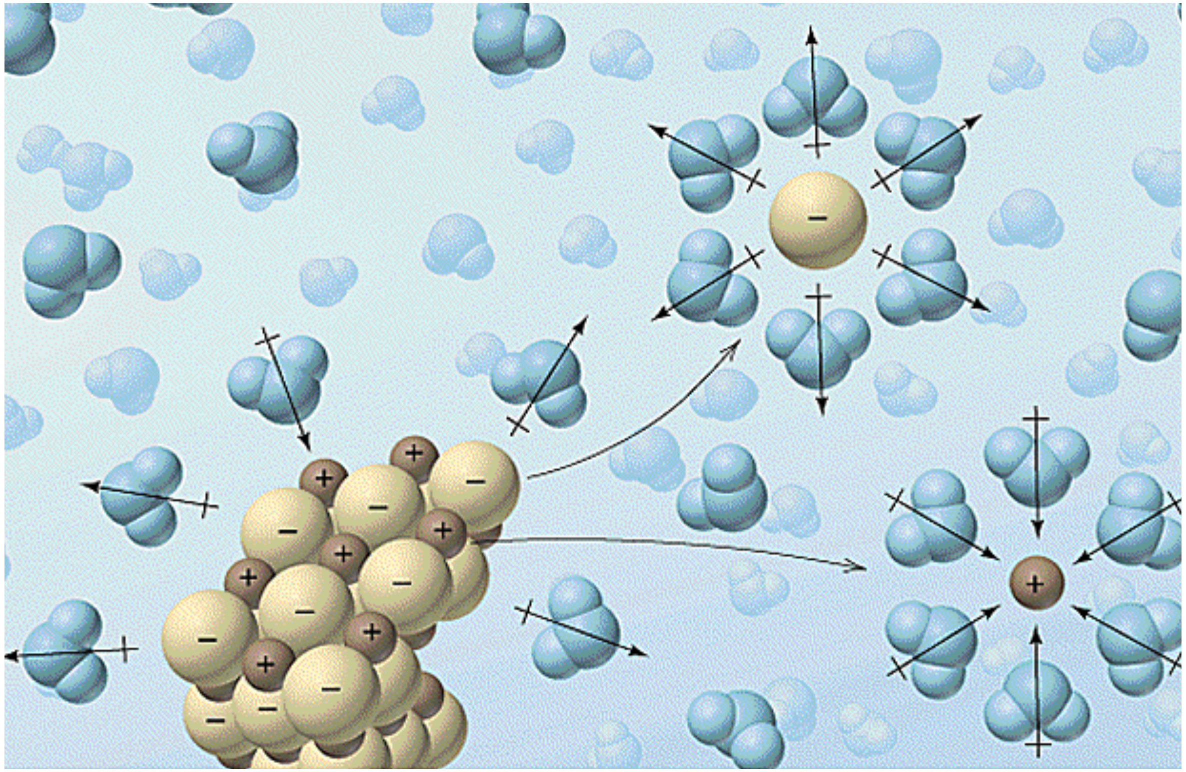
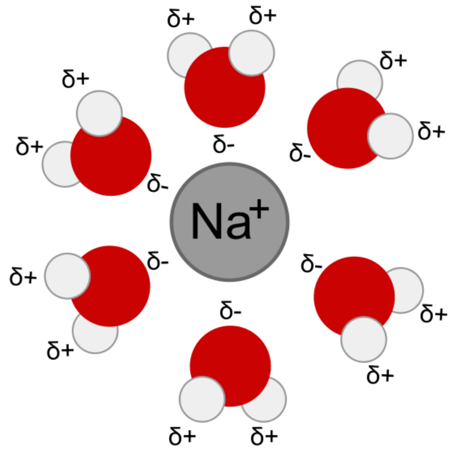
Polymer electrolytes

Dissolving an ionic salt in water



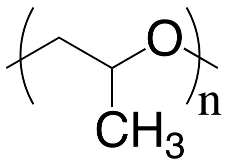


Polymer electrolytes

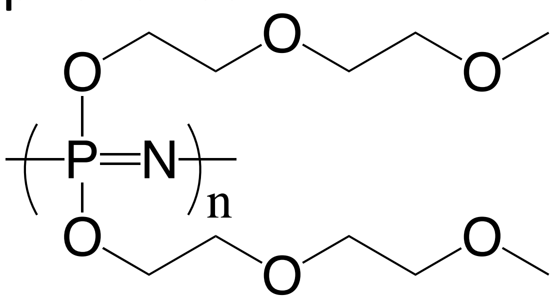
Polymer electrolytes *vs* **polyelectrolytes**

Polymer electrolytes = polymer (solvent) + ionic salt

"Solvating" polymers:
PEO (Tg≈ -60 ^{o}C, Tm≈65 ^{o}C)
PPO (amorphous)



Polyphosphazenes:



