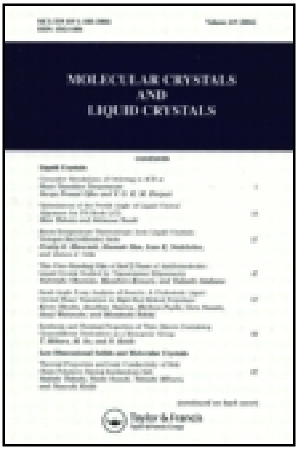

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STRUCTURAL STUDY OF POLYACETYLENE DOPED WITH TETRAHEDRAL ANIONS

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Abstract A structural study of polyacetylene doped with ClO_4, $FeCl_4$, $FeBr_4$, $GaCl_4$ and $InCl_4$ tetrahedral anions is presented. First stage intercalated CH/dopant structures are found. At doping levels where electronic properties change considerably, the dopants are found to cluster. Special attention has been paid to characterize the disorder and the amount of *cis-trans* isomerization in the undoped parts of the films. A relationship between these structural features and the presence of dopant induced elastic constraints is suggested.

I. INTRODUCTION

$(CH)_x$ has been subject to intense research since the report that its electrical conductivity is increased by more than eight orders of magnitude when doped with acceptor or donor chemical species. More detailed experiments have shown that the electrical conductivity increases rapidly to $1 (\Omega\ cm)^{-1}$ at about 1% doping concentration, while with higher dopant concentration, it increases more slowly to about $10^3\ (\Omega\ cm)^{-1}$. On the contrary, magnetic susceptibility stays at a small value to about 5% of dopant, then it increases to values usually found in metals.[1] These unusual electronic properties have opened a large debate. Several transport mechanisms including new kinds of excitations (polarons, solitons, . . .) have been proposed. However, until now, very little is known concerning the modifications brought by the dopant in the material: the disorder introduced, the homogeneity of the doping in the fibrils and the structural changes which may occur. The purpose of this study of $(CH)_x$ doped with tetrahedral anions is to shed light on these issues.

II. UNDOPED $(CH)_x$

Structural properties of undoped $(CH)_x$ has been reviewed recently.[2] We shall only point out here two aspects relevant for the present study:

a. $(CH)_x$ fibrils are highly crystalline. However, Bragg reflections observed are wider than the experimental resolution, which means that the crystalline order is spatially limited. In a crude model assuming the fibril is composed of crystallites of finite size L, this quantity is related to the intrinsic width $\Delta 2\theta$ of a reflection occuring at a Bragg angle θ by the Scherer formula $L=0.9\lambda/\Delta 2\delta \cos\theta$, where λ is the wavelength of the diffracting beam. Recent measurement of the width of two well defined (hk0) reflections shows, in fact, a decrease of L for θ increasing (L~85 Å and 60 Å for the (2,1,0) and (3,1,0) reflections respectively), which means that the crystalline periodicity is progressively lost in transverse directions of the fibril. Such a loss is probably due to fluctuations in the setting angle of $(CH)_x$ chains. A similar observation has been performed for the chain reflections $(0,0,\ell)$.[3] However, in that case, the loss of longitudinal co-herence might be due to conformational defects in the conjugation sequence.[2]

b. $(CH)_x$ prepared by the Shirakawa technique may be obtained in either a *cis* or a thermodynamically more stable *trans* isomer, by thermal annealing of *cis* materials. Earlier x-ray studies[4] have shown that the *cis* to *trans* isomerization process keeps constant the amount of crystallinity of the fibril and the crystalline coherence discussed above. With the increasing amount of *trans*, the continuous shift of lateral parameters was found to increase progressively the lateral compactness of the material,[4,5] while the constancy of the width of the lateral reflections (Fig. 1) showed that the crystalline coherence of the two dimensional network of projected $(CH)_x$ chains is preserved. This result and the observation in the *cis* rich mixed solutions of a progressive broadening toward the large Bragg angles of the (002) in chain *cis* reflection (which indicates a loss of lateral correlation between *cis* units)[4] means that isomerization occurs homogeneously with nearly random growth of *trans* chains or segments throughout the *cis* polymer.

