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Effects of order and disorder on field-effect mobilities measured in conjugated polymer thin-film transistors

E. R. Holland, D. Bloor, and A. P. Monkman

Organic Electroactive Materials Research Group, Department of Physics, University of Durham, Durham DH1 3LE, United Kingdom

A. Brown and D. De Leeuw

Philips Research Laboratories, P.O. Box 80 000, 5600 JA Eindhoven, The Netherlands

M. M. Bouman and E. W. Meijer

Department of Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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The morphology of conjugated polymer thin films has been controlled by exploiting the processes giving rise to solvatochromism in the initial polymer solutions from which the polymer films were deposited by spin coating. The material used was the substituted polythiophene, 3[2(S2-methylbutoxy)ethyl]-polythiophene. Starting with polymer dissolved in "good" solvent, various quantities of "bad" solvent when added lead to the reorganization of the solubilizing side chains attached to the conjugated polymer backbone. Ordering of these side chains increases with addition of bad solvent decreasing the flexibility of the backbone, yielding more rigid rodlike polymer chains. This in turn causes aggregation and finally precipitation. It is found that this molecular order can be transferred from solution to solid film during the spinning process, ascertained from optical spectroscopy. With these films acting as the active layer in a field-effect transistor structure, the mobility of the carriers injected into the films can be measured. It is found that as the molecular order and aggregation increases, carrier mobility decreases from $\sim 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $\leq 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in films displaying the highest degree of molecular order. This is ascribed to the increased interchain separation in the ordered systems along with effects due to macroscopic aggregate grain boundaries.

I. INTRODUCTION

Recently, there has been a substantial interest in the use of conjugated polymers as the active semiconductor in field-effect transistors (FET).^{1,2} From a technological viewpoint these materials offer a considerable advantage over inorganic semiconductors in their ease of processing. Spin coating, for example, can be used to produce high-quality thin polymer films. From a purely scientific viewpoint, the behavior of a polymer within a FET can provide useful information about the material, such as the charge carrier mobility.² The effect of order and disorder in the polymer film upon the carrier mobility can therefore be easily studied through the utilization of such structures.

It is generally accepted that for conjugated polymer materials, the degree of straight intrachain conjugation has an important effect on its conductive properties. This is mainly through increased conjugation leading to increased carrier mobility. In this work we use a FET structure in an attempt to probe the role of chain order on carrier mobility. We have achieved this by measuring field-effect mobility in polymer films showing both order and varying degrees of disorder. We affect this by treating solutions of one such conjugated polymer, the regioregular, chiral,³ 3[2(S2-methylbutoxy)ethyl]-polythiophene (PMBET) (Fig. 1) with a non-solvent and observing the effects on the resulting films spun onto the FET devices.

Using these FET devices allows the mobility of charge carriers in the film to be investigated. Furthermore, film con-

ductivity can be extracted from a study of the FET device characteristics. A typical device structure is shown in Fig. 2 and was operated in accumulation mode. To obtain values for carrier mobility and polymer conductivity the operation of the thin-film transistors was modeled using the equation⁴

$$I_{\text{DS}} = \frac{\mu WC_i}{L} \left((V_G - V_O) V_{\text{DS}} - \frac{V_{\text{DS}}^2}{2} \right) + I_{\Omega},$$

where I_{DS} is the source-drain current, μ the effective carrier mobility, W the source-drain channel width, L the source-drain channel length, C_i the gate capacitance/unit area, V_{DS} the source-drain bias voltage, V_G the gate bias voltage, V_O the offset voltage, and I_{Ω} the ohmic current.

The first term in this expression represents the gate-voltage-modulated source-drain current caused by the formation of an accumulation layer in the polymer, at the polymer-insulator interface, in the negative-gate-bias regimes. The second term represents ohmic conduction through the bulk of the polymer layer due to its intrinsic conductivity. This is proportional to V_{DS} , but independent of V_G .

For the case where $|V_G| > |V_{\text{DS}}|$ the source-drain current varies linearly with V_G . Therefore, a plot of I_{DS} vs V_G results in a straight line with gradient M , where

$$M = \frac{\mu WC_i V_{\text{DS}}}{L},$$

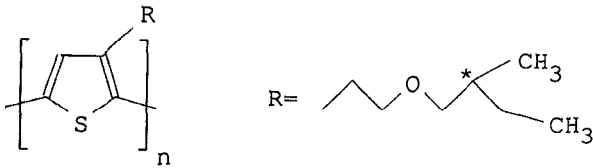


FIG. 1. Repeat unit structure of 3[2(S2-methylbutoxy)ethyl]-polythiophene (PMBET).

