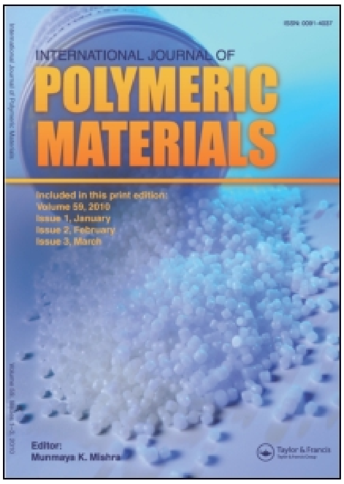

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Perconjugated Organic Polymers

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Factors affecting electrical conductivity of organic polymers are reviewed. Possibilities for new applications are discussed.

Keywords: Electrical conductivity; organic polymers; molecular structure perconjugation; polyacetylenes; thiophenes

INTRODUCTION

Ever since the fascinating field of electrically conducting polymers was discovered more than 30 years ago [1a, 1b], it has been the object of intense research. However, it took a long time to learn that the benefits of these polymers lie less in providing substitutes for conventional metals than in opening up new fields of application.

1. NEW MATERIALS WITH NEW PROPERTIES BY OXIDATIVE COUPLING

At the start of the 1960s, priorities centred on postulating and testing new structural principles for polymers. One approach, other than the classical polymerization methods, was that of oxidative coupling. By this technique, copper chloride and aluminium chloride were used to make an oligobenzene from benzene [1c]. This reaction was systematically extended and became established as the general "aufbau" method for synthesizing polyaromatics and polyheterocycles [1a].

To test the scope of the method, the following types of compounds were employed:

- aromatic compounds, substitution products and condensed systems, such as diphenyl, terphenyl, pyrene, anthracene and chrysene;
- unsaturated cyclic compounds, such as cyclopentadiene and cyclooctatetraene;
- heterocyclic compounds, such as thiophene, pyrrole and quinoline;
- metal complexes, such as phthalocyanines and ferrocene.

The potential afforded by the oxidant/Friedel-Crafts complexing agent reaction pair was extended considerably. In principle, all Friedel-Crafts catalysts and the usual dehydrogenation agents can be used for oxidative coupling. The degree of suitability is shown in decreasing order, from left to right, as tested on benzene/$CuCl_2$ (Eq. (1)) and as tested on benzene/$AlCl_3$ (Eq. (2)). Oxidizing Friedel-Crafts agents, such as $FeCl_3$, assume both functions.

$$\begin{aligned} AlBr_3 > AlCl_3 > FeCl_3 > MoCl_6 > NbCl_5 \\ > TaCl_4 > TiCl_4 > SnCl_4 > BF_3 > ZnCl_2 \end{aligned} \tag{1}$$

$$Pd^{II} > Co^{III} > Mn^{III} > Cu^{II} > Fe^{III} > \text{chloranil} > V^{III} > I_2 \tag{2}$$

The oligomeric and polymeric reaction products were characterized in terms of thermoelectric power and photo- and dark conductivities.

To our surprise, the reaction products, *e.g.*, polyphenylene and polythiophene, showed electrical conductivities of up to $5 \cdot 10^{-1}$ S/cm. Not only was this the highest value yet obtained for a polymer, but these were the first polymers capable of conducting electricity [1a].

The polymers also displayed photovoltaic and thermoelectric properties. After the great surprise and no less great incredulity as to "How can polymeric organic materials suddenly conduct electricity?" had subsided, the serious business of elucidating the structure, type of charge, mechanism, *etc.*, was pursued relentlessly and with some success.

2. CORRELATION BETWEEN SYNTHESIS CONDITIONS AND PROPERTIES

It is interesting to note that varying the reaction conditions opens up a broad spectrum of products with different properties (see Fig. 1). These include colour, which varies from pale yellow to dark brown and black [1d].

It can be seen that an increase in the number of constituents n^* is accompanied by a deepening in colour and an increase in electrical conductivity[†] and cross-linkages.

The stepwise synthesis of polyphenylene, for example, starts with a cationic radical and involves branching and cross-linking to produce layer lattices (like graphite). An indirect method for determining the molar mass consists in alkylation to convert the polymer to a soluble product.

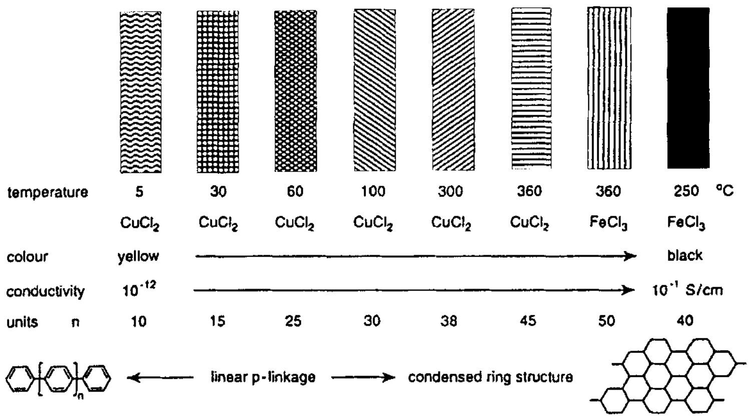

FIGURE 1 Conductivity of polyphenylenes as a function of number of aromatic units n and synthesis conditions [1a].

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[*] The number of constituents n was determined from IR spectra by calculating the ratio of monofunctional end groups to bifunctional centre groups, and comparing them with the known lower constituents: terphenl, quadriphenyl, *etc.*

[†] Unless otherwise stated. the term conductivity refers to the "dark conductivity" as measured in a cell by Beck [2] at 300 bar and room temperature.

3. CAN THE ELECTRICAL CONDUCTIVITY BE ALTERED?

As early as 1969, it was pointed out that complex formation between electron acceptors and electron donors increased the conductivity be several orders of magnitude [3]. Analogous effects can be achieved by

- increasing the degree of polymerization
- increasing the pressure
- raising the temperature
- irradiation.

In the search for easy-to-manufacture, highly stable compounds with a known number of double bonds, perylene derivatives of the imide and imidazole types [4] were studied for their electrical photo- and dark conductivities.

The crystal structures were elucidated later [5]. Interesting differences in the conductivity were found to be a function of the *R* substituents and the crystallinity of the samples. The formation of charge-transfer complexes with tetracyanoquinone dimethane, tetracyanoethylene and iodine (I_2) increased the conductivity by factor of 1,000 thereby allowing a conductivity similar to that of graphite (10^{+1} S/cm) to be attained in some cases.

