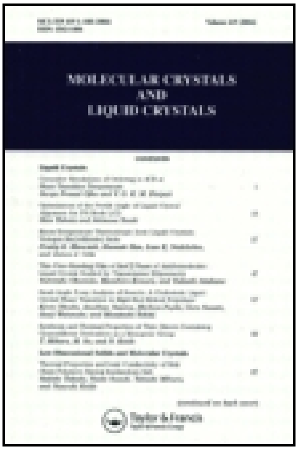

Molecular Crystals and Liquid Crystals

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New Routes to Conducting Polymers and New Insights into Structure-Properties Relations

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NEW ROUTES TO CONDUCTING POLYMERS AND NEW INSIGHTS INTO STRUCTURE-PROPERTIES RELATIONS

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Abstract The structure of conducting polymers is discussed in comparison to simple, so-called organic metals derived from naphthalene and similar arenes. In this context the conducting polymers are viewed as ion-radical salts of the backbone-units. This view is substantiated by recent results from X-ray investigations on electrochemically oxidized p-quaterphenyl as a model for poly(p-phenylene), poly-pyrrol salts of detergent ions and oxidized, highly oriented polyacetylene.

INTRODUCTION

Despite extensive studies of the so-called conducting polymers with regard to the nature of charge transport both by experimental and theoretical means surprisingly few hard facts are known about the solid-state structure, packing and packing interactions of these materials.
Even the chemistry necessary to produce a conducting polymer from an insulating precursor polymer is still under debate. It is now generally accepted that conductivity arises by oxidation or reduction of a suitable precursor polymer with concomittant production of a salt in which charge resides on the polymer backbone counterbalanced by gegenions derived from the redox reaction applied. Nevertheless the proper stoichiometry of the reaction is not known for a single case despite lengthy discussions on the use of this redox chemistry for electrochemical energy storage. In the light of these uncertainties we want to discuss the relations between the better known structures of low-molecular weight organic metals (ion-radical salts of arenes) and the polymeric salts. The insights gained from this comparison can be used to either construct new types of structures as

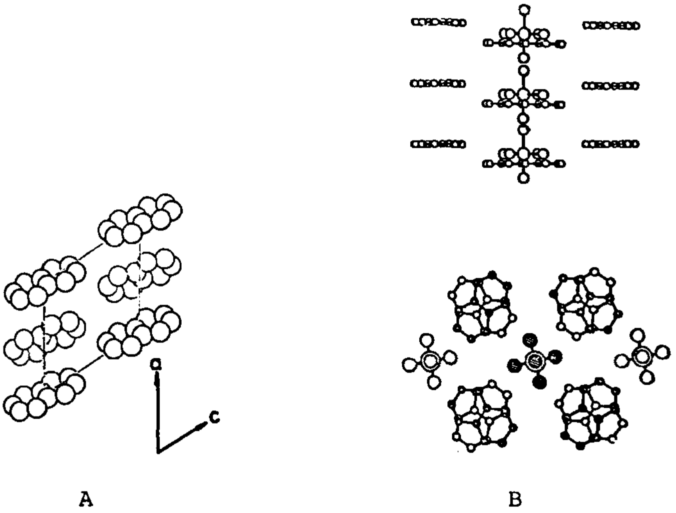


FIGURE 1 The crystal structure of neutral naphthalene (A) and of the cation-radical salt $(\text{naphthalene})_2^{\bullet+}\ PF_6^-$ (B).[3]

demonstrated in the case of poly(pyrrole)-detergent salt-layered structures or for interpretation of structural data as will be shown for oxidized polyacetylene.

