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Effects of CoCl_2 and other Additives on the Oxidative Chemical Synthesis and Properties of Poly(3-hexylthiophene)

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SUMMARY

The chemical oxidative polymerisation of 3-hexylthiophene (3HT) by FeCl_3 and the effects of reaction modifiers on the properties of the resulting polymer (P3HT) have been investigated. The process of polymerisation was identified using inhibitors that each affected one possible reaction mechanism. Gel permeation chromatography (GPC), UV-visible spectroscopy and proton nmr spectroscopy were employed to investigate the effects of the organic inhibitors and of added cobalt (II) chloride. Polymerisation appeared to proceed by two different mechanisms, one of which was strongly inhibited by cobalt chloride, whilst the other was favoured. CoCl_2 was found to increase the molecular weight of the polymer substantially, and to make it more regioregular. As a result, the electronic conductivity of lightly iodine-doped P3HT was also enhanced.

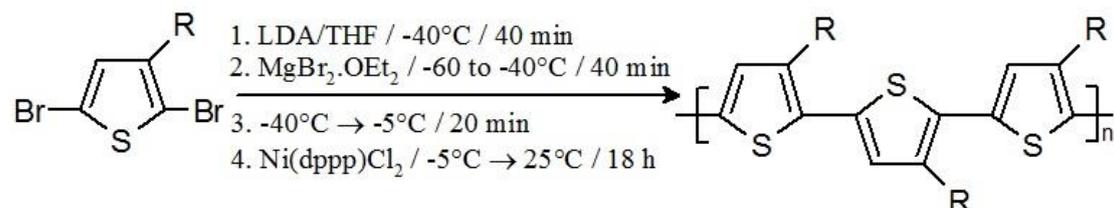
Keywords: Conducting polymers; poly(3-hexylthiophene); oxidative polymerisation;

1. INTRODUCTION

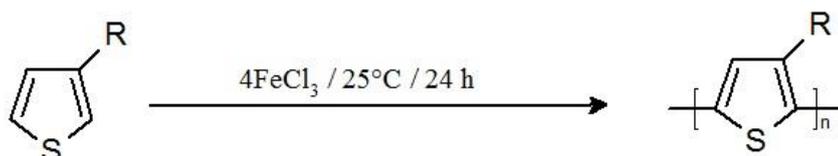
Poly(3-alkylthiophene)s (P3AT) are of great commercial and scientific interest because of their electrical conductivity, stability in air and processability¹. These applications all depend to some extent on the polymer being regioregular with respect to head-to-tail (HT) linkages. Other linkages give rise to steric hindrance and twisting of the backbone, causing a loss of conjugation².

Scheme 1:

Organometallic Polymerisation



Oxidative Chemical Polymerisation



Several general methods (such as those shown in Scheme 1) are available for the synthesis of P3ATs³. These include organometallic coupling, which produces highly regioregular polymer⁴, but involves expensive multi-step synthesis; electrochemical polymerisation which produces comparatively irregular polymer of low-to-medium molecular weight⁵; and oxidative chemical polymerisation which produces relatively high molecular weight polymer using cheap chemicals such as FeCl₃ in a one-step process⁶. The final method is a more commercially viable option for the mass production of P3AT, and is the subject of the present work. The product, whilst being more regioregular than electrochemically-synthesised polymer, is much less regioregular than those made by organometallic coupling, and is not generally suitable for applications in optoelectronics. For reactions initiated by FeCl₃ in particular, the effects of experimental variables on the properties of P3AT have been studied⁷, and this initiator has been found to give a largely regioregular polymerisation of 3-(4-octylphenyl)thiophene⁸. It has been reported that the polymerisation of 3-hexylthiophene by FeCl₃, with the addition of a small amount of a nickel (II) catalyst, resulted in a more regular polymer⁹; however, the mechanism for this process was not studied. Other workers studying the oxidative polymerisation of thiophene derivatives have used catalysts based on vanadium acetylacetonate¹⁰ or mixtures of palladium and copper acetates with trifluoroacetic acid¹¹.

We have observed a very beneficial effect from the use of catalytic amounts of cobalt (II) chloride with FeCl₃ to polymerise thiophenes under appropriate conditions:

the mechanism of polymerisation of 3-hexylthiophene and the influence of cobalt (II) chloride on the mechanism, polymer structure and properties, are the subject of this paper.

2. EXPERIMENTAL

2.1. Monomer Synthesis

(All the chemicals used were obtained from Sigma-Aldrich.) The monomer, 3-hexylthiophene, was prepared by reacting 3-bromothiophene with hexylmagnesium bromide catalysed by nickel bis[(diphenylphosphino)propane]nickel(II) chloride, as described by Tamao *et al*¹². Typical yields of about 75% were achieved. The monomer was characterised by GC-MS, ¹H nmr and infrared spectroscopy, and was found to be 100% pure after vacuum distillation (80° C; 0.5 mmHg).

ν_{\max} (liquid film, NaCl/cm⁻¹ 2956s, 2927s (alkane CH), 1465m (thiophene), 1409w, 1378w (alkane CH), 771s (thiophene); δ_{H} (300 MHz, CDCl₃), 0.99 - 1.04 (3H, t), 1.33 - 1.51 (6H, m), 1.69 - 1.79 (2H, m), 2.71 - 2.76 (2H, t), [7.00 (s), 7.02 - 7.03 (d of d), 7.30 - 7.32 (d of d)]3H; δ_{D} (300MHz, CDCl₃), 14.2, 22.7, 29.1, 30.5, 31.8, 77.1, 119.8, 125.1, 128.3, 143.3; m/z (GC-MS) (M⁺ 168); C₁₀H₁₆S requires 168), 139, 125, 111, 98 (100), 85, 84, 69, 53, 45 and 41.