Translating the system to polymeric charge-transfer complexes of the types polymer with donor + acceptor monomer, polymer with donor + polymer with acceptor, and polymer with acceptor + donor monomer led to a new class of compounds [6] that have electrical conductivities of up to 10^{+2} S/cm.

The idea of inserting electron acceptor and donor groups alternately in one molecule was realized in the synthesis of substituted ladder-like polyquinones with —S— and —NH groups [7].

4. STATUS OF RESEARCH AND APPLICATION

As mentioned above, after donor/acceptor complexing, the new electrically conducting organic materials exhibited astonishingly high conductivity values for that time (1969). Additional properties were thermoelectric power, photoconductivity and, especially, high thermal stability. A large number of potential applications suggested themselves:

Thermostable polymers, coatings, organic electrical contacts, photoelectric devices, photocells [1], as well as pigments with outstanding light fastness and thermal stability [1d]. Other potential applications are: resistance thermometers, thermistors, photoconductors, photodiodes, photoelements, solar batteries, electrical reproduction of information, electroluminescence, electrostatic storage batteries, image storage, and catalysis in chemical and biochemical systems [8].

5. WHAT ABOUT STABILITY?

The importance of stability was recognized early on and, in particular, oxygen absorption and storage stability were investigated.

Stability is a relative term, being generally understood to mean the constancy of material properties. In practice it means that the properties of the materials used to make a product should undergo no changes during normal use (including storage), at least for the duration of their life cycle.

Cuprene in particular, which is produced in large quantities in Reppe's COT synthesis as a film-like wall deposit with a metallic lustre

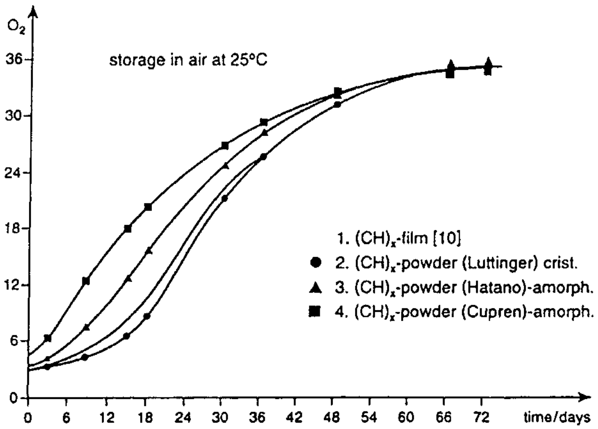


FIGURE 2 Autooxidation of polyacetylene [28].

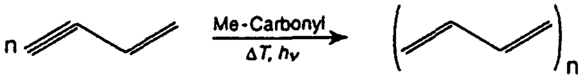
like that of copper or nickel, was the starting point for extensive studies [11]. These studies that polyacetylenes have the lowest degree of cross-linking and the greatest crystallinity and electrical conductivity, and that such highly crystalline polymers have the lowest capacity for absorbing oxygen. Furthermore, oxygen absorption considerably reduces the crystallinity.

These results spurred researchers on to make better polymers.

6. CONSEQUENCES: NEW TYPES AND METHODS

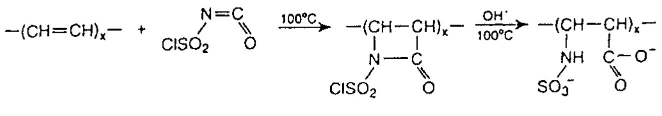
(a) The search for easy-to-manufacture, highly stable compounds with a known number of double bonds also focused on perylene derivatives. Further investigation led to the concept of ribbon-like polymers (*e.g.*, by repetitive Diels-Alder addition [12]) and ladder-like self-dopant systems [13].

(b) An interesting method is the polymerization of butenyne [14].



(c) A variety of chemical modifications result from radical additions or cyclo-additions to the $(CH)_x$ backbone, *e.g.*, with chlorosulfonyl isocyanate.

The ring of the adduct thus formed can be opened by alkalis. The reaction scheme for cyclo-addition of chlorosulfonyl isocyanate and ring opening to substituted hydrophilic polyacetylene is as follows:

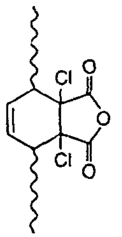


With 3-chloroperbenzoic acid, the dominant reaction is the formation of oxirane structures, which can react further.

Metal carbonyls, *e.g.*, $Fe_3(CO)_{12}$, react only with cisoid units. Otherwise, the metal atoms combine with two different units of the polyacetylene; or isomerization occurs, resulting in *cis* configurations. All these types of reaction have been confirmed by IR spectroscopy.

CO insertion can also be observed with molybdenum carbonyls. Cyclo-addition of maleic anhydride (MA) and 3,4-dichloromaleic anhydride (DCMA) leads to adducts like that shown below. The adduct formed by DCMA is worth mentioning because it gives rise to a fusible polyacetylene (165–180°C) [15].

(d) In all cases, the unmodified polyacetylenes proved to be extremely sensitive to oxygen.



DCMA modified $(CH)_x$

This also applied to Shirakawa's [16] polyacetylene films, formed at –78°C on $Al(ethyl)_3/Ti(OBu)_4$ using a high concentration of the catalyst in toluene.

Some years later the Penn Group [17] reported doping Shirakawa polyacetylene with the electron acceptor I_2 or Br_2, resulting in charge-transfer complexes with conductivities of 0.5–30 S/cm.

A comparison of the various types of polyacetylene [11] revealed some astonishing correlations: conductivity was directly proportional to crystallinity and inversely proportional to the number of sp^3 orbitals. This discovery was the key to the production of new polyacetylene types with fewer defects and greater stability.

Another important advance was the modification of the polymerization conditions, *e.g.*, using silicone oil or other viscous media. For instance, $(CH)_x$ can be polymerized at room temperatures to yield a new N-$(CH)_x$ polyacetylene of at least the same quality as the standard S-$(CH)_x$ obtained at – 78°C. Table I contains the results [18].

TABLE I Properties of the different $(CH)_x$ types

	Crystallinity[a] (%)	*Conductivity*[b] (*S/CM*)		*sp*^{3} *content*[c] (*rel*%)	*Surface*[d] *area* (m^2/g)	*Configuration*[e] *Cis content* (%)
		Undoped	*Doped with* I_2			
S-$(CH)_x$	70	10^{-6}	30	4	300	50
N-$(CH)_x$	65	10^{-8}	100,000	0	100	80

[a] Phillips diffractometer CuK_α radiation; [b] Four-probe measurement; [c] Determined by ^{13}C-NMR spectroscopy; [d] BET (Branauer–Emmett–Teller) method; [e] Determined by IR spectroscopy.

