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Polymerization of 3-alkylthiophenes with $FeCl_3$

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We report on the mechanism of direct oxidation of 3-alkylthiophenes using ferric chloride ($FeCl_3$) as the polymerization oxidant/catalyst to produce high molecular weight poly(3-alkylthiophenes) (P3ATs), conjugated polymers that have potential as electrically and optically active polymers. This study shows that the $FeCl_3$ must exist in the solid state in the reaction mixture to be active as an oxidant in the polymerization of P3AT. A feasible polymerization mechanism for 3-alkylthiophene was developed on the basis of the crystal structure of $FeCl_3$ and quantum chemical computations of thiophene derivatives. The polymerization is hypothesized to proceed through a radical mechanism rather than a radical cation mechanism.

(Keywords: 3-alkylthiophene; poly(3-alkylthiophene); polymerization; ferric chloride; radical; cation)

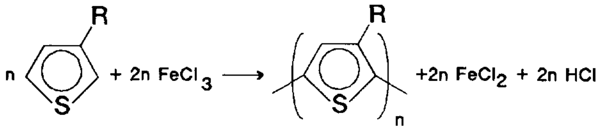
INTRODUCTION

The poly(3-alkylthiophenes) (P3ATs) represent a new generation of both solution and melt processable conjugated polymers. Furthermore, when P3ATs are treated with electron acceptors or electron donors, i.e. when the polymer chains are partially oxidized or reduced, they show remarkable changes in their physical and optical properties[1–3].

3-Alkylthiophenes can be polymerized to the corresponding P3ATs either by electrochemical or chemical polymerization methods. Sato *et al.* have shown that flexible, freestanding films of electrically conducting P3ATs are obtained if 3-alkylthiophenes are polymerized electrochemically[1]. After electrochemical reduction to the non-conducting state, these films are soluble in common organic solvents. Electrochemical polymerizations exhibit, however, several drawbacks as compared to chemical polymerization techniques, such as lower yield and generally higher degree of regio-irregularities which results in decreased π-electron delocalization and decreased solubility as compared to P3ATs obtained by chemical methods[4].

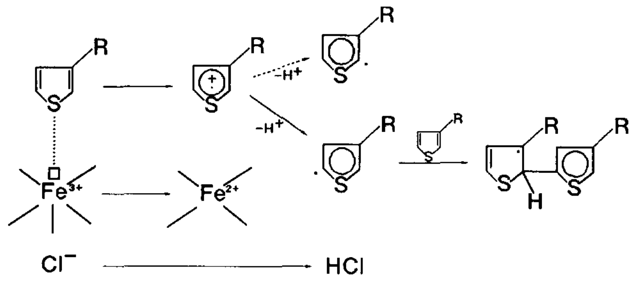
Jen *et al.* and Österholm *et al.* have used Grignard coupling to chemically prepare P3ATs[2,3]. Sugimoto *et al.* reported on the direct one-step oxidation of 3-alkylthiophenes, in which monomer (0.1 M) and transition metal halides (0.4 M), such as $FeCl_3$, are mixed in chloroform at room temperature[5]. In both cases, P3ATs were obtained in which the thiophene rings are essentially completely 2,5-coupled (increased π-delocalization) and completely soluble in organic solvents. The direct oxidation of P3AT using $FeCl_3$ as the oxidant/catalyst offers great advantages over the Grignard coupling route, due not only to its simplicity but also to the fact that polymers of much higher molecular weights are obtained[2,3].

However, the polymerization process raises several questions: What makes $FeCl_3$ so active an oxidant? Which form of $FeCl_3$ has the oxidative function? What are the roles of the solvent and the evolved hydrogen chloride (HCl(g))? Why is $FeCl_3$ needed in twice the stoichiometric proportion indicated by equation (1)?