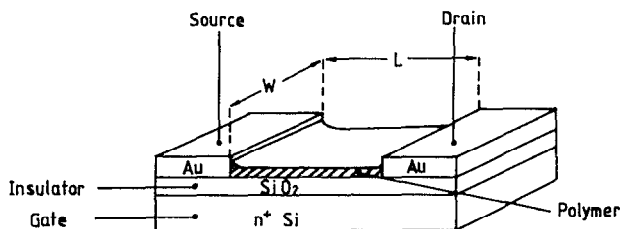
from which the effective carrier mobility can be extracted since all other parameters are known. Mobility measurements were thus made from devices operating in the $|V_G| > |V_{DS}|$ “linear” regime.

II. EXPERIMENT

To obtain PMBET with various degrees of chain order, we have exploited the well-known technique used in the field of polydiacetylenes (PDA) of adding quantities of nonsolvent to solutions of PDA in good solvent.⁵ In the case of PDAs such a 9BCMÜ,⁶ this would be chloroform (good solvent) and hexane (bad solvent). In the case of PMBET, the solvent used is THF, and the nonsolvent added to it is methanol.

Throughout this work, a typical set of solutions was studied. The ratios of solvent to nonsolvent used are given in Table I. All samples were first made up by dissolving 0.02 g of PMBET in 4 ml THF. After all the polymer had dissolved, the varying quantities of methanol, nonsolvent, were added. In solution a solvatochromic effect was observed. Progressive methanol addition caused the originally orange-red solution to become dark orange, red, and then dark red. When the ratio of methanol:THF exceeded 4:10 a red precipitate was formed. From these solutions, films of PMBET could be spun, using a photoresist spinner at 1000 rpm onto the FET structures, as shown in Fig. 2, and glass substrates. The solvatochromic effects observed in the initial spinning solutions are “transferred” to the resultant films; however, the red shifts are enhanced in the solid state. These effects were quantified by UV/vis spectroscopy.

Typical conditions employed throughout to obtain mobilities and conductivities from the FETs were V_{DS} fixed between -1 and -5 V and V_G scanned from -20 to -10 V.



BASIC FET STRUCTURE

FIG. 2. Field-effect-transistor structure used throughout the work to measure mobilities and conductivities. Typical $W=20$ μm and $L=10$ μm , polymer layer thickness ~ 100 Å.

TABLE I. Preparation conditions used for film spinning.

Sample	Ratio of THF:CH ₂ OH (by vol)	Solution color
1	100% THF	yellow orange
2	10:1	dark orange
3	10:2	red
4	10:3	dark red
5	10:4	dark red

All measurements were made using devices with dimensions $W=20$ mm and $L=10$ μm . Readings taken at several values of V_{DS} enable repeated measurements of μ . The polymer conductivity was measured using the I_{DS} vs V_{DS} characteristics when $V_G=0$ V. The film thickness was estimated at ~ 100 Å by comparison of the absolute absorption of samples to the absorption coefficient of PMBET. All electrical measurements were made using a Hewlett-Packard HP 4140B pA meter/voltage source.

III. RESULTS

A. UV-vis spectroscopy

The absorption spectrum of a PMBET film spun from pure THF solution (sample 1) shows a main peak at 546 nm with a shoulder at around 600 nm (Fig. 3). PMBET films spun from solutions with increasing methanol content show this main peak to shift to longer wavelengths, 552 nm for sample 2 and 564 nm for sample 3. The peak absorbance decreases in intensity. A new peak emerges from the shoulder at 600 nm and also shifts toward longer wavelengths as the methanol content of the spinning solution is increased. For sample 3 the new peak is seen at 610 nm, while for films spun from sample solutions 4 and 5 it is at 628 nm. It was noticed that the films spun from methanol treated solutions were scattering. This scattering was greater for films spun from the solutions with higher methanol content. This could also be the cause of increased absorption in the UV, e.g., the onset of absorption around 300 nm.

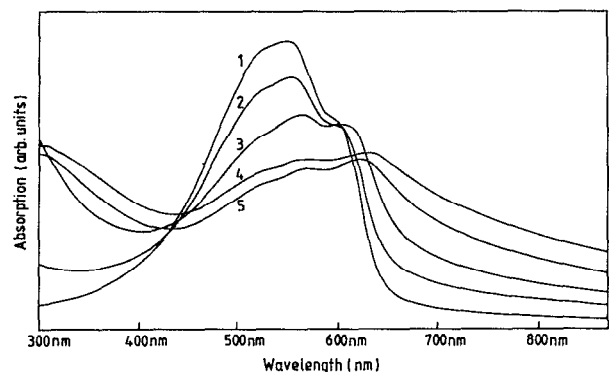


FIG. 3. Optical spectra of spun PMBET films showing the effects of increasing bad solvent addition to the spinning solution (increasing bad solvent content 1–5). Precise spinning solution compositions are given in Table I.