Ageing of the standard catalyst brings about another surprising improvement in the $(CH)_x$ properties. The resulting reduction in the number of sp^3 orbitals, *i.e.*, the production of a defect-free system, is of great benefit. Special techniques were applied to orient the $(CH)_x$ in order to attain high conductivities (*i.e.*, values greater than 100,000 S/cm [19]) and parallel fibrils.

Similarly, it is possible to make transparent $(CH)_x$ film with a conductivity of over 5,000 S/cm. The polyacetylene is produced on a plastic film and stretched together with the supporting material. Later it is complexed, *e.g.*, with iodine, under standard conditions.

Figure 3 illustrates two types of polyacetylene. The standard Shirakawa type (Fig. 3a) is cross-linked and contains an sp^3 fraction of approx. 2%.

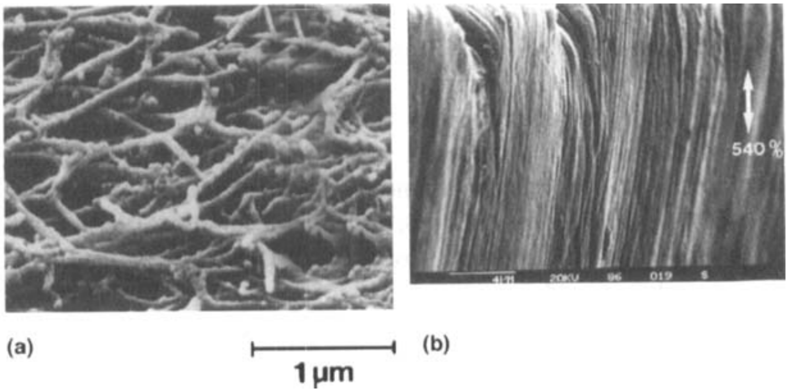


FIGURE 3 Scanning electron micrographs of iodine-doped polyacetylene; (a) Standard cross-linked polyacetylene (conductivity ca. 30 S/cm); (b) Stretched polyacetylene (conductivity > 100 000 S/cm) [38].

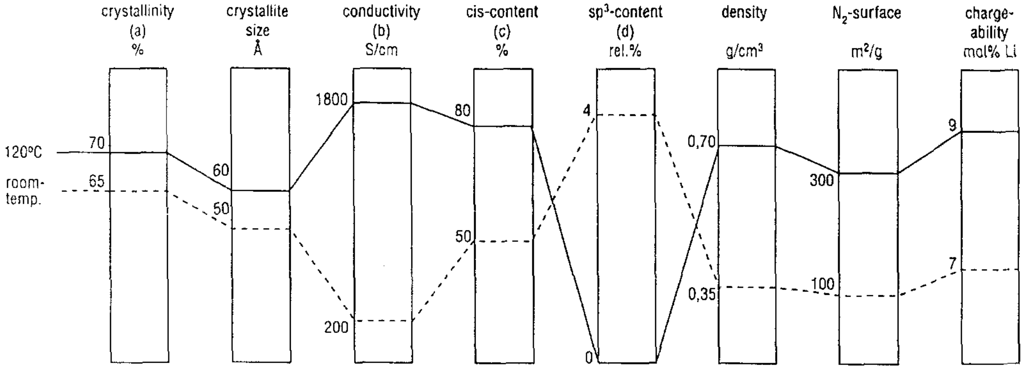


FIGURE 4 Comparison of $(CH)_x$ produced by unannealed --- and annealed catalysts — (120°C); (a) determined: Phillipsdiffractometer, CuK radiation, influenced: molratio Al/Ti, polym. temp., CH≡CH pressure; (b) determined: J_2-doped [19a], fourprobe measurement, status 1985; influenced: impurities; (c) determined: IR spectroscopy, influenced: catalyst type and preparation, CH≡CH quality; (d) determined: ^{13}C-NMR spectroscopy, influenced: type of catalyst solvent (silicon oil *etc.*), annealing process (time and temperature).

TABLE II Conductivities of some metals and different types of polyacetylene [38]

Metal or polyacetylene	*Conductivity (volume), S/cm*	*Density,[d] G/CM*$_3$	*Conductivity (weight), S/ cm*$^{-2}$*g*$^{-1}$
Hg	10 365	13.54	767
Pt	101 522	21.45	4 733
Cr	77 519	7.19	10 781
Fe	102 986	7.87	13 085
Au	470 588	19.3	24 382
Ag	671 140	10.49	63 972
Cu	645 000	8.94	72 147
Shirakawa polyacetylene [17a]	897[a]		813
	30[b]	1.23 (0.40)	22
Shirakawa polyacetylene, oriented in liquid-crystal matrix [17b]	1 600[b]	1.10 (0.50)	1 750
BASF polyacetylene, oriented [19a]	23 000[c]	1.12 (0.85)	20 000
BASF polyacetylene with additional reducing agent, oriented [19a]	120 000[c]	1.15 (0.90)	104 347

[a] Doped with $FeCl_3$.
[b] Doped with I_2 vapour.
[c] Doped with a saturated solution of I_2 in CCl_4.
[d] Densities for polymers denote values after doping; values before doping are given in parentheses.

The new BASF technique involves polymerization at room temperature (instead of – 78°C) and the use of a tempered catalyst. The stretched polyacetylene product has parallel fibrils.

Processes for modifying polyacetylene in a solution of polymers such as rubbers, polyisobutene, *etc.*, have been described in detail in Government Report 03 C 1340 [15] and will not be discussed further here. This also applies to work involving polymerization in high-viscosity media other than silicone oil.

Of general interest, however, are stability studies on the new type of polyacetylene N-$(CH)_x$.

8. STABILITY STUDIES ON THE NEW TYPE OF POLYACETYLENE N-$(CH)_x$

All organic polymers degrade on exposure to oxygen, particularly in the presence of sunlight, but the extent of degradation varies markedly with the structure of the polymer. Normal $(CH)_x$ is particularly susceptible to reaction with oxygen (Fig. 3).

Figure 5 shows the normalized conductivity of $(CH)_x$ doped with I_2 in CCl_4 solution *versus* exposure time in air.

The stability of $(CH)_x$ synthesized with different catalysts increases in the order:

Luttinger type L-$(CH)_x$ < Shirakawa type S-$(CH)_x$ < new type N-$(CH)_x$

N-$(CH)_x$ is the optimum material. Owing to its special method of synthesis, it has a minimal sp^3 fraction, high *cis* content (80 % *cis* isomer synthesized at RT), high density, very thin fibrils, and high conductivity after doping with iodine.