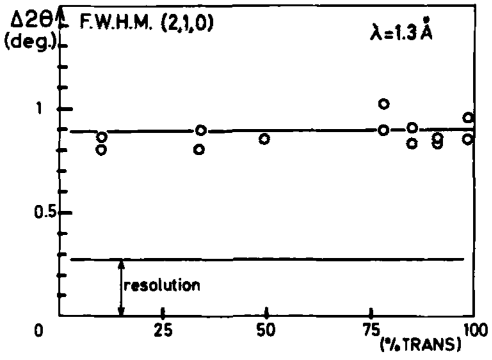

Figure 1
Full width at half maximum (F.W.H.M.) of the non-overlapping (210) lateral reflection as a function of isomerization.

III. DOPED $(CH)_x$

Earlier structural studies of $(CH)_x$ doped with iodine have shown that the doping is inhomogeneous:[6] in the heavily doped parts, the dopant intercalates regularly between $(CH)_x$ plane forming a new structure,[6,7] while in the lightly doped or undoped part it triggers a *cis* to *trans* isomerization of the starting material.[6] We shall examine here these features in $(CH)_x$ chemically doped with $FeCl_4^-$, $FeBr_4^-$, $GaCl_4^-$, $InCl_4^-$ anions[8] and $(CH)_x$ electrochemically doped during about 4 days with ClO_4^- anions. $[CH(ClO_4)_y]_x$ samples used here have also been the subject of correlated electrical, magnetic and optical measurements.[9]

a. CH/Dopant Structures

A typical Debye Scherrer x-ray pattern of a stretched heavily doped $[CH(ClO_4)_y]_x$ sample is shown in Fig. 2. It shows[4] broad rings, corresponding to d spacings 8.6 Å, 5.3 Å and 4.0 Å at different positions from those found in pure $(CH)_x$. The overall size of a tetrahedran of ClO_4 including the outer Van der Waals radius of oxygen atoms is of about 4.8 Å, thus, the 8.6 Å spacing corresponds closely to the repeat periodicity along a of alternating planes of ClO_4 tetrahedra and of $(CH)_x$ chains (of size $\sim a_{trans}/2 = 3.7$ Å). The other lateral spacing 4.0 Å is close to the repeat distance of $(CH)_x$ chains in the b direction (b_{trans} = 4.1 Å) and of that of interpenetrating ClO_4 tetrahedra with oxygen atoms in close contact (~4.2 Å). However, the in chain spacing, 5.3 Å, is slightly larger than the size of a tetrahedra (4.8 Å) and twice the repeat distance of a *trans* $(CH)_x$ unit ($2C = 4.92$ Å). From the width of these reflections one can estimate that ClO_4 tetrahedra intercalate between [100] planes of $(CH)_x$ over about 40 Å in the (100) direction, with an order over 20 A in (001) chain direction, and more limited along the other (010) lateral direction.

Similar x-ray patterns are found for $(CH)_x$ doped with $FeCl_4$, $FeBr_4$, $GaCl_4$ and $InCl_4$ (Fig. 3). The new d spacings obtained are shown in Table I. From the position and width of the two reflections of lowest Bragg angles, the CH/dopant intercalate structure appears to be similar and of the same size as that of $[CH(ClO_4)_y]_x$.

TABLE I. New d Spacings Obtained from the Microdensitometer Readings Shown in Fig. 3.