Tg=-83 ^{o}C

Upon addition of ionic salt: Tg and viscosity increase

Polymer electrolytes

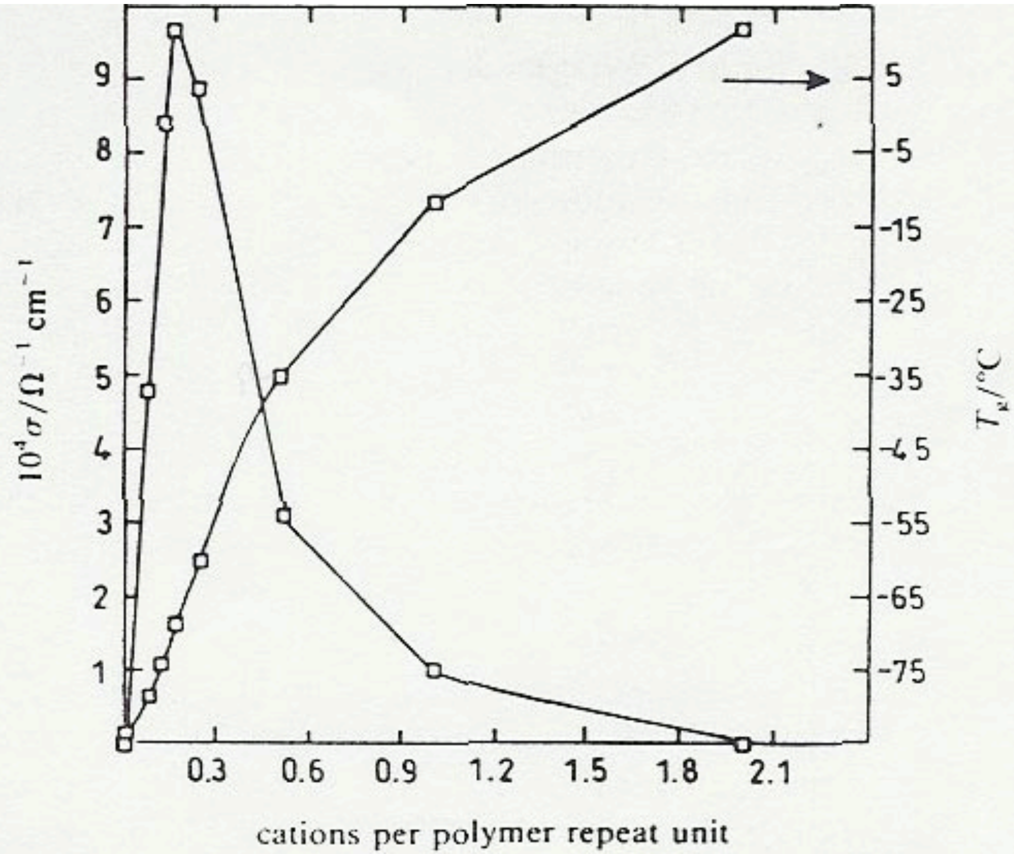


Fig. 2. Conductivity and glass-transition temperature of MEEP complexes containing $AgCF_3SO_3$. Note that the glass-transition temperature increases monotonically with salt concentration, and that the ionic conductivity maximizes at relatively low salt concentration. From ref. (22).

Polymer electrolytes

"Non solvating" polymers:

PMO — $(CH_2O)_n$

PTMO — $(CH_2CH_2CH_2O)_n$

Spacing and conformational flexibility of the monomers

Solvation – interaction between the oxygen atom (Lewis acid) and the cations (Lewis base)

Cations: metals and lanthanides
Anions: $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$ (suppresses crystallinity in PEO/Li^+)

Cations act as ***transient cross-linking agents***

Polymer electrolytes

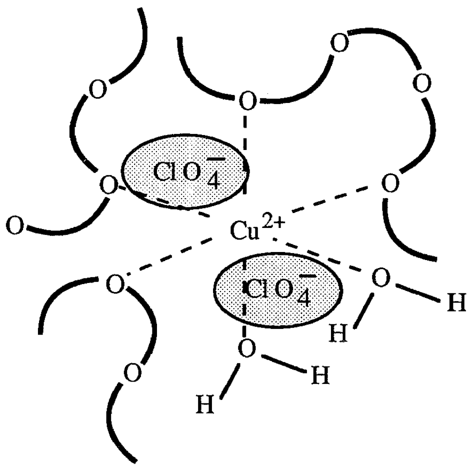
Samples (films) preparation:

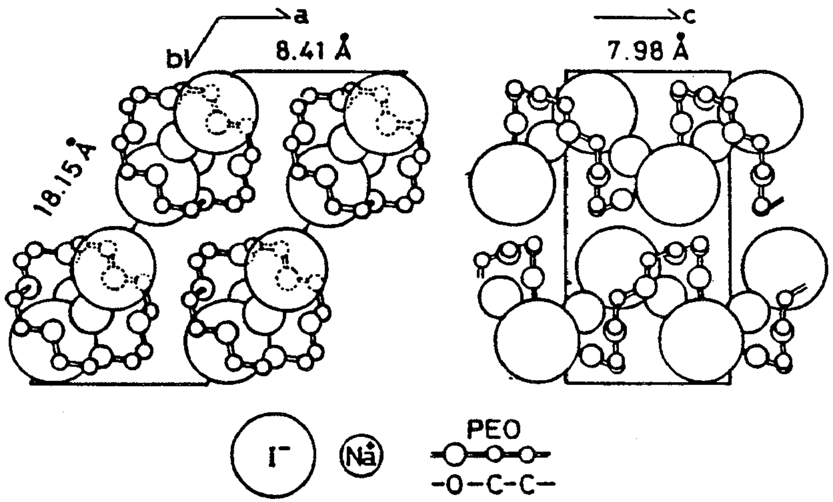
1. Mixed solution followed by solvent evaporation (solvent casting)
2. Addition of the ionic salt to the polymer melt
3. Mixing of the solid at low temperature followed by pressing

- When using (semi)crystalline polymers, such as PEO, there may be formed crystalline phases containing the salt.
- Salt is distributed between crystalline and amorphous domains
- Ionic conductivity due to the salt in the amorphous regions (only ?).