Both N-$(CH)_x$ and highly stretched $(CH)_x$ have greater stability than the usual systems (such as those of Shirakawa and Luttinger),

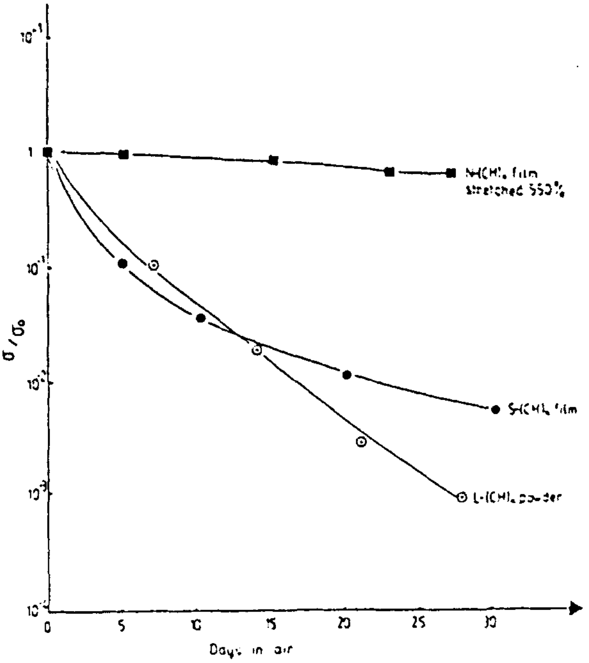


FIGURE 5 Normalized conductivity of iodine-doped $(CH)_x$ synthesized with different catalysts *vs.* exposure time in air [19a].

probably due to the higher density and very low defect rate of the former.

The mechanism of polymer degradation usually entails the absorption of energy (thermal or UV), leading to the formation of active free radicals that partake in chain scission and crosslinking.

Pristine S-$(CH)_x$ appears to undergo some spontaneous or "thermal" degradation at all practical temperatures. Even at −78°C, *cis-trans* isomerization occurs.

The *cis* content (%) of N-$(CH)_x$ film *versus* storage time in months at 22°C under nitrogen (Fig. 6) decreases very slowly compared with that of S-$(CH)_x$ to reach 78% after three months. This higher stability of N-$(CH)_x$ at 22°C is also confirmed by thermal isomerization studies, which show a higher energy barrier (25 kcal/mol) for N-$(CH)_x$ compared with 17 kcal/mol for typical S-$(CH)_x$.

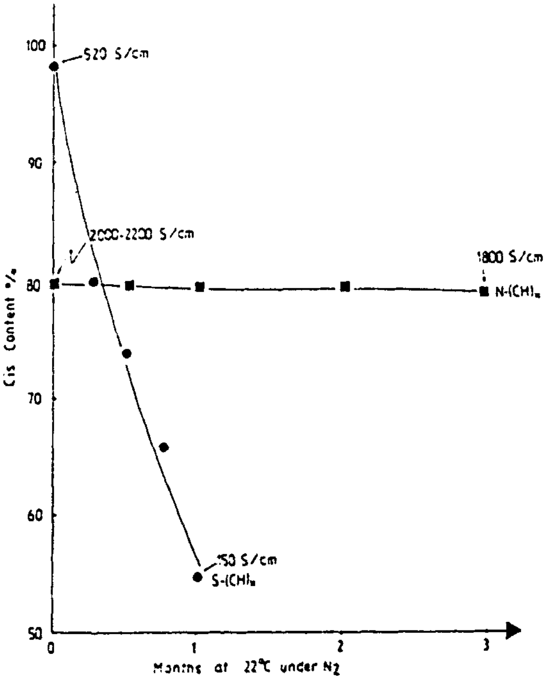


FIGURE 6 *Cis* content (%) of N-$(CH)_x$ and S-$(CH)_x$ films *vs*. storage time in months at 22°C under nitrogen [19a].

Also, we observed that N-$(CH)_x$ film that has been stored for three months under nitrogen gives, after doping with iodine, conductivities as high as 2000 S/cm, whereas one-month-old S-$(CH)_x$ gives only 150 S/cm (Fig. 5).

The infrared spectrum of the three-month-old sample is similar to that of the initial one.

9. WHAT IS THERE BESIDES POLYACETYLENE?

Polypyrrole and polythiophene, both first described in 1963 as electrically conducting materials [1a], experienced a renaissance when Diaz and Street gave new attention to the electrochemical oxidation of pyrrole [21], and Garnier to the "polythiophene field transistor".

Polyphenylene vinylene, polyaniline, polyphenylene sulfide, polycarbazole, polyindole, polypyrene and polyene fulvene are just a few of the large number of electrically conducting polymers with specific properties and interest [22].

10. CONTINUOUS ELECTROCHEMICAL POLYMERIZATION OF POLYPYRROLE-ANOTHER STEP FORWARD

In contrast to polyacetylene, polypyrrole is exceptionally stable and can be quite easily produced continuously by electrochemical techniques (Fig. 7).

Some general considerations apply to the choice of anion. If it is organic, smooth flexible films that can be readily detached from the

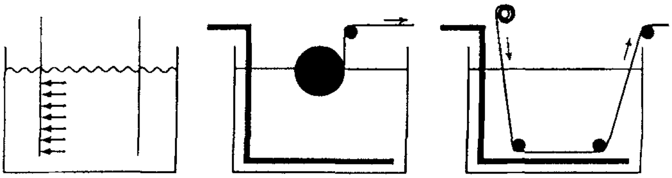


FIGURE 7 Electrochemical polypyrrole synthesis. Left: discontinuous process. Centre and right BASF methods: centre-continuous by rotating-drum electrode (U.S. Patent 4468291, June 27, 1983), and right-rotating band electrode.

anode are generally obtained. If it is hydrophilic. *e.g.*, ClO_4^- or BF_4^-, the polypyrrole formed is also hydrophilic- in contrast to polypyrroles in which a hydrophobic counterion is used.

11. COUNTERIONS: EACH TYPE OPENS UP NEW APPLICATIONS

The quality of the polymers is greatly influenced by many factors, *e.g.*, impurities, electrode material, pressure, concentrations, temperatures and comonomers.

The most crucial, however, are the current density and the electrolytes, especially the conducting anion X^-, because it is incorporated into the polymer as a counterion [23].

The properties of the counterion (*e.g.*, its size, geometry and charge) influence the properties of the polymer. The amount of counterion (anion) incorporated depends on the reaction conditions.

In general, one anion is incorporated for every three pyrrole units. Exceptions are pyrrole- and thiophene-sulfonic acids, where the counterion is coupled directly to the monomer (self-doping) [24].