(1)

In this study we report on the polymerization mechanism of direct oxidation of 3-alkylthiophenes using $FeCl_3$ as the oxidant/catalyst and we propose that the polymerization of 3-alkylthiophenes to the corresponding P3ATs proceeds through a radical mechanism rather than a radical cation mechanism. The proposed initiation mechanism is shown in *Scheme 1*.



Scheme 1

EXPERIMENTAL

The polymerizations of 3-octylthiophene (3-OT) were done according to Sugimoto *et al.*[5]: $FeCl_3$ (0.4 mol) was added to an appropriate solvent and mixed typically for 2–3 min. After that 3-OT (0.1 mol) was added at room temperature (e.g. 3.1 g 3-OT to a suspension of 10.2 g $FeCl_3$ in 125 ml $CHCl_3$). The mixture was stirred typically for 20 min, and then water was added to the

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reaction vessel to terminate the polymerization. The polymer was washed with water, precipitated with acidic ethanol and filtered.

To study the effect of the soluble portion of $FeCl_3$, $FeCl_3$ (2.4 g) was dissolved in $CHCl_3$ (125 ml) and 3-OT (0.9 g) was added to the stirred solution at room temperature. The synthesis was continued as mentioned above.

The effect of HCl gas on the polymerization reaction was studied in the following way: $FeCl_3$ (0.4 mol) was added to chloroform and mixed typically for 30 min in a flow of HCl gas. After that 3-OT (0.1 mol) was added and the mixture was stirred for 20 min in a continuous flow of HCl.

The titration experiments were done in the following way: the polarization or redox electrodes were placed in a stirred $CHCl_3$ solution and 3-OT (0.1 mol) was added. Subsequently $FeCl_3$ (0.4 mol) was added in small weighted portions. The titration curve was compared to similar titrations without 3-OT.

RESULTS AND DISCUSSION

Role of $FeCl_3$

$FeCl_3$ polymerized 3-OT in the absence of solvent and in any solvent that did not dissolve $FeCl_3$ fully (*Table 1*). In other words, the polymerization process requires solid $FeCl_3$. This result was verified in polarization and redox titration experiments: polymerization did not begin until solid $FeCl_3$ was present. For example in the synthesis where $FeCl_3$ was dissolved completely in $CHCl_3$, no polymer was produced.

The solubility of $FeCl_3$ in $CHCl_3$ explains ~ 50% of the need for the extra portion of $FeCl_3$ that is required initially. The yields of polymer were very low in the polymerizations in a continuous flow of HCl gas, and therefore the evolved HCl that consumes $FeCl_3$, probably by complexation[6] ($FeCl_4^-$), explains the need for the rest of the extra portion of $FeCl_3$.

Solvent is required to dissolve the P3AT formed, which otherwise would precipitate on $FeCl_3$ (s) and $FeCl_2$ (s) and make washing of the polymer difficult.

Crystal structure of $FeCl_3$

Ferric chloride has a layered lattice structure, where the chloride ions are arranged in hexagonally closest packing (hcp) and the iron(III) ions fill two-thirds of the octahedral holes in every other layer (*Figure 1*)[7]. The structure of the layer with iron(III) ions is shown in *Figures 2* and *3*. Figures were drawn by the PLUTO program[8] on the basis of the following initial data: $a = 6.605$ Å, $c = 17.44$ Å, $U = 556$ Å^3, $Z = 6$ and space group $R\bar{3}$ (C_{3i}^{2}) (ref. 9).