2.2. Polymerisation

Polymerisation was performed using anhydrous iron (III) chloride as an oxidising agent¹³. All glassware was dried in an oven overnight prior to use. The monomer (0.84 g) was then dissolved in chloroform (50 mL). Any additives that were being tested were added at this stage. The chloroform mixture was degassed with nitrogen for about 5 min. This solution was added to another stoppered conical flask with anhydrous FeCl₃ (1.62g) and chloroform (50 mL) to form a slurry, and the reaction mixture was stirred for 24 h. It was then added to methanol (100 mL) to precipitate the polymer, which was vacuum-filtered, collected and redissolved in chloroform (50 mL). The solution of P3HT was dedoped by refluxing with 15%

aqueous ammonia solution (50 ml) and then extracted with 0.1M aqueous disodium ethylenediaminetetra-acetate solution (50 mL). (The insoluble portion of the polymer product was separated from the reaction mixture and Soxhlet-extracted with chloroform to recover any remaining soluble component, which was added to the rest of the polymer solution.) The insoluble polymer was then Soxhletted with methanol to remove the residual iron chloride. The polymer was precipitated out using methanol (100 mL) and filtered. It was then purified by Soxhletting it with methanol until the methanol from the Soxhlet thimble was a clear colourless liquid and remained so after extracting the polymer for about 12 h. The additives used (individually) were as follows:-

Anhydrous cobalt chloride (2-10 mmol)

Phenol (10 mmol)

Benzoquinone (10 mmol)

2.3. Measurement

Gel Permeation Chromatography (GPC) was performed on 2 gL⁻¹ polymer solutions in THF using a Polymer Labs GPEL GPC column packed with Plgel[®] 10 µm MiniMIX-B gel, with a Waters 490 diode array detector and a Waters 600 pump. The GPC was calibrated using regioregular P3HT (Sigma-Aldrich), and toluene (0.1%) was used as an internal standard.

Conductivity measurement was done by van der Pauw's four point probe method¹⁴. The polymer was lightly doped with iodine vapour by leaving it in an open-topped container in a closed desiccator containing iodine crystals for 24 h. Polymer pellets were then pressed and they were replaced in the iodine vapour for a further 24 h.

¹H nmr spectroscopy was performed on polymer sampled dissolved in deuterated chloroform on a Bruker AC300 (¹H: 300 MHz) spectrometer.

UV-Visible spectroscopic analysis was carried out on thin films cast from polymer solutions in chloroform onto borosilicate glass slide covers. The films were scanned

between 800 and 300 nm using a Cary 100 UV-visible spectrophotometer.

The concentration of residual cobalt in the polymer was determined by ashing at 700 °C, dissolution of the residue in aqua regia and analysis by inductively-coupled plasma-atomic emission spectroscopy.

3. RESULTS AND DISCUSSION

3.1. The Effects of Inhibitors

P3HT was synthesised via chemical oxidation with and without various inhibitors to identify the main mechanisms of polymerisation. The reactions were carried out with additives such as phenol (a nucleophile), benzoquinone (a radical scavenger) and with no inhibitor. The polymers formed were analysed by GPC, and the traces are shown in Figures 1 to 3.

Figure 1. Molecular weight distribution of P3HT, not inhibited.