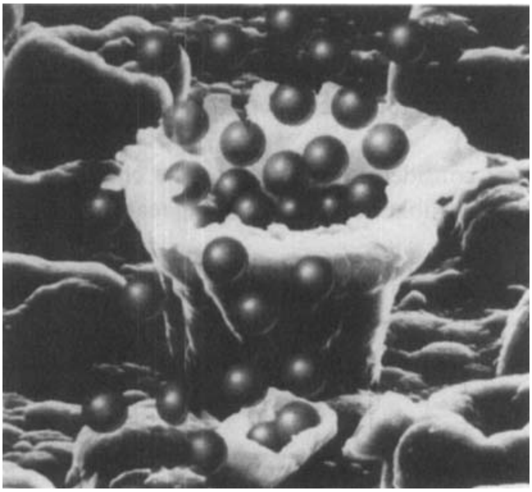


FIGURE 8 Polypyrrole with defined holes and counterions X^- [26, 28]. (See Color Plate I).

Some typical conducting anions are fluoroborate, perchlorate, aromatic sulfonic acids, penicillin [23], *n*-dodecyl sulfate [25], phthalocyanine sulfonic acid, polystyrene sulfonic acid, camphor sulfonic acid, styrene sulfonic acid and heparin [23].

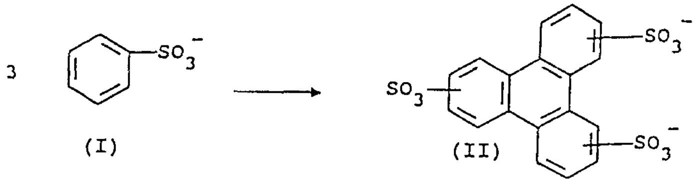
By changing the reaction conditions, polymers with different surface morphologies (*e.g.*, an open porous structure) can be obtained.

The anion X^- can also be released, *e.g.*, by applying a negative potential. Release can be specifically controlled, offering attractive possibilities for active counterions of medical significance (*e.g.*, heparin and monobactam) that can be incorporated into polypyrrole [26].

The conductive salt (X^-) used in the electrochemical synthesis is contained in the polypyrrole film as a dischargeable counterion. Interesting conductive salts that affect optical activity in polypyrrole are (+)- or (−)-camphor sulfonic acid (used for racemate separations), heparin, and other drugs such as monobactam.

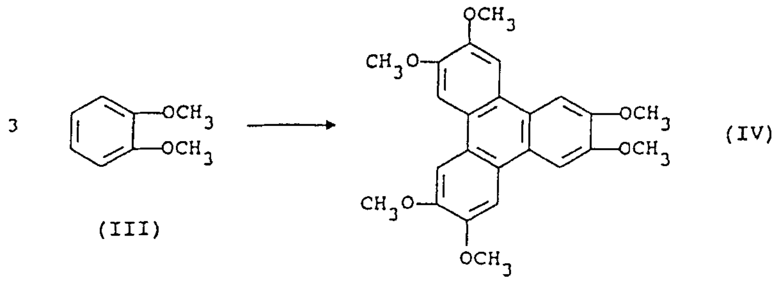
12. NEW MOLECULAR ARRANGEMENTS OF PERCONJUGATED SYSTEMS

Under oxidation conditions (electrochem. or chem.), starting from substituted benzenes or derivatives, triphenylene structures (benzo[1, 2:3, 4:5, 6]tris[arylenes]) are formed, *e.g.*:



If phenylsulfonic acid (I) is used as a counterion (current density [i] > 10 mA/cm^2), the trisulfonic acid of triphenylene is formed to some extent [23].

Another simple and convincing experiment is the conversion (trimerization) of *o*-dimethoxybenzene (III) to the analogous triphenylene ether (IV) [41].



Improved procedure: 120 g $FeCl_3$ was suspended in 500 ml H_2SO_4 (70%), and 30 ml *o*-dimethoxybenzene added under stirring. After 18 hours of stirring, 500 g ice was added and the precipitate filtered off. Washing with 1000 ml H_2O, 500 ml ethanol and 300 ml xylene and crystallization from trifluoroacetic acid yielded 13.8 g (46%) of 2,3,6,7,10,11-hexamethoxytriphenylene, mp > 300°C.

Condensed ring systems like naphthoquinone are trimerized analogously, and heterocycles can similarly be oxidized to "tris[hetarylenes]" [43a].

For example, using pyrrole as a starting monomer under strongly oxidizing conditions (electrochemical oxidation with current densities $> 10\,mA/cm^2$ or redox potentials $> 1.5\,V$), triphenylene structures were formed that could be oxidized to new macrocycle assemblies [40].

1. The resulting polypyrrole showed no C—H signals after pulsing (H NMR).
2. When tetradeutero(2,3,4,5)pyrrole was used as the starting monomer, the resulting polypyrrole showed no detectable amounts of D.
3. Polypyrrole degradation (pyrolysis at 600°C or anodic over-oxidation) gave benzene, indole, carbazole, *etc.*, fragments.
4. When a polypyrrole film was treated with an aq. $CuSO_4$ solution, Cu^{++} was sequestered (verified by spectroscopy).

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

This condensation seems to be a general approach to the synthesis of new types of disc-like tridentate polymeric structures. The pyrrole

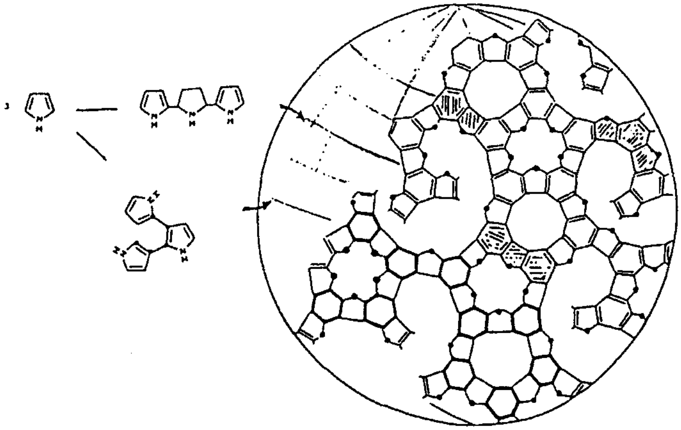


FIGURE 9 Polypyrrole macrocycles [36].

