

1. Introduction

The initial aims of the OMEC proposal were to synthesise, characterise, process and evaluate the device performance of novel, self-organising molecular materials of high purity which exhibit high carrier mobilities and which are suitable for the simple-in-principle manufacture of organic electronic devices on substrates useful for practical applications. These aims have remained valid throughout the course of the first year and this report presents a record of achievement in the first year.

2. Conjugated Polymer Synthesis

2.1 Preparation of Polycyclopentadithiophenes

Three protocols for the preparation of poly(4,4-dialkylcyclopentadithiophenes) have been investigated.^{1,2} The three methods afford soluble materials, free of mislinkages and showing extended conjugation in solution. Polymers obtained by an oxidative protocol show a higher molecular weight than those prepared by transition metal catalyzed polymerization. NMR spectroscopy and MALDI-TOF mass spectrometry showed that the moderate degree of polymerization (15-20 units) achieved by Kumada and Negishi type polymerization is probably due to incomplete formation of the organometallic intermediate. For these polymers the main chain conjugation can be directly correlated to the length of the polymer backbone. Extraction of the polymers using solvents of varying solubilising power led to fractions with increasing molecular weight. UV-visible spectra of the fractions show absorption maxima that increase with the average degree of polymerization as determined by GPC up a limiting value of around 20. These materials are not liquid crystalline as expected by analogy with the polyfluorenes and their mobilities are disappointing (see section 4) when compared to the analogous regioregular polythiophenes.³ The low mobilities are presumably due to the amorphous nature of the films obtained by spin coating from a range of solvents and after annealing at elevated temperatures.

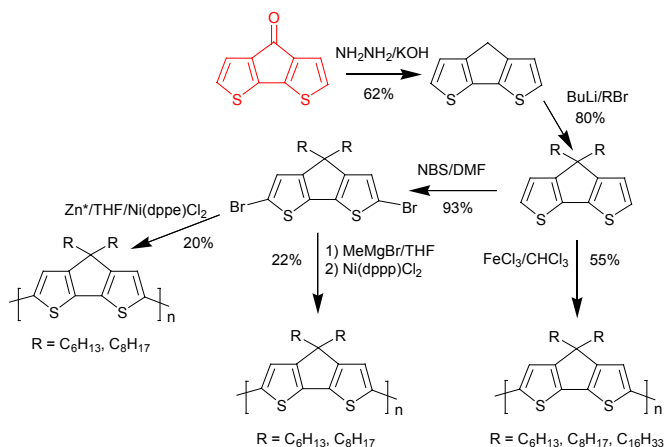


Fig. 1: Synthetic route to polycyclopentadithiophenes.

New derivatives have recently been prepared in which the alkyl chains are held in the plane of the polymer backbone (Fig. 2) and it is hoped that these materials pack more effectively in the solid state, leading to higher mobilities. An X-ray crystal study of the monomer (see Fig. 2) suggests that this may indeed be the case.⁴

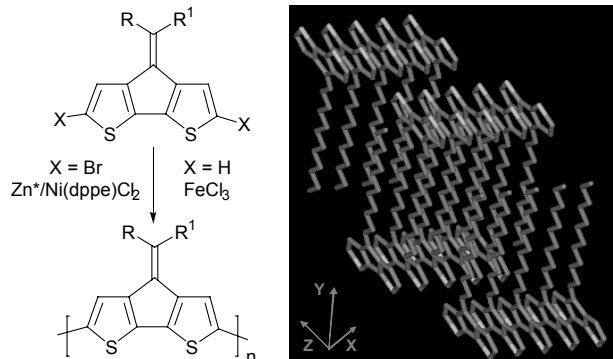


Fig. 2: Alkene bridged CPDT ($R=H$, $R^1=alkyl$, $R=R^1=alkyl$) and packing diagram of X-ray structure of monomer ($R=H, R^1=C_{11}H_{23}$)

2.2 Solid Phase Synthesis of Oligothiophenes

Preliminary work, prior to the start of the grant had established proof-of-concept for a novel method for the synthesis of oligothiophenes using a germanium-based linker model system *in solution*.⁵ The method consisted of an iterative synthesis in which cross-coupling yields for each iteration (i.e. addition of a thiophene monomer) could be driven to completion by 'double-coupling'. The ability to perform double-coupling was contingent upon the use of a silyl 'blocking' group at the α -position of each newly introduced thiophene monomer which needed to be stable to the cross-coupling conditions and able to be selectively removed without affecting the germanium-based linker. The model studies had established that a trimethylsilyl (TMS) blocking group in combination with a dimethylgermyl linker displayed these properties but had also alerted us to the fact that the TMS group becomes increasingly labile towards adventitious acid as the length of the oligomer increases. Consequently, before proceeding to the solid phase it was decided to re-engineer the system so as to define a more robust blocking group/linker combination that retained the possibility to perform double-coupling but that was significantly more robust towards acid. This first required the development of a completely new route to germanium-based linkers that would allow for variation of the 'spectator' ligands on the germanium centre. This was achieved in a manner that also circumvented the need to employ tin(IV) chloride, the achilles heel of the previous route (Fig. 3).

