

Herbert Naarmann

# Synthesis and Properties of Perconjugated Systems

This article focuses on the main developments in polymers containing conjugated  $-HC=CH-$  bonds. It begins with oxidative coupling, which at the start of the 1960s evolved through various stages of polyaromatic and polyheteroaromatic synthesis to culminate in the production of electrically conducting polymers.

During the last decades, various new syntheses have been developed, important correlations discovered, e. g. between orientation, defects and conductivity, and numerous potential applications found for organic electrodes and conducting foils and coatings. These include electrochemical energy storage, electromagnetic shielding, sensors, drug depot materials and electrochromic indicators.

## Introduction

Systems with polyconjugated  $-CH=CH-$  bonds are a fascinating area of research, which for years now has continually produced surprises as far as both syntheses and new applications are concerned. But just as important is the stimulating effect on other fields.

Figure 1 shows a complex system of developments resulting from pursuing certain lines of enquiry into new fields of exploration.

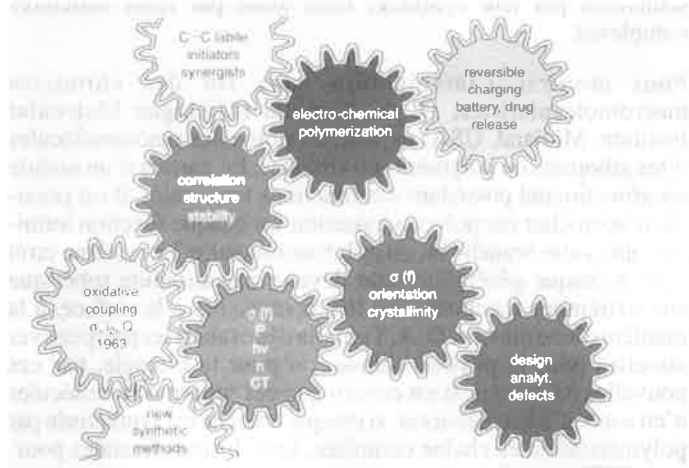


FIGURE 1. - Interrelationships and developments in the area of  $-CH=CH-$  conjugated systems.

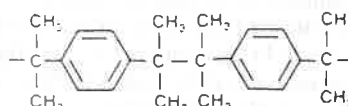
## Oxidative coupling

As is well-known, the oxidative coupling of compounds such as pyrrole, thiophene and benzene produces polymers [1], that are electrically conducting, shows a photovoltaic effect and have high Seebeck (thermoelectric) coefficients. Investigation of the products raised a number of questions :

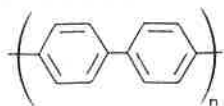
1. To which other structural classes can oxidative coupling be applied ?
2. What determines the electrical conductivity ?
3. How can the coupling products be characterized and is it possible to produce soluble polymers with electrical properties ?

Answering these questions, cf. Figure 1, has led to entirely new areas of investigation. In general, aromatic and heterocyclic compounds as well as metal complexes can be oxidatively coupled. However, the poor solubility or complete insolubility often makes unambiguous characterization difficult.

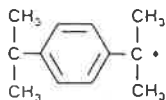
An interesting phenomenon is the oxidative coupling of substituted aromatics, e. g. mono (di) isopropylbenzene. A compound of the type



is obtained, which does not have the extreme thermostability of polyphenylene



(up to approx. 500 °C), but already begins to form radicals of the type

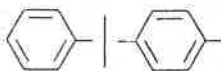


at ca. 180 °C. The latter act as radical initiators or as scavengers in processes such as combustion (flames are radical chain reactions) and are used in the production of self-extinguishing materials (e. g. styrene foams such as Styropor).

As early as 1969, it was pointed out that complex formation between electron acceptors and electron donors increases the conductivity by several orders of magnitude [2]. Analogous effects can be achieved by :

- Increasing the degree of polymerization ;
- Increasing the pressure ;
- Raising the temperature ;
- Irradiation.

The polymers are characterized by elementary analysis and spectroscopy. For example, the number of polymer (oligomer) units can be determined from the terminal/nonterminal group ratio



Attempts to make polycyclohexenones by cyclizing and condensing specific, soluble prepolymers, e. g. polyvinyl methyl ketone, led to the development of soluble precursors [3] (e. g. polyphenylene vinylene) as well as to so-called two-dimensional structures.

## Correlation between structure and stability

The introduction of links brings about a substantial change in the properties. Groups such as  $-NH-$ ,  $-CO-$ ,  $-S-$ ,  $=SO$ ,  $=SO_2$  and  $-O-$ , alone or in combination, can be used to convert polymers to high-technology polymers.

Another very important aspect is the dependence of stability on defects and orientation.