$[CH(FeCl_4)_{0.07}]_x$	9.3 Å	5.2 Å	4.65 Å	3.4 Å
$[CH(FeBr_4)_{0.03}]_x$	10.0 Å	5.7 Å	shoulder	~3.3 Å
$[CH(GaCl_4)_{0.04}]_x$	9.2 Å	4.9 Å		3.3 Å
$[CH(InCl_4)_{0.035}]_x$	9.7 Å	5.1 Å		~3.3 Å

With smaller ClO_4 concentrations, the observation of the 8.6 Å reflection depends on the samples. In all, the samples investigated, it has been only detected in those having a sizeable magnetic susceptibility ($\chi/\chi_{METAL} > 25\%$).[9] This behavior suggests that the proposed[9] commensurate-incommensurate transition and corresponding disorder induced "metallic" χ occurs when sufficient numbers of dopants have agglomerated and independent charged solitons can no longer be sustained. The confirmation of a relationship between the metallic behavior and the formation of a long distance intercalated structure needs investigation of other well-characterized samples for y close to the critical concentration 5%, and the study of other CH/dopant systems.

In contrast, the other new reflections remains visible for lower y values, although the in chain reflection, initially at 5.3 Å, belongs to a broad shoulder, centered at about 4.8 Å (which may also include the 4.0 Å reflection) on the left side of the strongest reflection of undoped $(CH)_x$ (Fig. 4). A similar observation has been done in the $CH/FeCl_4$ system. The number of agglomerated dopants per CH unit probably remains small enough for the charged solitons to be considered quasi-independent. This may occur in the absence of three dimensional ordering of the dopants.

Thus as ClO_4^- or $FeCl_4^-$ anions have a size comparable to that of a $(CH)_x$ unit, the intercalation of isolated anions costs so much elastic energy that the aggregation of dopant into columns or more likely into sheets is formed.[10] This two-dimensional clustering of dopant probably gives rise to the 4.8 Å broad reflection observed for the lowest y values. For the highest y values, a more regular packing between clusters of dopant and $(CH)_x$ chains develops, making possible the observation of the 8.6 Å (or 9.3 Å) periodicity. Thus, energy considerations lead to an inhomogeneous doping. In addition, the slow diffusion process of dopant into fibrils favors a preferential doping of its outer parts. However, as described below, this affects the undoped (or lightly doped) inner parts of the fibrils.

b. Undoped Parts of the Fibrils

Doping of $(CH)_x$ with ClO_4^- has the effect of decreasing progressively the lateral crystalline coherence defined in part IIa (Fig. 5) and inducing a progressive *cis* to *trans* isomerization (Fig. 6) of the undoped parts of $(CH)_x$, as thermal annealing does (see part IIb).

As the dopant introduces inhomogeneous elastic constraint in the fibrils, the "regular" arrangement of setting angles of $(CH)_x$ chains is certainly changed over long distances, increasing the loss of crystalline coherence even in the inner undoped parts of the fibrils. Furthermore, these elastic constraints tend to compress laterally the $(CH)_x$ chains. This, in addition to processes considered in ref. 6, may help the isomerization for it results in a gain of lateral compactness between $(CH)_x$ chains. The "undoped" regions may correspond to regions between the small two-dimensional "clusters" of dopants. Figure 5 suggests that these regions become smaller with increasing dopant concentration, as would be expected.

The *cis-trans* isomerization upon doping is best illustrated by Fig. 7, which shows the identity between the Debye-Scherrer pattern of a pure *trans* $(CH)_x$ (a) and that of a *cis* $(CH)_x$ electrochemically doped with 3.2% then dedoped to about 1.1% of ClO_4^- (b) [for this sample, the resulting amount of *trans* is indicated by the cross in Fig. 6]. In addition, from (a) to (b) Debye-Scherrer reflections broaden, indicating an increase in the disorder [more quantitatively measured by the cross in Fig. 5). Thus, the degradation of the fiber crystallinity upon doping and dedoping, as evidence here for even only one cycle, is an important parameter to consider for electrochemical applications of polyacetylene.