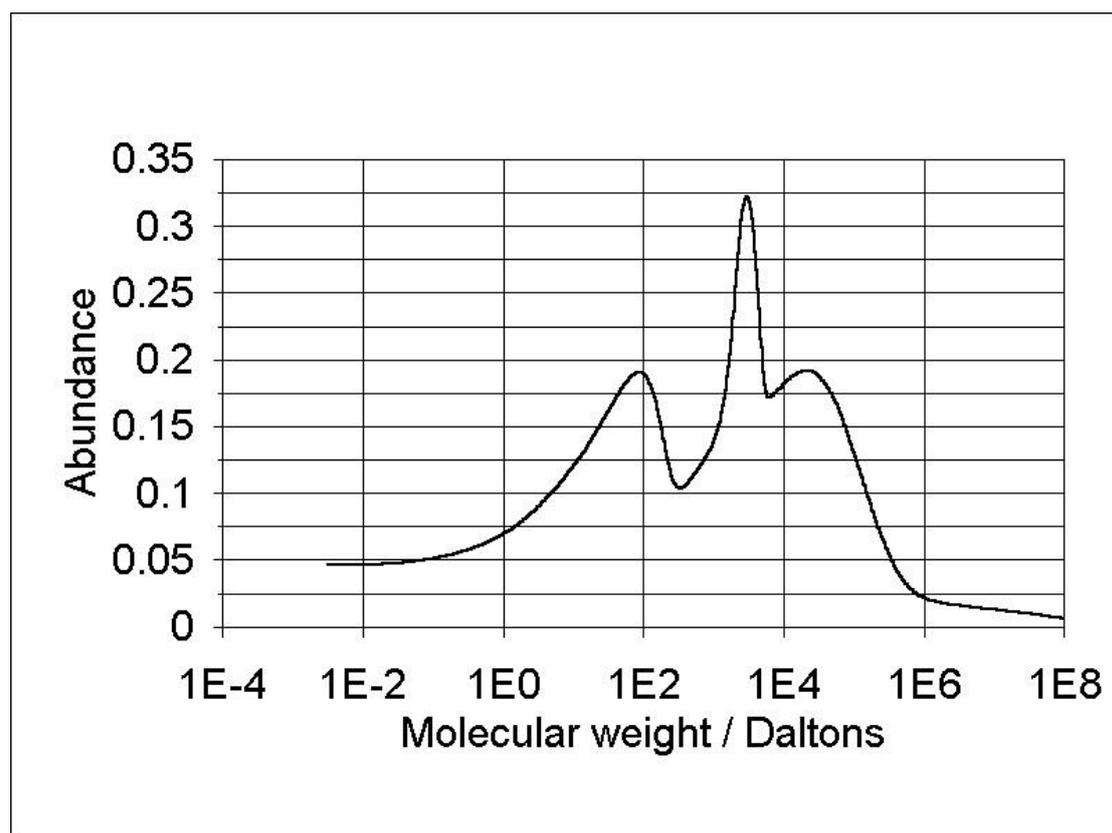


Figure 2. Molecular weight distribution of P3HT inhibited with phenol.

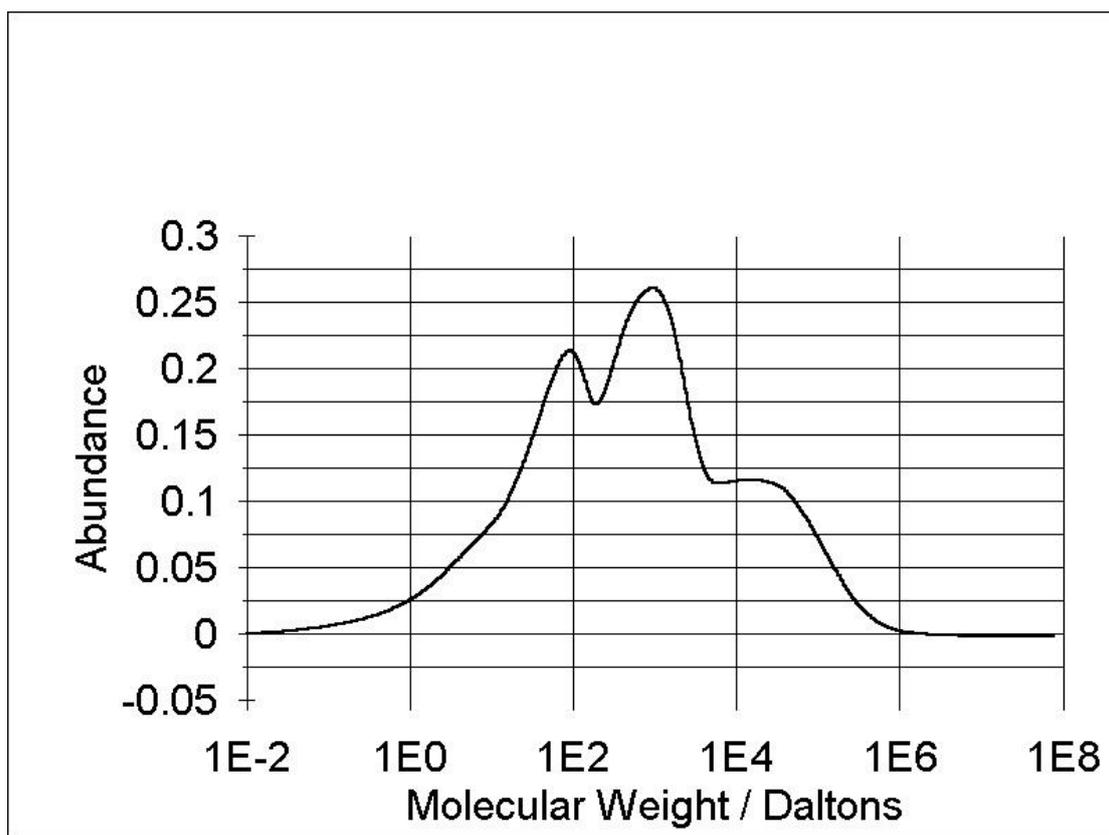


Figure 3. Molecular weight distribution of P3HT inhibited with benzoquinone.