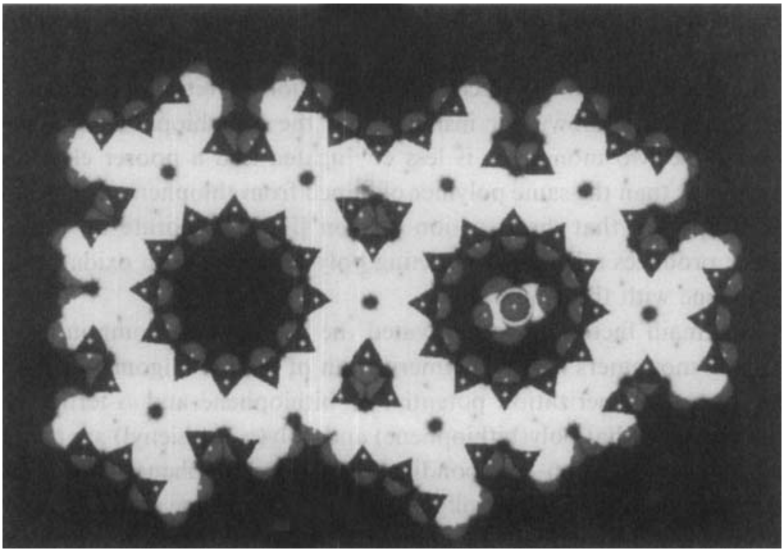


FIGURE 10 Model of polypyrrole macrocycle with counterion [34a]. (See Color Plate II).

units can be imagined to conform to a three-dimensional fullerene type structure in which one carbon from each of the pentagonal units is replaced by a nitrogen [40a].

It is worth mentioning that “indophenins”, including both oligomers and polymers, represent a new type of self-doped, electrically conducting, organic material. The electron acceptor and electron donor are assembled in one molecular unit (in the ratio 1:1), yielding conductivities of 10^{+1} S/cm without any additional doping agent. The materials are thermostable, no degradation in air occurring below 350°C.

13. SPECIAL THIOPHENES THIOPHENE OLIGOMERS [42a]

The synthesis and study of thiophene oligomers have attracted a great deal of attention for a number of years because of their activity against microorganisms, and recently because of their use as model compounds or synthetic building blocks for producing polymers that are able to conduct electricity. The monomers are polymerized chemically or electrochemically.

Studies based on the electropolymerization of bithiophene and α-terthienyl have shown for instance that the polythiophene obtained from these two monomers is less conjugated and a poorer electrical conductor than the same polymer obtained from thiophene. It has also been reported that direct action of iron [III] perchlorate on bithiophene produces a higher-conducting polythiophene than oxidation of thiophene with the same salt.

Two main factors have motivated the use of these compounds as starting monomers in the polymerization of thienyl oligomers. One is the lower polymerization potential of bithiophene and α-terthienyl. The second is that poly(bithiophene) and poly(α-terthienyl) are expected to have less non-α,α'-bonding than poly(thiophene). The same reasoning applies to higher oligomers of the thiophene series, with the advantage that the larger the number of thiophene rings in the monomeric unit, the higher the probability of obtaining purely α,α'-coupling by polymerization.

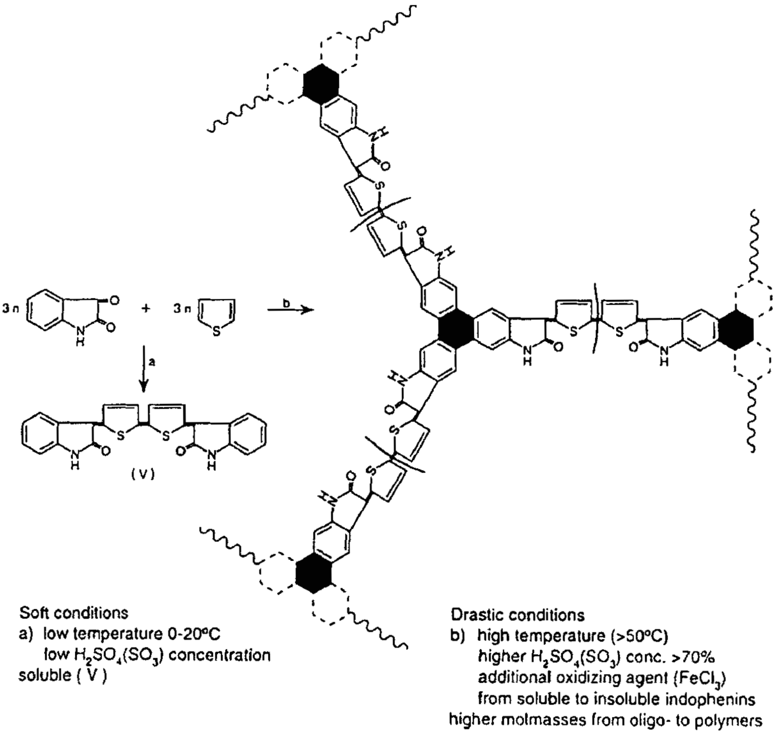
Physical data for thiophene oligomers (UV-visible, FT-IR, ^{13}C NMR, mass spectra and cyclic voltammograms (oxidation potentials)) are recorded in Table III.

By using oligothiophenes (thienyls) instead of the monomer thiophene in the indophenin reaction, for example (Fig. 11), the

TABLE III Physical and spectroscopic data of thiophene oligomers [42a]

	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
m.p.(°C)	33, colourless	95–96, yellow-green	214–215, chrome-yellow	258–259, orange	307–309, orange-red
UV/visible($CHCl_3$)	300 nm (in benzene)	354 nm	390	416	434
FT-IR (cm^{-1}) (Kbr pellet)	asym. C=C stretch. 1499 sym. C=C stretch. 1416 C—H bend. o.o.p. 827 C—H bend. 2,5-subst. – C—H bend. 2-subst. 694 Ring def. o.o.p. 458	asym. C=C stretch 1498 sym. C=C stretch. 1422 C—H bend, o.o.p 831 C—H bend 2,5-subst. 796 C—H bend 2-subst. 688 Ring def. o.o.p 455	asym. C=C stretch 1495 sym. C=C stretch. 1425 C—H bend, o.o.p 833 C—H bend 2,5-subst. 798 C—H bend 2-subst. 68 Ring def. o.o.p 454	asym. C=C stretch 1493 sym. C=C stretch. 1425 C—H bend, o.o.p 831 C—H bend 2,5-subst. 793 C—H bend 2-subst. 680 Ring def. o.o.p 457	asym. C=C stretch 1492 sym. C=C stretch. 1425 C—H bend, o.o.p 827 C—H bend 2,5-subst. 792 C—H bend 2-subst. 688 Ring def. o.o.p 457
^{13}C NMR (ppm)	C (2) 137.45 [b] C (3) 123.77 C (4) 127.66 C (5) 124.77	C (2) (2″) 137.07 [b] C (2′) (5′) 136.64 C (4) (4″) 127.10 C (5) (5″) 124.42 C (3′) (4′) 124.25 C (3) (3″) 123.64	C(2) (2″′) 134.63 [c] C (2′) 133.52 C (4) (4″′) 127.10 C (5) (5″′) 124.45 C (3′) (4′) (3″) (4″) 123.82 C (3) (3″) 123.08	138.0 [d] 135.6 125.9 123.9	136.4 [d] 135.1 126.3 123.9
Mass spectrum (m/e)	40, 83, 121, $\underline{166}$, 223 (M^+, 100%)	57, 124, 203, $\underline{248}$ (M^+, 100%)	165, 285, $\underline{330}$ (M^+, 100%)	206, 367, $\underline{412}$ (M^+, 100%)	247, $\underline{494}$ (M^+, 100%)
E_{ox}/Volts Ag/Ag^+ (0.5 M $LiClO_4$ in propylene carbonate)	0.43	0.21	0.12	0.08	0.04