Polymer electrolytes

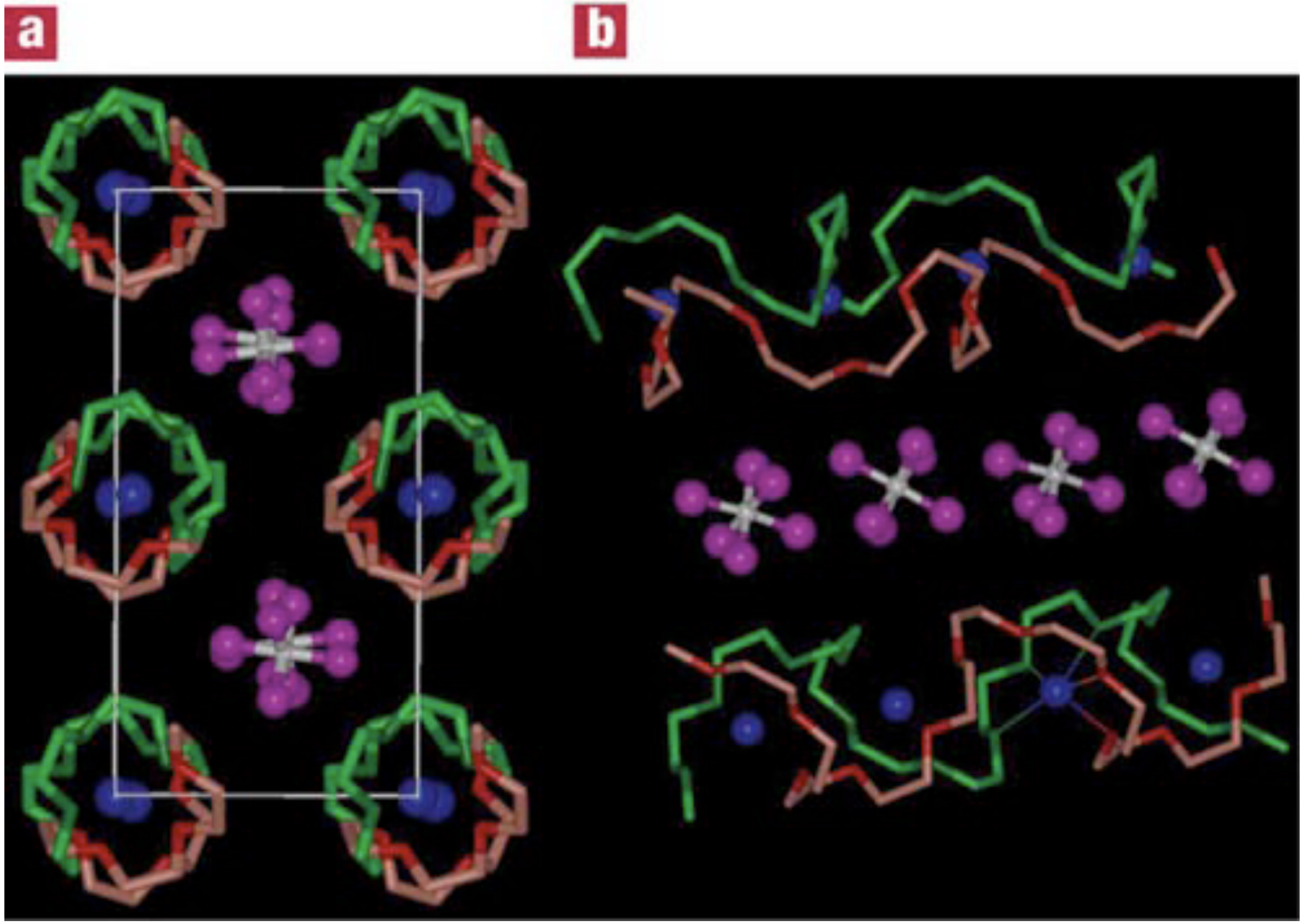
The most studied system: PEO + salt





Polymer electrolytes

Structure of crystalline PEO_6:$LiAsF_6$



Thin lines indicate coordination around the Li+ cation.
Blue spheres, lithium; white spheres, arsenic; magenta, fluorine; green, carbon; red, oxygen.

Polymer electrolytes

Ionic conductivity

Processes: Solvation and ionic mobility

In order to maximize ions concentration:

- Polymers with high dielectric constant
- Salts with low *lattice energy*

$$\sigma = \sum_i n_i Z_i \mu_i$$

In "conventional" solid electrolytes (crystalline materials)

($RbAg_4I_5$ (σ_{RT}≈0.2 S/cm); $Rb_4Cu_{16}I_{7-x}Cl_{13-x}$ (σ_{RT}≈1 S/cm)

$$\sigma = \sigma_0 e^{-\frac{E_a}{RT}}$$

Polymer electrolytes

Ionic conductivity

For polymer electrolytes:

Vogel, Tamman and Fulcher (VTF) equation

$$\sigma = A\,T^{-\frac{1}{2}}\,e^{-\frac{B}{T-T_0}}$$

A - constant, proportional to the ionic charge carriers concentration

T_0 – temperature at which the configurational entropy is zero,

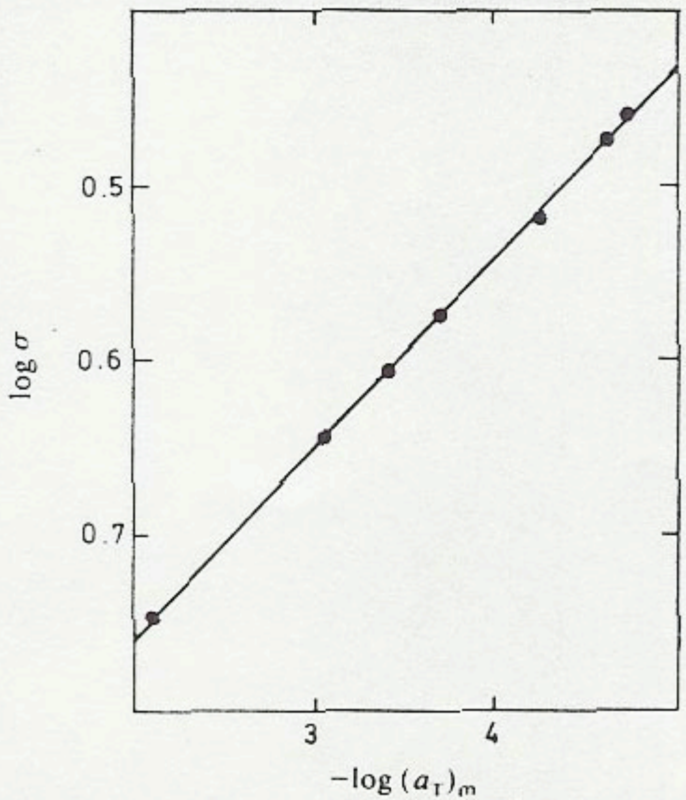
(in general varies from Tg-50 to Tg-20^{o}C)

VTH equation is equivalent to the empirical WLF equation (good fit from Tg up to Tg+100 oC)

$$\log\frac{\eta}{\eta_g} = \frac{-17.44(T-Tg)}{51.6+(T-Tg)} = -\log\frac{\sigma}{\sigma_g} = \log a_T$$

