

## Annealing behaviour of conductive poly(3-hexylthiophene) films

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We demonstrate that annealing conductive, solvent-cast poly(3-hexylthiophene) (P3HT) films under reduced vacuum improved their structural properties and induced higher conductivity. These preliminary results suggest that thermal processing of conductive polymers may be a useful step in their future device fabrication. © 1997 Elsevier Science Ltd. All rights reserved.

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### Introduction

Applications for semiconducting polymeric materials include their use in transistor, diode, optoelectronic and photovoltaic devices<sup>1</sup>. However, the results published for these experimental devices have been disappointing. The poor device characteristics have been explained by the material's high degree of amorphicity and large trap concentration<sup>2</sup>. These materials properties determine low charge carrier mobilities. The devices fabricated utilizing these materials showed rectifying polymer-metal junctions having poor thermionic theory fitting<sup>2</sup> and photovoltaic and photoconductive devices with small, inefficient output voltages<sup>3</sup> and currents<sup>4</sup> respectively.

Several authors have tried different techniques to overcome the poor structural ordering that occurs within conjugated conducting polymers. Anisotropic stretching of conducting polymer films and fibres has been observed to improve conjugated chain alignment in the stretch direction, and enhance conductivity values<sup>5</sup>. Mo *et al.*<sup>6</sup> reported that high temperature (380°C) annealing improved the degree of crystallinity of powdered, iodine doped polythiophene.

More recently the effect of these deficiencies has been reduced by materials and device development. Conducting polymers now show great promise as the active elements within electroluminescent devices<sup>7</sup> and light responsive devices<sup>8</sup>. Garnier *et al.*<sup>9</sup> have reported work on organic thin film FET transistors utilizing highly ordered vacuum deposited thiophene oligomers. These efficient devices possess characteristics close to those based upon amorphous silicon.

In this work we report improved structural properties of conductive poly(3-hexylthiophene) solvent-cast films after annealing them at 150°C in a partially evacuated ampoule. The heat-treatment of undoped solvent cast P3HT film also enhanced the materials conductivity.

### Experimental

Our preparation and characterization of very lightly doped P3HT film have been described earlier<sup>10</sup>. Solvent-cast films were fabricated by the evaporation of P3HT-chloroform solution (1 g l<sup>-1</sup>) on thoroughly cleaned glass microscope slides. The resulting film thickness depended upon the number of times this process was repeated, typically < 5 μm for visible absorption spectroscopy samples and up to 30–40 μm for X-ray and conductivity specimens. The films were found to contain a residual 0.4 at% of Fe from the polymerization reaction.

The van der Pauw conductivity<sup>11</sup>, X-ray diffraction and reflection FTi.r. and visible absorption spectra were recorded before the glass mounted P3HT film was loaded into a clean borosilicate glass ampoule and evacuated to approximately 10<sup>-5</sup> Torr before being sealed. The ampoule was placed in an oven and the temperature raised carefully up to ~ 150°C. The annealing process lasted for between 48 and 67 h before the oven was cooled to ambient temperature at about 1°C min<sup>-1</sup>. X-ray diffraction, reflection FTi.r. and visible spectroscopy were repeated on the same, but now annealed samples, while the conductivity measurements were made on previously unmeasured annealed P3HT film cut from the same large film as the untreated samples.

### Results

The reflection FTi.r. spectrum of annealed P3HT films showed no significant difference to that of untreated P3HT film. We were particularly concerned about the formation of carbon-oxygen bonds, which would have indicated some degradation of the conjugated P3HT chains. This observation is consistent with earlier thermal analysis indications that P3HT is stable up to about 250°C in air, and even higher temperature under a nitrogen atmosphere<sup>10</sup>. The average room temperature van der Pauw conductivity was measured as 4.2 × 10<sup>-5</sup> S cm<sup>-1</sup> before the annealing process and 12.8 × 10<sup>-5</sup> S cm<sup>-1</sup> after.

Assuming a direct-allowed band-band transition<sup>12</sup>, the semiconducting band gap of P3HT film was determined as 2.14 eV from the absorption edge of the

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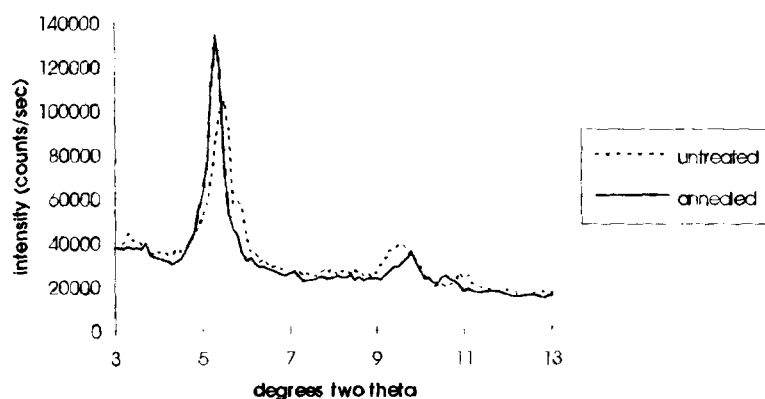


Figure 1 X-ray diffraction pattern of untreated and annealed P3HT film

Table 1 X-ray diffraction data for untreated and annealed P3HT film

	Peak ( $2\theta$ )		$d$ (Å)		$D$ (Å)	
	Before	After	Before	After	Before	After
Film 1	5.45	5.35	16.22	16.52	256.8	318.6
	10.9	10.6	8.11	8.35		
Film 2	5.45	5.3	16.22	16.67	261.0	318.4
	11.1	10.6	7.97	8.35		
Film 3	5.45	5.35	16.22	16.52	244.9	379.0
	11.0	10.6	8.04	8.35		
Film 4	5.4	5.3	16.37	16.67	346.1	397.9
	10.8	10.6	8.19	8.35		
Film 5	5.5	5.3	16.07	16.67	234.1	370.2
	11.0	10.65	8.04	8.31		

visible spectrum. This value is consistent with published work on polythiophene and its derivatives<sup>13</sup>. Upon annealing the band-gap was found to decrease to 2.08 eV.