[a] IUPAC names: n = 0.2,2′-bithiopene; n = 1,2,2′:5′2″-terthiophene; n = 2,2,2:5′,2″5″,2″′-quarterthiophene; n = 3,2,2′ 5′,2″5″′,2″′:5″′,2″″5′2″″-quniquethiophene; n = 4,2,2′5″,2″5″,2″′:5″′,2″″5″″,2″″′-sexithiophene; [b] $CDCl_3$; [c] DMSO-d_6; [d] MAS-CP ^{13}C NMR.



Soft conditions
a) low temperature 0-20°C
low $H_2SO_4(SO_3)$ concentration
soluble (V)

Drastic conditions
b) high temperature (>50°C)
higher $H_2SO_4(SO_3)$ conc. >70%
additional oxidizing agent ($FeCl_3$)
from soluble to insoluble indophenins
higher molmasses from oligo- to polymers

FIGURE 11 Isatin/thiophene condensation to indophenins [47a].

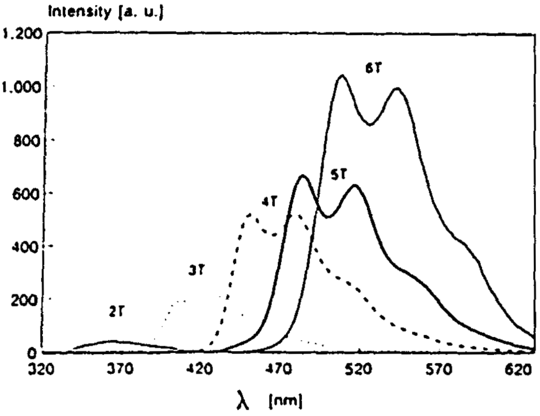


FIGURE 12 Fluorescence spectra of thiophene oligomers in dioxan (absorption ≤0.05, excitation at the band maxima).

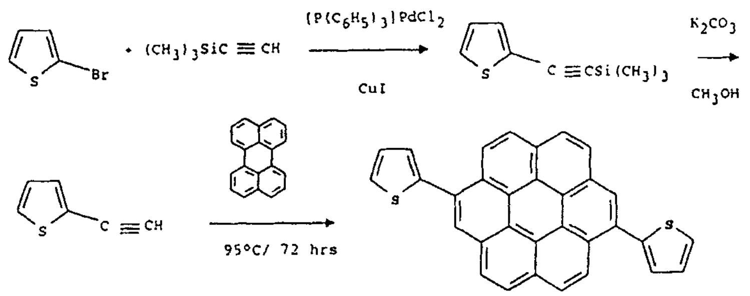
electron donor can be inserted into the indophenin molecule in a controlled manner, changing the physical properties, esp. the conductivity.

The results of time-resolved fluorescence studies are shown in Figure 12 [44].

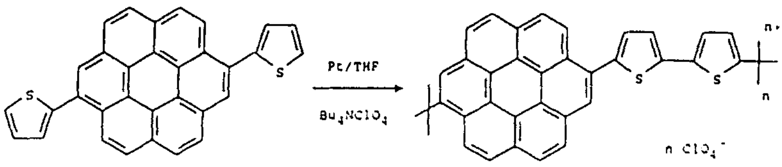
These materials also offer a potential application in the NLO field [44a].

The electrochemical polymerization of bisthienyl coronene represents another route to polymers containing thiophene units [45]. The synthesis scheme for bisthienyl coronene shown below illustrates the polymerization to the new polymer type.

Synthesis scheme.

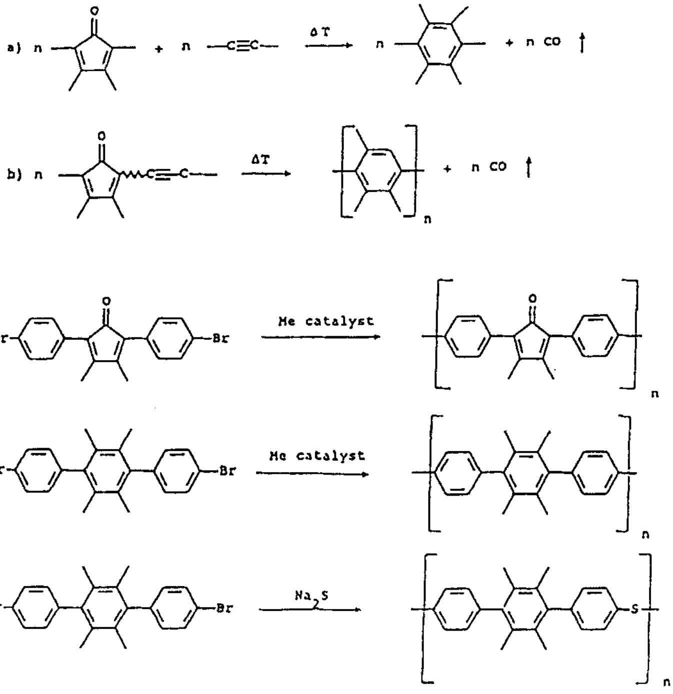


Electrochemical synthesis scheme.

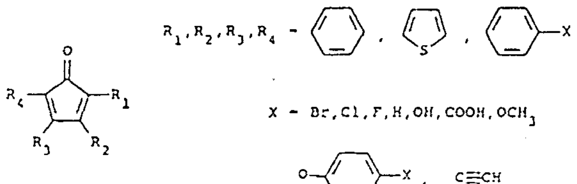


The 2-ethynyl thiophene used to synthesize the thiophene-substituted coronene offers another interesting possibility for synthesizing new polymers. *viz. via* tetraarylcyclopenta-dienones or thienyl-substituted cyclopentadienones to yield substituted terphenylenes [12, 46, 47].