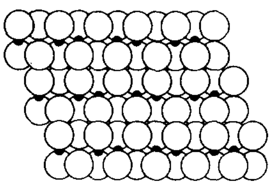


Figure 1 Layered lattice structure of $FeCl_3$

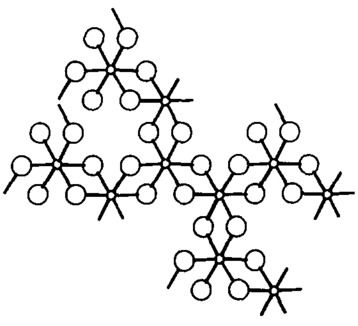


Figure 2 PLUTO drawing of the $FeCl_3$ crystal structure

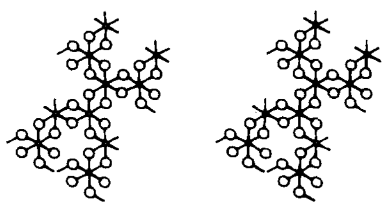


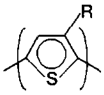
Figure 3 Stereoscopic PLUTO drawing of the $FeCl_3$ crystal structure

Table 1 Effect of different solvents on polymerization of 3-OT

Solvent	Solubility of $FeCl_3$	Polymerization
–		+
$CHCl_3$	Not completely	+
Toluene	Not completely	+
CCl_4	None	+
Pentane	None	+
Hexane	None	+
Diethylether	Completely	–
Xylene	Completely	–
Acetone	Completely	–
Formic acid	Completely	–

Proposed polymerization mechanism

Only a few mechanisms for the polymerization of non-alkylated thiophene have been presented in the literature[10,11], and it is not clear, therefore, why 3-alkylthiophenes polymerize, both chemically and electrochemically, to almost pure poly(3-alkyl-2,5-thienylenes)



with negligible regio-irregularities[3,12]. In recent studies Leclerc *et al.*[4] have shown by structural analysis that poly(3-alkyl-2,5-thienylenes) produced by chemical oxidation are more regular and contain fewer irregular couplings than those produced by electrochemical means. The $FeCl_3$ oxidant has not received detailed attention in the literature.

Role of iron in the polymerization. In solid $FeCl_3$, the iron(III) ions are mostly hidden within the crystal (*Figures 1–3*) where they are chemically inert. Each chloride ion is coordinated to two iron(III) ions. The structure is slightly different at the surface of the crystal: in order for the total charge to be neutral there must be a deficiency of chloride ions, and some of the chloride ions are coordinated to only one iron(III) ion. Thus each iron(III) ion at the surface of the crystal has one unshared chloride ion and one free orbital. The crystal structure

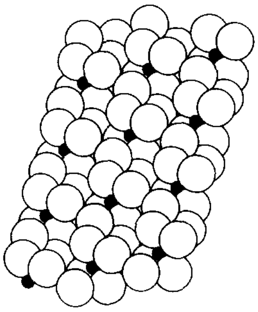


Figure 4 Crystal structure of $FeCl_3$ at the surface of the crystal

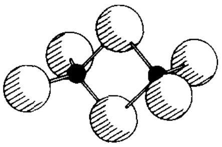


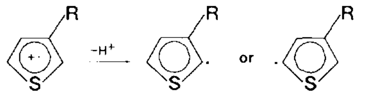
Figure 5 Dimeric Fe_2Cl_6

of solid $FeCl_3$ at the surface of the crystal is shown in *Figure 4*.

The active sites in polymerization are the iron(III) ions at the surface of the crystal, which have strong Lewis acid character because of the one free orbital. The Lewis acid character also explains the highly hygroscopic nature of $FeCl_3$. In chloroform the soluble part of $FeCl_3$ is inert because it exists in dimeric form (*Figure 5*) without free orbitals[13].

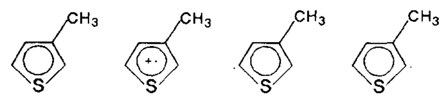
Thiophene molecules lying in close proximity to solid $FeCl_3$, will easily coordinate, through the free electron pair of the sulphur atom, to the iron(III) ions with one free orbital. This situation was simulated with the CHEM-X molecular graphics program and confirmed to be feasible. However, the oxidizing ability of the iron(III) ion is strong enough to oxidize the thiophene molecule to the radical cation.