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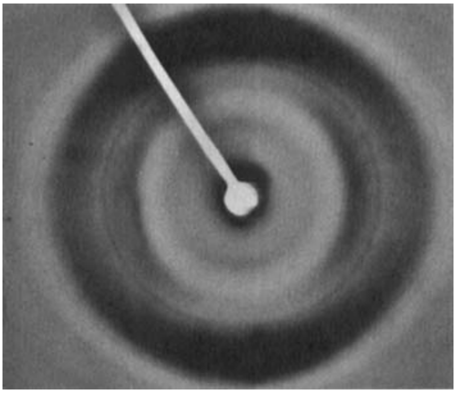
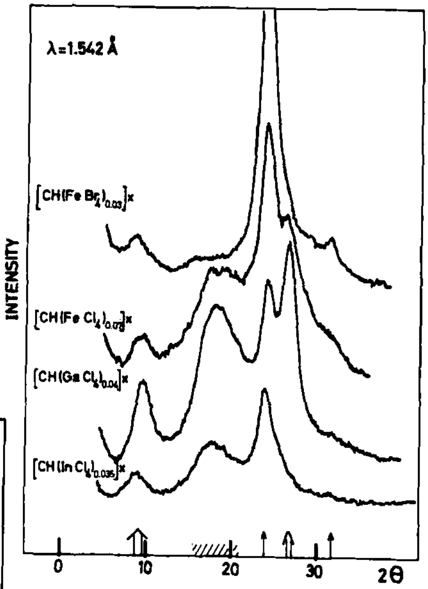


Figure 2
Debye-Scherrer x-ray pattern of $[CH(ClO_4)_{0.063}]_x$ stretched 2 times (the chain axis is horizontal). It shows new lateral d spacings at 8.6±0.1 Å, 4.0±0.1 Å and an in chain d spacing at 5.3±0.1 Å. (Thin rings of small intensity are contamination.)

Figure 3
Microdensitometer readings of Debye-Scherrer patterns of $(CH)_x$ doped with 3% of $FeBr_4$, 7% of $FeCl_4$, 4% of $GaCl_4$ and 3.5% of $InCl_4$. Single arrows point toward reflections of pure $(CH)_x$. Double arrows and the hatched segment indicate the position of new reflections.



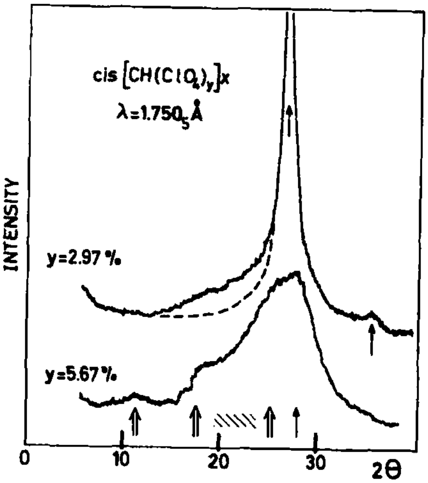


Figure 4
Microdensitometer readings of Debye-Scherrer patterns of $(CH)_x$ doped with 3% and 5.7% of ClO_4. For the lowest concentration, only a broad new reflection corresponding to the hatched segment ▨ is observed.

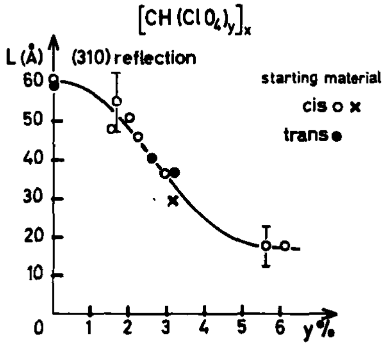


Figure 5
Apparent coherence length, L, deduced from the width of the (310) reflection as a function of the ClO_4 content. Note that the same values are obtained for *cis* and *trans* starting materials. This means that a sizeable broadening of this reflection coming from nonhomogeneous isomerization of *cis* samples can be excluded.

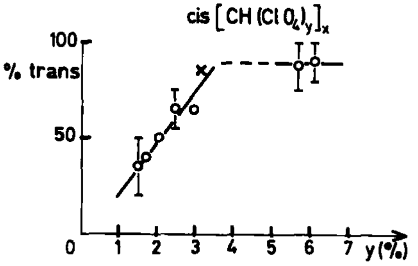


Figure 6
Isomerization of the undoped part of $(CH)_x$ as a function of the ClO_4 content. The quantity has been determined by the position of the 3 strongest (hk0) reflections according to ref. 4 and the ratio of the intensity of the (210) and (310) reflections.