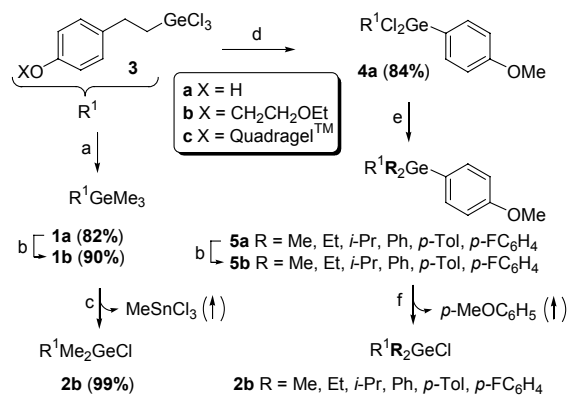


Fig. 3: (a) MeMgBr, toluene, 110 °C. (b) EtOCH₂CH₂Cl, *n*-Bu₄Ni, Cs₂CO₃, MeCN, 85 °C. (c) SnCl₄, MeNO₂, 50 °C. (d) i) *p*-MeOC₆H₄MgBr, THF, RT. ii) *c*.HCl, CH₂Cl₂, RT. (e) RMgBr, THF, 70 °C. (f) 1.0M HCl in Et₂O, RT

With this new route established a series of optimisation studies were performed using soluble linker model systems (having the spectator ligands indicated in **Fig. 3**) in combination with thiophene monomers having different silyl blocking systems (i.e. TES, TBDMS, and TIPS). As the result of these experiments it was decided that the best combination of blocking group and linker would

be: TBDMS blocking group with di-*p*-tolylgermyl linker. Preliminary studies in solution clearly established that this combination showed good stability towards acid whilst retaining the orthogonal stability of the two groups towards fluoride that forms the basis of the selective de-blocking procedure. Moreover, the greater stability of the TBDMS group towards bases as compared to the TMS group allowed for the development of a more robust Suzuki-type cross-coupling protocol than had been possible in the previous work. Using this combination of groups preliminary work on the solid phase have been performed this year. Three solid supports have been evaluated: Merrifield resin [i.e. lightly DVB cross-linked polystyrene (PS)], Hypogel[®] (a grafted PS resin with a distribution of 3-6 oxyethyl repeats) and Quadragel[®] (a grafted PS resin with 4 oxyethyl repeats). The Quadragel[®] was found to be the optimal from both a chemistry point of view and also from the perspective of giving the highest quality MAS-NMR spectra. To date, synthesis has been carried out to the dimer stage,⁶ work that has unambiguously established the utility of the double-coupling tactic for enhancing iteration efficiency as measured by HPLC of cleaved samples of the bithiophene (**Figs. 4 & 5**).

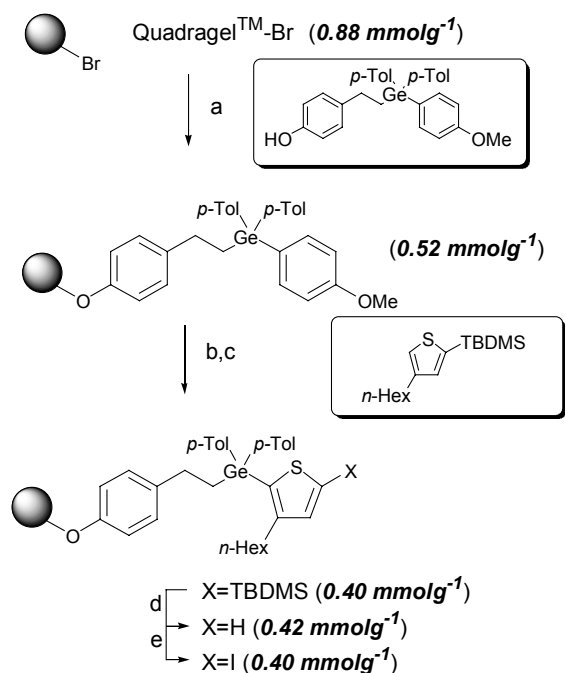


Fig. 4. *n*-Bu₄Ni, Cs₂CO₃, MeCN, 85 °C; (b) 1.0M HCl in Et₂O, RT; (c) LDA, THF, 40 °C; (d) CsF, DMF, 110 °C; (e) (i) LDA, -50 °C, (ii) ICH₂CH₂I, dark