Polymer electrolytes

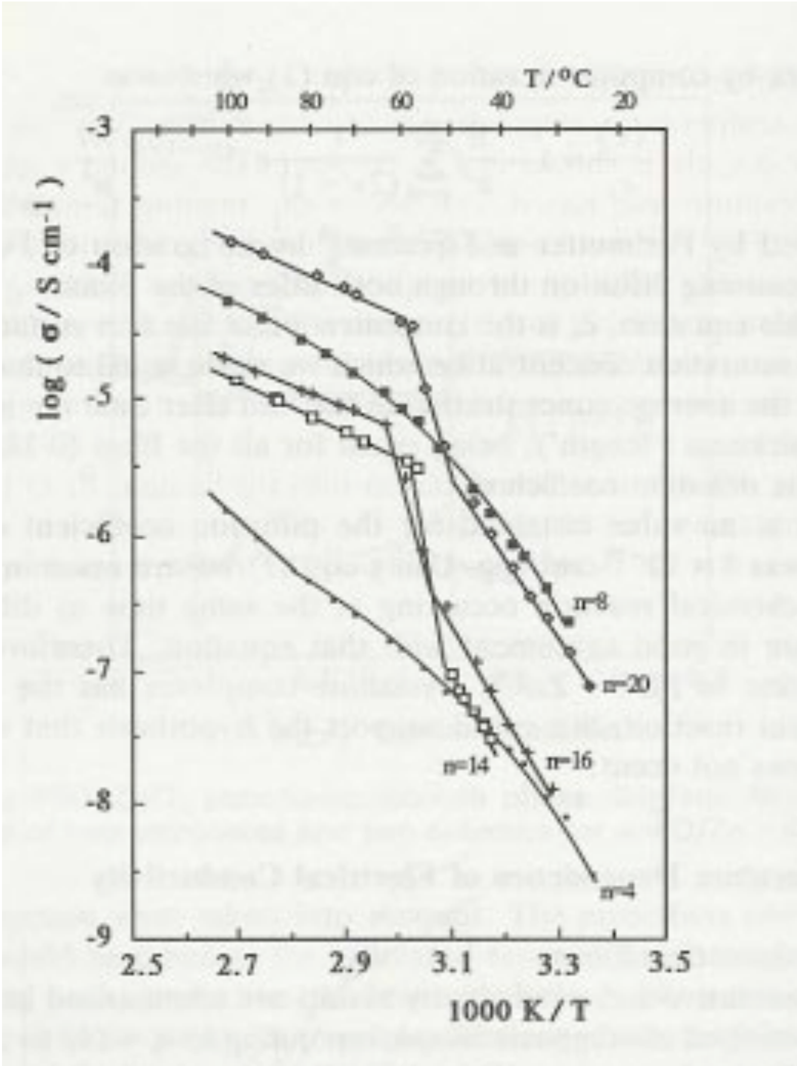
Ionic conductivity



'ig. 1. Correlation between the shift factor a_T describing physical relaxation and the conductivity or PEO networks, with low concentrations of salt. The direct proportionality, with slope of unity, nplies conductivity inversely proportional to viscosity, as assumed in the Stokes-Einstein relationship or Walden relationship. From ref. (25).

Polymer electrolytes

Ionic conductivity



Polymer electrolytes

Ionic conductivity

- *The equivalence between VTF and WLF equations means that the ionic conductance is associated to structural movements of the polymer chains – **transient cross-links.***

- *Both VTF and WLF equations rely on the concept of free volume. The VTF equation can be derived from the configurational entropy model.*

Polymer electrolytes

Room temperature ionic conductivity

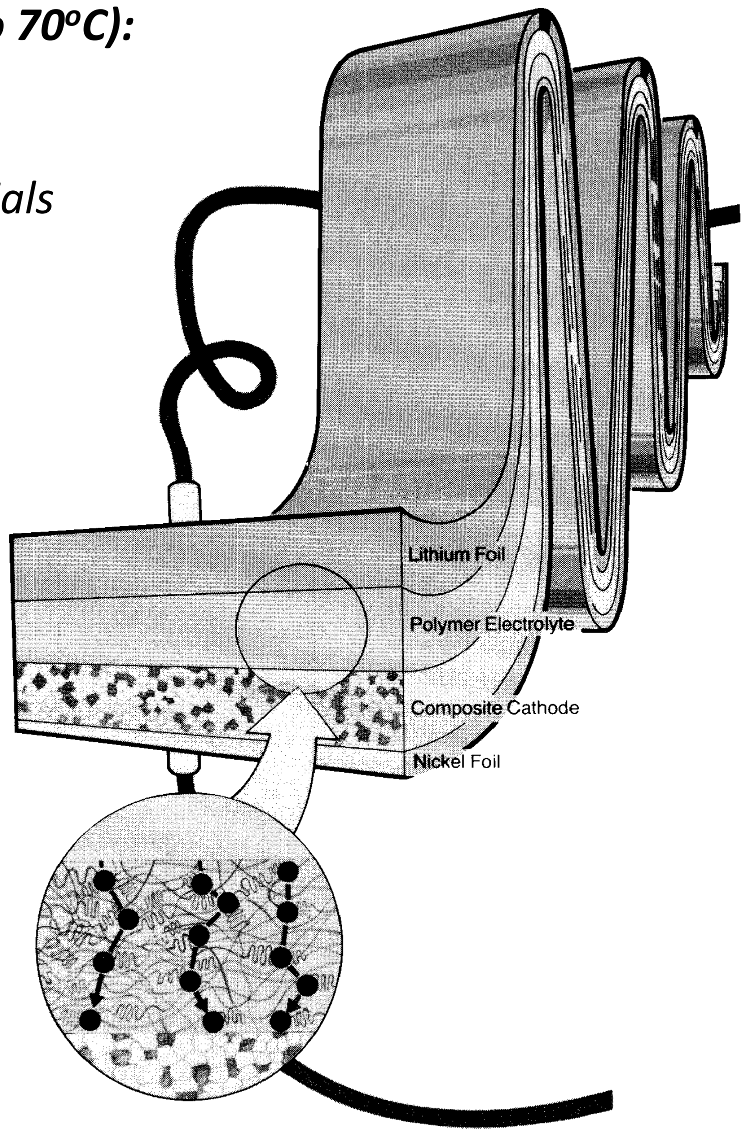
Eléctrólito polimérico Polymer electrolyte	T_g(°C) *Polímero* Polymer	T_g(°C) *Electrólito* Electrolyte	T_f (°C)	σ a 25°C (S/cm)
$(POE)_8\ LiClO_4$	-60	-15	65	$\approx 10^{-8}$
$(POE)_{50}\ LiClO_4$	-60	-43	n.d.	$\approx 10^{-6}$
$(POE)_8\ [LiN(SO_2CF_3)_2]$	-60	-40	53*	$\approx 10^{-5}$
$(POP)_8\ LiClO_4$	-60	0	amorfo	$\approx 10^{-8}$
$(MEEP)_4 LiClO_4$	-83	-58	amorfo	1.7×10^{-5}
$(MEEP)_4 LiSO_3CF_3$	-83	-62	amorfo	1.5×10^{-5}
$(MEEP)_8 LiSO_3CF_3$	-83	-69	amorfo	1.5×10^{-5}
$(MEEP)_4 LiN(SO_2CF_3)_2$	-83	n.d.	amorfo	6.5×10^{-5}
$(MEEP)_4 LiBF_4$	-83	n.d.	amorfo	1.7×10^{-5}

* A T_f parece estar associada a POE puro. Os complexos POE-Li são amorfos

Polymer electrolytes

Requirements for applications in batteries (-40 to 70^{o}C):

- *σ in the range 10^{-4} to 10^{-3} S/cm*
- *Thermal and dimensional stabilityl*
- *Chemical compatibility with the electrode materials*
- *Electrochemical stability window*



Lithium batteries

Li(s)/Polymer electrolyte/cathode

Cathode-Composite materials

(V_6O_{13}, TiO_2,…)

