Conducting Polymers

One can distinguish between three types of conducting polymers:

- Electron-conducting polymers
- Proton-conducting polymers
- Ion-conducting polymers

Each polymer type has already found widespread use in many, mainly optical and electronic applications such as batteries, displays, plastic wires, optical signal processing, information storage, solar energy conversion, etc.. Although conducting polymers have been known for at least 25 years (reports on the synthesis date back to the last century), it was only in the early 90s that a tidal wave of renewed and amplified interest in these materials has catalysed many new developments, both on a fundamental level as well as from the manufacturing side. In particular the discovery of light-emitting polymers in 1990, in the Cavendish Laboratory at Cambridge University, was a major if not the turning point in the fortunes of plastronics, i.e. the use of polymeric materials as substitute for metal and their derivatives in electronic devices. Serious problems like oxidative stability and device lifetimes have to be overcome, but one does not have to be a soothsayer to predict that one day in the not so distant future we will all go to the beach, carrying our table-set sized flexible LED display with us. Solar-powered, we will sit down and read our paper, surf the net or simply be watching TV.

This part of the fourth year lecture course will present an overview on the synthetic strategies of synthesising electron-conducting polymers.

1. Introduction

Polymers (Plastic) shape our lives because polymers can be shaped! Is it really necessary to point this out? Maybe not, but it is the major driving force behind most research that tries to design plastics fit for electronic applications. Polymers have the advantage that they are so much more easily to be processed than metals for example. One can very easily cover large surfaces with a spin-coated polymer solution. Once the solvent has evaporated one is left with a layer of polymer chains. Most plastics can be deformed reversibly and they also do not break easily, which is not true for metals. These properties and the ease with which polymers can be shaped into complex multi-polymer architectures are the reasons that have enticed many scientist and industrialist looking for novel applications and new products.

The ability to synthesise what we have identified to be the ideal molecular structure is paramount to a successful and fruitful exploitation of polymers for the sake of plastronics. In the following we will emphasise on synthetic strategies and methodologies used in the synthesis of conducting polymer rather than covering the almost limitless structural variations that one can introduce.
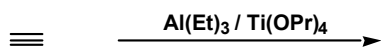
2.   Electron-conducting Polymers
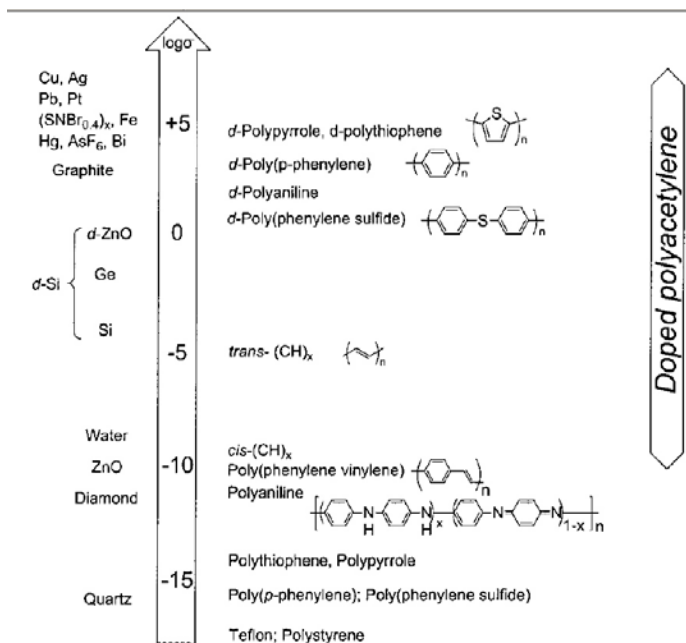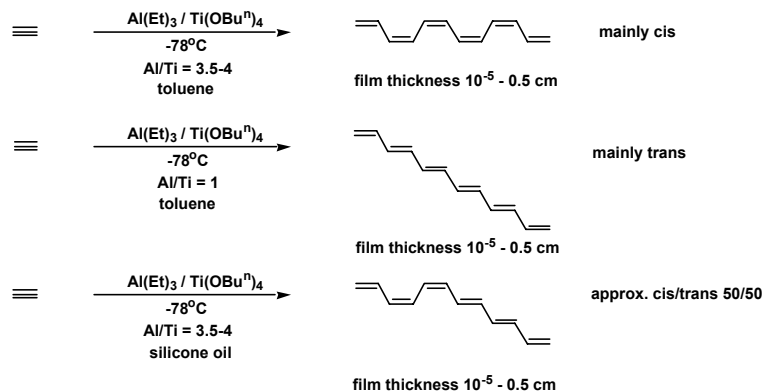

2.1.   Poly(acetylene)s

The first conducting polymer synthesised was poly(acetylene). The first reports on acetylene polymers date back to the last century. Cuprene, a highly crosslinked and extremely irregular product of acetylene polymerisation in the presence of copper-containing catalysts being a typical example for the initial efforts. Poly(acetylene) is the simplest conjugated polymer. In its linear form it precipitates as a black, air sensitive, infusible and intractable powder out of solution and can not be processed. Ant et al. were the first to polymerise acetylene in hexane using a mixed catalyst of alkyl aluminium and titanium tetraalkoxides:

Natta's route (1958) to poly(acetylene) resulting in intractable, infusible, air sensitive black powders.

Shirakawa's route (1970s; Nobel Prize for Chemistry 2000) to poly(acetylene) yielding polymer films of up to 0.5 cm thickness. The first example of conducting poly(acetylene) upon doping with halogens or AsF_5.

Al(Et)$_3$ / Ti(OBu^n)$_4$
-78°C
Al/Ti = 3.5-4
toluene
mainly cis
film thickness 10^{-5} - 0.5 cm

Al(Et)$_3$ / Ti(OBu^n)$_4$
-78°C
Al/Ti = 1
toluene
mainly trans
film thickness 10^{-5} - 0.5 cm

Al(Et)$_3$ / Ti(OBu^n)$_4$
-78°C
Al/Ti = 3.5-4
silicone oil
approx. cis/trans 50/50
film thickness 10^{-5} - 0.5 cm

Reaction conditions allow to control the morphology of the conjugated polymer obtained as powder, gel, spongy mass or a film. Iodine doping renders these polymers conducting and values of up to 10^5 S/cm have been claimed. Films can be stretched

The inherent insolubility and infusibility of poly(acetylene) coupled with its sensitivity to air imposes a barrier to the processability of the polymer. As a result considerable research efforts have been directed towards obtaining processable poly(acetylene) by means of polymer analogous transformation. Two syntheses are of particular importance.

Dehydrohalogenations of poly(vinyl chloride)

CI CI CI CI CI CI CI CI

CI CI CI CI CI CI CI CI CI

head to head   **tail to tail**
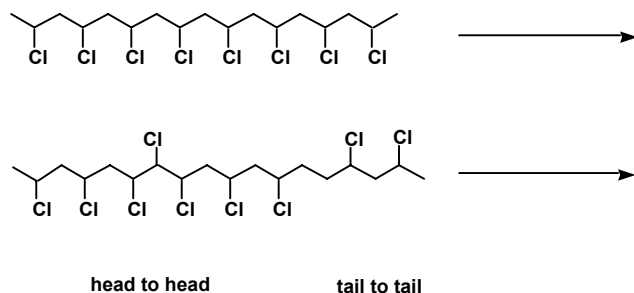
Drawbacks of this route are short conjugation length, structural defects and crosslinks. Thermally convertable prepolymers (Precursor routes)

F$_3$C
F$_3$C
ROMP
F$_3$C
F$_3$C
n
heat
n
heat
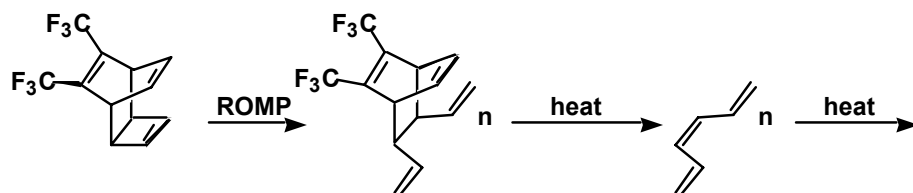
Durham Route

Property advantages of poly(acetylene) prepared by precursor routes:

- Continuous solid films with densities of 1.05-1.10.
- Controlled morphology range; amorphous, semi-crystalline, crystalline.
- Films can be stretched during or prior to conversion
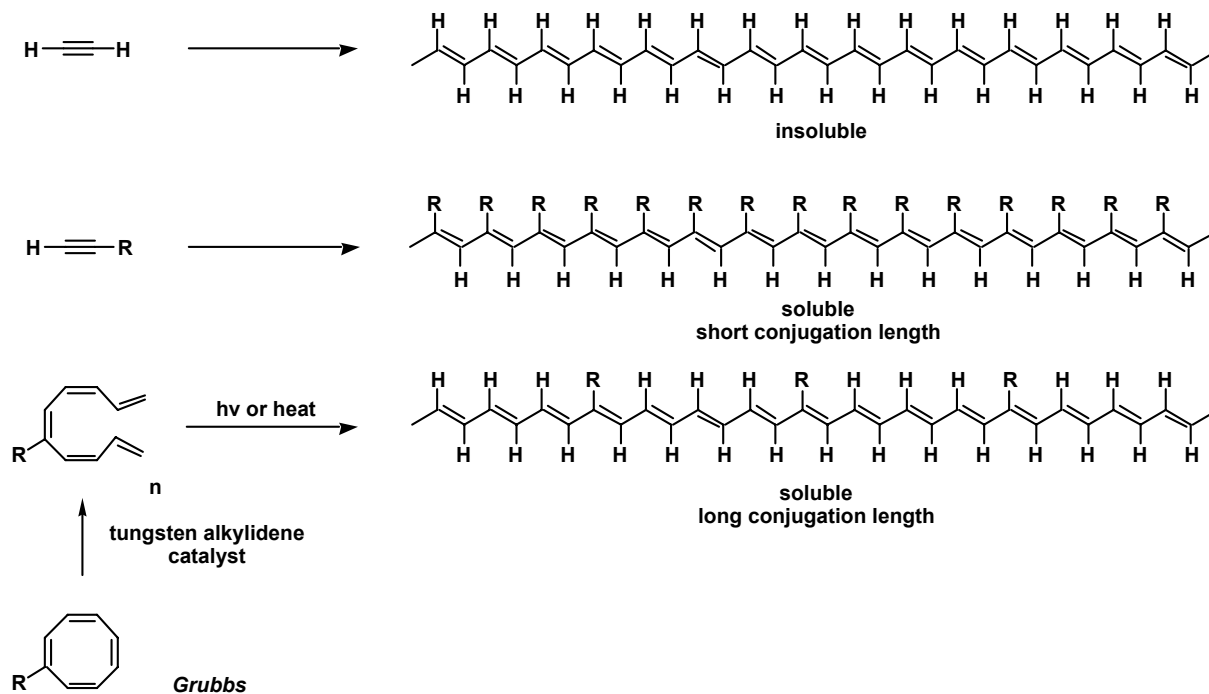
The conductivity of all substituted poly(acetylene) analogues reported to date is significantly lower than that for poly(acetylene) itself. The reduction in conjugation length is attributed to steric repulsions between adjacent side groups which causes the polymer chains to twist (rotation barrier single bond: 6 kcal/mol). Grubbs showed that monosubstituted cyclooctatetraenes can be "ROMPed" to give partially substituted poly(acetylene)s that are both soluble and highly conjugated.

2.2.   Theory of Conductivity

Poly(acetylene) provides the limiting case of a polyene of infinite conjugation length. The Hückel energy levels for any polyene with n unsaturated carbon atoms and with equal bond lengths can be obtained by appeal to the Frost mnemonic for linear polyenes in which a polygon of order 2n+2 is inscribed in a circle of radius 2ß. At the limit of infinite chain length, this relationship still holds, except the polygon is a circle itself. Projection of the semicircle containing the equal density of energy levels along the circumference produces an envelope of energy levels commonly referred to as the density of states. Significantly, the HOMO-LUMO energy difference, or band gap, vanishes. Population of the conduction band requires no energy and thus the system should be metallic.

This non-sensical result arises from the error in assumption of equal bond lengths and resonance integrals. A half-occupation of the conduction bands leads to a Jahn-Teller distortion for quasi-one-dimensional systems called the Peierls distortion. The result of this is two inequivalent ground states "R" and "L" with alternating bond lengths and a non-zero gap requiring activation energy for the intervconversion of the two forms and thus forming an insulating material.
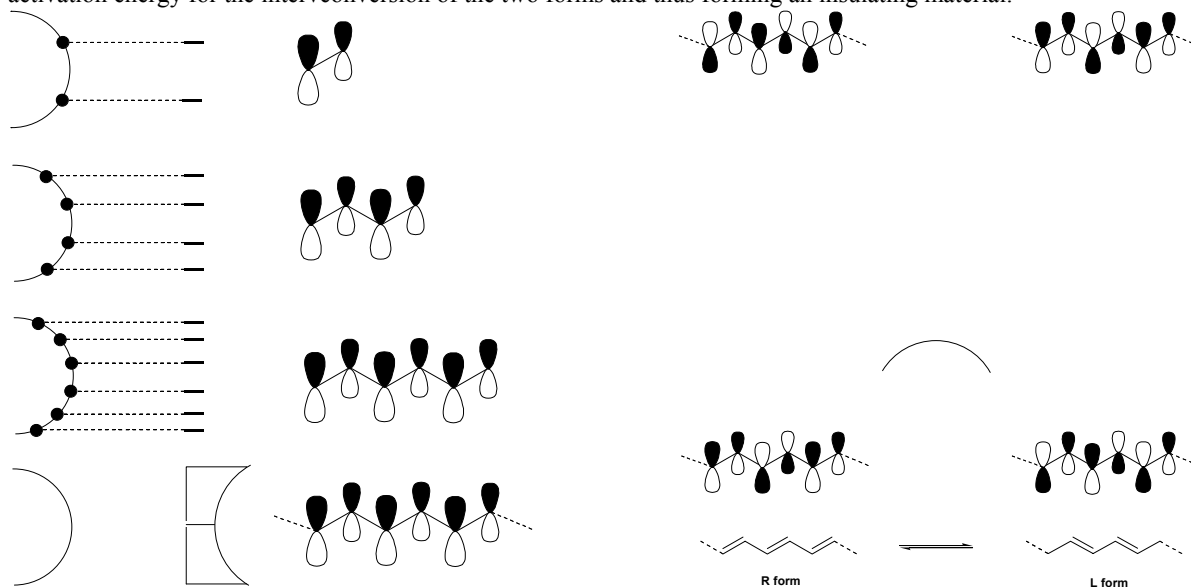
The Peierls distortion corresponds to a thermally forbidden energy level crossing problem in the Woodward-Hoffmann rule sense. The HOMO for a polyene of arbitrary length is characterised by bonding interactions between the "doubly"-bonded carbon and antibonding interactions between "singly" bonded carbon. The LUMO is analogous, except that anti-bonding interactions are found between "doubly" bonded carbon and bonding between "singly" bonded carbon.

As a result the symmetric HOMO of the "R" form corresponds to the LUMO of the "L" form and vice versa.

Let us restate the above in other words: As predicted by theory, the low dimensional structure of a polyene (of equal bond length and resonance integral) is unstable and the coupling of electrons and phonons with lattice distortions leads to a localisation of single and double bonds which lifts the degeneracy and results in a localisation of π electrons with the opening of a bandgap (E_g) generally larger than 1.50 eV.

The HOMO-LUMO energy gap of a linear conjugated system (ΔE) and the E_g value of the resulting material are usually determined from the low energy absorption edge of the electronic absorption spectra. Both values can also be determined from solution oxidation and reduction potentials (CV).
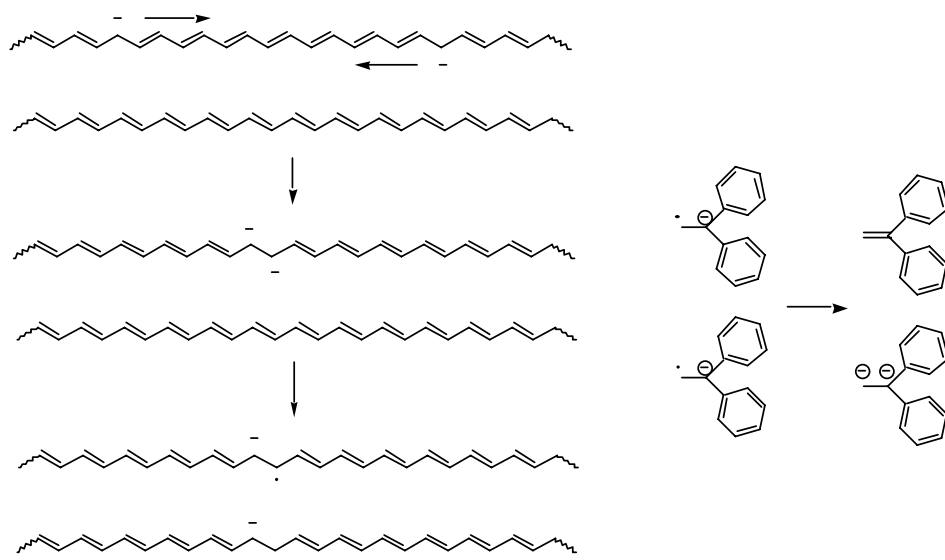
2.2.1. Conduction mechanism

Again, poly(acetylene) is taken as an example to illustrate principles of conduction mechanisms in conducting polymers.