A preliminary communication detailing much of the above work is in press⁷ and a full paper is in preparation. A UK patent application has also been filed in conjunction with Avecia Ltd.⁸ Work is ongoing towards the synthesis of the corresponding hexamer (i.e. HT-3-hexylsexithiophene) by a [1+1+2+2] strategy in which the bithiophene already prepared is partially cleaved from the resin with concomitant boronate formation to provide a 'bithiophene monomer' for cross-coupling (x 2) to the resin bound bithiophene to give the required hexamer.

Additionally, and in parallel with the above work, efforts have focussed on developing new methods for the cleavage of oligothiophenes from the germanium-based linker so as to concomitantly install useful functionality at the point of attachment. Specifically, new protocols have been developed by which cleavage can be achieved concomitant with:

- Boronic ester formation using BCl₃/pinacol,
- Friedel-Crafts type acylation using the appropriate acid chloride and AlCl₃,
- Germyl-Stille type cross-coupling to introduce an aryl group using Pd(0) catalysis, KF, and the appropriate aryl halide.

Work is ongoing to delineate the scope of these new methods and to make them as reliable as possible for generating end-group functionality that is useful either for block co-oligomer synthesis or as terminating groups for the oligomers.

2.3 Synthesis of Anthraquinone Polymers

Quinones are involved in various natural electron transfer processes such as photosynthesis and oxidative phosphorylation. Anthraquinone is a well-studied member of this family. It has excellent chemical and thermal stability and its electron accepting properties have been extensively studied. This project concerns the design, synthesis and characterisation of novel n-type polymers based on anthraquinones.

The few publications that report polymers with anthraquinones in a conjugated backbone show that the materials have very low solubilities unless a 1,4-linkage is chosen. In order to allow the synthesis of copolymers, using Suzuki coupling, a range of dibromo-substituted anthraquinone monomers were prepared (see **Fig. 6**). The synthesis of several 4-bisarylanthraquinones was also carried out in order to prepare model compounds and new monomers for polymerisations. An X-ray structure of bis-(4-bromophenyl)anthraquinone showed that the phenyl rings and anthraquinone groups are rotated out of the plane with respect to each and hence are not conjugated but the packing diagram does show extensive π -stacking of the anthraquinone groups.

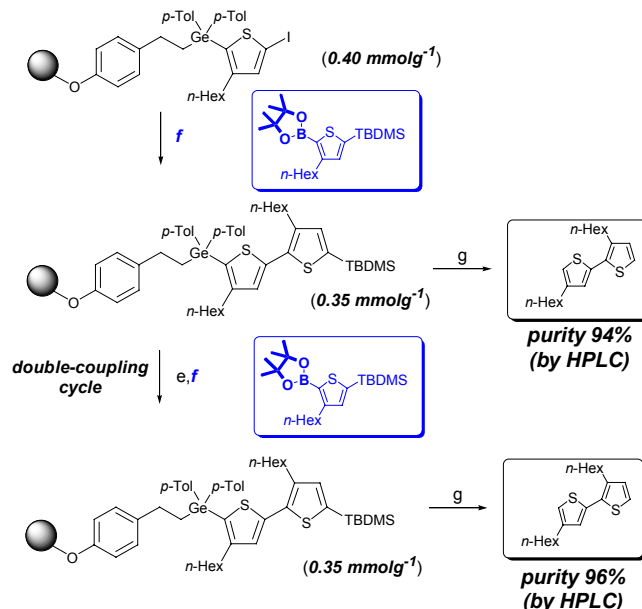


Fig. 5. (d) CsF, DMF, 110 °C; (e) (i) LDA, -50 °C, (ii) ICH₂CH₂I, dark; (f) K₂PO₄, Pd(PPh₃)₄, DMF, 60 °C; (g) (i) CsF, (ii) TFA