Polymer electrolytes

Crystalline polymer electrolytes

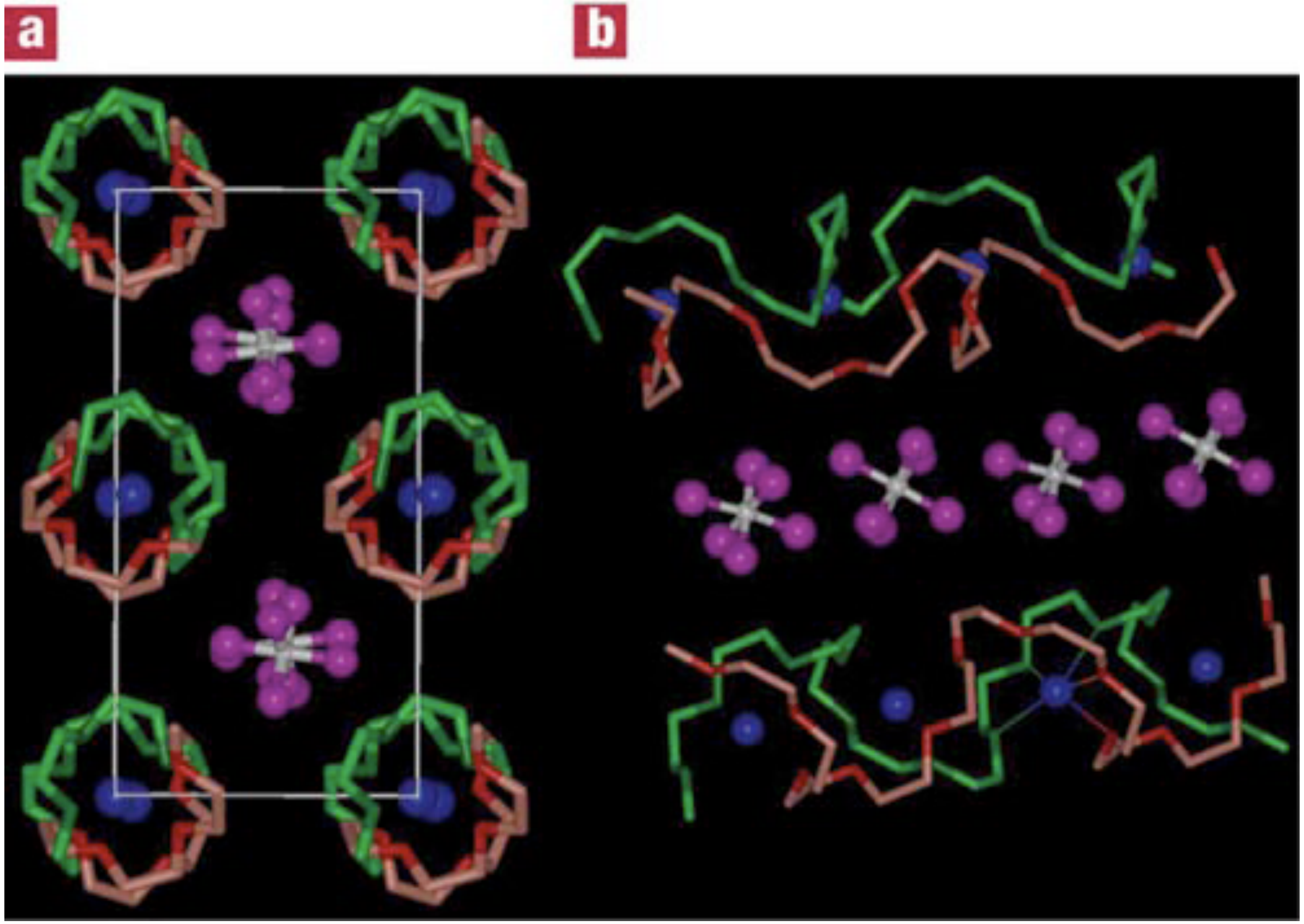
For 30 years it has been accepted that ionic conductivity in polymer electrolytes occurred exclusively in the amorphous phase, above the glass transition temperature Tg. Crystalline polymer electrolytes were considered to be insulators.

But recent studies have shown that this is not the case: the 6:1 crystalline complexes PEO_6:$LiXF_6$; X = P, As, Sb demonstrate ionic conductivity. The Li^+ ions reside in tunnels formed by the polymer chains.

ZLATKA GADJOUROVA, YURI G. ANDREEV, DAVID P. TUNSTALL & PETER G. BRUCE, "Ionic conductivity in crystalline polymer electrolytes", Nature 412, 520 – 523 (02 August 2001);

Polymer electrolytes

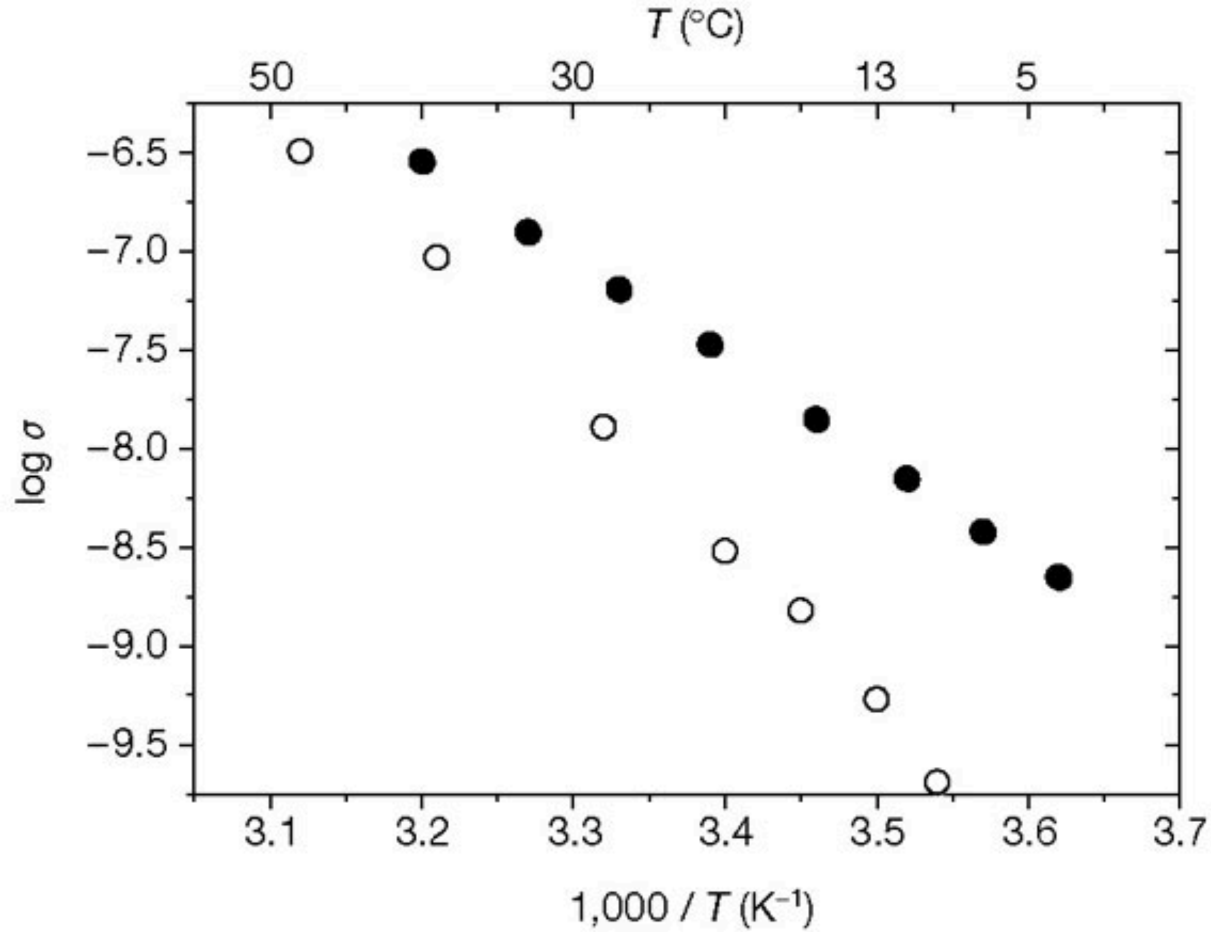
Structure of crystalline $PEO_6:LiAsF_6$