L form   **R form**   *soliton*
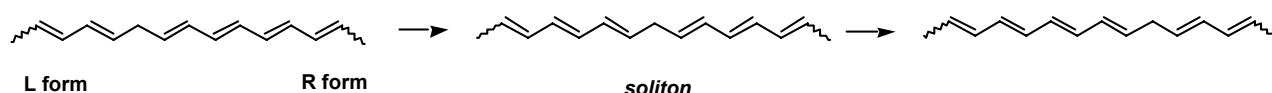
As a necessary consequence of the asymmetry of the poly(acetylene) ground state, two equivalent polyene chains R and L are interconverted through the intervention of a mobile charge carrier, a soliton. The soliton is a mobile charged or neutral defect, or a "kink" in the poly(acetylene) chain that propagates down the chain and thus reduces the barrier for interconversion.

The charge carrier in n-doped (negatively charged) poly(acetylene) is a resonance-stabilised polyenyl anion of approximately 29-31 CH units in length, with highest amplitude at the centre of the defect. This description is backed up by chemical shifts found in the ^{13}C NMR spectrum, which indicate increased charge density at the centre of such anions. Also advanced theoretical calculations (MNDO) are in agreement with this description.

So how does a soliton manage to travel from one end of a sample to the other? This can be explained by the bipolaron hopping mechanism:

Most experimental data is consistent with a rate-limiting interchain charge transport. If short chains are involved, conduction in poly(acetylene) requires some mechanism for transfer of charge from one chain to another (e.g. intersoliton hopping). Current theories for interchain charge transfer centre around the Kivelson "percolation" mechanism. For n-type solitons (Carbanions) this involves electron transfer from the anion to a neutral soliton (radical) in a neighbouring chain in an isoenergetic process. However the lattice distortion associated with interpolaron hopping (hopping between a radical

carbanion and a neutral polyene chain) is thought to present inaccessible energy barriers. A solution to this dilemma is provided by organic carbanion chemistry. Charge transfer between carbanions often involves a disproportionation equilibrium between a neutral/dianion pair (ion triplet) and a radical anion pair. It is recognised that at the moment this mechanism most closely matches the charge transport energetics.

Bipolarons in poly(p-phenylene)

A)

B)

C)

π-conjugated segment   large substituent   flexible segment
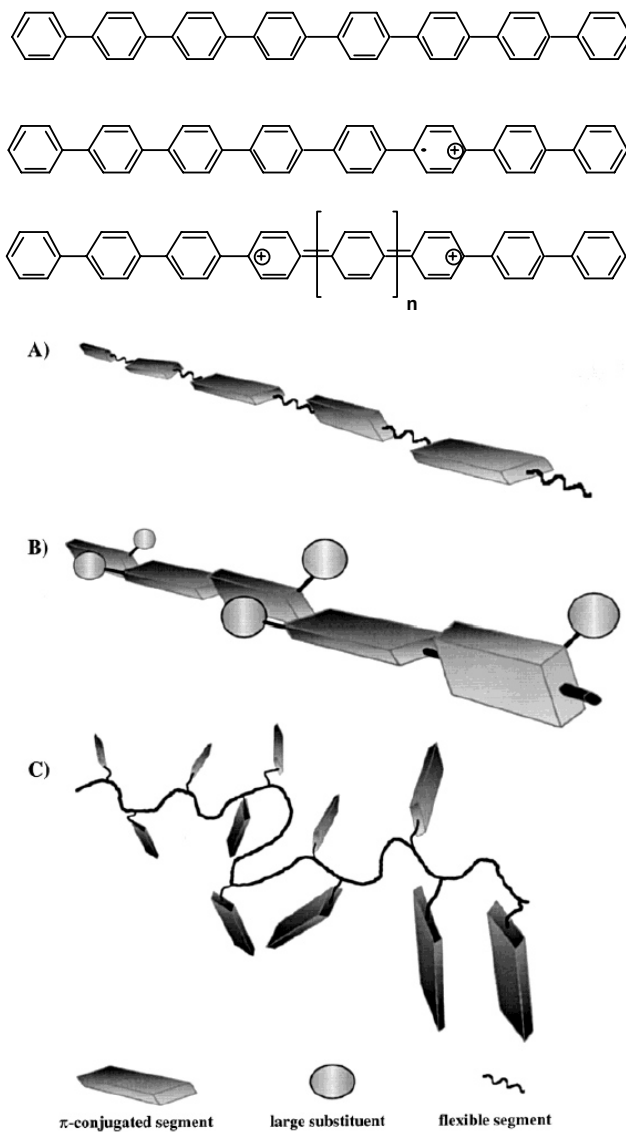
2.3.   Poly(diacetylene)s

Poly(diacetylene)s are prepared by the topochemical polymerisation of diacetylenes.

2.4.   Poly(phenylene)s

Four synthetic routes have been employed for the preparation of poly(phenylene)s. Oxidative coupling, organometallic coupling, dehydrogenation of poly(cyclohexylene)s and cycloaddition reactions.
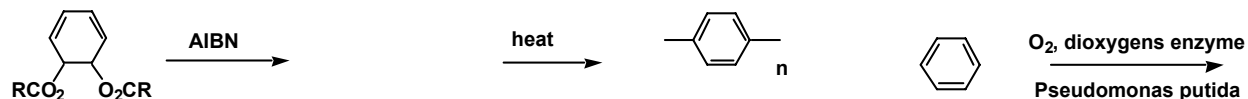
Oxidative coupling
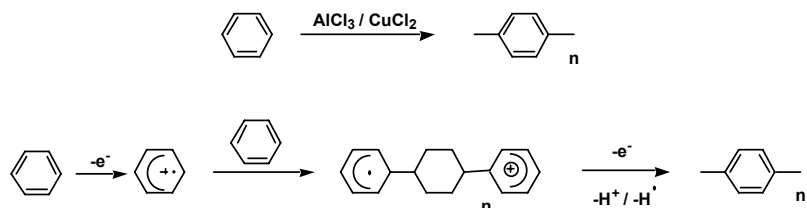
The structural features (meta or ortho linkages) and physical properties of the polymer prepared by oxidative coupling depend to a large extend on the nature of the oxidising reagent. Ortho linkages can be introduced by using more substituted benzenes rather than the parent compound. Polymers substituted in the para position are in general more difficult to process, i.e. they are more ordered and thus π stacking is more efficient.

Organometallic coupling

Ullmann and Wurtz-Fittig reactions have been utilised for the synthesis of phenylene oligomers but these methods can not be applied to the synthesis of poly(phenylene)s since yields are low.
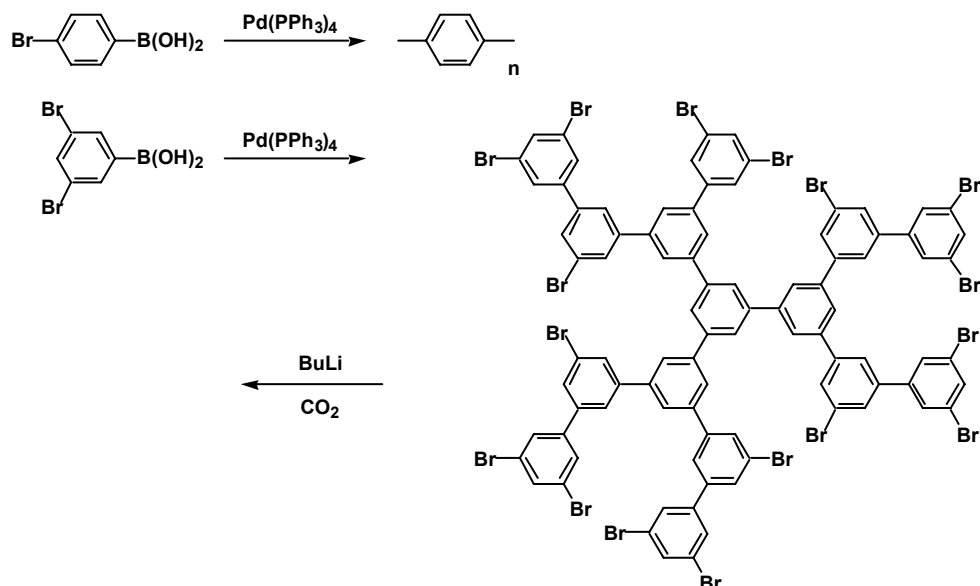
Dehydrogenation of poly(cycohexylene)s

Diester derivatives of 5,6-dihydroxy-1,3-cyclohexadiene have been polymerised radically after which the resulting poly(cyclohexylene)s were converted to poly(phenylene)s by pyrolysis. Best results were obtained with methyl carbonate derivatives. The dihydroxy monomer precursor is accessible through enzymatic oxidation of benzene. An environmentally friendly route to conjugated/conducting polymers.