STRUCTURAL CHEMISTRY OF CONDUCTING ION-RADICAL SALTS

The experimental and structural requirements necessary to produce a so-called organic metal are well known.[1] It is important to start with a compound which can be oxidized or reduced to an ion-radical state of a life-time long enough to form a complex with the neutral precursor. This complex must then crystallize into an organic salt structure characterized by ordering of the ion-radical complex into stacks with a face-to-face-arrangement of adjacent molecules.[2]
The simplest organic metals can be produced from naphthalene[3] and similar arenes such as pyrene, perylene, fluoranthene or triphenylene[4-6]. Crystals of the general stoichiometry $(\text{arene})_2{}^+X^-$ ($X=ClO_4$, BF_4, PF_6, SbF_6, AsF_6 etc.) are obtained, if these compounds are electrochemically oxidized in an inert solvent containing e. g. $(C_4H_9)_4N^+X^-$ as the supporting electrolyte. The counterion X^- serves to provide electroneutrality to the salt crystals growing from the anode. They balance

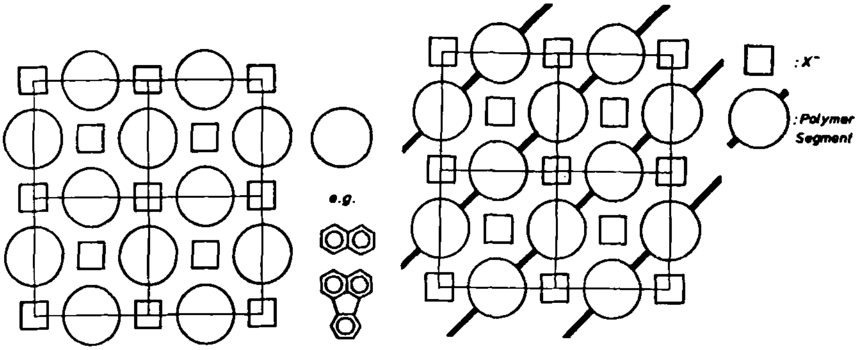


FIGURE 2

a) Packing scheme of cation-radical salts $Ar_2^{+}\cdot X^-$

b) Proposed packing of polymer cation-radical salts $[(\text{segment})_2^{+}\cdot X^-]_n$

the charge located on the aromatic cation-radical stack (comp. figure 1).

As a typical example figure 1 shows a comparison of the crystal structures of neutral naphthalene and the corresponding organic metal of the composition $(\text{naphthalene})_2^{+}\cdot PF_6^-$ ($\sigma_{298} \gtrsim 500\Omega^{-1}cm^{-1}$ in stack direction). The typical features of the ion-radical salt are the columns of naphthalene molecules which are close packed as to leave channels in which the counterions X^- are located. Within the columns individual naphthalene units are spaced at a distance of ca. 320 pm and adjacent units are rotated by 90° with regard to each other. In a formal sense every second molecule carries a positive charge and a spin. In reality charge and spin are smeared out through the whole stack and all molecules are crystallographically identical. The counterions serve to keep electroneutrality and are "spectators" with regard to the electronic properties which in turn are a property of the sublattice formed by the organic residues.[7]

In the language used in the field of conducting polymers[8] going from neutral naphthalene (figure 1A) to the cation-radical complex (figure 1B) may be called "doping" of naphthalene. In fact, the same type of complexes are obtained, if solid arenes are treated by AsF_5, SbF_5 and similar oxidizing reagents. Consideration of the facts indicates however that the term "doping" is totally inadequate in this case. We rather deal with oxidation of the arene and with the formation of a totally new structure which has nothing in common with the initial naphthalene structure. In addition, the electronic properties of the organic metal arise from intermolecular interaction between the units within the stack; thus the packing of the molecules is at the origin of all considerations relating to the electronic properties.

The structure of the (arene)$_2^{+\cdot}$X$^-$ complexes may be generalized with regard to the design of polymeric organic metals[9] as it is shown by figure 2. Several unit cells are depicted in figure 2a showing in general terms how the stacks of the ion-radicals are densely packed together leaving channels for the counterions X$^-$. If we - in a Gedankenexperiment - connect the organic ions within the same lattice plane and along a lattice direction by chemical bonds, as shown in the other part of figure 2, we create the model of the packing of a polymeric organic metal. The circles now depict the segment of the polymer chain which supports the cation-radical site and the black bars are the bonds connecting these segments.

