

The effect of molecular weight and crystallinity on the conductivity of a conducting polymer

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Recent theories have related the molecular-weight dependence of the conductivity of a conjugated polymer to the relative importance of interchain and intrachain charge transport processes. This prompted an experimental search for this effect using a series of fractionated poly(3-octylthiophenes). No significant molecular-weight dependence was found over the range $30\,000 \leq M_w \leq 400\,000$, indicating that interchain transport does not limit the macroscopic conductivity of these samples. However, even small differences in the degree of crystallinity among the polymer samples were determined to have a profound effect on the conductivity.

(Keywords: conducting polymer; conductivity; crystallinity; molecular weight; poly(3-octylthiophene))

INTRODUCTION

In order for a conducting polymer to attain an electrically conducting state it must first be doped with a chemical agent that either donates electrons or, more typically, withdraws electrons from the macromolecule. This process creates the charge carriers that support conductivity and results in a delocalization of electrons along the polymer backbone. However, conductivity on a macroscopic length scale must involve not only charge transport along the polymer chain (intrachain transport) but charge 'hopping' from the polymer to neighbouring molecules (interchain transport) as well.

Charge transport by these two mechanisms can be modelled by two characteristic times: the mean lifetime of a charge carrier on an individual polymer chain, τ_c , and the time that would be required to completely explore the polymer chain, τ_i . While τ_c is considered an intrinsic characteristic of the polymer, the magnitude of τ_i is a function of molecular weight. In the limit of $\tau_c \gg \tau_i$, the conductivity of random-coil polymers is limited by interchain hopping and will be a linearly increasing function of molecular weight given by:

$$\sigma \propto \frac{ne^2 aL}{kT \tau_c} \quad (1)$$

Here L is the length of the polymer and is proportional to the molecular weight, a is the persistence length of the chain, n is the charge carrier density and e is the charge per carrier. However, the opposite limit of $\tau_c \ll \tau_i$ will be approached by sufficiently high-molecular-weight polymers, for which the conductivity is independent of

molecular weight:

$$\sigma \propto \frac{ne^2}{kT} a \left(\frac{D_i}{\tau_c} \right)^{1/2} \quad (2)$$

Here $D_i \propto L^2/\tau_i$ is the diffusion coefficient for the charge carriers along the chain and is independent of L . A more complete development of these arguments is presented in refs. 1–3.

The following experimental work was undertaken to determine whether a molecular-weight dependence of the conductivity is observed, and thus to infer the relative importance of interchain *versus* intrachain charge transport. Preliminary experiments were performed on poly(3-octylthiophene) (P3OT) films of varying molecular weight that had been prepared and doped under uniform conditions. The results were somewhat surprising, since they did not correspond to either of the theoretical limits described above: the conductivity was found to decrease with increasing molecular weight of the samples, even though a constant doping level was determined for all films.

Although we had been careful to prepare our samples under uniform conditions, we had not considered the possibility of varying crystallinity among the solution-cast P3OT films. Owing to their greater mobility, the lower-molecular-weight chains would be expected to crystallize to a greater extent than those of higher molecular weight. This led us to propose two possible mechanisms that would explain an inverse dependence of conductivity on molecular weight as a result of differing crystallinity:

(1) The ordered packing in the crystalline regions produces a high degree of local chain orientation, which

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is likely to result in higher conductivity^{3,4}. The dense packing may also reduce the energy required for interchain charge transport, also contributing to a conductivity increase.

(2) In the undoped state, the molecules are highly flexible and entangled with each other. When the polymer is doped, the chains need to extend if they are to establish delocalized π -orbitals, which facilitate conductivity⁴. The increased rigidity of poly(alkylthiophene) upon doping has been observed in dilute solution by neutron scattering⁵. In the bulk state, the polymer chains may be 'pinned' by crystallites or entanglements, which restrict their mobility. The chain ends, however, are free to achieve their optimum configuration, which enhances the conductivity. Because the lower-molecular-weight polymers have a higher proportion of material at the chain ends, they would have a higher conductivity.

Our first experiments were repeated and X-ray diffraction analysis was used to evaluate the crystallinity of our solution-cast films. In addition, a second set of films having a lower degree of crystallinity were prepared by heating above the melting point and quickly quenching below the glass transition temperature. The resulting conductivity of the less-crystalline films might be expected to increase or decrease, depending on which scenario proposed above is correct:

(1) If the conductivity is greater in the crystalline regions, the conductivity of the quenched films should be lower than in the solution-cast films.

(2) If the conductivity is suppressed by chain pinning, the quenched films should achieve a higher conductivity.