As mentioned above, most electrically conducting polymers are insoluble and crosslinked. Orientation of such products in a preferred direction is almost impossible or occurs only to a very minor extent.

This is due to the crosslinking sites in the polymer, the number of which can be ascertained by  $^{13}C$  NMR determination of the  $sp^3$  fraction. The synthesis of a BASF polyacetylene [4] that was almost totally free of defects was the first time that high stretching rates could be achieved.

For instance, polyacetylene that has been produced in silicone oil with a specially treated catalyst shows surprisingly high conductivities after being doped with iodine ( $CCl_4$  saturated with iodine at 25 °C).

Figure 2 reveals significant differences between a crosslinked  $(CH=CH)_x$  which cannot be oriented [5] and defect-free polyacetylene prepared at room temperature with an aged catalyst [4].

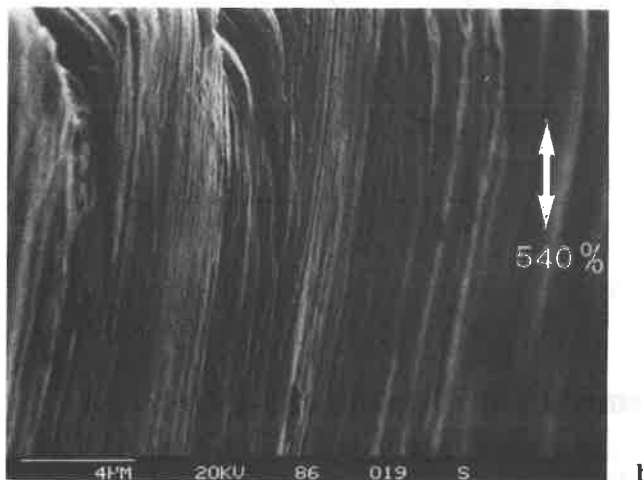
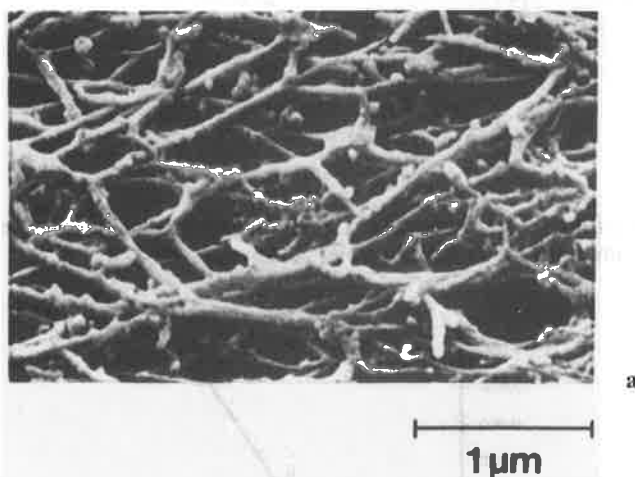


FIGURE 2.

The Shirakawa type on the Figure 2a is crosslinked and contains approx. 2 %  $sp^3$ . The polyacetylene shown on the Figure 2b has been prepared by the new BASF technique. It is linear (no  $sp^3$ ), is thus highly orientable (up to 660 %) and has a conductivity of more than 100,000 S/cm.

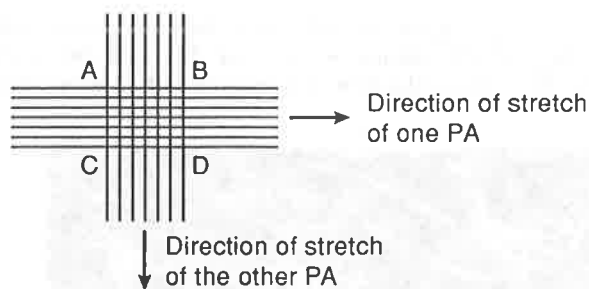
In general, the stability of the polyacetylene depends on the method of preparation.

Order of stability : Luttinger  $L-(CH)_x$  < Shirakawa  $S-(CH)_x$  < new BASF  $N-(CH)_x$  [6].

The greater stability of the  $N-(CH=CH)_x$  samples is probably due to the absence of defect sites of high crystallinity.

A parallel phenomenon as that of high anisotropy in the stretched sample. Figure 3 shows the dependency of conductivity on the degree of stretching ( $\perp$ ) and the direction of stretching ( $\parallel$ ).

The anisotropy of the stretched polyacetylenes permits the construction of a polarizer. When polyacetylene (PA) strips are laid across each other, polarized light is extinguished in the region of overlap ABCD of the anisotropic polymer :



Orientation by liquid-crystal or Langmuir-Blodgett techniques or with other polymers (polypyrrole) is also possible [7].