Thin lines indicate coordination around the Li^+ cation.
Blue spheres, lithium; white spheres, arsenic; magenta, fluorine; green, carbon; red, oxygen

Polymer electrolytes

Ionic conductivity sigma (S cm^{-1}) of amorphous (open circles) and crystalline (filled circles) PEO_6:$LiSbF_6$ as a function of temperature



Polymer electrolytes

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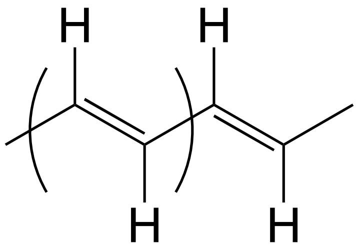
Conjugated polymers

Polyacetylene



Trans-polyaceylene

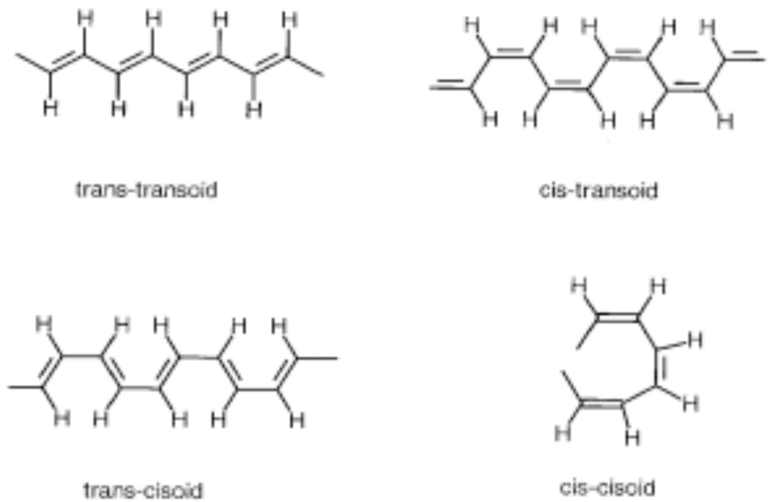
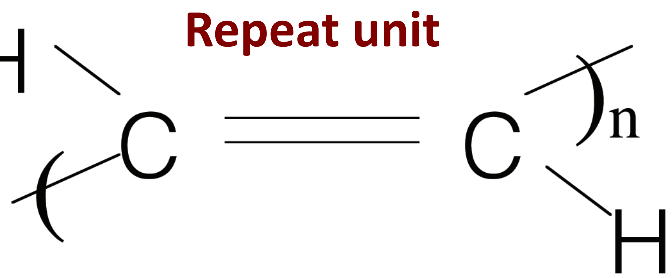
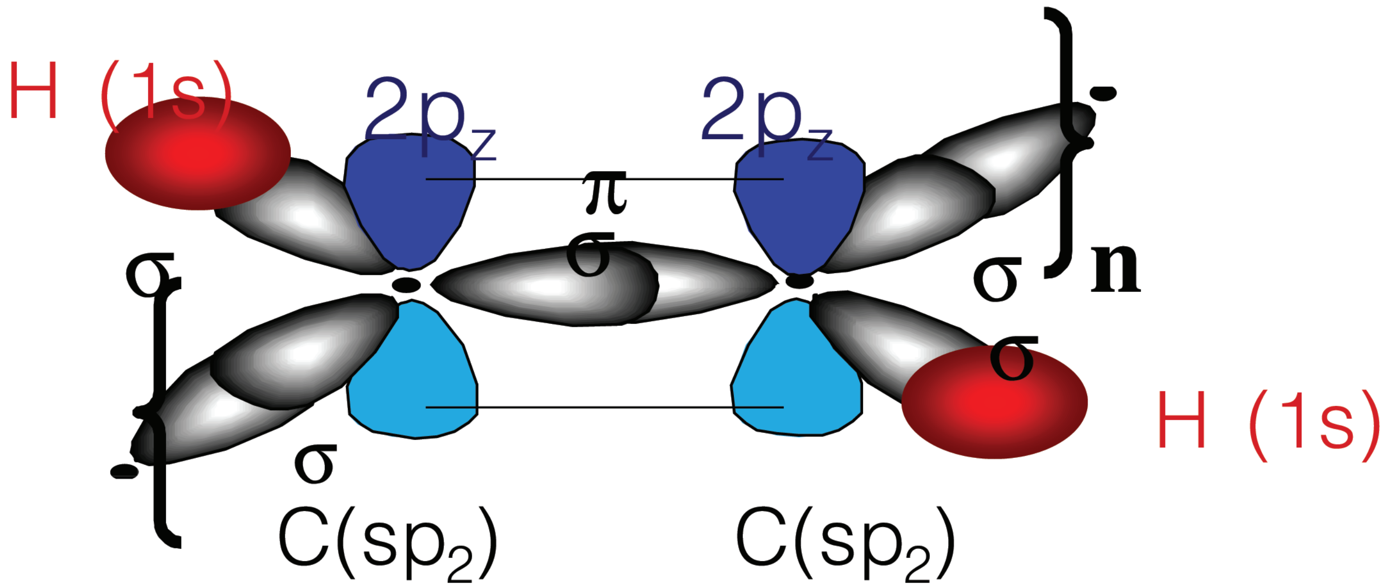


Chart 4 Four isomeric structures of polyacetylene **12**.