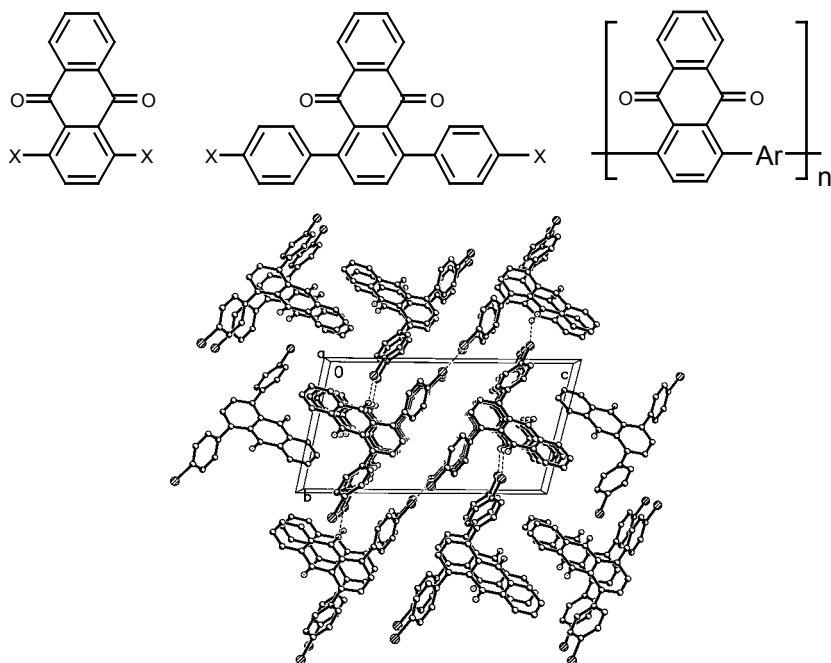


Fig.6: Anthraquinone monomers and polymers and copolymers (Ar = Ph, dioctylfluorene) plus packing diagram of X-ray structure of bis-(bromophenyl)anthraquinone.

molecules with low mobilities ($\mu_e \sim 10^{-6-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and have very limited processability from solution phase. The key issues with the n-type carrier's remains the stability of the materials to ambient (mainly stability to O_2), the very high threshold voltages in operation and the poor processability. These all need to be addressed before a "good" material is identified. Air-stable, solution processible polymer/oligomeric n-type materials having high mobility ($>10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are not available at present and as such we remain interested in poly and oligo anthraquinones. To date polyanthraquinones prepared in this project were found not to have a measurable FET mobility up to a gate voltage of +80V. Copolymers of anthraquinone and substituted variants are currently evaluation focusing upon the ability of non-conjugated polyanthraquinones to π -stack.

3. New Insulators for Field Effect Transistors and New Device Architectures.

In the first year of OMEC, we have successfully established an organic field-effect transistor characterization lab in the Department of Physics, University of Sheffield, enabling the measurement of the current between source and drain versus drain voltage (output characteristic) and versus the gate voltage (transfer characteristic), while simultaneously monitoring the gate leakage current. A temperature stage has also been set-up that allows the measurement of transistor performance from -190 C to temperatures exceeding 300 C . This allows the morphology of the semiconductor in the channel (near the interface with the gate insulator) to be controlled. The system can also be used in the future to study accelerated ageing in transistors.

At the same time, an anodisation bath was built and the anodisation process perfected using evaporated aluminium, and commercially available aluminium on Mylar foil. Using the underlying aluminium as a gate electrode, and the anodised aluminium oxide (Al_2O_3) as a gate dielectric, very promising transistors have been built. As active semiconductor, state of the art commercial semiconductors, regio-regular poly(3-hexyl thiophene) and pentacene have been employed, as well as semiconductors provided by our OMEC partners; gratifyingly, a collaboration with Avecia resulted in a publication this year.⁹ Two further manuscripts relating to the low voltage operation of OFETs using very thin, high-capacitance inorganic gate insulators have been submitted (J. Phys. D; Synth. Met.). Solution-processible polymers have also been used as gate insulators, e.g. poly(vinyl alcohol) (PVA), a polymer with a relatively high dielectric constant of 5 – 8. It has been shown that pentacene OFETs with gold top contacts and PVA gate insulator display a threshold voltage that depends on the thickness of the pentacene film, which is at variance with the standard theory of the organic transistor. This variance is the result of injection barriers at the gold-pentacene contact,¹⁰ as standard theory assumes ohmic contacts. Further studies have shown how this barrier may be mediated by the formation of Schottky contacts; and this is the subject of a submitted manuscript (APL).

Collaborators at Avecia have determined FET mobilities of a range of fused ring thiophene oligomers and polymers (synthesised by methodology reported in Section 3.1) using a standard bottom gate configuration OFET fabricated on a glass substrate (see **Table 1**). Work is still in progress but the results indicate that the presence of the bridging carbon in CPDT has a significant effect on stability (c.f. F8T2), mobility (c.f. rr-P3HT) and in certain cases solubility. Devices fabricated in the absence of air and with no annealing have to date given the best mobilities. Doping, especially with Fe remains an ongoing issue; however, cyclopentadithiophene polymers continue to be class for further evaluation.

