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THE STATE OF ORDER AND THE RELEVANCE OF PHASE TRANSITIONS IN CONDUCTING POLYMERS

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Abstract Highly conducting polymers exhibit a salt like structure in which positive or negative charges are located on the polymer backbone and are counterbalanced by gegenions whose main role is to provide electroneutrality of the system. The electric conductivity is a property of the sublattice build by the charged segments of the polymer. The polymeric salt structure is formed via a redox-reaction from the initially insulating non-polar precursor polymer. The so-called doping of polymers is thus understood as a heterogeneous chemical reaction with simultaneous change of phase.

Examples are given from the area of polypyrrole where new systems with layered structures are described; recent results on the crystal structure of poly(acetylene hexafluoroantimonate) and the preparation of highly oriented polyacetylene are reported. Similarly, the structure and redox chemistry of poly(phthalocyaninatosiloxane) is described as an other example for the above mentioned ideas.

INTRODUCTION

The structural background of the electrical and electronic properties of certain highly conducting polymers has developed into a field of controversies ever since the seminal work of Mc Diarmid, Heeger and coworkers.[1-3] These authors showed how to convert originally insulating polymers to highly conducting ones by chemical treatment. This treatment was called "doping" by these authors fostering the idea of similarities in behaviour between conventional semiconductors and polymeric materials such as polyacetylene.
R. H. Baughman and his group,[4-5] B. Street et al[6] and many other groups widened the field by showing that a variety of polymers with different backbone structures such as poly-p-phenylene, poly-p-phenylene sulfide, polypyrrol etc. could be "doped" as well and thus be made conductive. It soon

turned out that "doping" really means oxidation or reduction of the initally insulating polymer and that the conductivity is a property of the oxidized or reduced polymer in its solid-state structure.[7,8] The term redox-polymer invented long ago for polymers which are able to undergo reversible oxidation or reduction without degradation of the backbone[9] is thus the appropriate name to classify these polymers as well. They have the additional property of being conductive in their oxidized and/or reduced form. The redox-properties are readily identified carrying out the oxidation or reduction electrochemically whereby the polymer is used both as the electrode and the electroactive medium.[3,10] In a suitable arrangement the redox-polymers may be put together to form a secondary electrochemical cell and their use for the fabrication of unconventional batteries has been amply discussed.

The controversies start over the proper description of the stoichiometry of the oxidation or reduction; it is debated whether the redox reaction leading to conductivity proceeds homogeneously or heterogeneously meaning that some authors believe that the redox reaction proceeds with simultaneous production of the new phase of the conducting polymer, other workers in the field believe in a homogeneous solid-solution type aggregation of charged and uncharged chains or segments of the chains as the intermediate of the "doping"

In earlier reports we have drawn attention to the fact that very "simple" organic metals can be produced by electrochemical oxidation of a variety of arenes like naphthalene, pyrene, perylene, fluoranthene etc. in the form of rather perfect single crystals and that these materials can be understood as models for the "doped" (oxidized) polymers.[8,11] The important electrode processes leading to the growth of these so-called cation-radical salts are essentially the same as those leading to the conductive state of the polymers for which polyacetylene is the most prominent example. In the following we want to substantiate these ideas with examples taken from recent work in our laboratory which show that the conducting polymers possess a well defined salt-like structure.

Polypyrrole Alkylsulfonates and Alkylsulfates

The anodic oxidation of pyrrole dissolved in a suitable electrolyte leads to the growth of polymeric films at the surface of the anode. These films show metal-like conductivity somewhat depending on the preparation conditions;[12,13]

Due to the lower redox-potential of polypyrrole (PPY) the films formed are immediately oxidized in situ and incorporate the counterion X^- of the supporting electrolyte in order to achieve charge neutrality. Diaz et al. and G. B. Street et al. have shown that various types of films of the polypyrrole salts with good mechanical quality and conductivities of typically 100 S/cm may be obtained, if the polymerization is carried out in non-aqueous solutions (e. g. acetonitrile) of tetrabutylammonium salts (TBA^+X^-)with $X^-=BF_4^-$, PF_6^-, AsF_6^-, ClO_4^-, H_3C-C_6H_4-SO_3^-, CF_3-SO_3^- etc. The elemental composition of these films corresponds to a structure with one positive charge residing on the chain for every 3-4 pyrrole units and the appropriate amount of counterions derived from the electrolyte solution.[12] The films are reported to be totally amorphous.[12,13]

The chemical oxidation gives in principle rise to the same or similar products, however, in powderform, if pyrrole and the oxidizing agent (e. g. $FeCl_3$) are mixed by stirring. Films of the conducting polymer may be easily obtained, if pyrrole vapour is allowed to contact the quiescent solution of an oxidizing reagent from the surface.[14]

We have now found that films of conducting PPY can be prepared which show layer-type order effected via proper design of the counterions. These films contain tensides as counterions and can be readily prepared from an aqueous electrolyte, which contains only the alkali salt of a tenside as the supporting electrolyte and pyrrole monomer. The films show good conductivities, good mechanical and environmental stability and interesting structural and electrical properties. The tensides used were sodiumalkyl-sulfates, H-$(CH_2)_n$-$OSO_3^-Na^+$, and sodiumalkyl-sulfonates, H-$(CH_2)_n$-$SO_3^-Na^+$, with various values for n between n=4 and 18. In addition 1,10-decanedisulfonate, $Na^{+-}SO_3$-$(CH_2)_n$-$SO_3^-Na^+$ was used as an example of a difunctional component.