The X-ray diffraction pattern of P3HT film before and after annealing is shown for angles between 3 and 13 degrees  $2\theta$  in Figure 1. The rest of the X-ray diffraction spectrum was dominated by a broad amorphous hump and is not shown. Upon close inspection, the peaks observed at 5.45 and 10.9 degrees  $2\theta$  move to slightly lower angles (larger  $d$ -spacings) after heat-treatment. These diffraction peaks also become much sharper. The diffraction peak at about 9.7 degrees  $2\theta$  is a machine fault.

The crystallite size was estimated by applying the Scherrer equation (i), where  $D$  is the crystallite size (Å),  $\lambda$  is the radiation wavelength (1.5418 Å) and  $\beta$  is the peak width at half maximum peak height (in radians), to the 5.45 degrees  $2\theta$  peak. The results are tabulated in Table 1, and show that annealing increases the crystallite size.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (i)$$

### Discussion

The aim of this work was to find a way of improving the mobility of the charge carrier (polarons and/or bipolarons) along the polymer conjugated chain. This requires the formation of more perfectly aligned conjugated polymer chains in which more efficient carbon  $2p$  orbital overlap occurs and less defect sites for polaron trapping and/or annihilation exist.

The conductivity ( $\sigma$ ) of a material is given by equation (ii),

$$\sigma = ne\mu \quad (ii)$$

where  $n$  is the number of charge carriers,  $e$  the electron charge and  $\mu$  the charge carrier mobility. Assuming that the unintentionally present Fe doping agent remains in the same chemical state during the annealing process (i.e. the number of charge carriers remains constant), then it is possible to believe that the measured increase in conductivity is due to improved charge carrier mobility.

If it is assumed that each Fe atom is electrically active as an acceptor, then the concentration of acceptors ( $n$ ) can be estimated as  $2 \times 10^{19} \text{ cm}^{-3}$  from

$$\text{acceptors per cm}^3 = \frac{4 \times 10^3 \times \rho \times N_{AV}}{M_W}$$

where  $\rho$  is the density of P3HT ( $1.10 \text{ g cm}^{-3}$ ),  $N_{AV}$  is Avogadro's number and  $M_W$  is the relative molecular mass of 3-hexylthiophene monomer. Inserting this value of  $n$  into (ii) gives a room temperature charge carrier mobility of about  $1.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is consistent with values determined for undoped P3HT films by Assadi *et al.*<sup>15</sup>. The charge carrier mobility of annealed P3HT film can be estimated from (ii) as about three times faster than for untreated P3HT film.

The small decrease in band gap of P3HT film after the annealing process suggests that the conjugated sequences have been more efficiently aligned. Using band-gap data determined for oligothiophenes of 3, 4, and 5 monomer units an estimate of the effective chain conjugation length ( $l$ ) can be calculated by extrapolating a graph of  $(1-2)^{1/3}$  vs observed band-gap energy<sup>16</sup>. The average effective conjugation length estimated for untreated P3HT film (band-gap = 2.14 eV) was 11.1 monomer units. This is much smaller than the average polymer chain length (about 130-220 monomer units)<sup>12</sup>. Upon annealing P3HT film (band-gap = 2.08 eV, the average effective conjugation length increases very slightly to 12 monomer units. The improved alignment of the conjugated polymer chain would result in a higher charge carrier mobility.

The two peaks observed on the X-ray diffraction pattern of untreated P3HT film occurred at 5.45 and 10.9 degrees  $2\theta$ , and since their angles are of the ratio 1:2 it suggests the reflections originate from a family of planes. The  $d$ -spacings were determined as 16.2 Å and 8.1 Å, respectively, using the Bragg equation.

The structure of polythiophene and its derivatives is not fully established despite a number of published studies<sup>6,14,17,18</sup>. It has been reported that poly(3-alkylthiophenes) have an almost planar chain with interplanar distance of 3.8 Å, and an interchain distance

which is dependent on the alkyl chain length<sup>14</sup>. The interchain distance of stretch oriented P3HT has been given as 16.8 Å<sup>14</sup> and is comparable to the value determined in this work. The *d*-spacing of annealed P3HT film was about 0.3 Å larger than that determined for untreated P3HT film.

The X-ray diffraction data (*Table 1*) also suggests that microstructural alignment of P3HT has occurred during the annealing process, as the average crystallite size became larger for each P3HT film after heat-treatment. However, one would expect that upon improved microstructural properties the *d*-spacings would decrease as the chains moved into a more perfect and relaxed conformation. The data summarized in *Table 1* proposes that the polymer chains move approximately 0.3 Å apart after heat-treatment. Mo *et al.*<sup>6</sup> have observed a smaller but similar trend for heat-treated polythiophene powder.

### Conclusion

We have shown that electrical conduction in undoped P3HT film can be enhanced upon annealing under reduced vacuum. This exciting feature may result from an improvement in the alignment of the conjugated straight chain sequences, which would induce more efficient carbon 2*p* orbital overlap and increase the mobility of the charge carriers. This suggests that annealing should be one of the process steps in the fabrication of conducting polymer devices.

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