Cycloaddition reactions

1,4-cycloadditions of bis-cyclopentadienones with bisacetylenes can yield high molecular weight polymers which contain approximately equal amounts of meta and para substituted phenylene units.
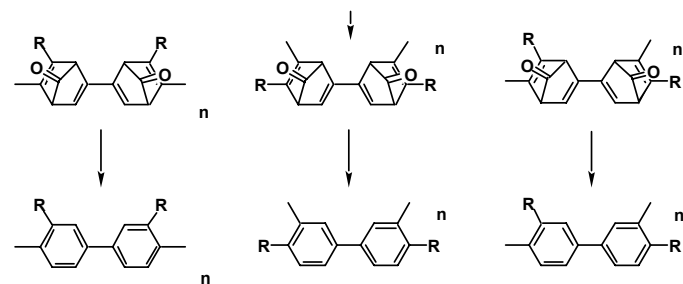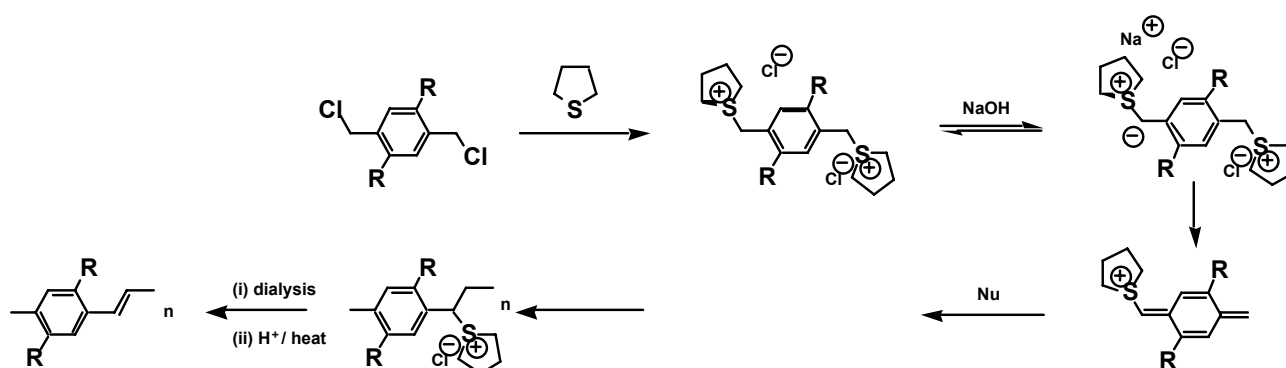

Suzuki coupling of p-bromophenyl boronic acid offers another convenient route to poly(phenylene) although substituted analogues require elaborate syntheses of monomer units. An interesting extension of this methodology is the synthesis of hyperbranched poly(phenylene)s from an AB_2 monomer. In general branching improves solubility and processibility compared to the linear parent polymer, which is also true in the case of highly conjugated polymers such as poly(phenylene)s.

Pd(PPh₃)₄ → (over schemes)

Br—⟨benzene⟩—B(OH)₂ →[Pd(PPh3)4] (—⟨benzene⟩—)n

Br / ⟨benzene⟩ —B(OH)₂ (3,5-dibromophenylboronic acid) →[Pd(PPh3)4] (dendritic polybrominated polyphenylene structure)

←[BuLi / CO₂]

2.5. Poly(phenylene vinylene)s

Poly(phenylene vinylene) (PPV) possess a chemical structure which is intermediate between that of poly(acetylene) and poly(phenylene). Oriented PPV is highly crystalline, mechanically strong and environmentally stable. Early attempts utilised dehydrohalogenation or Wittig condensation reactions which resulted in the formation of intractable oligomeric powders. The Wessling-Zimmermann precursor is a water-soluble PPV prepolymer (cf. Durham route) which allows the reproducible formation of high molecular weight free standing films.

PPVs were originally synthesised via the popular Gilch route which uses the bis(chloromethyl)benzene precursor monomer in THF in the presence of t-butoxide as non-nucleophilic base. The reaction leads to a rather il-defined product with limited conjugation length and defects along the polymer backbone. The precursor sulfonium electrolyte is prepared in aqueous solution (Wessling route to PPV, less defects, longer conjugation, milder) by the base induced polymerisation of the appropriate bis-sulfonium monomer. The polymerisation is quenched by addition of dilute acid and the reaction mixture is then dialysed against water to separate the high molecular weight fraction as well as the sodium and chloride ions. A study of the polymerisation mechanism revealed the existence of a quinoid intermediate during the early stages of the polymerisation. An alternative radical mechanism has been considered but ruled out by the experimental evidence.

(Reaction scheme: bis(chloromethyl)benzene + THF (S) → bis-sulfonium chloride →[NaOH] sodium chloride sulfonium species →[Nu] quinoid intermediate → sulfonium prepolymer —[(i) dialysis (ii) H⁺/ heat]→ PPV)

An interesting group of electron-deficient PPVs are the cyano substituted PPVs which are prepared by a Knoevenagel condensation reaction between an aromatic diacetonitrile and an aromatic dialdehyde.

The versatiliy of the Knoevenagel condensation reaction renders this route suitable for the synthesis of heteroaromatic cyanopolymers including well-defined alternating copolymers. As always important in the context of conducting polymers is the ability to influence the bandgap in a molecular predictable fashion so that their electronic properties can be tuned and tailored according to the desired application.

2.6.   Oligomers

How planar is a PPV molecule? Drawn PPV films were analysed by X-ray diffraction and NMR. The results demonstrated that the average tilt of the phenylene ring relative to the chain axis was 7.7^o, close but not exactly equal to the 9.2^o predicted for a trans-stilbene-like structure. Highly oriented PPV shows high electrical conductivity upon vapour-phase doping with AsF_5 but iodine doped films show only modest conductivities.

PPV oligomers have been synthesised by the Wittig reaction in order to obtain model compounds for physical characterisation studies aimed at a more detailed understanding of the conduction mechanism present in doped conjugated polymers.
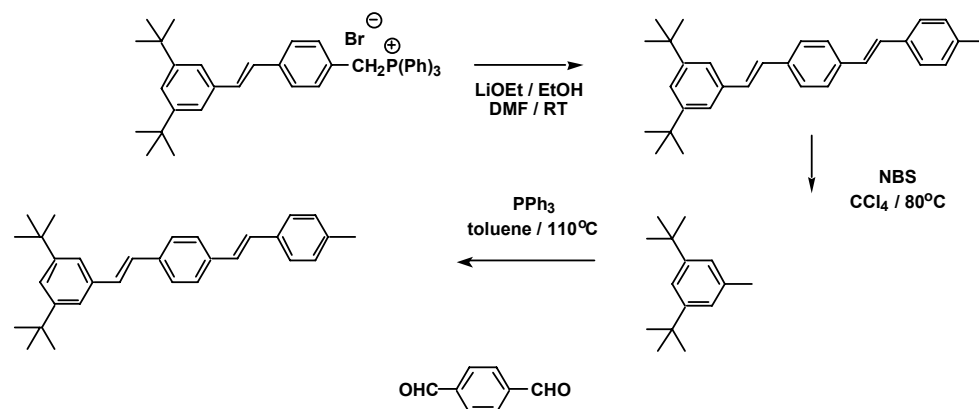
It is a challenge to prepare PS oligomers!!!

## 2.7.   Ladderpolymers

2.8.   Poly(thiophene)s

Heteroaromatic polyarylenes can be prepared employing similar synthetic strategies as those described for poly(phenylene)s and poly(phenylene vinylene)s. Not only has the heteroatom an influence on the chemical and physical properties of the polymeric product, it also has to be taken into account when preparing the required monomer (cf. aromatic heterocycles lectures).

Polythiophene like many other linear polyaromatic compounds is insoluble in organic solvents (rigid backbone) and substitution in the 3 and/or 4 position is necessary to render the polymer soluble.

With the introduction of 3-substituents, a number of different regioisomers are possible. These are head-to-head, tail-to-tail and head-to-tail. and random configurations. The issue of regioregularity pervades all of polymer chemistry and is present even in simple linear polymers such as polystyrene and poly(methyl methacrylate). Potentially any α-olefin is prone to polymerise to yield all of these regiochemical variations. Thus it is a significant challenge to find polymerisation reactions and/or reaction conditions to allow to control the sequence of regioisomers at will.