Once the effect of crystallinity on conductivity was established, it was also possible to determine the influence of molecular weight alone.

EXPERIMENTAL

Throughout the sample preparation, doping and conductivity measurements, all experimental conditions were maintained as uniform as possible among the five samples.

Materials

A series of different molecular-weight samples were fractionated from a single batch of poly(3-octylthiophene) by preparative gel permeation chromatography (g.p.c.). The unfractionated sample had a molecular weight of 94 000 as measured by g.p.c. calibrated with polystyrene standards and a polydispersity M_w/M_n of 2.9. The five fractions used in this study (shown in Table 1) had molecular weights ranging from 30 000 to 400 000, and similar polydispersities between 1.65 and 2.1. Further details of the characterization of P3OT will be described elsewhere⁶.

Table 1 Molecular-weight characterization of P3OT samples

Sample	M_w^a	M_w/M_n^b
1	390 000	2.07
2	197 000	1.74
3	105 000	1.65
4	54 200	1.71
5	32 500	2.04

^a By light scattering

^b By g.p.c. calibrated with polystyrene

Film preparation and doping

Thin films of each polymer fraction were prepared by pouring a chloroform solution ($c = 10 \text{ mg ml}^{-1}$) into flat glass dishes, followed by slow evaporation of the solvent in air for 4 h. The films were then dried completely under vacuum at room temperature. The resulting films were fairly transparent and appeared visually homogeneous and free of inclusions. Five narrow strips of constant width (ca. $0.2 \times 2 \text{ cm}^2$) were cut from each film for conductivity measurements. The strips were measured and weighed prior to doping. The thicknesses of all the films were $20 \pm 5 \mu\text{m}$.

A second set of films with reduced crystallinity was also prepared. A portion of each solution-cast film was placed between sheets of fluoropolymer film, sandwiched between two thin aluminium plates, and heated in a hot press at 200°C for 5 min. The sample was then removed and immediately placed in a cooling bath of dry ice in isopropanol. The quenched films were easily peeled from the fluoropolymer sheets and dried under vacuum. Multiple thicknesses of the lower-molecular-weight films were required in order that the thickness after melting was in the same $20 \pm 5 \mu\text{m}$ range as the solution-cast films. The experimental procedure then proceeded in the same manner as for the solution-cast films. X-ray measurements indicated that the crystallinity of quenched films held at room temperature remained constant for at least several days.

The polymer was doped using a 1.0 M solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in nitromethane. The films were placed in individual vials containing 3 ml of the dopant solution. After immersion for 1 h, the films were withdrawn and allowed to soak in pure nitromethane for 5 min in an effort to remove any dopant that was not incorporated by the polymer. The films were then rinsed in clean nitromethane and dried under vacuum at room temperature. The doped samples were reweighed to determine the amount of dopant uptake.

Conductivity measurement

The conductivity of polymer films was measured using the collinear four-point probe method⁷. The polymer film was fastened to wire contacts using conductive carbon paint (Structure Probe Inc.). The sample was then sealed in a flask, and a current was applied to the outer electrodes (Lake Shore Cryotronics 120 current source). The resulting voltage across the inner electrodes was recorded (Keithley 195A digital multimeter) after the flask had been evacuated under vacuum for 3 min. The conductivity of the sample was calculated according to the formula:

$$\sigma = Id/VA \quad (3)$$

where I is the applied current, d is the distance between the inner electrodes, V is the measured voltage and A is the cross-sectional area of the film. The average cross-sectional area of each film was determined gravimetrically from a sample of known length, using 1.20 g cm^{-3} as the density of doped P3OT⁸. The measured conductivity remained constant as the current density was varied over several decades (typically $0.02\text{--}20 \text{ A cm}^{-2}$).

Researchers⁹ have noted that there is an optimal doping time to achieve maximum conductivity in P3OT; the dopant requires a reasonable amount of time to diffuse into the polymer, but doping for too long appears to

over-oxidize the polymer and reduce the conductivity. A similar effect has been observed in electrochemically synthesized polymers¹⁰. In order to determine the optimal doping time, films of the unfractionated polymer were prepared in the manner described above and doped for periods ranging from 30 to 120 min. The conductivity as a function of doping time is shown in *Figure 1*. The highest conductivity was observed in samples doped for 60 min, and this is the time we adopted for the subsequent doping of the fractionated samples.

The variable thickness of the polymer films might conceivably affect their macroscopic conductivity if the dopant could not equally penetrate the entire depth of the sample. This possibility was quickly investigated by doping two films differing in thickness by a factor of 2 to obtain the data in *Figure 1*. At each time the measured conductivities are in agreement within experimental error, leading us to conclude that film thickness does not have a significant effect on conductivity for films of this size doped in this manner.