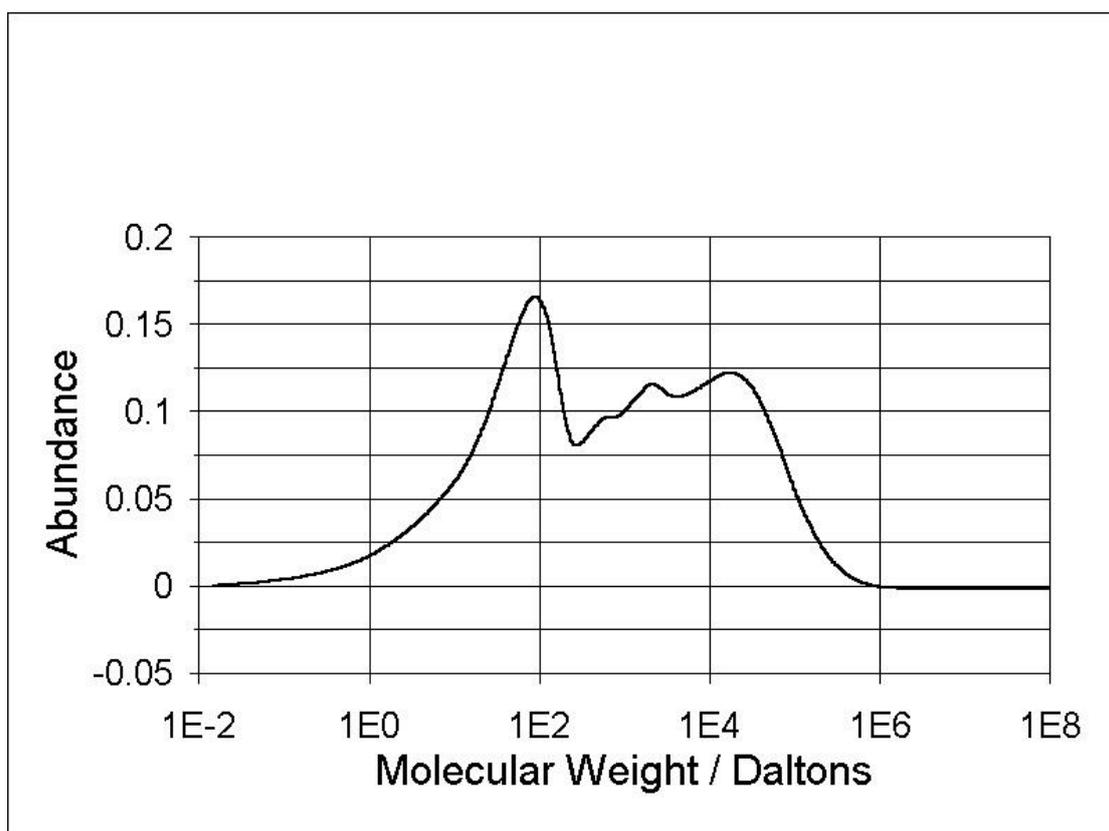
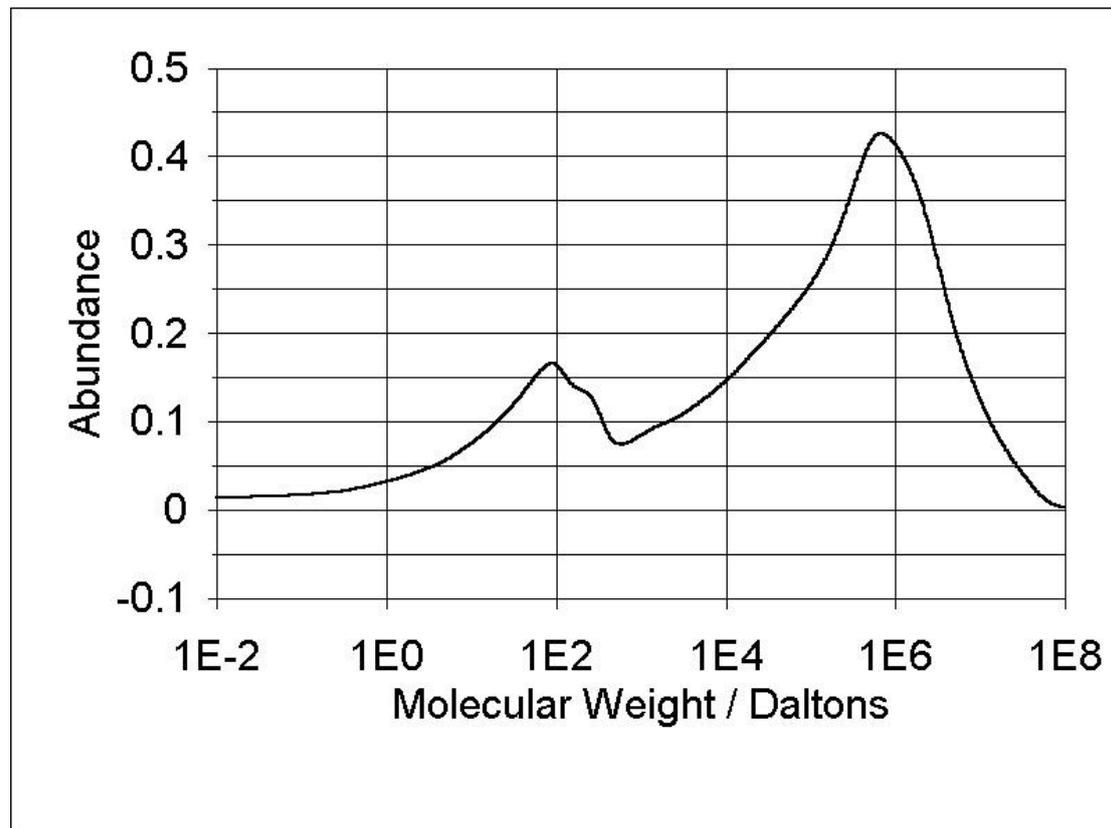


Figure 1 shows the molecular weight distribution of P3HT without any inhibitors. There are two main polymer peaks (the third peak at just under 100 Daltons is the toluene internal standard). This suggests that two reaction mechanisms were involved in the polymerisation. When a nucleophile such as phenol was added (Figure 2) the higher molecular weight peak was reduced, suggesting that the mechanism for this peak was cationic in nature. Figure 3 shows that benzoquinone had the opposite effect, suggesting that the lower molecular weight peak was the result of a radical chain mechanism.