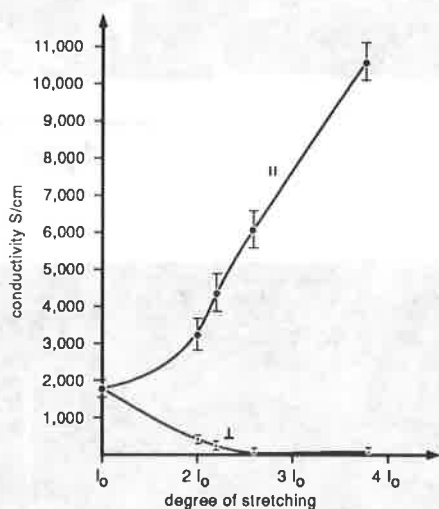
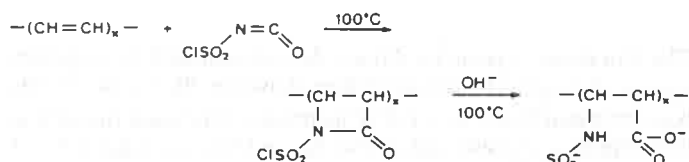


FIGURE 3.

## Chemical modification of $(-\text{CH}=\text{CH}-)_x$

Interesting chemical modifications are cyclo-additions on the  $(\text{CH})_x$  backbone, *e.g.* with chlorosulfonyl isocyanate. The ring of the adduct thus formed can be opened by alkalis.



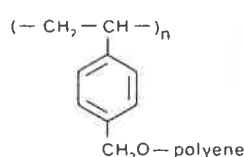
Cyclo-addition of chlorosulfonyl isocyanate and ring-opening to substituted hydrophilic polyacetylene.

The dominant reaction involving 3-chloroperbenzoic acid is the formation of oxirane structures, which can react further. Metal carbonyls, *e.g.*  $\text{Fe}_3(\text{CO})_{12}$ , react only with cisoid units. Otherwise, the metal atoms combine with 2 moles of the en-component, or isomerization occurs and leads to *cis*-configurations. Both types of reaction are confirmed by IR spectroscopy.

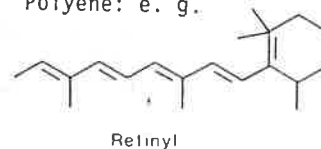
CO-insertion can also be observed with molybdenum carbonyls. Cyclo-addition with maleic anhydride (MA) and 3,4-dichloromaleic anhydride (DCMA) leads to adducts. The adduct formed by DCMA is worth mentioning because it gives rise to a fusible polyacetylene (165 - 180 °C).

With the Wittig reaction, it is easy to synthesize polymers with polyene side groups [8].

Type I

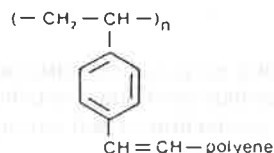


Polyene: *e.g.*



Or higher molecular polyene site groups :

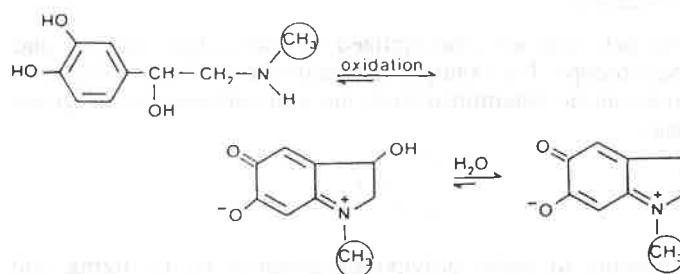
Type II



In all cases, the basic idea was to try to use compounds of types I-II as molecular wires to transport electrical charges and conduct impulses.

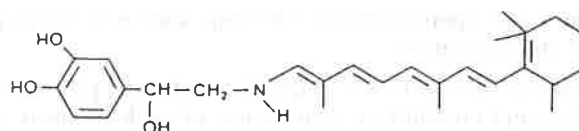
A completely new class of sensors are those based on, for example, adrenaline (or homologous derivatives), type III [9].

Type III



Replacing the methyl group in adrenaline with a polyene side group in the presence of mild oxidizing agents, *e.g.*  $\text{K}_4(\text{FeCN})_6$ , creates an impulse - as in the formation of the quinoid cyclic system by ring closure to give an indole derivative (pyrrole). In such a model system, the quinoid component acts as an intramolecular doping system, forming an intramolecular CT complex that is electrically conducting, the  $\pi$ -double bonds in the polyene allowing the electrical charge transportation (in the body, the adrenaline is responsible for nerve stimulation).

Type IV



This substance (type IV) can be used as a powerful colorimetric sensor for changing electrode potentials.

## Electrochemical polymerization

In contrast to polyacetylene, polypyrrole and polythiophene are exceptionally stable and can be quite easily produced continuously by electrochemical means [10].