Conjugated polymers

Trans-polyacetylene

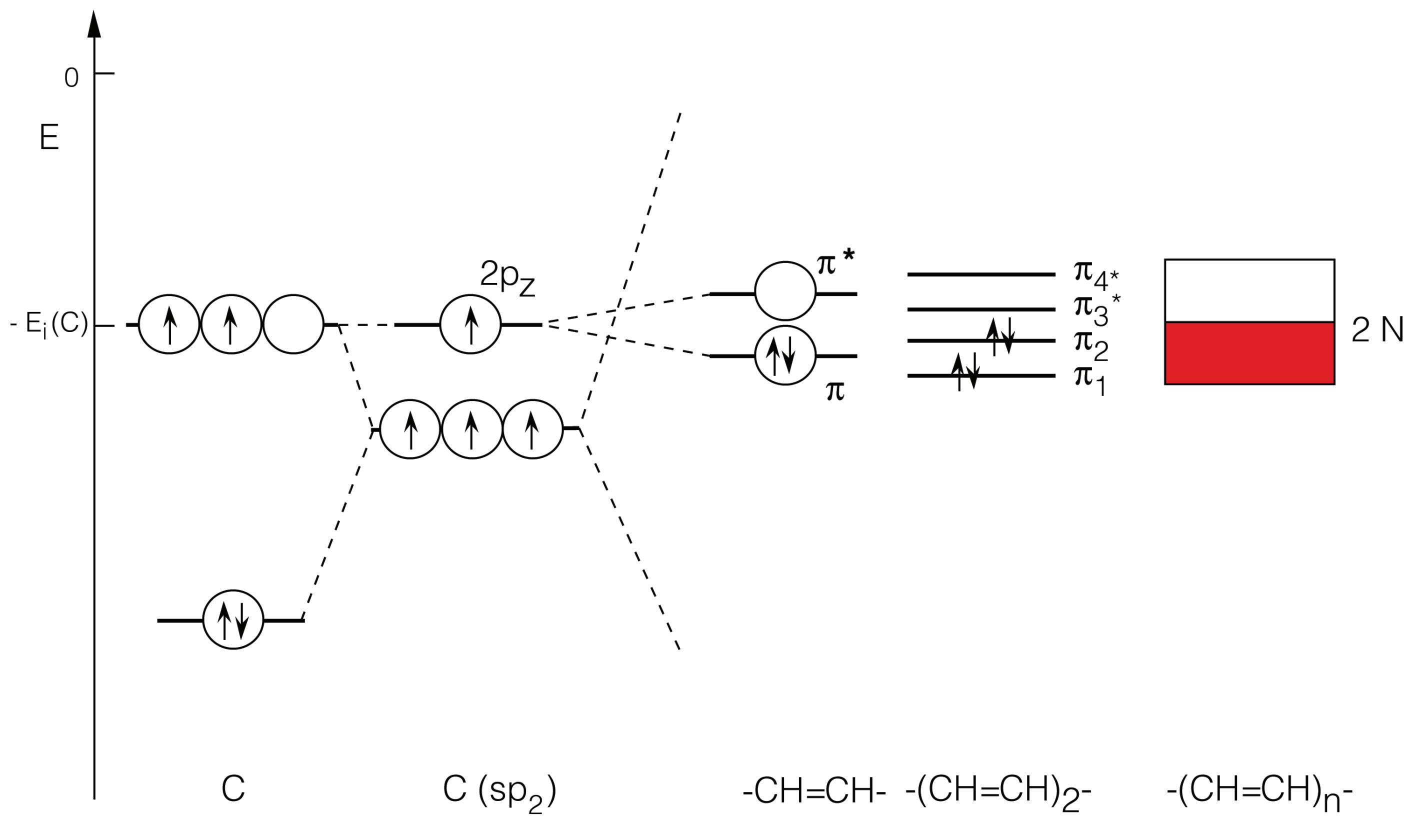




Conjugated polymers

Uniform infinit chain of trans-polyacetylene

Delocalized π orbitals

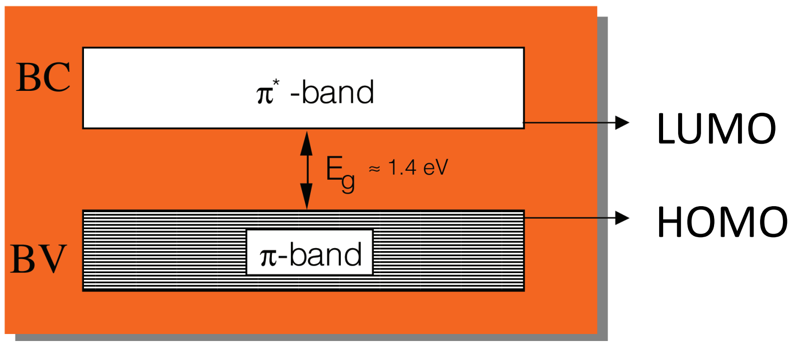


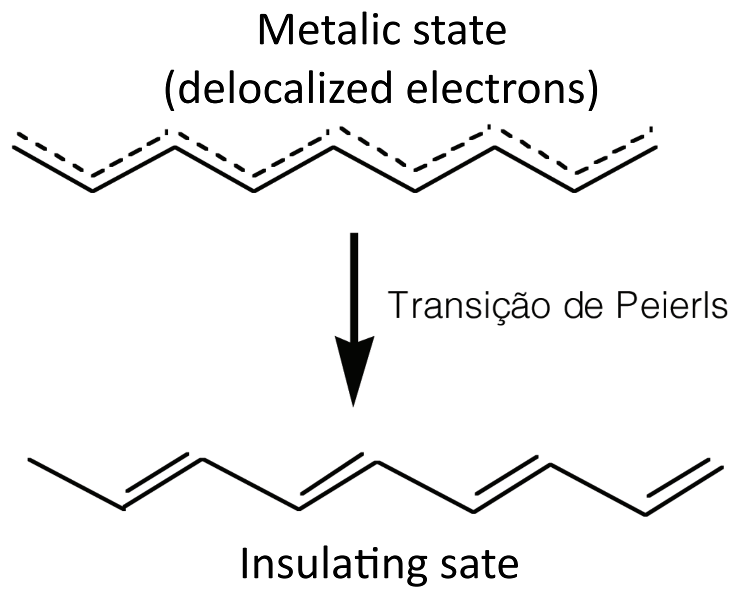
Conjugated polymers

Real trans-polyacetylene

- π electronic density is not uniform
- Bond alternation
- "Localization" of single and double bonds (Peierls transition)