Studies on regioregular poly(thiophene)s, that have become accessible recently via a number of elegant routs, have shown that crystallinity increases with stereoregularity and that the possibility of sidechain crystallinity is essential for the development of optimal properties. For regiorandom polymers the optimal chain length for properties like conductivity and optical non-linearities has been determined to be in the range of 7-9. In contrast doped regioregular 3-substituted poly(thiophene) reaches

its optimal conductivity (1000 S/cm) with an dodecyl sidechain (octyl for the regiorandom polymer (20 S/cm)). 3,4-disubstitution reduces conductivity in the case of methylene groups (loss of coplanarity) because of steric hindrance. This can be overcome by substituting the methylene group with an oxygen.
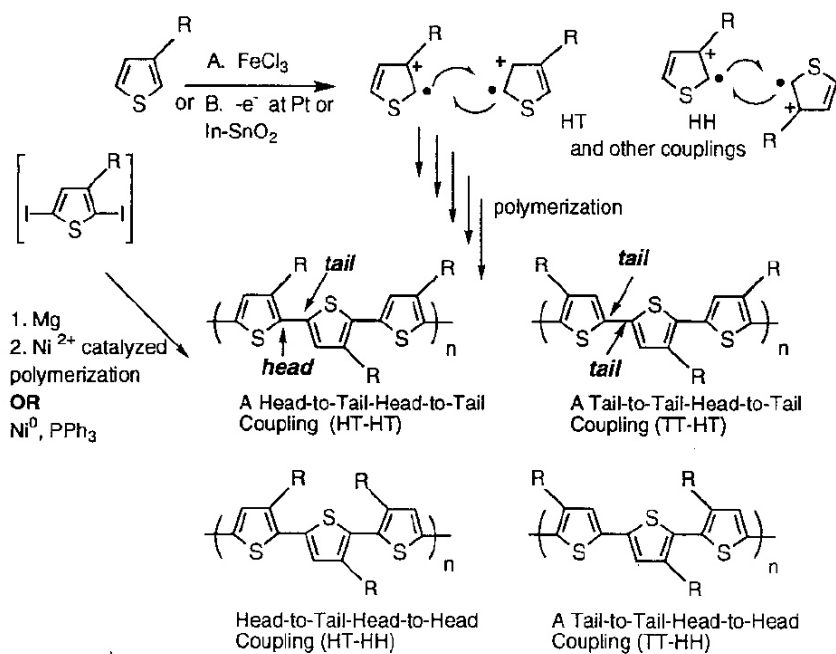
McCullough's route to regioregular poly(thiophene)s (98% HT; 70%).
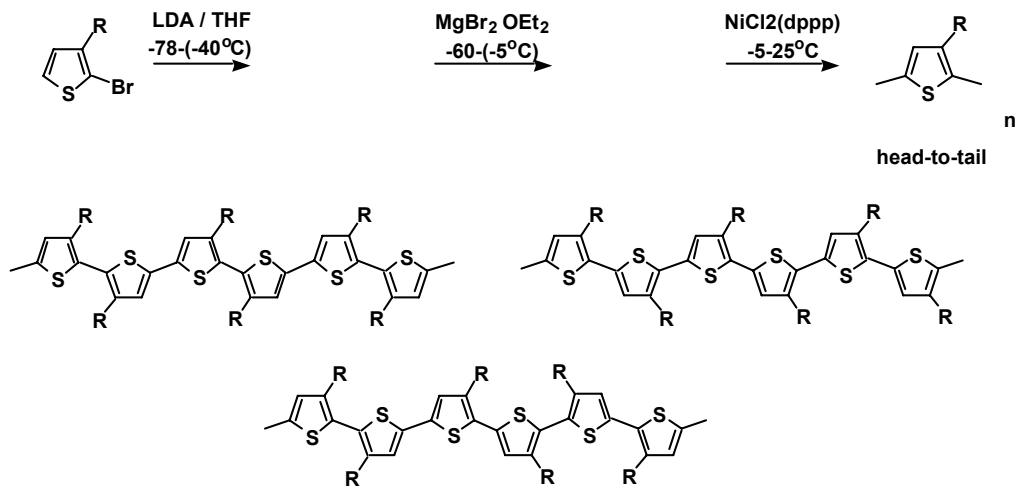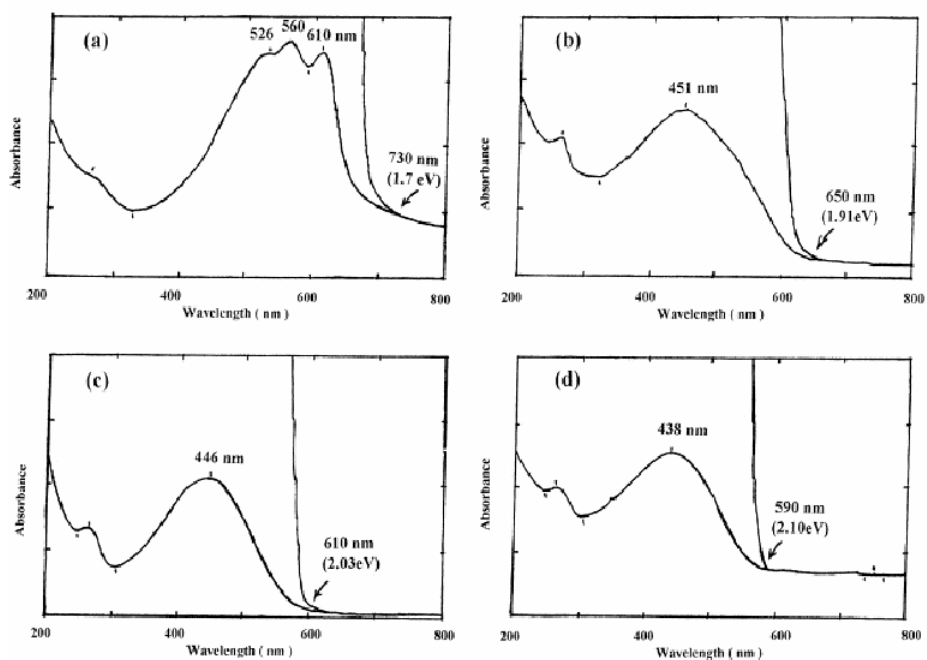
Solid-state UV–vis absorption spectra for films of poly(3-hexylthiophenes) with different regioregularity: (a) HT>89.5%; (b) HT:HH=70:30; (c) HT:HH=65:53; (d) HT:HH=50:50.

Oxidative coupling to poly(thiophene)s using FeCl$_3$ has also been shown to produce regioregular polymers with up to 94% HT.

An interesting and intriguing property of substituted poly(thiophene)s is the temperature dependence of the UV absorption. An increase in temperature causes the λ_{max} to shift to shorter wavelengths. This thermochromism arises from the conformational change in the aromatic backbone as a result of an increased disorder of the alkyl sidechains. Two distinct structures are possible depending on solvent and temperature; a predominantly coplanar structure in an aggregated form in a poor solvent (or low temperatures) and a conformationally disordered non-planar structure in a good solvent (high temperature).
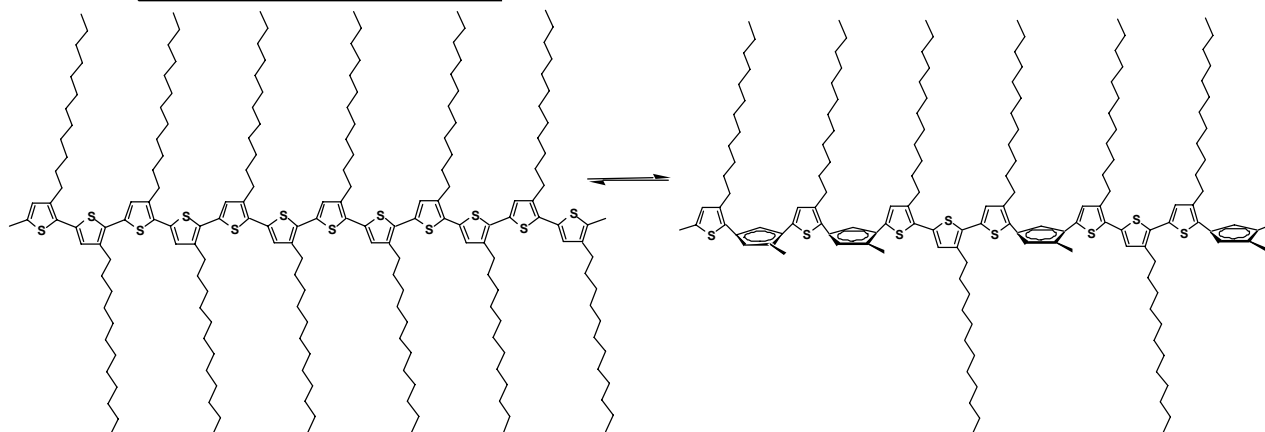