Using the electrochemical technique (Figure 4), the polypyrrole, etc. can be produced under various conditions from  $-40\text{ }^{\circ}\text{C}$  up to more than  $100\text{ }^{\circ}\text{C}$ . The film is drawn off the anode under tension so that it is stretched, and orientation forces are applied when it is found onto a reel.

Another important point is the exchange of counterions. These can be excluded specifically, making it possible to release optically active counterions or active ingredients, e. g. those of medical interest such as heparin or monobactam, which are incorporated in specific quantities as counterions into polypyrrole [11]. Finally, it is worth mentioning that under the oxidation conditions used (electrochem.  $> 10\text{ mA/cm}^2$  or redox potential  $> 1.5\text{ V}$ ) triphenylene structures are formed and, in analogy, pyrrole could be oxidized to new macrocycles [11] (figure 5).

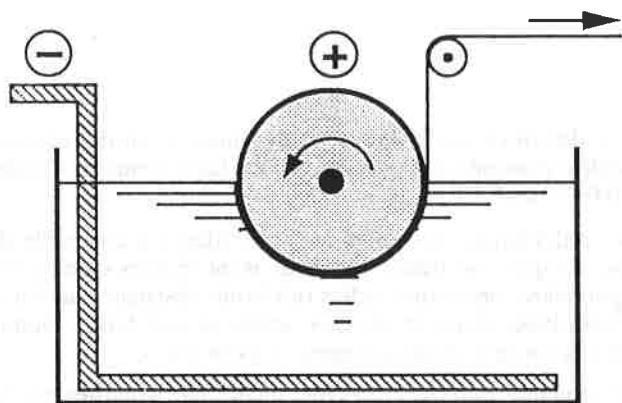


FIGURE 4. - Continuous polymerization.

1. The resulting polypyrrole showed no C-H signals after pulsing (H-NMR).
2. When, for example, tetradeutero (2, 3, 4, 5) pyrrole was used as a starting monomer, the resulting polypyrrole showed no detectable amounts of D.
3. Polypyrrole degradation (pyrolysis at  $600\text{ }^{\circ}\text{C}$ , or anodic overoxidation) gave benzene, indole, carbazole, etc. fragments.
4. When a polypyrrole film is treated with an aq.  $\text{CuSO}_4$  solution,  $\text{Cu}^{++}$  is sequestered (verified by spectroscopy).

All these phenomena are in accordance with the proposed macrocyclic structure and not with a linear one.

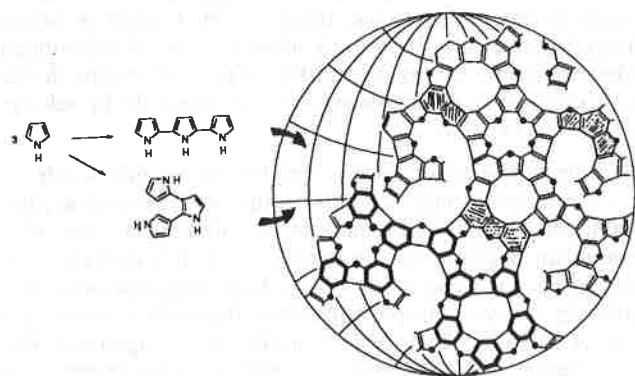


FIGURE 5. - Model of polypyrrole macrocycles.

Force-field calculations yield similar models with inner volumes (up to  $11\text{ \AA}$  in diameter) big enough to contain large counterions.

There is a strong correlation between *application and design*, each application being determined by the form assumed by the product during a particular process. Electrically conducting polymers can be reproducibly manufactured as powders, oriented films, coatings [12] and fibres. The benefit lies less in providing substitutes for conventional metals than in opening up new application areas. This calls for creativity and innovation.

#### Acknowledgements

I would like to thank my colleagues at BASF for their efficient teamwork, especially Chem. Ing. Hellwig (model substances), Dr Haberkorn (structural investigations), Dr Heckmann (morphology), Dr Denig (analysis), Dr Simak/Dr Passlack (IR spectroscopy), Dr Voelkel (NMR spectroscopy), Dr Schlag (conductivity measurements), Dr Naegele (electrochemistry), Dr Penzien/Dr Köhler (synthesis of polyacetylene, polypyrrole, etc.), Dr Theophilou (polyacetylene, stretched), Dr Cosmo (polyacetylene, modified).

Special thanks are also due to the partners in the BMFT projects, Professors Hanack, Müllen, Wegner, Schwoerer and Dormann and their colleagues, for fruitful cooperation.

Lastly, I would like to thank Dr F. Beck (now Professor in Duisburg) who measured the electrical conductivity of polyconjugated systems at the beginning of the 1960s.

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