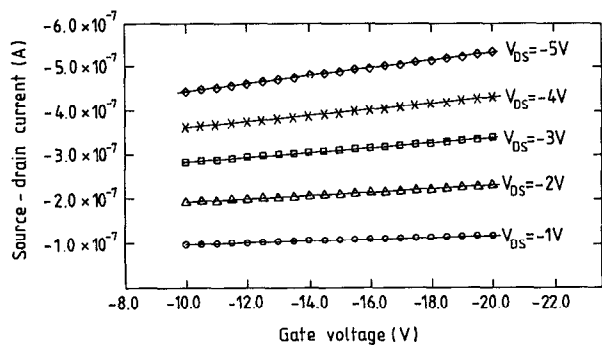


FIG. 4. A typical set of I - V characteristics obtained from a PMBET FET. PMBET film spun from purely good solvent.

This shoulder and new peaks which are clearly evident in the subsequent spectra are ascribed to vibronic bands. In all cases the lowest energy band is the 0-0 transition with the first vibronic side band being 190 meV higher in energy (in all cases). This is very consistent with the electronic transition being strongly coupled to the C=C stretch of the polymer backbone. Typically for most thiophenes the C=C stretch occurs at $\sim 1500\text{ cm}^{-1}$ or 185 meV. This energy separation is independent (to within a few meV) of chromic shift. These results from spun films are consistent with those reported by Rughooputh *et al.*⁷ in solutions of polyalkylthiophenes.

B. FET characterization

As previously stated, all mobility measurements were performed with devices operating in the $|V_G| > |V_{DS}|$ regime, and accumulation mode⁸ with V_{DS} scanned so as to give a set of measurements from which mobility can then be calculated. A typical set of results for a PMBET film is shown in Fig. 4. As predicted by theory, each V_{DS} line is linear allowing accurate values of mobility to be determined. For each film sample (1–5) such measurements were made, the mobilities calculated from them are shown in Table II. Sample 5 displayed no measurable modulation of the source-drain current with applied gate voltage. Along with this mobility data, the sample conductivities estimated from I_{DS} vs V_{DS} measurements at $V_G = 0\text{ V}$ are also given, the measured conductivity of sample 3 appears somewhat low; this we ascribe to an overestimate of the film thickness. A correlation between methanol content and measured mobility is found. In all

TABLE II. Measured field-effect mobilities and polymer film conductivities. For film preparation conditions see Table I.

Sample	Conductivity (S cm^{-1})	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
1	1.7×10^{-5}	4.0×10^{-5}
2	7.3×10^{-6}	1.5×10^{-5}
3	6.1×10^{-9}	1.5×10^{-8}
4	3.0×10^{-8}	1.5×10^{-8}
5	9.5×10^{-9}	unmeasurable

cases, increased methanol content in the spinning solutions yields lower carrier mobility and bulk conductivity.

IV. DISCUSSION

From the optical-absorption measurements, it can be seen that generally as poor solvent is added to the spinning solutions, the absorption of the subsequent films red shifts, with increased UV absorption being observed along with increased film scattering. The observed shift in absorption toward longer wavelengths is interpreted as an increase in the effective intrachain conjugation length. This arises because the average length of rigid rod along the polymer chain increases as the concentration of methanol (nonsolvent) in the solution is increased. Similar effects are well documented in the side-chain polydiacetylenes. In this case the addition of hexane to solutions of BCMU PDA derivatives⁶ causes solvatochromic shifts. Here chains occur as random wormlike coils in good solvent, addition of poor solvent causes the individual chains to collapse down on themselves via intramolecular interactions such that sections of the chain form into rigid rods.⁹ These more rigid chains readily aggregate, even in dilute solution. The driving force for this collapse is not hydrogen bonding¹⁰ but an intramolecular attraction. In the BCMUs it is still not clear whether the aggregates are amorphous or fringed micelles which have partial crystallinity.

The appearance of the films, becoming progressively more cloudy as the nonsolvent content of the spinning solution increases, suggests an increase in the crystalline fraction of the films or that aggregation of the polymer chains occurs in solution prior to spinning. This explains why we observe the scattering trail on the low-energy side of the $\pi \rightarrow \pi^*$ transition of the polymer. Further evidence for this comes from the gain in oscillator strength of the 0-0 and vibronic side bands, indicative of more one-dimensional polymer chains which would be the case in the crystalline fractions.