An immediate prediction from this model is that the conductivity in polymeric systems should be rather independent from chain length, since the electronic properties should arise because of the same principles as in the low-molecular weight analogues. The missing link between the low-molecular weight organic metals and the polymers has in fact been found in the case of the cation-radical salts of ter- and quaterphenyl.[10,11] These are prepared as described for the other (arene)$_2^{+\cdot}$X$^-$ materials by anodic oxidation and exhibit the structure predicted from the model shown in figure 2b.[11] They are models for the organic metal obtained by oxidation of poly(p-phenylene).[12]

POLYPYRROLE-SALTS WITH DETERGENTIONS: LAYERED STRUCTURES

Figure 2b can be considered in terms of a layered structure as well; this aspect is strengthened, if the highly symmetrical gegenions discussed so far, are replaced by anisometric ions such as the ions of detergent molecules without, however, changing the stacking of the segments of the polymer.

We have realized this idea in the case of poly(pyrrole) salts prepared by electrochemical oxidation of pyrrol in the presence of a supporting electrolyte which contains simple detergent ion.[13-15] Suitable detergents are n-alkyl sulfates, -sulfonates,- phosphates and

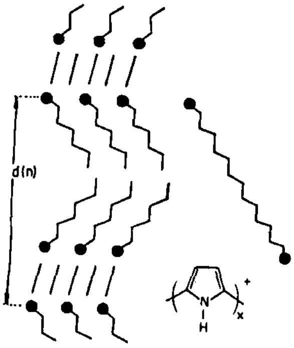


FIGURE 3 Idealized structure[13-15] (short range order) in poly(pyrrole) detergent salts, seen along the polymer chain axis. The short black bars represent PPY-chains, the zigzag lines the alkylchains of the detergents and the black dots stand for the ionic head groups. Note the stacking of the polymer chains as in figure 2b.

phosphonates. These salts give rise to a small-angle X-ray peak which scales with the number n of carbon atoms per alkyl chain as $d(n)=0.19\cdot n+1.2$ (nm). The structure of these salts is schematically depicted by figure 3; they exhibit conductivities $10<\sigma\leq 150$ somewhat depending on the length of the alkyl chains introduced. A surprising fact is the very small temperature dependence of σ in these materials.[14]

STRUCTURE OF POLY(ACETYLENE) AND ITS CATION-RADICAL SALTS

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

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

($R=nC_4H_9$) 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. Similarly, iodine, AsF_5 or other reagents may serve as oxidants to produce the ion-radical salt with appropriate counterions in each case. This formulation does not intend to neglect the possible disproportionation or further oxidation of the ion-radical to a spin-less two-valent state ("bipolaron").

The structure of these highly conducting salts could, so far, only be guessed by interpretation of limited data available from powder patterns or poorly oriented samples of the so-called Shirakawa-poly(acetylene).[9,13,16] This situation has changed with the advent of a new route to polyacetylene via a soluble precursor polymer