The monomers have been polymerised by Yamamoto and Suzuki couplings to prepare homopolymers and copolymers with fluorene units. The structure of the materials was characterised by NMR, IR, GPC, TGA and DSC. The UV-vis absorption, the fluorescence and the electrochemical behaviour of the different compounds were analysed.

In considering the use of n-type materials, the mobility of the material is probably not the most important factor as the stability of the n-doped materials to ambient conditions and the operational voltages (threshold voltages) also need to be taken into account to a much greater extent than for the p-types. Whilst there have been some notable publications on n-types, generally the majority of the literature is patchy at best and has usually reported only the mobility factor. Any data regarding stability and turn-on voltages is, on the whole, very poorly (if at all) reported. Of the materials that have been reported, the majority have been used as electron injection layers in SMOLEDs and are generally vacuum evaporated small

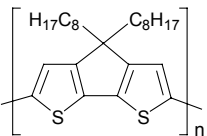
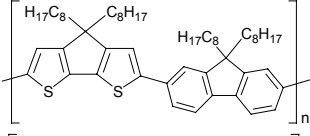
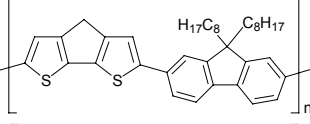
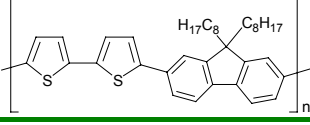
Polymer	M_n	FET mobility (cm ² /Vs)	Conditions
	6,000	No FET mobility	Air and annealing
	30,000 - High [Fe]	2×10^{-3}	Vacuum at RT
	30,000 - Low [Fe]	7.9×10^{-5}	Vacuum at RT
	5,000	7×10^{-7}	Vacuum at RT
	3,000	5×10^{-6}	Air and annealing
	2,700	1.5×10^{-3}	Air and annealing

Table 1: OFET mobilities for polycyclopentadithiophenes and fluorene copolymers

Finally, in a very exciting development the first all-organic ferroelectric memory device, the FerrOFET has been developed. Poly(*m*-xylylenediamine-*alt*-adipic acid) (MXD6) has been utilised as the gate insulator in pentacene OFETs. This polymer dielectric displays a ferroelectric-type electric displacement vs electric field ($D - E$) hysteresis in the amorphous phase. Consequently, OFETs with MXD6 gate insulator may be either ‘on’ or ‘off’ at zero gate voltage, depending on the most recent poling bias. These studies are the subject of a submitted manuscript¹¹ and a patent application for the FerrOFET has been filed.¹²

4. Surface Studies

The main focus of the scattering studies was to investigate order and morphology at the semiconducting polymer surface during annealing. Both these factors affect mobility, ordering being beneficial and roughness detrimental for the channel of a FET device. The main techniques employed are grazing incidence X-ray diffraction (GIXRD) and atomic force microscopy (AFM). This latter technique has also led to an unforeseen complementary programme investigating the electrical properties of the semiconducting polymers on the nanoscale using electrostatic force microscopy (EFM). The structural and electrical aspects of the programme are now outlined in turn.

4.1 Surface Ordering and Roughening Kinetics

Mobility generally improves with increased ordering – hence one might expect crystallisation to be beneficial. However, crystallisation of polymer films leads to poor surface morphology due to the significant density difference between the crystalline and amorphous regions of the film.

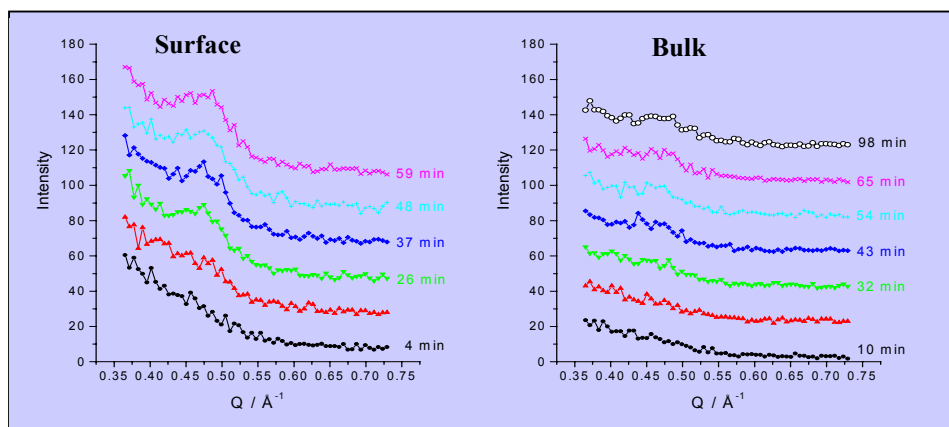


Fig 7: GIXRD scans of Q close to the surface normal during annealing of F8 at 87°C