In good solvent the side chains of the PMBET molecules will have plenty of free volume enabling them to move rapidly. This degree of side-chain freedom will cause the polymer chain to take up a wormlike configuration.¹¹ This will in turn cause a twisting of neighboring rings along the polymer backbone. This deviation from planarity of the conjugated backbone will drive the system to a more localized geometry.¹² These effects are locked in when films are spun as the solvent will evaporate rapidly (from the very thin films), not giving the chains and side groups time to reorient. As poor solvent is added to the solution this degree of freedom is reduced, via an intramolecular interaction as in the case of the BCMUs, introducing order (rigid rod character) to the chains, allowing aggregation to occur. Thus, the chains can return to a more planar and hence more conjugated form, shifting the $\pi \rightarrow \pi^*$ absorption to lower energy. Again after film spinning the chain configuration is locked in. At very high nonsolvent content, aggregation dominates, leading to the observed high degree of scattering from the films.

The effects of these changes in chain configuration and aggregation can clearly be seen in the measured mobilities and conductivities of the cast films. At first sight our findings are counterintuitive, with mobility and hence conductivity

falls (markedly) as nonsolvent is added to the spinning solution, but at the same time effective conjugation length of each chain within the film increases. Within the more ordered regions of the film the conjugated backbone will be more rigid. This rigidity will decrease the degree of freedom of the side groups, causing them to order. This ordering of the side groups will on average increase the interchain separation of the conjugated backbones, thus reducing the hopping probability between chains reducing the carrier mobility and hence conductivity. These results are in good agreement with those of Paloheimo *et al.*⁸ who have quantitatively shown that increasing the size of the substituent on the thiophene backbone, thus increasing chainchain separation, also leads to a decrease in carrier field-effect mobility.

On comparing our values of mobility with those quoted by Horowitz *et al.*¹³ for various thiophene systems, nothing untoward is seen. The value of $4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ obtained for PMBET films cast from a purely good solvent is high for a substituted polymer, but not unduly so. Thus, the observed effects on mobility must be caused by the effects of either order or aggregation or both. Recent work in the field of oligomeric thiophenes^{13,14} has shown that interchain transport is all important. Compared to α substitution, β substitution drastically reduced carrier mobility, due in part to loss of crystallinity and because the adjacent, facing thiophene rings are much further apart, although it is observed that a β -substituted dodeca thiophene has a mobility of $5 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a value approaching that which we have measured for PMBET. From these findings we deduce that in the pristine films of PMBET, there is a fair degree of order between the more closely spaced chains, as the optical spectrum of such a film displays vibronic structure, hence interchain transport is high with a concomitant high carrier mobility. As nonsolvent is added to the spinning solution chain rigidity and increased conjugation ensues, corresponding to increased order within the film, aggregation occurs, as deduced from increased scattering. The mobilities within such films falls; however, this we ascribe to the effects of increased chain separation on a microscopic scale and to the effects of grain boundaries on the macroscopic scale. These boundaries between the individual aggregate particles disrupts bulk mobility, which is measured in our experiment, although within a particle the mobility may well be higher.

V. SUMMARY

We have used a metal-insulator-semiconductor FET structure to measure charge-carrier mobility and conductivities of PMBET films, spun from solvent:nonsolvent mixtures. Optical characterization of films spun from solutions containing varying ratios of THF methanol (nonsolvent) shows clear vibronic structure on the $\pi \rightarrow \pi^*$ transition. Sol-

vatochromic shifts are maintained in the spun films due to the rapid evaporation of the solvent from the (thin) films during the spinning process. This rapid evaporation locks in chain structure. As the nonsolvent content of the spinning solution is increased, films show increased conjugation, i.e., red shift of the visible absorption. This we ascribe to increased rigidity, and hence longer conjugation lengths along the polymer chain. Accompanying this, films appear more scattering, this we ascribe to aggregation within the solutions, and the films produced from them.

This latter observation is very important when considering the measured carrier mobilities in the films. As nonsolvent content increases the mobility in the films spun from these solutions decreases. This can be ascribed to effects on both the microscopic and macroscopic scale. On the microscopic scale, increased chain rigidity will cause the side groups to order increasing interchain separation and hence reduce the interchain hopping probability. The presence of macroscopic grain boundaries associated with the aggregation particles in the films affects the bulk mobility within the films. These results should be kept in mind when considering devices made with high-mobility oligomers, as again grain boundaries may be limiting the maximum attainable carrier mobilities and thus, ultimate device performance. Experiments such as microwave electrical conductivity will help to differentiate between these effects, and are underway at present.

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