Arylation *via* cyclopentadienones [47 a]



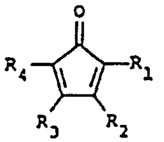
Reaction (b) represents the AB type leading directly to polymers.



VI

The general formula VI shows the wide variety of substitution possibilities. Mixed types are also possible. The polymers are stable (> 300°C) and have electrical conductivities ($FeCl_3$-doped) of around 10^{+2} S/cm.

Monomers containing thienyl groups:



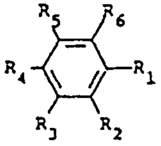
VII

R_1 / R_4 = thienyl

or

R_2 / R_3 = thienyl

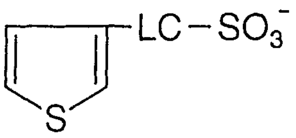
and



VIII

R_5/R_6 = thienyl (or R_1/R_4 or R_2/R_3 in formula VII or VIII) offers the possibility of undergoing the indophenin reaction (like thiophene).

A thiophene substituent in the 2-position with a liquid–crystal chain (LC) containing, for example, an SO_3^- group represents a type of monomer that, once electrochemically polymerized, contains its own counterion (in one molecule), and whose morphology can be organized by the LC unit [46].



14. APPLICATIONS

The following list demonstrates the large variety of possible applications:

- drug release, *e.g.*, heparin and penicillin [27]
- deposition of conducting materials, *e.g.*, pyrrole, on nylon, glass fibre fleeces and carbon fibres [26, 29]

- deposition of metals, *e.g.*, copper, on electrically deposited conducting polymers (printed circuits) [30]
- deposition of structured electrically conducting polymers by irradiation [31]
- elastic polypyrroles (elongation > 100%) [32]
- polymeric shish kebab structures [33]
- piezoceramic elements [34]
- ion-exchange membranes [35]
- self-dopant systems [36] with ionic side groups or CT-complexing in the main chain
- optical data storage [37]
- separation of DNA on polypyrrole films [48]

An interesting alternative is the chemical oxidation of heterocycles (*e.g.*, thiophene or pyrrole) dissolved in an organic solvent (*e.g.*, ethanol) on the surface of various materials. Conductive coatings (thickness 0.01 µm) can be produced on films of poly(phenylene sulfone), block copolymers of butadiene and styrene (Ultrason, Styrolux), poly(vinyl chloride), and other polymer films to give transparent, antistatic films with conductivities of about 0.001 S/cm. Ceramics and glass can also be coated in this way. In addition, porous materials (*e.g.*, wood, fabrics and open-celled foams) and fibres (*e.g.*, polyamide, glass and carbon fibres) can be modified and rendered antistatic by this method.

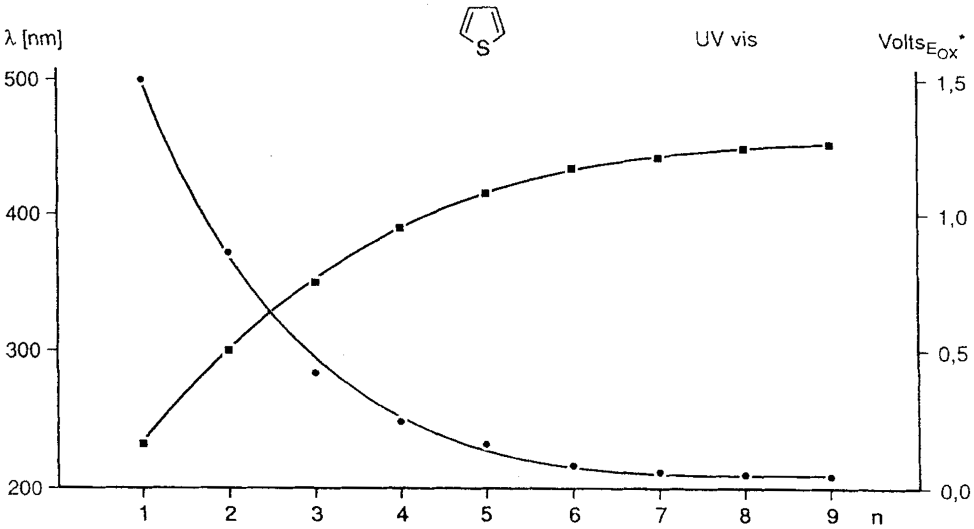
Excellent coatings are obtained when the polymerization process is initiated by irradiation ($h\nu$). Irradiating through a mask yields excellent depositions with resolutions of approx. 3 µm.

Chemical oxidation can also be used to produce conductive powders (*e.g.*, polypyrrole) with a particle size of about 0.1 µm and conductivities of up to 10 S/cm, which can be incorporated as fillers in thermoplastics. These materials can serve as chip carriers.

The conductivity of polypyrrole films suggest applications such as flexible conductive paths in printed circuits, heating films, and film keyboards.

Polypyrrole films show good electromagnetic shielding effects of about 40 dB over a wide range of frequencies (10 – 1,500 MHz).

Polypyrroles in which the counterion is 4-hydroxyphenyl sulfonic acid do not undergo any change in conductivity when exposed to



*) 0.5 m ET_4NBF_4 in CH_3CN V/versus sat. calomel electrode

FIGURE 13 Correlation between "*n*", absorption and oxidation potential.

nitrogen for two months at 140°C. Nor was any change in conductivity observed when these polymers were stored in the laboratory for three years at room temperature and 5% relative humidity. Polypyrrole is sensitive to moisture because this leads to leaching of the counterion and hence to a decrease in conductivity. This can be avoided by using appropriate hydrophobic or polymeric counterions [*e.g.*, camphor sulfonic acid or poly(styrene sulfonic acid)] or by incorporating hydrophilic compounds. Polypyrroles obtained by synthesis in aqueous electrolytes maintain a conductivity of about 20 S/cm. Polypyrroles with a perchlorate counterion are unstable under atmospheric conditions, but can be used as electrodes in rechargeable batteries.

The advantage of polymer electrodes is that they can be easily shaped, allowing novel battery designs (*e.g.*, for the electronics sector) and less expensive production methods. Polymer cells with polypyrrole and lithium electrodes have been developed. In the flat cell, the polypyrrole and lithium films are sandwiched together; in the cylindrical cell, the two films are wound concentrically. Their energy per unit mass and discharge characteristics are similar to those of the nickel-cadmium cells now on the market. Over 500 charging and recharging cycles have been achieved with laboratory cells. Applications include dictaphones and pocket radios [38].

Acknowledgements

This article is a short résumé of my many years of research activity (1960 – 1995 at BASF) and represents a selection from more than 500 patents and 100 scientific publications as well as numerous internal reports.

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