Table 1 shows the composition of a series of these polypyrroles with different anions. The analytical oxygen and hydrogen contents indicate the incorporation of water molecules into the layers. As can be seen from this table 3 to 4 pyrrole units carry one positive charge in the doped polymer.

The conductivities, σ, at ambient temperature lie between 1 S/cm and 160 S/cm. The reproducibility of the conductivity values for two polypyrrole samples seemingly synthesized under the same conditions is only within one order of

TABLE 1. Composition of the polypyrrole-tenside salts

Tenside Anion	Pyrrole Units per Anion	"Crystal"-water	Weight Fraction of Anions	Typical values of conductivity 1) $\sigma/\Omega^{-1}cm^{-1}$
$\underline{1}H(CH_2)_{12}OSO_3$	3.8...4.2	1	0.515	$6<\sigma<60$
$\underline{2}H(CH_2)_{16}OSO_3$	3.8	1	0.565	10
$\underline{3}H(CH_2)_4\ SO_3$	3.5	1	0.375	10
$\underline{4}H(CH_2)_6\ SO_3$	3.5	1	0.421	$30<\sigma<70$
$\underline{5}H(CH_2)_8\ SO_3$	3.0	1	0.497	150
$\underline{6}H(CH_2)_{10}\ SO_3$	3.0		0.531	20
$\underline{7}H(CH_2)_{16}\ SO_3$	3.9	0.7	0.546	10
$\underline{8}SO_3(CH_2)_{10}SO_3$	8.0	3	0.365	10

1) measured by four-probe technique at 25°C

magnitude. Thus trends of conductivity vs length of the alkylchains which may be present are buried under this uncertainty. The temperature dependence of σ is exceptionally small. Fig. 1 shows $\sigma(T)$ for three samples of the new PPY-tenside salts in comparison to the corresponding values of PPY-fluoroborate and PPY-tosylate grown from acetontrile as solvent.

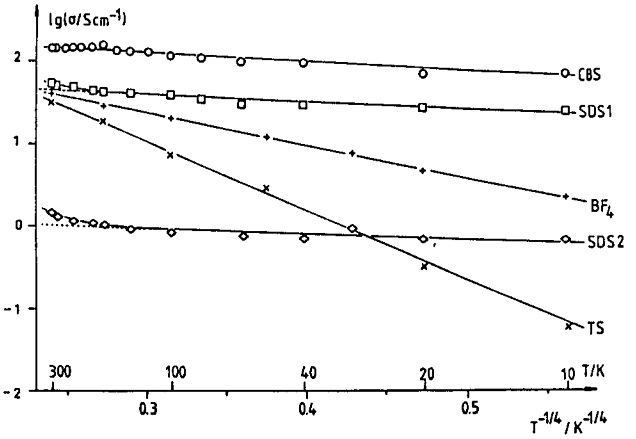


FIGURE 1. Temperature dependence of polypyrrole-tenside salts, CBS: PPY-octanesulfonate,($\underline{5}$), SDS: PPY-dodecylsulfate ($\underline{1}$), BF: PPY-hexafluoroborate and TS: PPY-tosylate. SDS2 and SDS2 are samples of the same tenside anion from different batches.

Except the curve from the PPY-dodecylsulfate samples (SDS) all data exhibit a perfectly linear relationship of lg(σ) and $T^{-1/4}$. This form of the T-dependence of σ is predicted by a model for 3D variable range hopping by N. F. Mott.[15] The weak T-dependence indicates that the barriers for the hopping process must be very low in these materials with respect to more "conventional" polypyrroles.

Fig. 2 shows the X-ray diffraction pattern from a film of PPY-octanesulfonate, (Tab. 1, 5). The occurence of a small-angle peak below $2\ \theta = 5$ deg and a broad distribution of scattered intensity around $2\ \theta = 20$ deg is typical for the whole series of PPY-sulfonates and -sulfates. The position of the small-angle peak is correlated to the number of CH_2-groups, n, of the alkylchains of the tenside anions incorporated in the polymer. The width of this peak and the fact that no higher order is observable implies that the underlying structure in the polymer is very distorted, probably liquid like. Nevertheless, a typical periodictiy d(n) (layer spacing) can be extracted[14] which is plotted in Fig. 3 vs. the number of carbon atoms in the alkyl chains of the tenside anions, n. The series of d spacings for the PPY-alkylsulfonates obeys the linear relationship $d(n) = (0.19 = n + 1.2)$ nm. The values of d determined for PPY-dodecylsulfate are approximately equal to those expected for PPY-dodecylsulfonate, as can be expected from the similar chemical structure.