structural ordering in poly(9,9-dioctylfluorene) (F8) during *in-situ* annealing. The scattering arising from ordering normal to the surface is shown in **Fig. 7**. The surface-sensitive scans were obtained using an incident angle α of 0.16° and the bulk scans with an α of 0.6°. The results indicate that there is a narrow range of temperature in which the surface orders more rapidly than the bulk of the film. The x-ray flux at Daresbury is insufficient to probe the ordering in the plane of the surface. This will be probed in an experiment at ESRF Grenoble scheduled for February 2004.

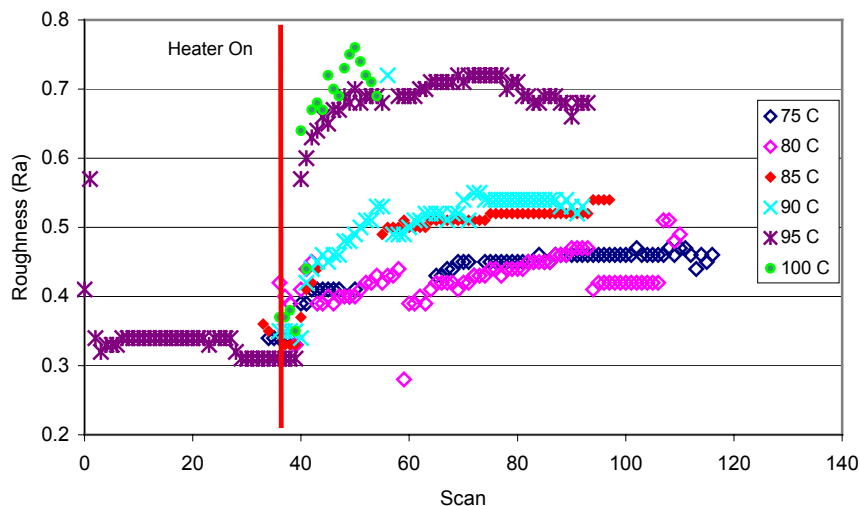


Fig. 8: Mean roughness (in nm) of the F8 surface during annealing.

5. Nanometer Scale Semiconducting Polymer Networks

While spin-coating films of decreasing thickness, we found that networks of polymer strands formed on the surface (**Fig. 9**). We

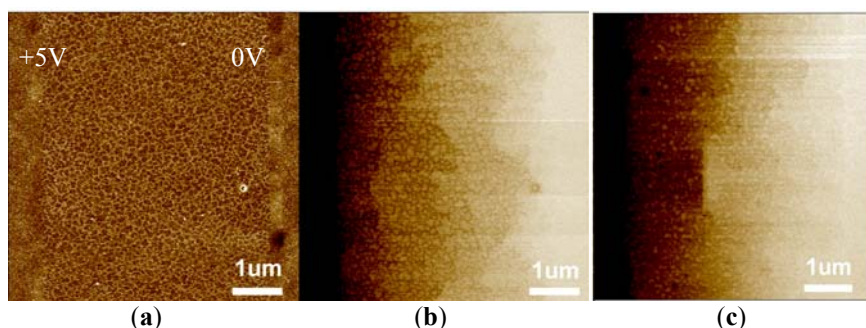
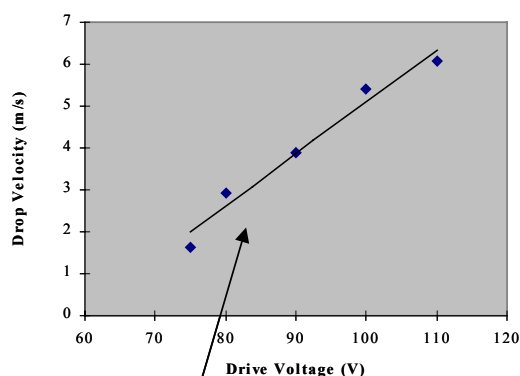


Fig. 9: (a) Topography of the polymer network (the Au electrodes have been artificially flattened in the image to show the network contrast) (b) an EFM-phase image of the surface potential (c) as for (b) following a mechanical vertical cut of 2 μm with the AFM tip, confirming the electrical nature of the signal

7. Processing of Conjugated Polymers

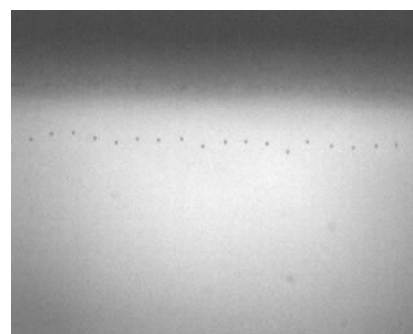
Inkjettable formulations of polycyclopentadithiopenes have been developed and their jetting performance evaluated using a Spectra Galaxy 128 head (see **Fig. 10**). Fluids were found to show model behaviour. Devices were fabricated and FET mobility was found to be comparable to spin coated devices (see above).