Quantum chemical computations. Quantum chemical computations were done to find out whether the polymerization proceeds through the radical cation or through the radical formed from the radical cation by proton abstraction:



(2)

The computations were done with the Gaussian 88 program[14] with STO-3G geometry. 3-Methylthiophene was chosen as the model compound to minimize the computation time. Total energies and total atomic charges were computed for the following thiophene derivatives:



1 **2** **3** **4**

In addition, a full population analysis was carried out for the radical cation 2 (*Figure 6*).

From the total energies (*Table 2*) we can see that radical 3 is slightly more stable than radical 4 (difference 1.456 kJ mol^{-1}). The total atomic charges of the thiophene rings are shown in *Table 3*.

Discussion of alternative mechanisms. There are four possible, alternative mechanisms:

1. radical cation reacts with neutral thiophene
2. radical reacts with neutral thiophene
3. two radical cations react with each other
4. two radicals react with each other

Alternatives 3 and 4 can be neglected, because the chloride ions at the surface of the crystal prevent the radical cations or radicals from assuming positions suitable for dimerization.

As illustrated in *Figure 7*, if a neutral thiophene molecule reacts with a 3-alkylthiophene radical cation, a new C–C bond will be formed between the most negative carbon of the 3-alkylthiophene (carbon 2, *Table 3*) and the carbon of the radical cation that has the highest odd electron population (carbon 2, *Figure 6*). This time however, there will be many tail-to-tail links.

By contrast, when the neutral thiophene molecule reacts with the more stable radical, as illustrated in *Figure 8*, there will be fewer regio-irregularities. The radical mechanism has the further advantage that, in coupling, the hybridization of carbon atoms changes $sp^2 \rightarrow sp^3 \rightarrow sp^2$ only once, whereas in the radical cation mechanism the similar hybridization changing occurs twice. The low dielectric constant of chloroform further supports the radical mechanism, because the chloride ion that is no longer coordinated to the iron(III) ion when

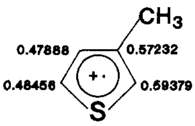


Figure 6 Coefficients of odd electron population in different atoms for radical cation 2

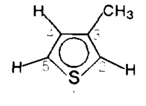
Table 2 Total energies of thiophene derivatives

Derivative	E (kJ mol^{-1})
1	−1542251.240
2	−1541494.490
3	−1540546.388
4	−1540544.932

Table 3 Total atomic charges of thiophene derivatives[a]

	Derivative			
Atom	1	2	3	4
1 S	0.395509	0.890940	0.363064	0.363736
2 C	−0.473563	−0.528244	−0.468221	−0.152381
3 C	−0.051790	−0.008051	−0.045442	−0.123106
4 C	−0.236226	−0.142905	−0.290425	−0.216387
5 C	−0.461390	−0.518705	−0.149354	−0.464442
2 H	0.257716	0.351469	0.263186	
4 H	0.245386	0.352820	0.255502	0.251127
5 H	0.261942	0.358035		0.266175

[a]