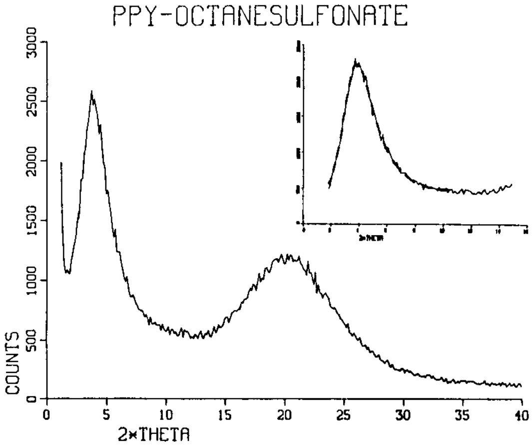


FIGURE 2. X-ray diffraction pattern of polypyrroleoctanesulfonate (C8S). The insert in the upper left shows a comparison of the fitted theoretical lineshape, dashed line, and the experimental one.

The d-value of PPY-α,ω-decanedisulfonate, (S), d=1.96 nm, is only 60 percent of the d-Value of PPY-decane (mono)sulfonate. The stoichiometry of this compound implies that there are 8 pyrrole units per tenside , which yields one positive charge per 4 pyrrole rings on the polypyrrole chain as in the compounds containing monovalent anions.

From the fact that the d-value for the PPY-n-alkylsulfonates increases by 0.19 nm per CH_2-unit and from the fact that the contour length of a single alkyl chain grows only by 0.125 nm if one CH_2 unit is added, it can be concluded that the monosulfonates form a kind of double layered structure as depicted by Fig. 4, α,ω-disulfonates in contrast seem to produce a single layered structure, see Fig. 4 left side.

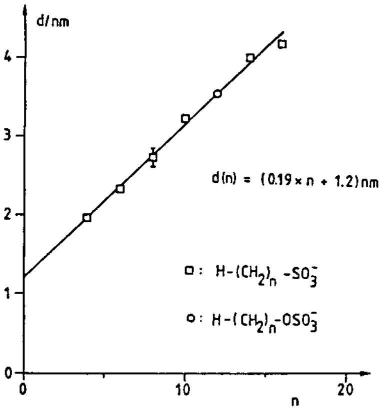


FIGURE 3. Plot of the fitted-d-values of the first peak for a series of polypyrrole-sulf(on)ates vs the number of carbon atoms, n, in one alkylchain of the incorporated tenside ion.

Fig. 4 represents a hypothetical model of an idealized structure of the short range type. The stack of polypyrrole chains perpendicular to the plane of drawing in Fig. 4 (row of simple black lines between the tenside ion double layers) are postulated in analogy to the structure of the radical cation salts of simple arenes[11,16] and to our structural model of SbF_6-doped polyacetylene.[17] It should be kept in mind that the real structure of these doped polypyrroles is rather distorted and should better be considered as a liquid like short range order.[14] Nevertheless the use of tensides as anions obviously offers the possibility to separate the conducting polypyrrole containing regions by presumably isolating alkyl chain layers of freely selectable thickness. With regard to possible applications it is worthwile noting that the synthesis requires only inexpensive, nontoxic

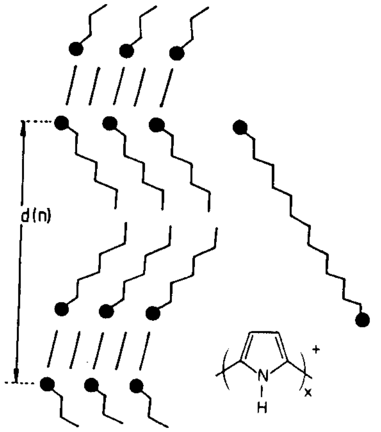


FIGURE 4. Idealized proposal for the short range order in the PPY-tenside salts, seen along the polypyrrole chain axis. The simple black lines represent the PPY-chains, the zig-zag lines symbolize the alkylchains of the tensides and the black dots stand for the ionic $-SO_3$ or $-O-SO_3-$ groups.

solvents (water!) and "dopands" (a sodiumsulf(on)ate soap). The resulting material is much more stable than e.g. polyacetylene and can be made to posses acceptable mechanical strength.