Drive Voltage vs. Drop Velocity at a Constant Pulse Width of 6.0 μs



Well controlled jetting performance

- Low viscosity
- Anisole default solvent



75V, 6.0 μs , 323 μs delay (Velocity: 1.64 ms^{-1})

While GIXRD can in principle be used to monitor the surface roughness during annealing via reflectivity experiments, it is difficult to obtain the required time-resolution for *in-situ* studies. AFM provides information direct images of the morphology in addition to spatially-averaged surface roughness. We have performed such AFM measurements during *in-situ* annealing (**Fig. 8**). It is technically demanding to follow the rapid changes that occur in the first few minutes after the heater is switched on, nevertheless the changes in morphology are clearly seen. It is clear that the roughness increases rapidly between 90°C and 95°C. The combined GIXRD and AFM results therefore point to a temperature range around 86-90°C in which an ordered, yet relatively smooth, surface can be generated. This work is being prepared for publication.

We evaporated two electrodes 5 μm apart and applied 5V to the left electrode with the other electrode earthed. Using a new EFM-phase approach we could image the surface potential directly with the AFM while imaging (**Fig. 9b**). The electrical nature of the signal was confirmed by cutting molecular strands with the AFM tip in contact mode: the molecules to the right of the cut are at reduced potential because they are indirectly connected to the electrode around the cut (**Fig. 9c**). We are currently investigating the electrical properties of these networks. One paper has been published¹³ and another submitted on this work.¹⁴

Fig. 10: Ink-jet printing of polycyclopentadithiophene from anisole solution.

8. Research Output to November 2003

8.1 Oral Presentations.

- (1) 18th November 2002: University of Leicester, "Conjugated Materials for Polarised Electroluminescence and Polymer Electronics"
- (2) 28th November 2002: Meville Polymer Laboratory, University of Cambridge, "New Synthetic Routes to Polycyclopentadithiophenes"
- (3) 11th Dec 2002: White Rose symposium, York University: "Opportunities for solid phase synthesis using organogermanium linkers"
- (4) 1st February 2003: TU Graz, Austria, "Conjugated Materials for Polarised Electroluminescence and Photovoltaic Devices"
- (5) 19th February 2003: University of Liverpool, "New Synthetic Routes to Polycyclopentadithiophenes"
- (6) March 2003: University of Birmingham, A. Das, C.H. Lei, M. Elliott, and J.E. Macdonald, "EFM investigation of organic macromolecular networks"
- (7) 7-10th April 2003: UK SPM Conference, Swansea, A. Das, C.H. Lei, M. Elliott, and J.E. Macdonald, "Morphology and electrical behaviour of nanoscale semiconducting polymer networks."
- (8) 20-25th April 2003, Spring Meeting of MRS, San Francisco, USA, "A novel strategy for the synthesis of ultra pure organic semiconductors".
- (9) 8th May 2003: Avecia CASE symposium, Grasmere, "Preparation of Solution Processible Cyclopentadithiophene based Polymers and Copolymers for Plastic Electronics"
- (10) 16th May 2003: Bayer CropScience, Frankfurt: 'Opportunities for solid phase synthesis using organogermanium linkers'.
- (11) 30th July 2003: Sixth International Conference on Materials Chemistry, University of Sheffield, "Preparation of Solution Processible Cyclopentadithiophene based Polymers and Copolymers for Plastic Electronics"
- (12) 4th September 2003: CPFilms, Martinsville, VA, USA, "Conjugated Polymers – Synthesis and Applications"
- (13) 10th September 2003: Fall meeting of ACS, New York, USA, "Synthetic Routes to Solution Processable Polycyclopentadithiophenes"
- (14) 22nd Sept 2003: 1st University of Glasgow-Organon Symposium on Synthetic Chemistry: 'Opportunities for solid phase synthesis using organogermanium linkers'.
- (15) 24th Sept 2003: RSC Heterocyclic meeting Novartis Horsham: 'The development of organogermanium linkers for solid phase heterocycle synthesis'.
- (16) 26th September 2003, Third European Conference on Organic Electronics Research, Imperial College, Wye, Kent, "The First All-organic Single Transistor Ferroelectric Memory Device."
- (17) 22nd Oct 2003: the University of Leeds: 'Solid phase synthesis using organogermanium linkers'.
- (18) 27-31st October 2003: 9th International Symposium on Radiation Physics, Cape Town, J E Macdonald, "Applications of Surface X-ray Diffraction to Polymer Interfaces".