Electrochemical polymerisation of thiophene is used as a convenient route to prepare thin conducting films with controlled film thickness. The proposed polymerisation mechanism is proposed to include a dication of two thiophene rings.
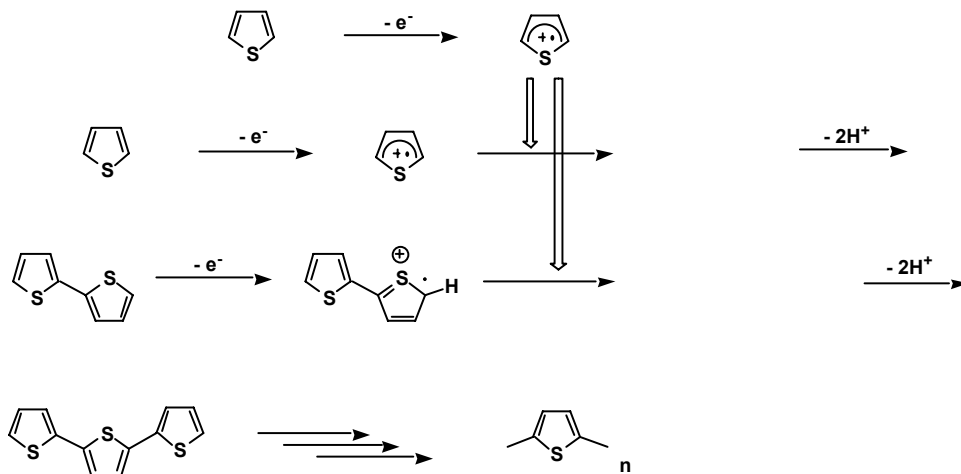
The synthesis of poly(pyrrole)s is very much related to that of poly(thiophene)s. However there is one distinct difference and that is the reactive nitrogen-hydrogen bond. Thus protection of the amine is required to prevent sidereactions such as crosslinking to occur. As in so many cases in polymer chemistry the t-Boc group serves well as stable protecting group which subsequently can be removed easily through acidic or thermal deprotection.
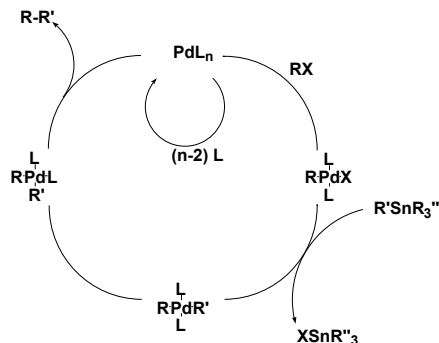
2.9.   Poly(pyrrole)s

Poly(pyrrole) prepared by the Stille coupling/thermolysis sequence.
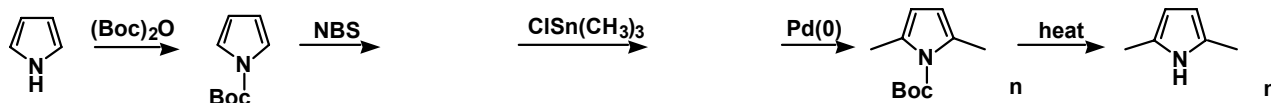

2.9.1.   Stille Coupling
(as an example for a variety of cross-coupling chemistries; Suzuki, Shonganishira, Yamamoto, Heck))

Stille coupling. Catalytic cycle.

2.10.   Poly(aniline)s

Oxidation of aniline is the most widely employed synthetic route to polyaniline and can be performed either electrochemically or chemically. The reaction is usually carried out in acidic medium with a chemical oxidising agents such as ammoniumpersulfate. Branching or even crosslinking during polymerisation occurs through the formation of radicals at the 2 and 6 position.
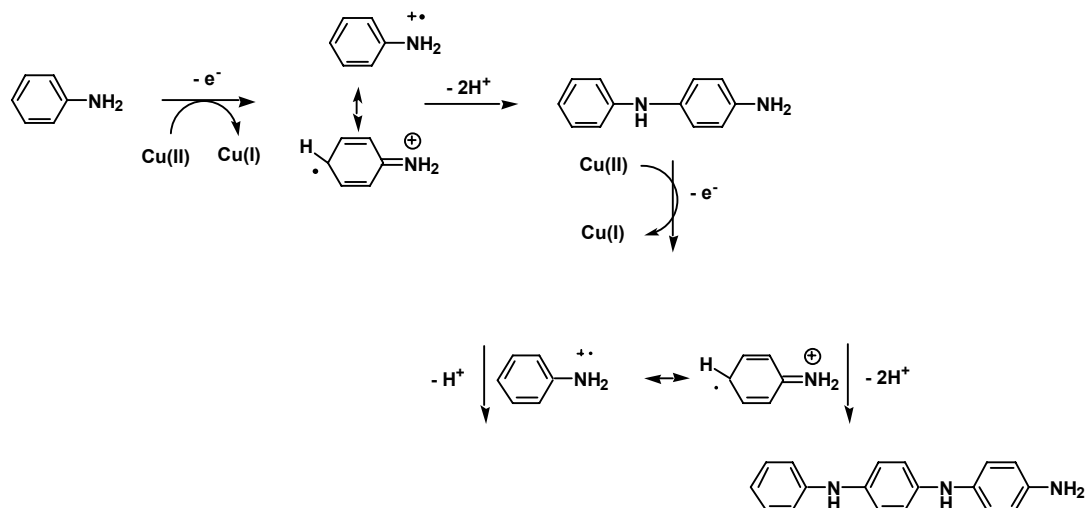
Polyaniline can occur in a number of well-defined oxidation states. The different states range from the fully reduced leucoemeraldine via protoemeraldine, emeraldine and nigraniline to the fully oxidised pernigraniline. Unlike most other polyaromatics, the fully oxidised state in polyaniline is not conducting as are all the others too!. Polyaniline becomes conducting when the moderately oxidised states, in particular the emeraldine base, are protonated and charge carriers are generated. It is this process, generally called protonic acid doping, which makes polyaniline so unique. No electrons have to be added or removed from the insulating material to make it conducting.
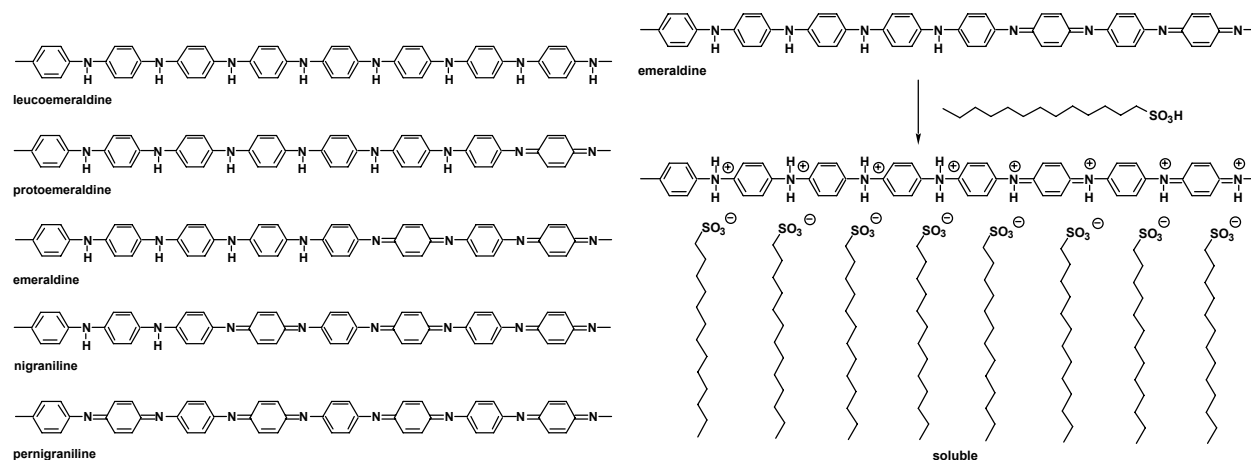

The different oxidation states of polyaniline can also be generated by doping with oxidants such as iodine but the resulting conductivity is lower than that obtained via protonic acid doping. The conduction mechanism is believed to involve polarons. In the case of the protonated emeraldine a delocalised poly(semiquinone radical cation) is the polaronic carrier.

The conductivity is affected by the water content. Completely dry samples are five times less conductive than samples containing some water.