Crystallinity determination

The crystallinity of each sample was determined both prior to and after doping by X-ray measurements performed using Cu K α radiation ($\lambda = 0.154$ nm) generated at 45 kV and 40 mA (Seifert SN60 X-ray tube). Measurements were made over an angular range of $2^\circ \leq 2\theta \leq 40^\circ$ using a Scintag X-ray diffractometer (model XDS-2000), with continuous intensity sampling every 0.05° at a detector speed 1° min^{-1} and a detector slit width of 0.5 mm. The areas under the crystalline peaks, A_c , and the broad amorphous peak, A_a , of the angular intensity profile were calculated in order to estimate the percentage crystallinity of each sample¹¹:

$$\text{crystallinity (\%)} = [A_c / (A_c + A_a)] \times 100 \quad (4)$$

Owing to the small amount of crystalline material in most samples, these measurements may not accurately reflect the absolute degree of crystallinity, but reproducible relative values were consistently obtained.

RESULTS AND DISCUSSION

X-ray diffraction measurements were made in order to determine the percentage crystallinity of the P3OT

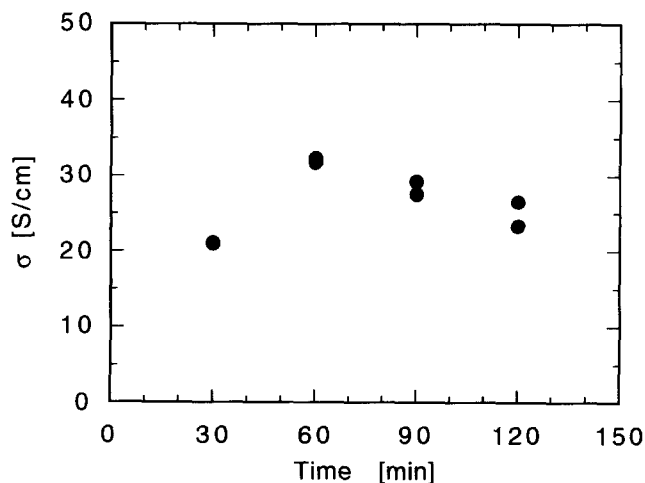


Figure 1 The influence of doping time on the conductivity of P3OT doped in 1.0 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in nitromethane. The optimum conductivity is achieved after 60 min

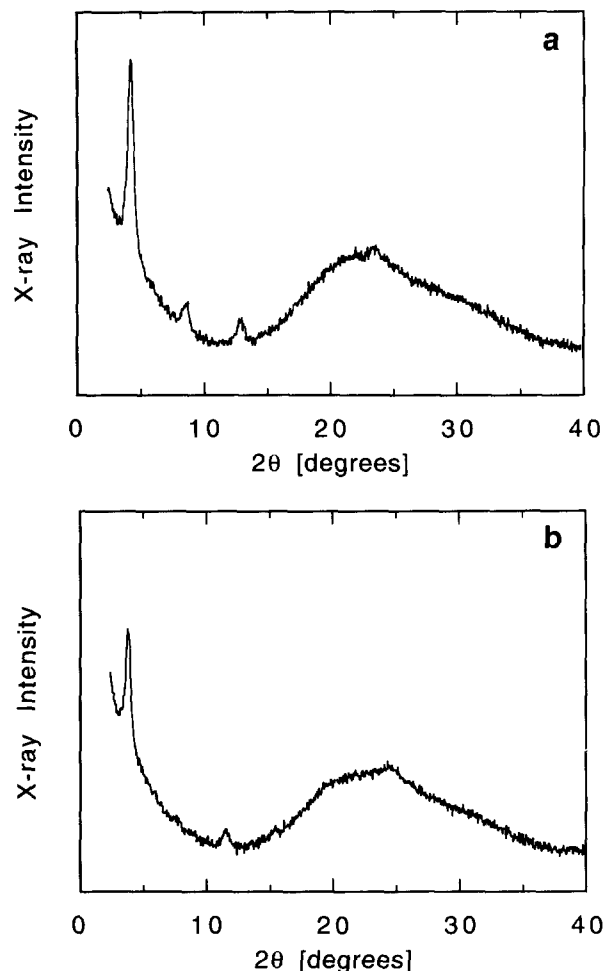


Figure 2 X-ray diffraction scans of solution-cast P3OT films (sample 3): (a) neutral film; (b) film doped with ferric chloride