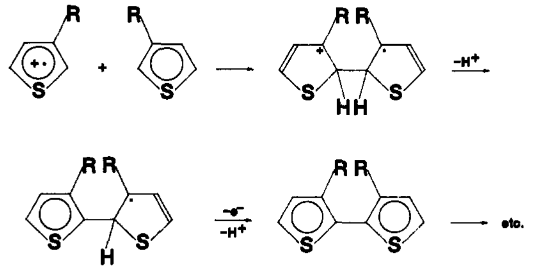


Figure 7 Radical cation mechanism

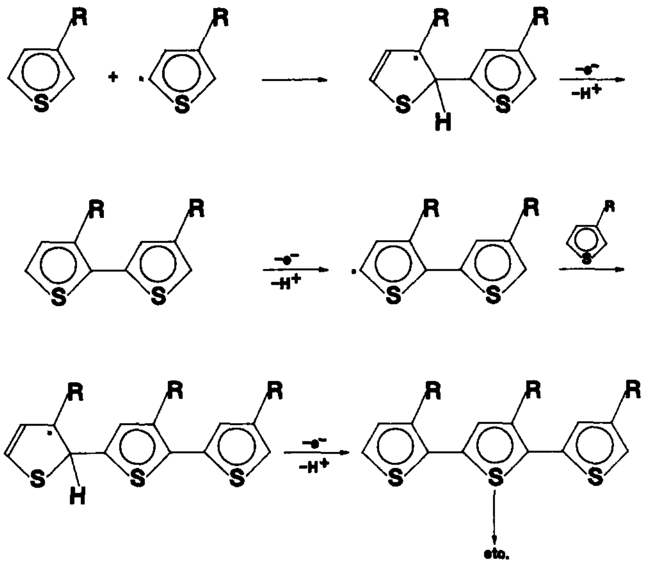


Figure 8 Radical mechanism

the radical cation is formed, will directly capture a proton from the radical cation forming a neutral HCl molecule.

CONCLUSIONS

We found that FeCl$_3$ must be solid to be active as a polymerization oxidant for 3-alkylthiophenes. The soluble part of FeCl$_3$ seems to be inert. The solubility of FeCl$_3$ in chloroform and the consuming effect of evolved HCl gas explain the extra portion of FeCl$_3$ that is needed initially to get high conversion in polymerization.

The role of FeCl$_3$ in the polymerization synthesis is described and a feasible polymerization mechanism for 3-alkylthiophenes was developed on the basis of quantum chemical computations of thiophene derivatives. The polymerization is proposed to proceed through a radical mechanism rather than a radical cation mechanism, because the polymer produced by the former mechanism will have fewer regio-irregularities than the polymer produced by the latter mechanism.

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REFERENCES

1 Sato, M., Tanaka, S. and Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* 1986, 873
2 Jen, K. Y., Miller, G. G. and Elsembaumer, R. L. *J. Chem. Soc., Chem. Commun.* 1986, 1346
3 Österholm, J.-E., Laakso, J., Nyholm, P., Isotalo, H., Stubb, H., Inganäs, O. and Salaneck, W. R. *Synth. Met.* 1989, **28**, C435
4 Leclerc, M., Diaz, F. M. and Wegner, G. *Makromol. Chem.* 1989, **190**, 3105
5 Sugimoto, R., Takeda, S., Gu, H. B. and Yoshino, K. *Chem. Express* 1986, **1**, 635
6 Friedman, H. L. *J. Am. Chem. Soc.* 1952, **74**, 5
7 Wooster, N. *Zeit. Kristallog.* 1932, **83**, 35
8 Motherwell, W. D. S. and Clegg, W. 'PLUTO 78', University of Cambridge, 1978
9 Pearson, W. B. Structure Reports Vol. 27 for 1962, A. Oosthoek's Uitgeversmaaschappij N. V., Utrecht, 1971, p. 440
10 Kossmehl, G. *Makromol. Chem., Macromol. Symp.* 1986, **4**, 45
11 Kossmehl, G. and Chatzitheodorou, G. *Makromol. Chem., Rapid Commun.* 1981, **2**, 551
12 Hotta, S., Soga, M. and Sonoda, N. *Synth. Met.* 1988, **26**, 267
13 Vertes, A., Nagy-Czako, I. and Burger, K. *J. Phys. Chem.* 1978, **82**, 1469
14 Frisch, M. J., Head-Gordon, M., Schlegel, H. B., Raghavachari, K., Binkley, J. S., Gonzalez, C., Defrees, D. J., Fox, D. J., Whiteside, R. A., Seeger, R., Melius, C. F., Baker, J., Martin, R. L., Kahn, L. R., Stewart, J. J. P., Fluder, E. M., Topiol, S. and Pople, J. A. 'Gaussian 88', Gaussian Inc., Pittsburgh, 1988