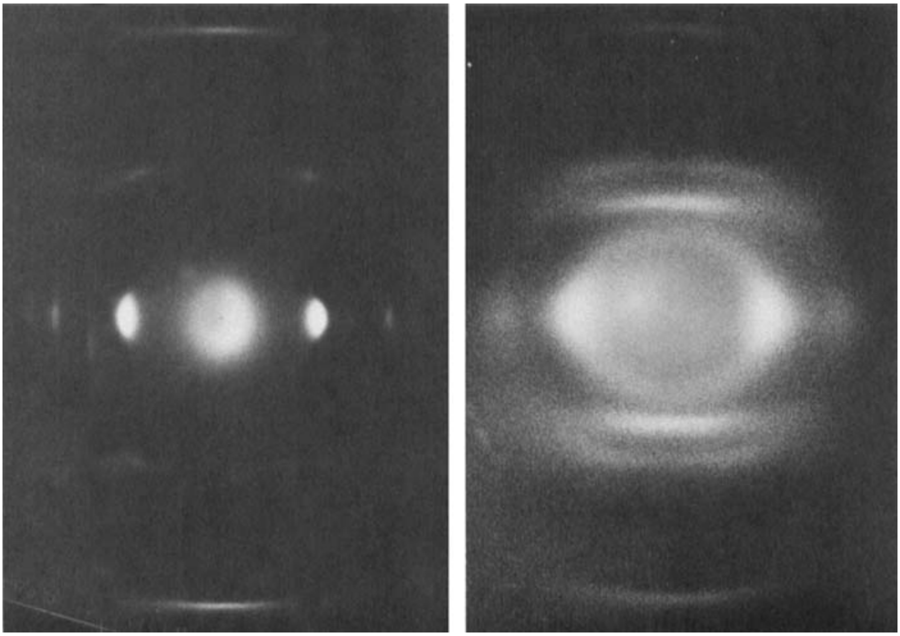


FIGURE 4 a(left). Fibre diffraction pattern (EM) of stretched trans-polyacetylene obtained by the route of Edwards and Feast. b(right). Fibre diffraction pattern of the same polymer after treatment with iodine ($\sigma_{298} \geq 10 \Omega^{-1} \mathrm{cm}^{-1}$).

first described by Edwards and Feast.[17] Adopting this method we realized[13] that highly oriented trans-poly (acetylene) can be obtained through stretch alignement with concurrent pyrrolysis of the precursor polymer. Figure 4a shows the fibre pattern obtained from such material. It can be indexed in an orthorhombic unit cell (Pnam)with a=7.20 Å, b=4.15 Å, c=2.44 Å, ρ=1.18 gcm^{-3}, Z=2. The ratio of the axes a/b equals exactly $\sqrt{3}$ indicating the possibility of a pseudohexagonal arrangement (with disorder) of the polymer chains. Note also, that the space group Pnam is incompatible with the bond alternation along the zig-zag-chain; it only arises because of positional disorder along the fibre axis. Figure 4b shows the fibre pattern of this material after exposure to iodine, i.e. of the conducting phase. Note the pronounced occurence of streaks along the lines indicating the positional disorder of nematic type in this material. Their positions at the meridian correspond to d-values of 3.13, 1.86, 1.55, 1.35, 0.92, 0.80 and 0.70 Å all incommensurate with regard to the periodicitiy of trans-polyacetylene.

Figure 5 shows the X-ray diffraction patterns of fibres of trans-poly(acetylene) a) exposed to iodine and b) electrochemically oxidized as to obtain the SbF_6^--salt. The latter was analyzed in more detail. The pattern arises basically from the anion sublattice, the structure factor of the polymer-segment-sublattice being comparatively small. The streak at the first layer line (d=5.4 Å) indicates the periodicity of positionally disordered rows of SbF_6^--ions parallel to the fibre axis. Together with the equatorial reflections which are described in a densitometer trace by figure 6 a unit cell with a=8.45 Å, b=16.8 Å, c=5.02 Å, α= 90°, β= 90°, γ= 99.3° can be assigned. The c-value is somewhat arbitrary and was only used to satisfy the conditions for calculations with regard to the packing in the a,b-plane. The structure derived from this pattern and optimized by packing calculations is shown in figure 7. This structure is well established with regard to the anion positions and is open to further improvement with regard to the setting angle of the polymer chain. It is, however, certain that the chains are packed with the zig-zag-planes facing each other along a stack and they cannot face the counterions as assumed by C. W. Chien et al.[16] in the case of the iodide-salt.

A good fit between observed and calculated intensities of the equatorial reflections is obtained for this structure as indicated in figure 6. The structure has a fairly large unit cell with 4 chains per 3 rows of counterions; note also that the zig-zag-geometry of the chains is incommensurate with the counterion periodicity of 5.4 Å except one would assume a very large unit cell.