8.2 Poster Presentations

- (1) 3-7th March 2003: APS March Meeting 2003, Austin, Texas, U.S.A, C.H. Lei, A. Das, J.E. Macdonald and M. Elliott, "EFM Investigations of Macromolecules at the Nanometer Scale".
- (2) 20-25th April 2003, Spring Meeting of MRS, San Francisco, USA, P. Coppo, D. C. Cupertino, S. G. Yeates, M. L. Turner, "Investigation of the electronic properties of cyclopentadithiophene polymers and copolymers".
- (3) May 2003: IOP Nanophysics Meeting, Reading, C.H. Lei, A. Das, M. Elliott and J.E. Macdonald, "Electric Force Microscopy Investigation of Organic Macromolecular Networks".
- (4) 28th July – 1st August 2003: Sixth International Conference on Materials Chemistry, University of Sheffield. J. Gautrot, Dr A. Ben Haida and P.Hodge, "Synthesis of novel n-type conjugated polymers based on anthraquinone".
- (5) 28th July – 1st August 2003: Sixth International Conference on Materials Chemistry, University of Sheffield. P. Coppo, D. C. Cupertino, S. G. Yeates, M. L. Turner, "An investigation of the optical and electronic properties of solution processed polycyclopentadithiophene thin films."
- (6) 10-14th September 2003, Seventh European Conference on Molecular Electronics, Avignon, France, J. Gautrot, Dr A. Ben Haida and P.Hodge, "Synthesis of novel n-type conjugated polymers based on anthraquinone".
- (7) 23-27th September 2003, Third European Conference on Organic Electronics Research, Imperial College, Wye, Kent, L.A. Majewski, R. Schroeder and M. Grell "Flexible OFETs with high gate capacitance"
- (8) 23-27th September 2003, Third European Conference on Organic Electronics Research, Imperial College, Wye, Kent, R. Schroeder, L.A. Majewski and M. Grell "Organic field-effect transistors with non-ohmic contacts"
- (9) 23-27th September, 2003: Third European Conference on Organic Electronics Research, Imperial College, Wye, Kent, C. H. Lei, A. Das, M. Elliott and J. E. Macdonald, "Surface potential determination of conjugated polymer films by EFM-phase with high resolution"

8.3 Papers/Patents Published and Submitted

- (1) P. Coppo, D.C. Cupertino, S.G. Yeates and M.L. Turner, *J. Mat. Chem.*, 2002, **12**, 2597-2599;
- (2) P. Coppo, D.C. Cupertino, S.G. Yeates and M.L. Turner, *Macromolecules*, 2003, **36**, 2705-2711
- (3) P. Coppo and M.L. Turner, *Mat. Res. Soc. Symp. Proc.* **2003**, 771, 61-64.
- (4) P. Coppo, H. Adams, D.C. Cupertino, S.G. Yeates, and M.L. Turner, *Chem. Comm.*, 2003, 2548-2549
- (5) A.C. Spivey, D.J. Turner, M.L. Turner, and S. Yeates, *Org. Lett.* 2002, **4**, 1899-1902
- (6) D. Turner, A. Spivey, D. Cupertino, P. Mackie, R. Anemain, S. Yeates, *Mat. Res. Soc. Symp. Proc.* **2003**, 771, L8.8.1.
- (7) A.C. Spivey, D.J. Turner, M.L. Turner, and S. Yeates, *Synlett* 2003, *in press*
- (8) A.C. Spivey, D.J. Turner, *UK patent application*; Avecia Ltd. 2002, published 2003.
- (9) L.A. Majewski, M. Grell, S.D. Ogier, J. Veres, *Organic Electronics* 2003, **4**, 27-32.
- (10) R. Schroeder, L.A. Majewski and M. Grell, *Appl. Phys. Lett.*, 2003, **83**, 3201-3203.
- (11) R. Schroeder and M. Grell, *Adv. Mater.*, submitted.
- (12) R. Schroeder and M. Grell, *UK patent application*, 0318522.0.
- (13) C H Lei, A Das, M Elliott and J E Macdonald, *Appl. Phys. Lett.*, 2003, **83**, 482-484.
- (14) C H Lei, A Das, M Elliott and J E Macdonald, *Nanotech.*, submitted.