Structure of polyacetylene hexafluoroantimonate

Polyacetylene can be electrochemically oxidized in the presence of tetrabutylammoniumhexafluoroantimonate as the supporting electrolyte to give an ionic solid of metal-like conductivity. The oxidation may be described as a half-cell reaction

$$..-(CH=CH)_n-.. + R_4N^+(SbF_6^-) \longrightarrow ..\left[(CH=CH)_n^{+\cdot} X^-\right] + R_4N^+ + e^- \quad (1)$$

($R = nC_4H_9$) in which segments of the polymer chain with n double bonds are oxidized to form a cation radical located on the chain and counterbalanced by a gegenion provided by the supporting electrolyte. A seemingly simple but important question which is not yet solved in a quantitative way is the stoichiometry of the polymeric cation-radical salt; in other word, the charge density on the polymer-chain has not been unambigously determined nor do we have a theoretical basis to make safe predictions. The question cannot be answered from elemental analysis of the conducting salt alone since both chemical and electrochemical oxidation does not proceed without side reactions; available polyacetylene does not allow to differentiate in a simple way between the reactivity of the surface, of the disordered and of the crystalline part of the total sample (comp. also Fig. 9). This questions can be tackled by crystallographic methods which also give information on the chain-chain and chain-gegenion interaction, another matter of debate since long.

In a previous paper we have shown that polyacetylene undergoes major structural changes upon oxidation.[18] Partially oxidized ("doped") polymer is analyzed as a mixture of the neutral polymer unaffected by the oxidation and of the oxidized ionic(salt) structure based on inspection of the X-ray or neutron diffraction pattern.[19-21] This seems to be generally true for all polymers which can be made conducting by oxidation.

Due to the apparently high degree of disorder of the crystalline regions the information that is available from X-ray diffraction patterns of "doped" polymer samples is rather limited. Nevertheless it is possible to get some insight into the structure of the SbF_6^- complex by testing structural models on their packing properties and on their compatibility with the available X-ray data. The following results were obtained by Monkenbusch and Wieners[17] in our laboratory and only the salient features of their work will be reported here. Details of the experimental procedure and the packing caluculations may be found in ref. 17.

Free standing films of polyacetylene ("as polymerized") were electrochemically "doped" by anodic oxidation in a solution of $(n\text{-}C_4H_9)_4\overset{+}{N}SbF_6^-$ (0.1 mol/l) in dry CH_2Cl_2.[18] The oxidized sample had a room temperature conductivity of σ_{RT}=300 S/cm at an average of x = 10.2 percent SbF_6^- ions/CH-unit.

In Fig. 5 the diffraction data (Cu-K_α-radiation) of the "doped" PA sample are plotted after the subtraction of a constant background (curve a), (b) is the synthetic target composed of 4 gaussians.

The hatched area in the region $25^o<2\theta<30^o$ indicates a probably present weak third group of peaks. The triangle at $2\theta \sim 10$ deg represents the resolution of the X-ray diffraction set-up. The "doped" material shows a reflection at about 2θ = 10 deg, according to a d-value of 8-9 Å and the broad distribution of scattering intensity around 2θ=20 deg.

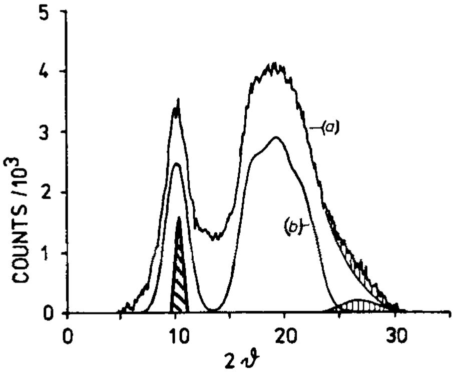


FIGURE 5. Diffraction data from PA$^+$SbF$_6^-$,(a) and background-corrected synthetic curve derived from them, (b).

These features are characteristic for other doped PA's, too.[21] A peak analogous to the $2\theta = 10$ deg peak in PA has also been observed in doped PPP.[6,7] In the range of $35\ 2\theta<100$ deg no further peaks have been observed which could be discriminated from the background radiation.

The existence of a -spacing of 8-9 Å can be used as a guideline to design structural models. In Fig. 6 several projections of tentative arrangements of (CH)$_x$-chains (ellipses) and SbF$_6^-$ counterions (circles) are shown.

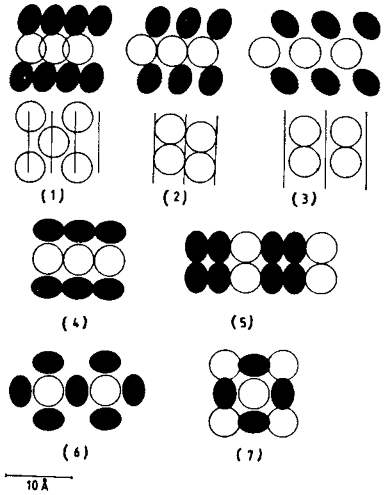


FIGURE 6. Tentative molecular arrangements for $|(CH)_x(SbF_6)_y|_n$ ellipses: (CH)$_x$-chains; circles: counterions; vertical lines in (1)-(3): CH$_x$-chain axis.