Table 2 Percentage crystallinity of P3OT samples determined by X-ray diffraction measurements

Sample	Solution-cast films		Quenched films	
	Neutral	Doped	Neutral	Doped
1	12.5	8.0	3.6	2.8
2	12.7	8.1	3.7	3.1
3	18.3	10.9	6.4	4.8
4	20.3	13.6	10.0	6.5
5	25.4	17.9	11.5	9.8

films used in this work. Typical X-ray diffraction curves for both neutral and doped samples are shown in *Figure 2*. Peaks are visible at 4, 8, 12 and 23° , in agreement with the peak assignments of $(h00)$ and $(hk0)$ crystalline reflections of P3OT described by Winokur *et al.*¹². The broad peak occurring between 10 and 40° is attributable to scattering from the amorphous polymer. The intensity of the crystalline peaks is diminished upon doping, as shown in *Figure 2b*. The reduction in crystallinity is indicative of the structural reorganization that is necessary to accommodate the dopant ions, apparently disrupting the order of the crystalline regions. The percentage crystallinity calculated from the X-ray measurements is given in *Table 2*. In each case the doped polymer was found to be less crystalline than the neutral polymer by 20–40%. It is also evident from *Table 2* that

the quenched films are, as expected, much less crystalline than the solution-cast films, although they are not completely amorphous.

The data obtained in our first experiments on solution-cast films demonstrate a decrease in conductivity with increasing molecular weight, as shown in Figure 3 (filled circles). The average of five independently measured values of the conductivity is shown, with error bars representing ± 1 standard deviation of the data. Also shown are the results obtained upon repeating the experiment, demonstrating excellent reproducibility of the observed trend.

A comparison between the conductivities of the solution-cast films and quenched films is shown in Figure 4. The conductivity of the quenched films was found to be lower for all molecular weights. Furthermore, in both cases the conductivity varies by a factor of 2 over the range of molecular weights studied, approximately corresponding to the difference in crystallinity. These results are expected if the conductivity of the crystalline polymer is greater than that of the amorphous polymer, as discussed previously.

The amount of dopant incorporated into the polymer films as measured by their weight gain is shown in

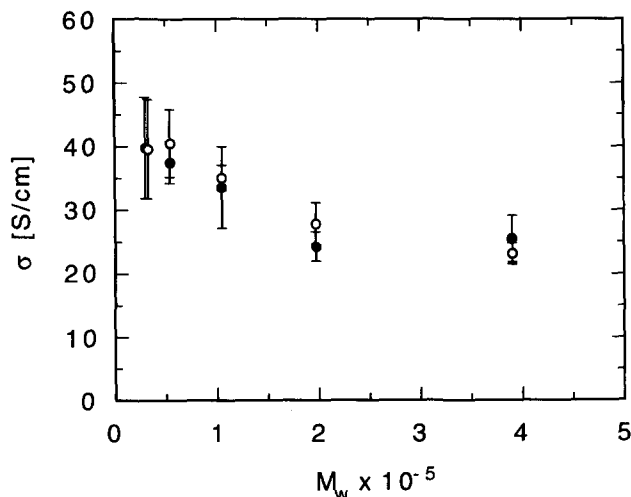


Figure 3 Conductivity of solution-cast P3OT films as a function of molecular weight. The open and filled symbols correspond to the same experimental procedure performed two different times. Average values are plotted; error bars indicate ± 1 standard deviation of the data

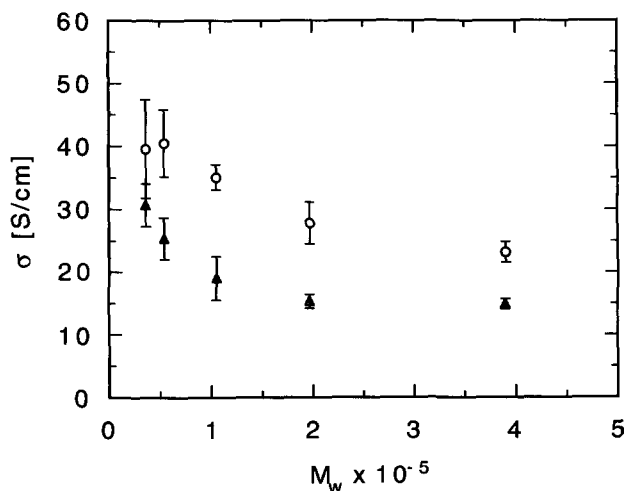


Figure 4 Conductivity of solution-cast (○) and less-crystalline quenched (△) P3OT films as a function of molecular weight