Energy gap in the "π band"





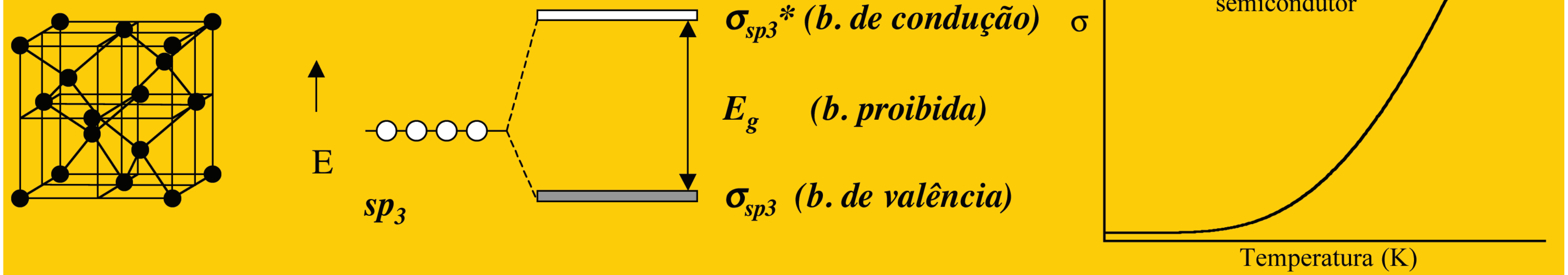
Semiconductor!

- Optics
- Electronics
- Doping

Conjugated polymers

Silicon_typical semiconductor

Semicondutores /isoladores cristalinos:



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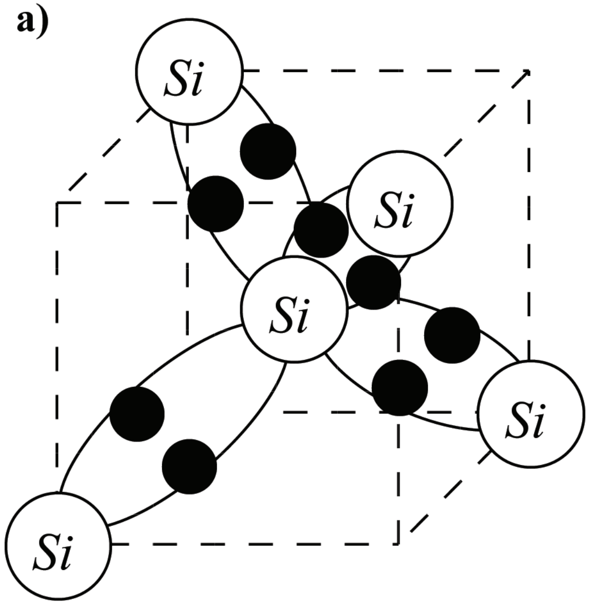

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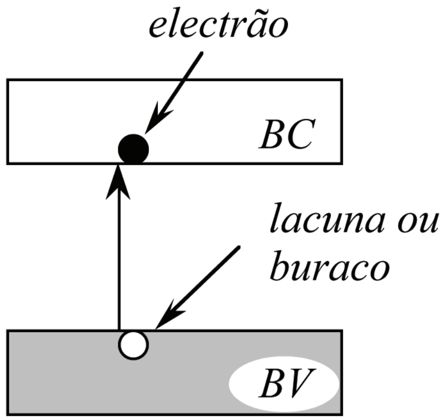
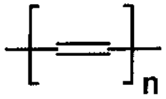


Conjugated polymers

Insoluble conjugated polymers



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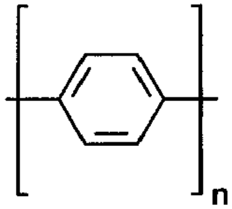

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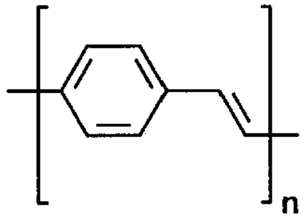

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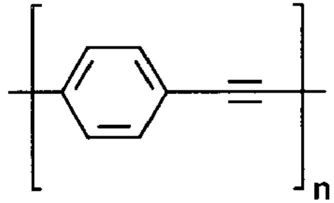

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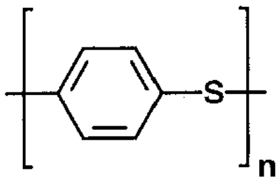

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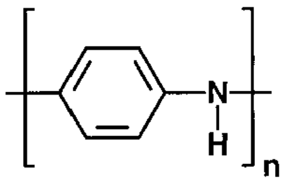

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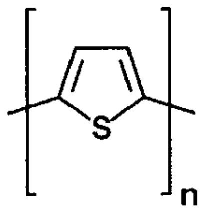

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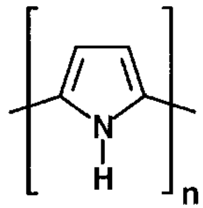

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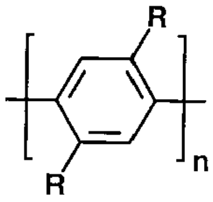
Conjugated polymers

Soluble conjugated polymers



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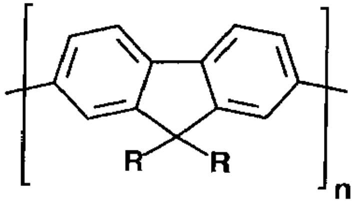

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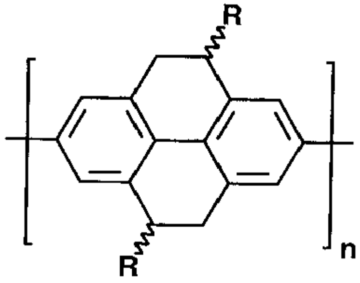

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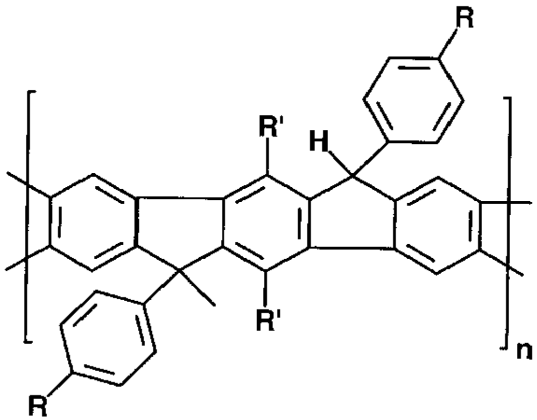

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Chart 10 Dialkyl-PPP **53**, step-ladder PPP **49** and **50** and LPPP **52**.

References

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