In all models the axes are chosen as follows: The chain direction is always parallel to c; the planes that give rise to the d-value of 8.5 Å are approximately perpendicular to a; b connects the $(CH)_x$-chains within these planes.

Starting from arrangement (1) the structure depicted in Fig. 7 was obtained by packing refinement procedures. The lattice parameters are: a = 8.63 Å; b = 5.39 Å; c = 7.53 Å; $\alpha = 41.2^o$; $\beta = 85.0^o$; $\gamma = 83^o$.

The unit cell contains one SbF_6^- ion and 6 CH-units, thus the stoichiometry (doping level) implied by this structure is 0.167 anions/CH-unit times the occupation probability of the anion positions. In other words, $n \doteq 3$ in Eq. 1.

The corresponding calculated diffraction pattern is shown in Fig. 8. The dotted line has been calculated for 100 percent ion occupation probability. A slight improvement of the agreement of the calculated curve (solid line) to the experimental data is achieved by assuming a 91 percent occupation probability of the anion positions. The minimal nonbonding contact distances in this structure are $d^{min}_{H...F} = 2.5$ Å; $d^{min}_{F...F} = 2.75$ Å and $d^{min}_{C...C} = 3.26$ Å.

All other packing arrangements shown in Fig. 6 did not lead to a satisfactory agreement between calculated and observed diffraction pattern or an unreasonably low occupation probability had to be invoked. The resulting "doping level" in the formula $(CH)(SbF_6)_x$ is x = 0.152 for the best fit between calc. and obs. diffraction data as compared to our maximum experimental "doping level" of x = 0.14 which can be reached without severe overoxidation of the sample. The validity of the structure model (Fig.7) thus developed could have major implications on the theoretical models of the electrical conduction. The close structural analogy with the structure of the radical cation salts of simple aromatic molecules[11,16] suggests also an analogy in the conduction mechanism. The radical cation salts are conductive due to a rapid electron transfer between the aromatic molecules in a stack.[23] Therefor one has to conclude that in oxidized PA with a structure according to Fig. 7 the electron transfer between two neighbouring chains is easy and may be of great importance for the observed macroscopic conductivity.

The analogy between low molecular weight cation-radical salts and "doped" polymers is further supported by recent work of V. Enkelmann and coworkers[24,25] in our laboratory.

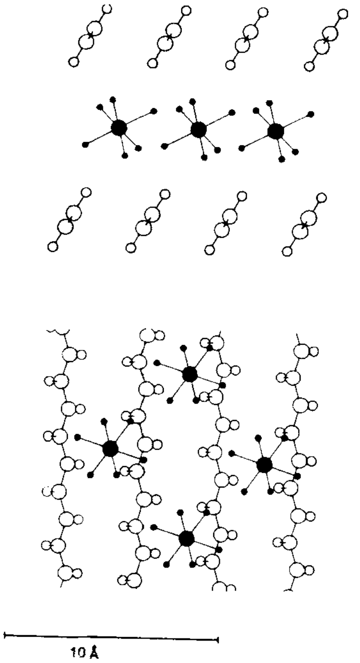


FIGURE 7. Structure model obtained by refinement of arrangement(1) in Fig. 2. Upper half: projection along the $(CH)_x$-chain direction; lower half: projection perpendicular to the plane defined by the chain stacks.

It was shown that p-quaterphenyl (QP) which may be considered as an oligomer model of poly-p-phenylene can be anodically oxidized to give single crystals of the general stoichiometry $(QP)_nX^-_m$. The crystallographic analysis shows that in the case of $X=SbF_6$ n=2, m=1 and that the QP molecules are stacked in an analogous fashion as commonly observed in other cation radical salts.