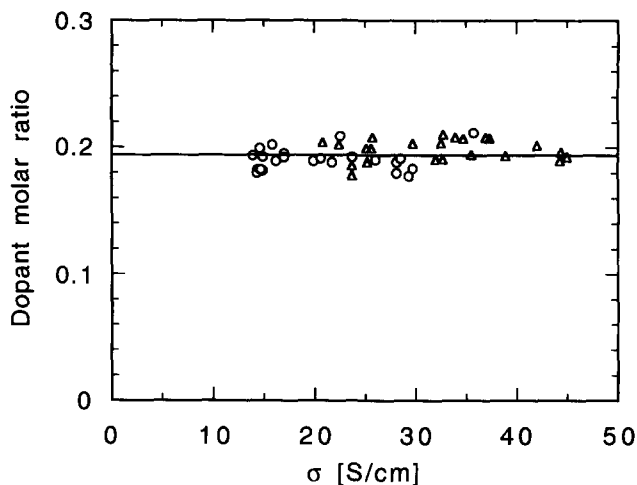


Figure 5 Dopant weight ratio (weight gain upon doping divided by weight of the neutral polymer) as a function of the conductivity of solution-cast (○) and quenched (△) P3OT films. The average value is 0.198

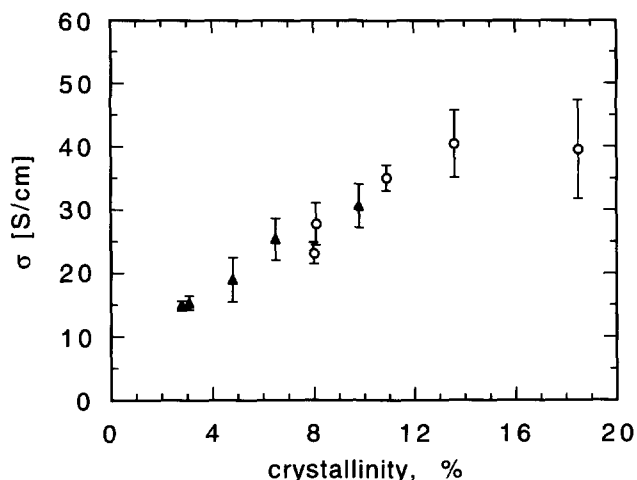


Figure 6 Conductivity of solution-cast (○) and quenched (△) P3OT films as a function of percentage crystallinity

Figure 5. There is no significant difference between the doping level of solution-cast and quenched films. Most importantly, the doping level is constant and independent of the film conductivity, confirming that any observed difference in conductivity is due solely to differences in the polymer and not the quantity of dopant. When ferric chloride is used as a dopant, FeCl_4^- ions are created as counterions for the positively charged polymer chain, while the formation of FeCl_2 maintains the stoichiometric balance¹³. Assuming that both species remain in the doped polymer, we calculate a saturation doping level of one counterion for approximately every eight repeat units.

The direct relationship between crystallinity and conductivity of P3OT is illustrated in Figure 6, which suggests that the conductivity is initially a linear function of crystallinity. The completely amorphous polymer would appear to have a conductivity of about 10 S cm^{-1} , while just 10% crystallinity increases that value by a factor of 3, demonstrating the dramatic role that crystallinity can have in the charge transport processes of conducting polymers. Such an effect may explain, at least in part, the high conductivity recently reported for poly(dodecylthiophene) synthesized with a high degree of regiospecificity¹⁴, which would be expected to

crystallize more readily due to the regular spacing of the alkyl side groups.

Since all the conductivity data fall on the same curve in Figure 6 regardless of molecular weight, we conclude that there is no significant effect of molecular weight on conductivity in the range studied. This agrees with recent results obtained by Osawa *et al.*¹⁵ on electrochemically synthesized poly(3-hexylthiophene), which indicate that although the conductivity initially increases with molecular weight, it is relatively constant for molecular weights above 30 000. Reflecting upon our earlier discussion, we may infer from these results that P3OT of moderate molecular weight is characterized by charge transport in the limit $\tau_c \ll \tau_i$, and conductivity is not limited by interchain transport.

REMARKS

Conductivity is almost certainly not a linear function of crystallinity over the entire range of crystallinity. Polymer films with a greater degree of crystallinity might be prepared by annealing them prior to doping. This would allow a larger database from which to model the relationship between conductivity and crystallinity. However, the loss of crystallinity accompanying the doping process will continue to be a problem unless a less intrusive doping agent is found. Annealing the polymer after doping is not a possibility owing to the occurrence of thermal dedoping at elevated temperatures¹⁶.

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