Figure 7 is only to be understood as a schematic picture especially since the data give the best fit, if only 85 percent of all SbF_6^--sites are actually occupied (one reason for the appearance of the streak).

These results, although of still limited accuracy, clearly indicate that the conducting salts of polyacetylene are fully within the scope of other, less complicated cation radical salts, at least as far as the crystal chemistry is concerned.

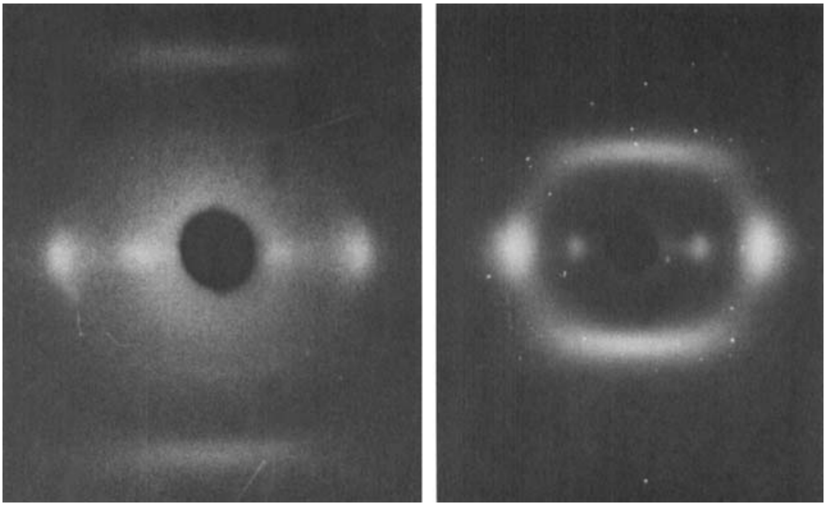
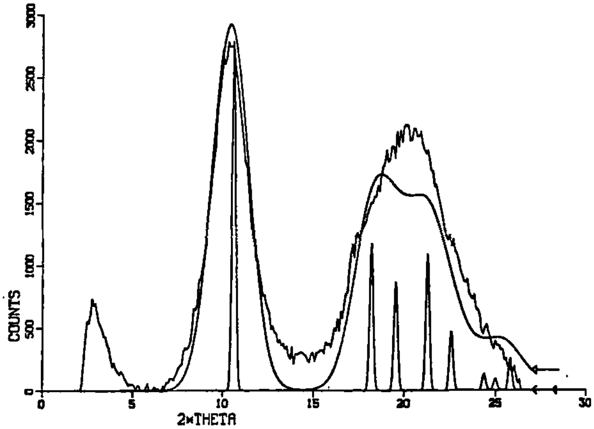


FIGURE 5 X-ray fibre diagrams of trans-poly(acetylene) a) (left):I_2-treated; b) (right): electrochemically oxidized, SbF_6^--counterions.

FIGURE 6 Intensity distribution along equator of pattern shown in figure 5b; calc. intensity based on unit cell shown in figure 7 marked by arrow. Sharpspikes: expected positions and intensity of (001), (030), (1$\bar{3}$0), (200), (130), (1$\bar{4}$0) reflections.



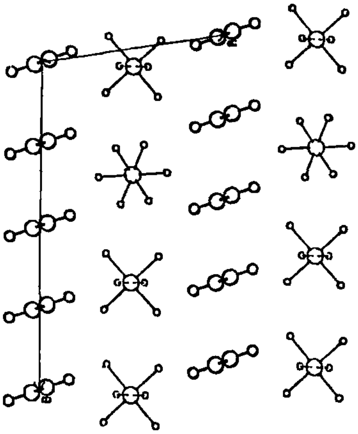


FIGURE 7 Proposed ideal structure of the trans-poly(acetylene)$^+$SbF$_6^-$-salt; note that in the real structure part of the anionsites (≥15 percent) are probably not occupied.

ACKNOWLEDGEMENT

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