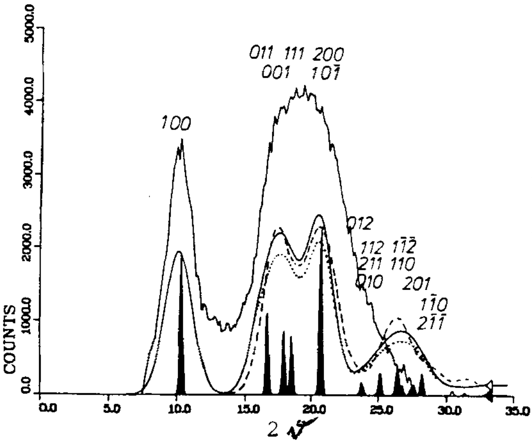


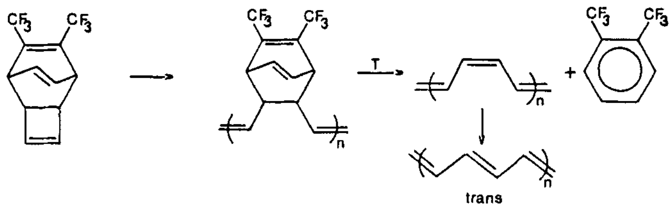
FIGURE 8. Calculated diffraction pattern for the structure shown in Fig. 7. Solid line: 91 percent of the anion positions occupied. Dotted line: all anion positions occupied. The sharp black peaks denote the contributions of the different lattice planes. Dashed line: Scattering from a slight variation of model(1)(see ref.17).

Polyacetylene with new morphology and high orientation

The morphology of polyacetylene as obtained by transition metal catalyzed polymerization of acetylene is complex. The two most commonly used procedures to obtain the polymer in the form of thin sheats which are formed in situ apply conditions described by Ito, Shirakawa and Ikeda[26] (Ziegler-catalyst) and by Lieser, Wegner et al.[27] (Luttinger-catalyst).[28] Films with essentially the same properties are obtained by both methods. The question of concern is the chain orientation with regard to the morphological features, the degree of crystallinity of the samples and the dependence of the morphological features on various parameters of the synthesis and handling of the sample (see ref.29 for a discussion of this subject).
A discussion of this subject is not intendend here; the complexity of the problem is only demonstrated by Fig. 9 showing electron micrographs of two samples of polyacetylene obtained under seemingly similar conditions by a Luttinger-catalyst at -78°C.

The sample shown in Fig. 9a was formed directly on a microscope grid and the total conversion was small (<10 percent). The sample of Fig. 9b was formed in suspension and only subsequently transfered to the microscope grid. Both samples were washed and handled under the same conditions prior to the preparation for microscopy and both were identified by the same diffraction pattern (mainly cis-polyacetylene with some trans-content).

The feature common in both samples is the very high surface area and that they have a tissue-like or porous structure of intertwinned morphological subunits. This makes the problem of orientation, in other words the formation of true fibre-like textures so difficult. In fact, good X-ray fibre diagrams as they are commonly obtained for conventional polymers have not been reported so far in the literature.



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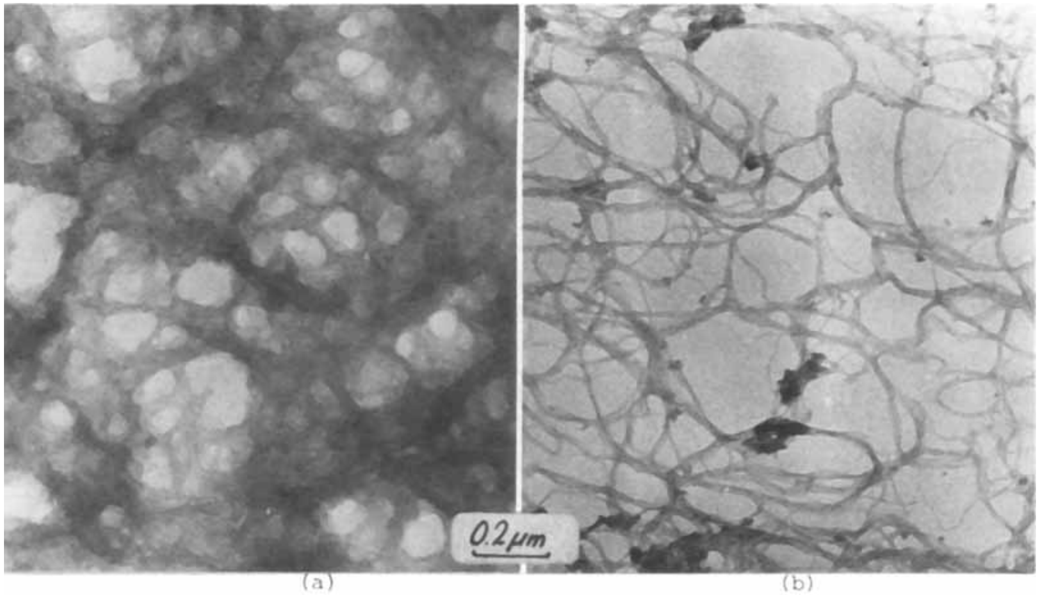


FIGURE 9. Two samples of polyacetylene obtained by Luttinger's catalyst at -78^{O}C under similar conditions (see text); micrographs courtesy of Dr. G. Lieser.