To study the effect of cobalt chloride on the polymerisation, P3HT was synthesised with the addition of CoCl_2 at 10% of the monomer concentration. The polymer produced was analysed by GPC, as shown in Figure 4.

Figure 4. Molecular weight distribution of P3HT made with $10 \text{ mmol dm}^{-3} \text{ CoCl}_2$ in the reaction mixture.

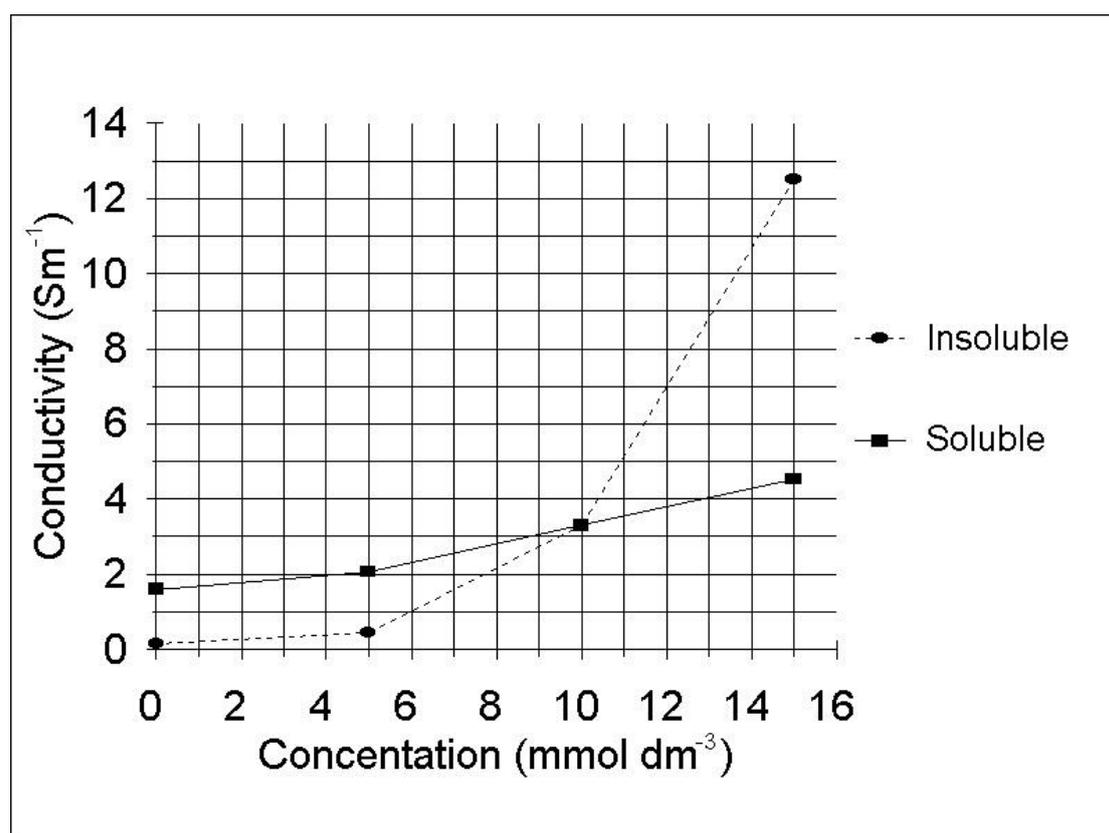


Only the higher molecular weight peak is now present, and this peak also appears

at a higher molecular weight than that of the polymer made without cobalt (II) chloride. This suggests that CoCl_2 is an effective radical scavenger, and that the cationic mechanism is aided by it.

Samples of P3HT were synthesised with a range of concentrations of cobalt chloride, from 2 to 10 mmol dm^{-3} . These were lightly doped with saturated I_2 vapour at 20°C (ca. 0.3 mm Hg), then they were pressed into pellets and their conductivities were measured.

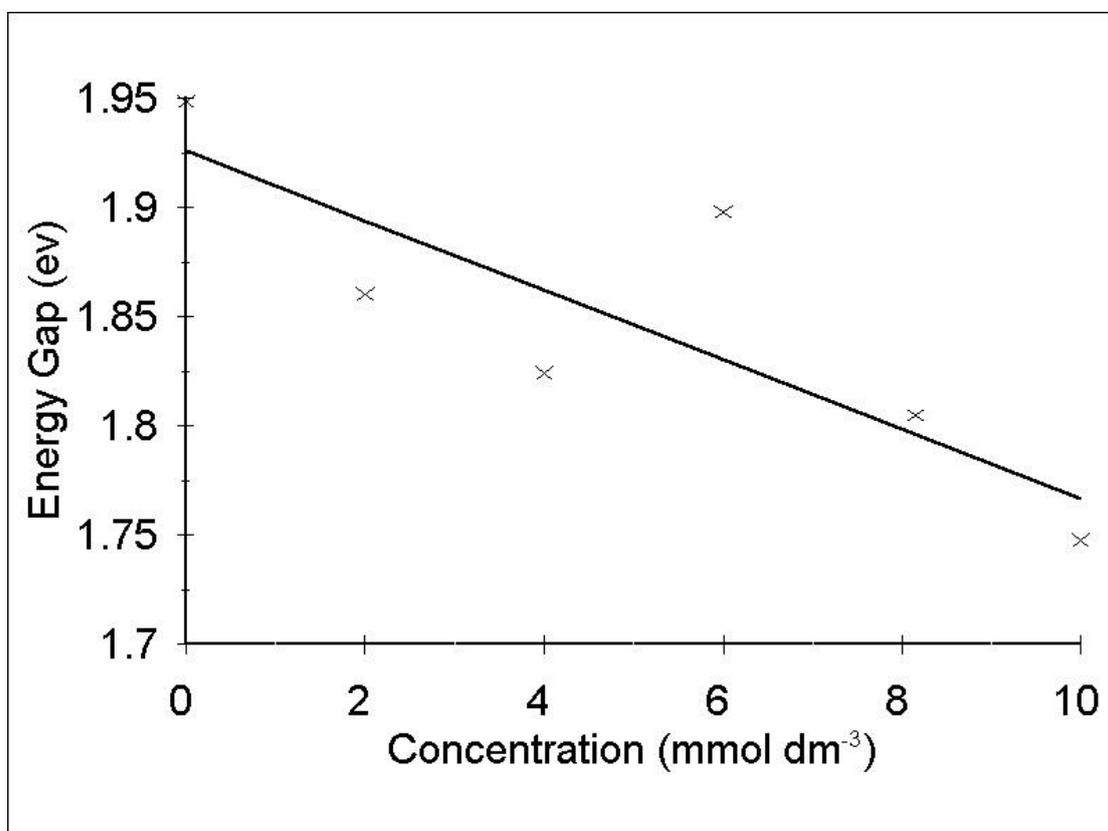
Figure 5. Variation of conductivity of P3HT with concentration of CoCl_2