Self-doped polyaniline, containing sulphonic acid substituents has been synthesised by sulphonation of the emeraldine base.
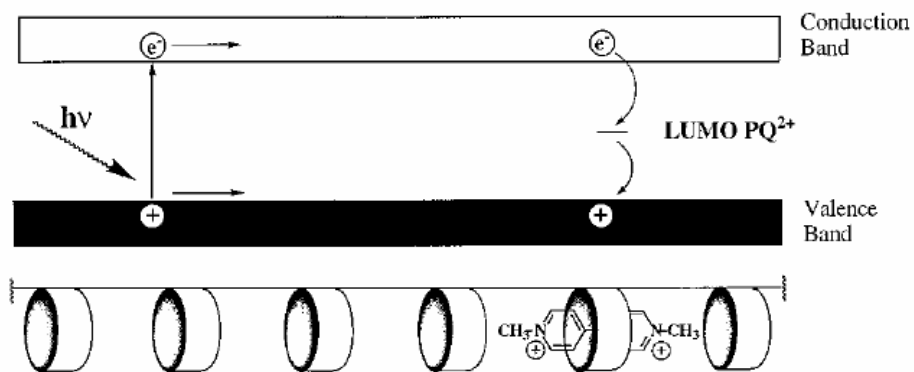
A different approach to the production of polyaniline (instead of long alkyl sidechain e.g.) is the use of n-alkyl sulphonic acids as proton donor (and ionically anchored aliphatic sidechains).

Stable thin films of polyaniline that can be processed out of solution are prepared from the emeraldine base with camphorsulphonic acid as dopant. m-Cresol as cosolvent is essential to obtain a chiral crystalline structure.
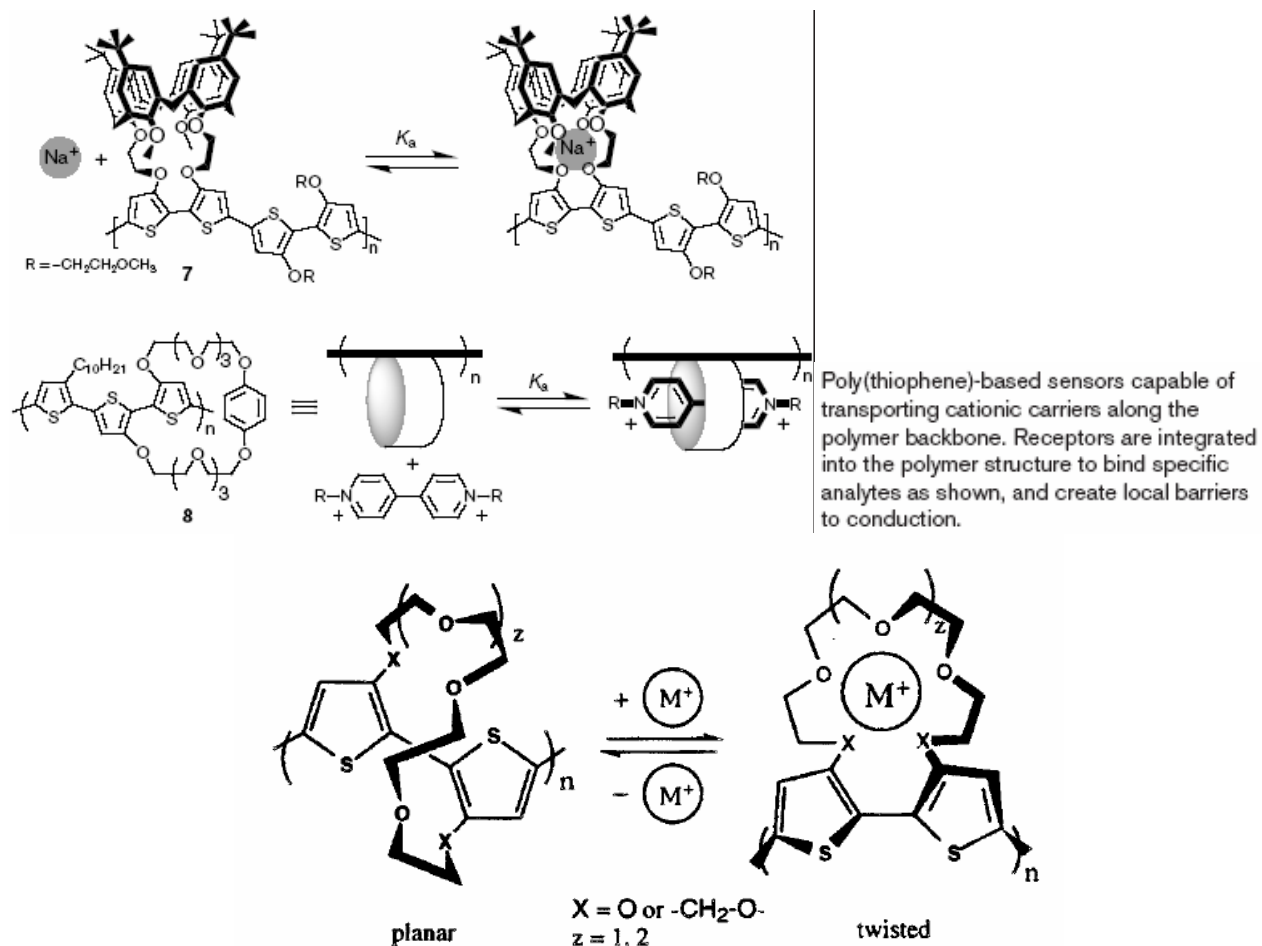
300 nm   700 nm
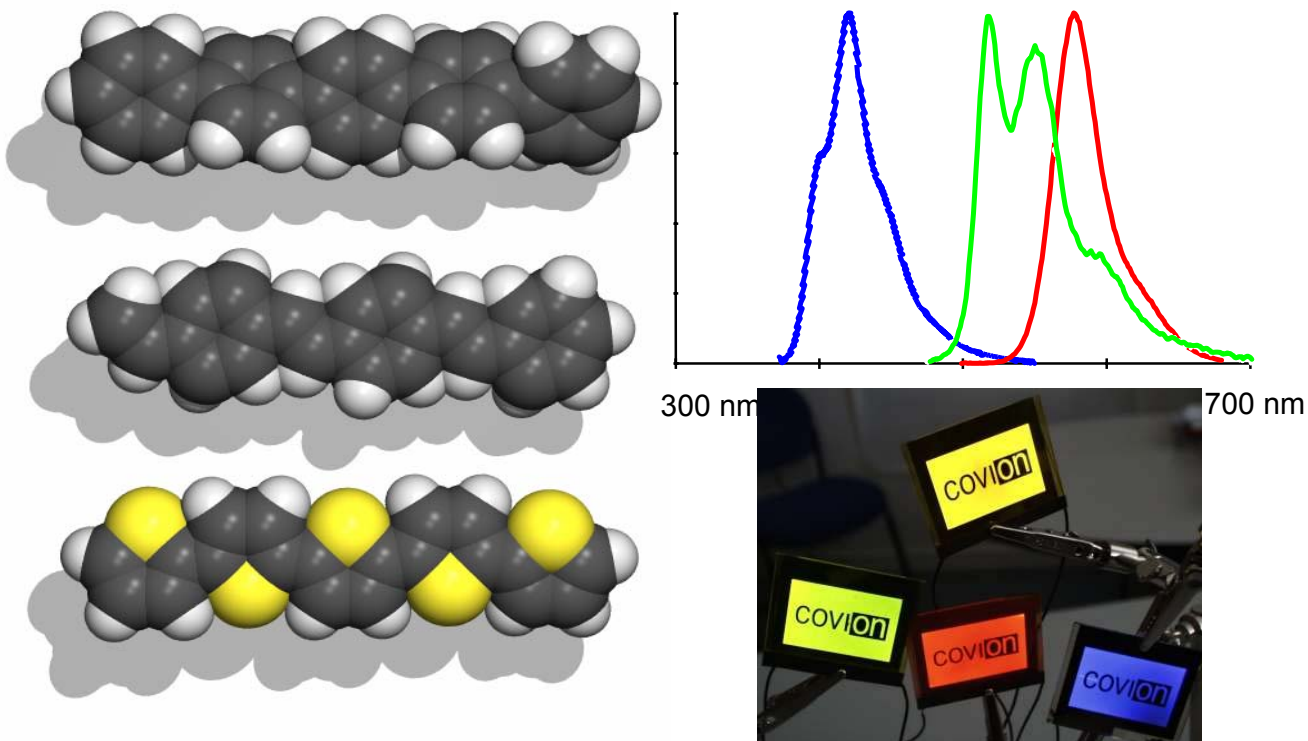
2.11 Conducting polyrotaxanes

Conducting polyrotaxanes as sensors - Mechanism

Examples of ion-selective polyrotaxane sensors.