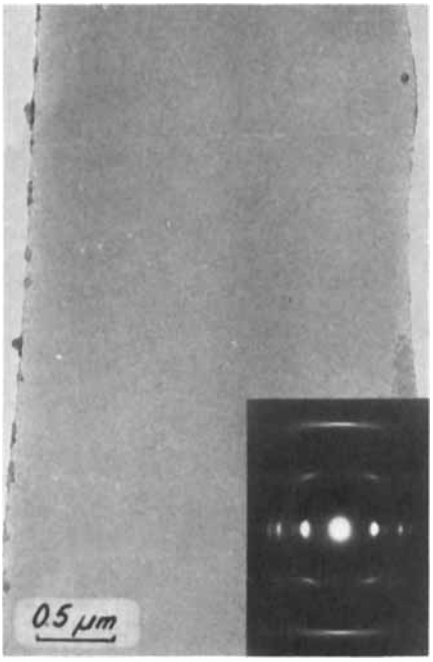


FIGURE 10. Highly oriented film of polyacetylene obtained by thermolysis of Feast's precursor polymer (eq.2) and electron diffraction pattern obtained from it; (photograph courtesy of Dr. G. Lieser).

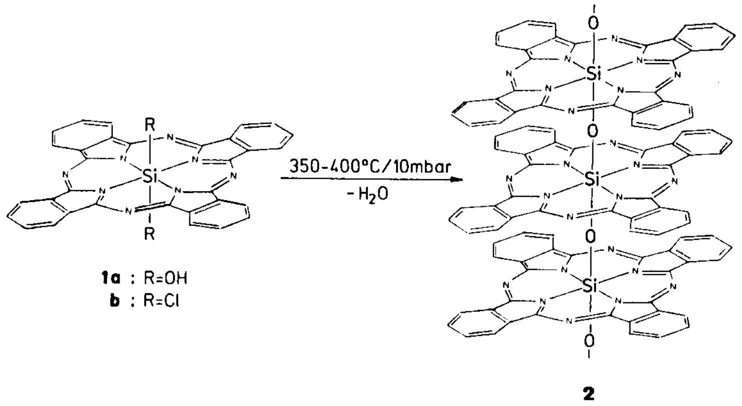
Edwards and Feast[30] have reported another approach to the synthesis of polyacetylene according to eq. (2).

A precursor polymer is synthesized first which can be cast from common solvents to form coherent films. These films are subsequently thermolyzed to give trans-polyacetylene and a volatile by-product. We have repeated this process in our laboratory[31] and were surprised to find that the polyacetylene obtained via this method was not only obtainable in the form of coherent films but also showed a reasonable to good crystallinity. Previous workers in the field[32,33] had claimed that the polyacetylene obtained in this way was amorphous. Films of a thickness between 20-60 μm could easily be oxidized by the same methods as commonly known for polyacetylene and became conducting. Treatment with iodine from the gasphase gave a conductivity of 4 Scm^{-1} at a total analytical content of I_2 of 12 percent. Electrochemical (anodic) oxidation gave values of $0.1<\sigma<4$ S cm^{-1} for SbF_6^-, BF_4^-, AsF_6^- and ClO_4^- as *gegenions* at an analytical content of the gegenions $1\le X\le 4$ mole percent/CH-unit.

Highly oriented trans-polyacetylene was obtained, if stripes of thin films of the precursor polymer were thermolyzed at 150°C with the ends fixed to a frame. Fig. 10 shows a piece of such a highly aligned film and the corresponding diffraction pattern. We believe this to be the "best" fibre diffraction pattern ever obtained from polyacetylene. All reflections can be indexed in terms of the unit cell discussed by Shimamura et al.[34] for oriented trans - polyacetylene obtained by the Shirakawa method although the arcing in our pattern is distinctly less and the d-values are slightly smaller than his.
The unit cell parameters derived from this pattern are $a = 720$ pm, $b = 415$ pm, c (chain direction) = 244 pm, $\rho = 1.18$ gcm^{-3}, $z = 2$ (orthorombic lattice). These values conform excellently with the ones theoretically predicted by packing calculations on trans-polyacetylene.[35] The pattern shown in Fig. 10 contains a number of further interesting features like continuous streaks on the layer lines giving evidence of certain types of disorder structures.
We are presently engaged in work to oxidize these highly oriented specimens in an attempt to obtain highly oriented "doped" polyacetylene.

Phthalocyaninatopolysiloxane: electrochemical oxidation and conductivity

The most important structural requirement for the design of organic metals is the crystallization of partially oxidized or reduced molecular entities (or segments of a polymer) in segregated stacks. In the case of metallo macrocycles, e. g. phthalocyanines, as these molecular entities the arrangement in stacks can be enforced by connecting adjacent rings with covalent bonds perpendicular to the ring planes via the central metal atoms. Cofacial stacks built from phthalocyanine rings can be obtained by condensation of phthalocyaninatosilicondihydroxid, $PcSi(OH)_2$.[36,37] (eq. (3)).
Highly crystalline polymer powders of considerable thermal stability with average degree of polymerization $10 < \bar{P}_n < 200$ are obtained.[36-38] Oxidation (doping) of these materials with I_2, Br_2, substituted quinones, nitrosylsalts etc. leads to partially oxidized samples with specific conductivities of $10^{-2} < \sigma < 1$ S cm^{-1}.