The general trend was an increase in conductivity with concentration of cobalt chloride. (The concentration of residual cobalt was negligible, being below the limit of detection by ICP.). This suggests that the polymer was either more regioregular and/or had a higher molecular weight. The existence of greater regioregularity (and hence more effective chain conjugation) was further supported by UV-visible spectroscopy of thin films of these polymer samples. The fundamental band-gaps were calculated from the onset of the lowest-energy absorption in the UV-visible

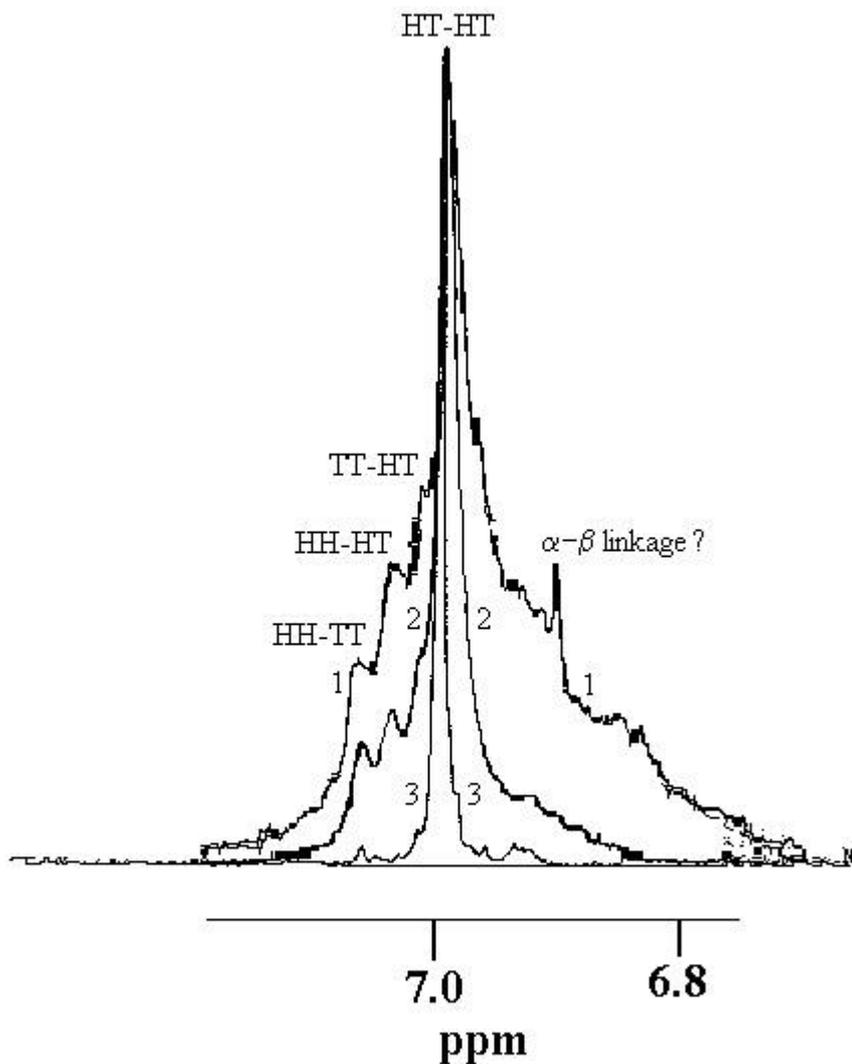
spectra, and the values are shown in Figure 6. (It should be noted that this method probably under-estimated the true semiconducting band-gap slightly, but a trend of decreasing interband energy with increasing CoCl_2 concentration appears to be established.)

Figure 6. The variation of band gap versus concentration of CoCl_2 .