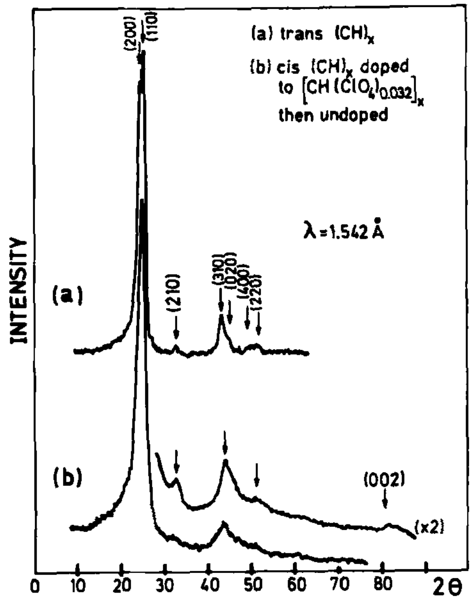


Figure 7
Comparison between microdensitometer readings of Debye-Scherrer patterns of a pure *trans* $(CH)_x$ (a) and of an about 80% *trans* $(CH)_x$ obtained after electrochemical doping of *cis* $(CH)_x$ with 3.2% of ClO_4^- and its dedoping to about 1.1% of ClO_4^-.

REFERENCES

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1. A.J. Epstein, H. Rommelmann, R. Bigelow, H.W. Gibson, D.M. Hoffman, and D.B.Tanner, Phys. Rev. Lett. 50, 1866 (1983).
2. J.P. Pouget, P. Robin, R. Comes, H.W. Gibson, A.J. Epstein and D. Billaud, Physica (under press).
3. C.R. Fincher, Jr., C.E. Chen, A.J. Heeger, A.G. MacDiarmid and J.B. Hastings, Phys. Rev. Lett. 48, 100 (1982).
4. P. Robin, J. P. Pouget, R. Comes, H.W. Gibson and A.J. Epstein, Phys. Rev. B 27, 3938 (1983) and Journal de Physique 44, C3-77 (1983).
5. G. Perego, G. Lugli, V. Pedretti and E. Cernia, Journal de Physique 44, C3-93 (1983); A. Bolognesi, M. Catellani, S. Destr, G. Morelli, W. Porzio, R. Tubino and M. Zocchi, Makromol. Chem. Commun. 4, 403 (1983).
6. P. Robin, J.P. Pouget, R. Comes, H.W. Gibson and A.J. Epstein, Polymer, 24, 1558 (1983) and Journal de Physique 44, C3-87 (1983).
7. R.H. Baughman, N.S. Murthy, G.G. Miller and L.W. Shacklette, J. Chem. Phys. 79, 1065 (1983); T. Danno, K. Miyasaka and K. Ismikawa, J. Polym. Sci., Polym. Phys. Ed. 21, 1527 (1983); K. Shimamura, F.E. Karasz, J.C.W. Chien and J.A. Hirsch, Makromol Chem. Rapid. Commun. 3, 269 (1982).
8. A. Pron, D. Billaud, I. Kulszewicz, C. Budrowski, J. Przyluski, and J. Suwaiski Mat. Res. Bull. 16, 1229 (1981); D. Billaud, et. al., this conference.
9. A.J. Epstein, R.W. Bigelow, H.W. Gibson, A. Feldblum, D.B. Tanner, J.P. Pouget, R. Comes, P. Robin, and S. Kivelson, these proceedings; X.A. Yang, D.B. Tanner, A. Feldblum, H.W. Gibson, and A.J. Epstein, these proceedings.
10. R.H. Baughman, N.S. Murthy, G.G. Miller, L.W. Shacklette and R.M. Metzger, Journal de Physique 44, C3-53 (1983).