Poly(thiophene)-based sensors capable of transporting cationic carriers along the polymer backbone. Receptors are integrated into the polymer structure to bind specific analytes as shown, and create local barriers to conduction.
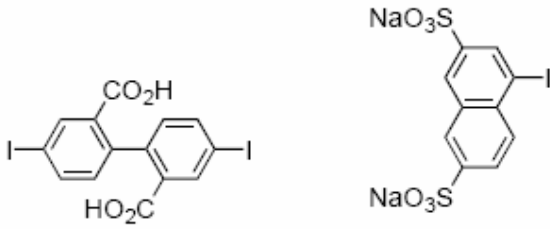
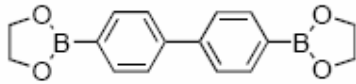X = O or -CH$_2$-O-
z = 1, 2

planar   twisted

Synthesis of an encapsulated molecular wire. PPP encapsulated with cyclodextrins employing the Suzuki couping as polymerisation reaction.

Strategy
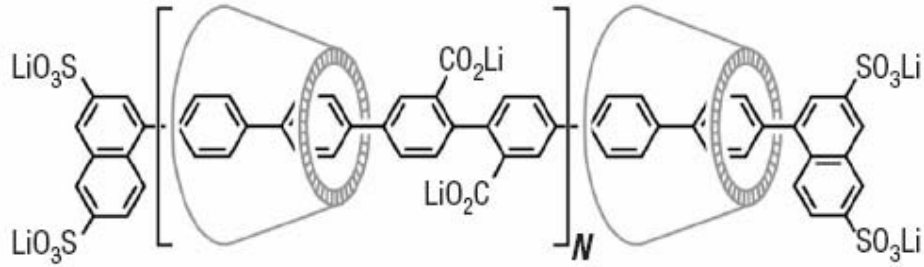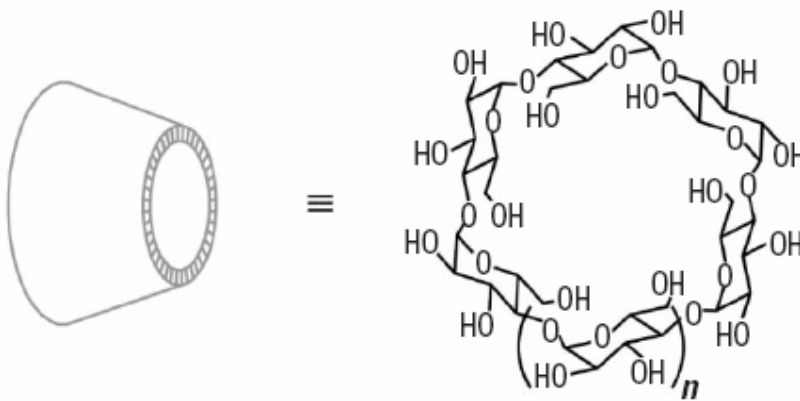

threading: hydrophobic binding

coupling: step-growth polymerization

capping
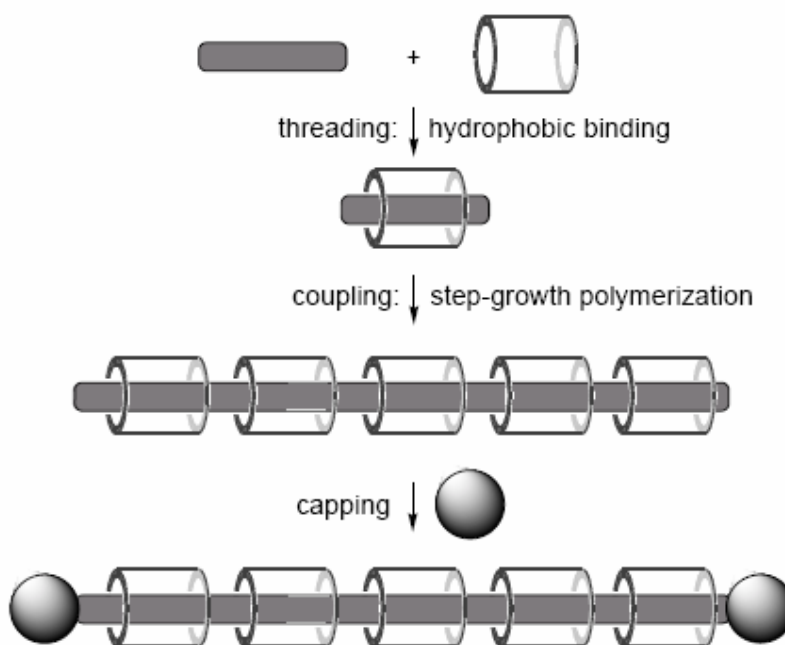
Monomers and stopper groups

Resulting polymer chain

β-CD-PPP

α-CD ($n=1$)
β-CD ($n=2$)

Effect on absorption and fluorescence.

— with β-CD
----- without β-CD

a PPP

1.0 nm
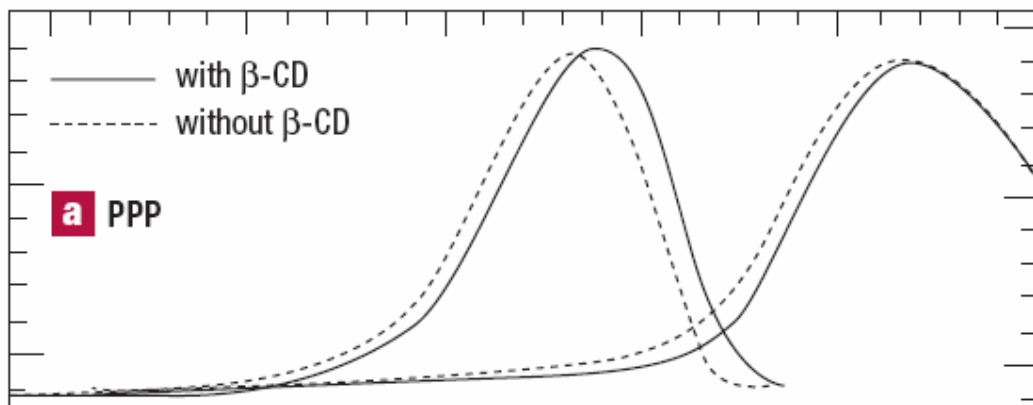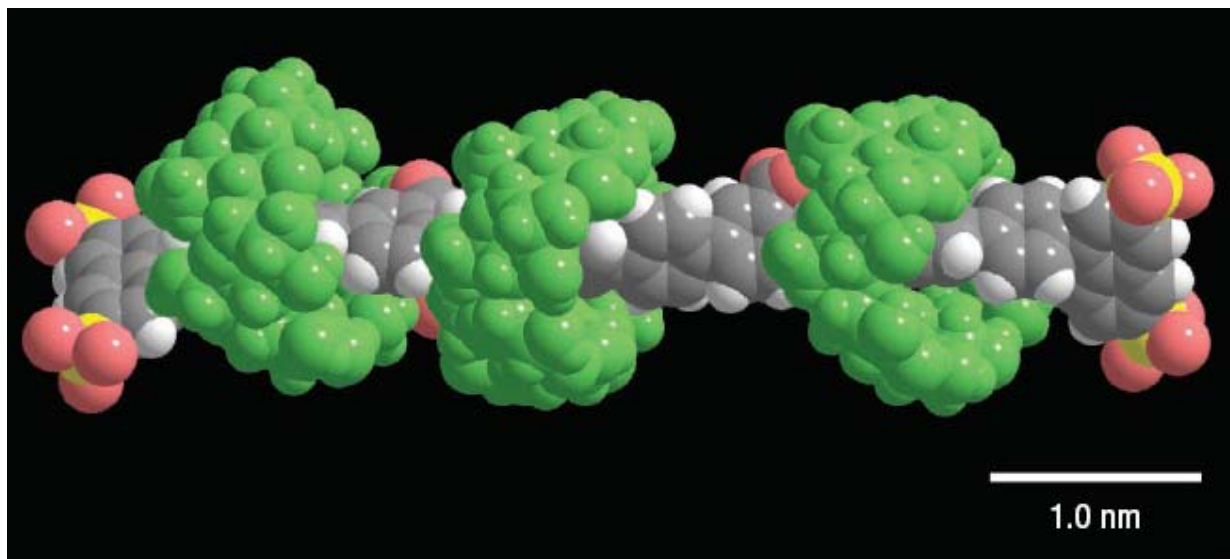
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