(3)

"Doping" from the gas phase has been described as inhomogeneous process and the dependence of conductivity on conversion has been treated using the percolation theory.[37]
The structure of the oxidized phthalocyaninatopolysiloxane $(PcSiO)_x$ has been described by pseudohexagonal packing of the partially oxidized stacks with counterions (e.g. I_3^-) located in channels between the stacks.

Since we consider these polymers to be excellent models to study the general behaviour of conducting polymers we have investigated their electrochemical oxidation and their chain length dependent conductivity.[38]
The degree of polymerization of the material obtained acc. eq. 3 was found to be related to the conversion p by Flory's eq. $P_n = 1/(1-p)$; thus, different molecular weights can be prepared adjusting p via the time and temperature of polycondensation.[38] The microcrystalline powdery polymer was electrochemically oxidized in a cell depicted by Fig. 11.

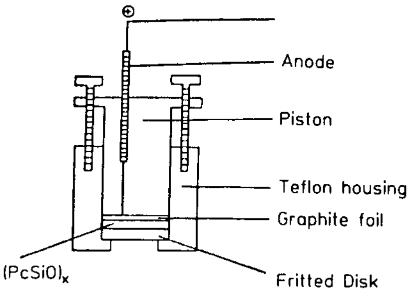


FIGURE 11. Cell for the electrochemical doping.

Specific conductivities σ were determined with the polymer pressed to pellets using a four-probe set-up.

The influence of different counterions on the specific conductivity of samples oxidized ("doped") electrochemically to the same extent is summarized in Tab. 2.

TABLE 2. Conductivities of phthalocyaninatopolysiloxane[1] after electrochemical oxidation[2]

Supporting electrolyte	Solvent	Conductivity (Ω^{-1}cm^{-1}) (pressed pellet)
$Bu_4N\ BF_4$	CH_2Cl_2	2,8 10^{-1}
$Bu_4N\ PF_6$	CH_2Cl_2	912 10^{-2}
$Bu_4N\ HSO_4$	CH_2Cl_2	5,3 10^{-2} 3)
Bu_4N Tosylat	CH_2Cl_2	3,4 10^{-2}
$Bu_4N\ SbF_6$	CH_2Cl_2	1,2 10^{-1}
$Bu_4N\ AsF_6$	CH_2Cl_2	1,9 10^{-1}
$Bu_4N\ ClO_4$	CH_2Cl_2	2,3 10^{-1}
$Bu_4N\ B(C_6H_5)_4$	CH_2Cl_2	3,0 10^{-8}
$LiClO_4$	H_2O	1,1 10^{-1}

1) $\overline{P}_n$ = 60, bulk polymerized samples

2) All samples electrolyzed galvanostatically: 0,5 F per mole of constitutive unit

3) Sulfur elemental analysis of this sample indicated a composition $|(PcSiO)\ (HSO_4)_{0.5}|_n$

It can be seen that the choice of solvent and supporting electrolyte has comparatively little effect on the conductivities, if the counterion is small enough to enter the channel between the stacks. The observation that samples electrolyzed in the presence of $|B(C_6H_5)_4|^-$ as counterion show a substantially lower conductivity qualitatively supports this structural model.

The X-ray patterns remain virtually unchanged. The fact that there is no detectable change in the Debye-Scherrer photographs is in accordance with the assumption that the anions occupy statistically disordered sites in the channel without changing the lateral packing of the polymer stacks.

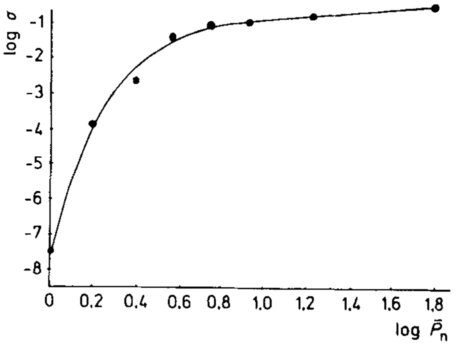


FIGURE 12. Romm temperature conductivity σ in $\Omega^{-1}\cdot cm^{-1}$ as a function of degree of polymerization.

The dependence of σ on the degree of polymerization is shown in Fig. 12. The function of the polmyer chain is obviously to bring about the desired packing of the macrocycles in stacks, but the actual chain length is of little consequence to the conductivity at least in samples of polycrystalline quality like the ones investigated here.

In summary, the general features seen in other conducting polymers including polyacetylene are seen in these metallomacrocycle polymers as well.

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