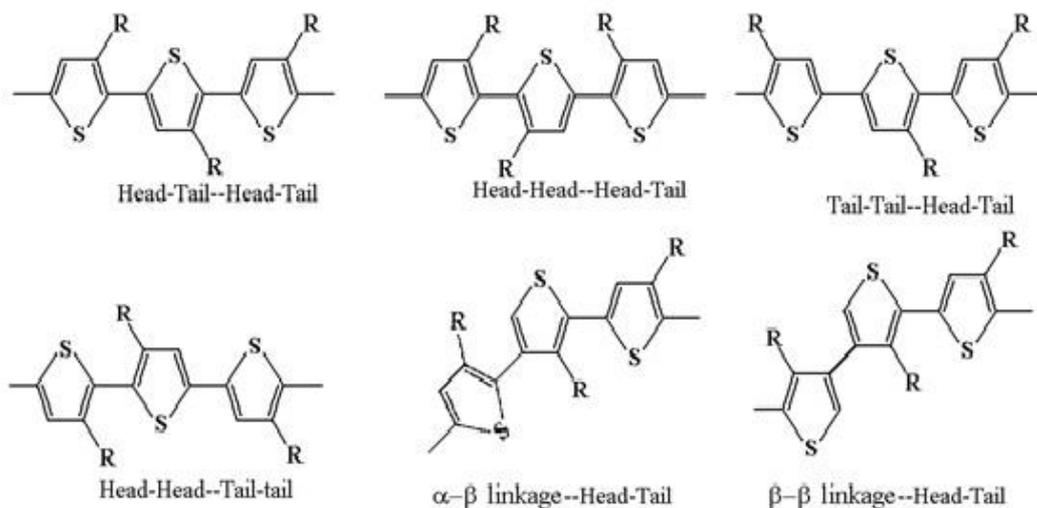
The question of whether cobalt was promoting the regioregularity of the P3HT was more directly investigated by ^1H nmr spectroscopy. The aromatic peak relating to the α -hydrogen has slight variations in chemical shift, depending on the regioisomer. Nmr spectra were run of polymers made with and without CoCl_2 , as well as a commercially-supplied regioregular sample (Sigma-Aldrich).

Figure 7. ^1H nmr spectra of P3HT showing the aromatic proton resonance, with the slight variations in chemical shift due to the different regioisomers. (Curve 1: no catalyst; Curve 2: with 5 mmol dm^{-3} CoCl_2 ; Curve 3: commercial regioregular polymer.)



The possible regioisomers and structural defects that may be present on the polymer chains are depicted in Scheme 2, and the corresponding assignments are marked on the spectra in Figure 7.

Scheme 2:



Whilst not being as regioregular as the commercial polymer, the cobalt chloride-catalysed polymer was significantly more regioregular than the one made without a catalyst.

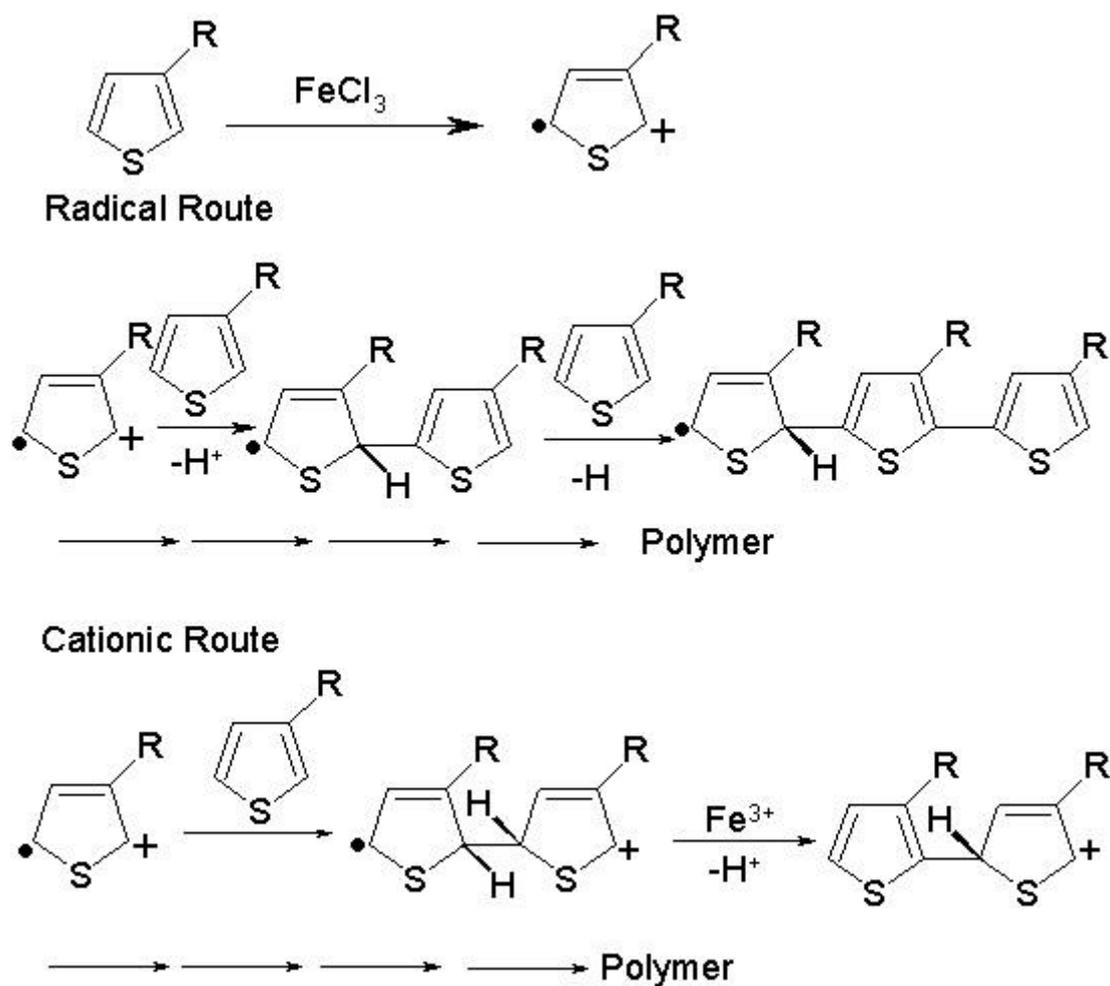
The main observations in this work are that:

1. Nucleophiles hinder the mechanism that produces higher molecular weight polymer. GPC analysis shows that radical scavengers hinder formation of the lower molecular weight polymer.
2. The addition of CoCl_2 causes an increase in the proportion and the molecular weight of the higher molecular weight polymer.
3. The absolute amount of the low molecular weight polymer is reduced by the presence of the metal halide.
4. The polymer produced with CoCl_2 present is more HT-HT regioisomerically pure as shown by ^1H nmr, an increase in the polymer's conductivity and a decrease in the band-gap with concentration of metal cations.

From the gathered evidence, the following can be deduced:

1. Polymerisation occurs by two mechanistic routes, a cationic and a radical one, such as those shown in Figure 8.

Figure 8. Reaction mechanisms for the polymerisation of 3-ATs.



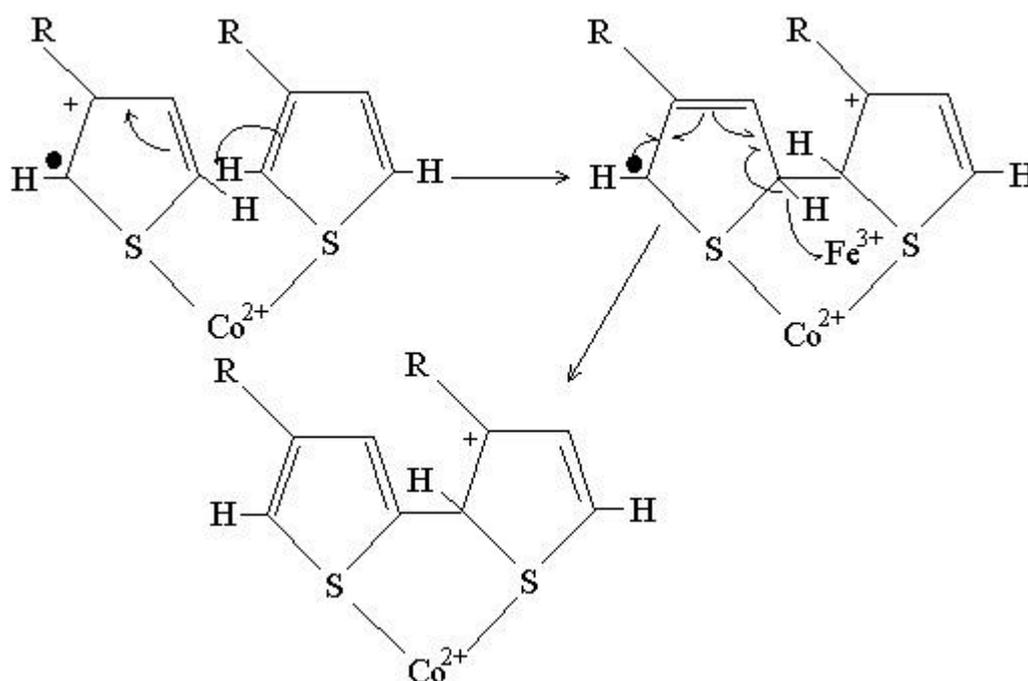
2. The cationic route produces polymer of higher molecular weight than the radical one.
3. The radical mechanism is retarded by CoCl_2 (probably via the metal cation acting as a radical scavenger). It seems likely that the unpaired d-electrons of the metal could readily pair up with the unpaired radical electron, inhibiting further reaction.

The complexation of the thiophene units to Co^{2+} cations may help to align them in the

correct position for the formation of regiospecific HT-HT polymer better than the complexation to FeCl_3 .

We propose that the metal cations hold two or more thiophenes in a favourable position for a cationic reaction, such as that shown in Figure 9.

Figure 9. Metal cation-assisted polymerisation of 3-alkylthiophene.



It should be noted that a purely radical coupling reaction would probably tend to create TT regioisomer which, due to steric hindrance, would be less reactive.

For comparison, a limited study has been made of the effects of the same additives but using electrochemical polymerisation, and to date, it has shown the same trends as for the chemical polymerisation by FeCl_3 .

4. CONCLUSIONS

The chemical oxidative route for synthesis of poly(3-alkylthiophenes) has been studied, as was the effect of cobalt (II) chloride on the reaction and on the polymer properties. It was found that the polymerisation proceeded by two competing routes,

one apparently being a radical mechanism and the other cationic. The cationic pathway produced higher molecular weight polymer than the radical one.

The addition of cobalt (II) chloride inhibited the radical mechanism and catalysed the cationic one. It also caused the polymer product to be significantly more regioregular. This was found to have positive effects on the properties of the polymer, and these could probably be enhanced further by thermal annealing¹⁵, to optimise the molecular organisation and crystallinity for practical applications such as organic electronics.

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