Macromol. Symp. ***175,*** *151–158 (2001)*

Synthesis and Properties of Self Organising Semiconducting and Luminescent Polymers and Model Compounds

W.J Feast,[a*] *F. Goldoni*[b], *A.F.M. Kilbinger*[a], *E.W. Meijer*[b], *M.C. Petty*[c] *and A.P.H.J. Schenning*[b]

a) IRC in Polymer Science and Technology, University of Durham, Durham DH1 3LE, U.K.
b) Laboratory of Macromolecular and Organic Chemistry, Dutch Polymer Institute, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands, and c) School of Engineering, University of Durham, Durham DH1 3LE, U.K.

SUMMARY: Oligothiophene-PEO-block-co-polymers and related model compounds have been synthesised and characterised. In the polymers well-defined oligothiophene blocks (with from two to six α,α-linked thiophene sequences) were alternated with poly(ethylene oxide) blocks of narrow polydispersity. Model α,α-linked sexithiophenes were prepared carrying chiral, achiral, mono and narrow polydispersity monomethyl PEO substituents at their terminal alpha positions. All the products were soluble in common organic solvents and organic/aqueous solvent mixtures. UV/vis and fluorescence studies in solution indicated that the oligothiophene segments were molecularly dissolved in good solvents like chloroform. Aggregation of the oligothiophenes occurred in dioxane/water mixtures, consistent with observed shifts of the UV absorption maxima towards the blue and quenching of the fluorescence. An oligothiophene length of three thiophenes (terthiophene) was necessary for aggregation to be observed. The materials formed well-organised transferable monolayers at the air water interface.

Introduction

Semiconducting conjugated organic compounds are of potential interest for application in electronic device structures because they offer potentially cheap materials which should be easy to fabricate via conventional processes. Early examples of conjugated polymers were generally ill-defined, they often displayed wide distributions of conjugation lengths and structural defects were rife. Progress in this field depended on the availability of much better defined materials and the synthesis of conjugated oligomers was attractive because such materials could be relatively easily purified, giving the products as monodisperse well-defined single compounds. Pure α,α-linked sexithiophene, was established as a promising organic semiconductor material for field effect transistor applications (FET).1) To be of practical interest organic semiconductors are required to be processable, preferably from solution; however, as the molecular weights of oligothiophenes increase their solubilities decrease which, of course, inhibits solution processing. In attempts to overcome this problem substituents have been attached to the oligothiophene units in either the α- or the β-positions,

CCC 1022-1360/00/$ 17.50+.50/0

by and large α-substituents did not provide practically useful solubilities,2-5) whereas β-substitution gave highly soluble derivatives.6-10) Many variants of polythiophene and oligothiophene homo- and co-polymers have been described but, as far as we are aware, usefully significant solubilities were only achieved with β-substituents. It has been suggested that substitution at sites other than the 4- or 5-carbons of the terminal rings of oligothiophene sequences twists the rings out of planarity and reduces π-overlap significantly with consequent reduction of useful electronic properties.11) The electronic and optical properties of conjugated oligomers and polymers depend on the planarity of the conjugated segment and interchain interactions, aggregation of conjugated sequences occurs in poor solvents and on cooling solutions of such materials in good solvents,1,2,12,13) the aggregates have properties reminescent of the solid state. This behaviour has been studied for several β- substituted poly- and oligothiophenes but there are few reports on the aggregation of α-substituted oligothiophenes or main chain polymers. A high degree of solid state order is necessary for the high carrier mobilities required if organic semiconductors are to find use in electronic devices such as FETs. In this paper we describe an approach to solution processable alternating oligothiophene-PEO-block-*co*-polymers and related model compounds in which the oligothiophene blocks are only α-substituted and some of the properties and characterisation data which demonstrate their aggregation and organisation in aqueous solution.

Concept

Our first approach to making polymers and model compounds containing oligothiophene units that could aggregate is shown in Figure 1 for the general case of a processable copolymer. The idea was to link α-functionalised segments of the eventual oligothiophene units via short flexible and soluble chains to give the BB-monomer shown in the bottom right-hand corner of the cartoon. This BB-monomer could then be coupled with an AA-monomer using any appropriate metal mediated aryl-aryl coupling technique.

Results and discussion

The concept outlined above is extendable to a variety of polymers and model compounds and examples of its application are outlined in Figures 2 and 3, the experimental details having been published elsewhere.14, 15) Figure 2 illustrates the route adopted for the synthesis of PEO-oligothiophene block copolymers containing six and five α,α-linked thiophene sequences. A similar process was followed for the analogous block copolymers containing di-, tri- and tetra- α,α-linked thiophene sequences and the molecular weights of the products are shown in the Table.

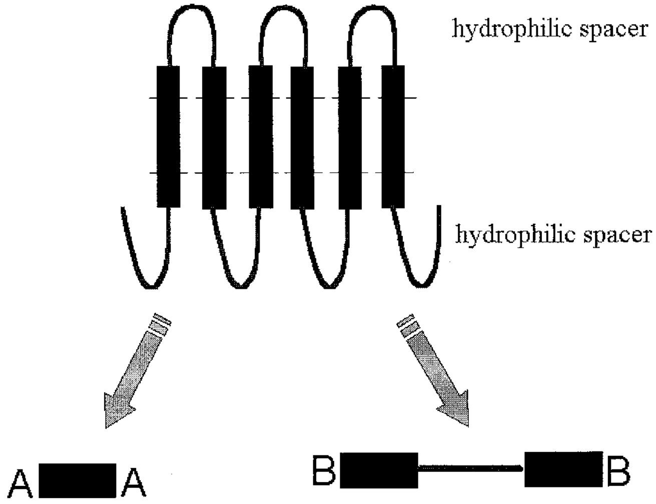

Figure 1. Cartoon illustrating the concept for the synthesis of solution proccessable polymers containing oligothiophene segments; solid rectangular blocks represent oligothiophene sequences, the simple lines represent flexible solubilising linkers, **A** and **B** are function groups used in the coupling reaction and the broken line indicates the polymer assembly points.

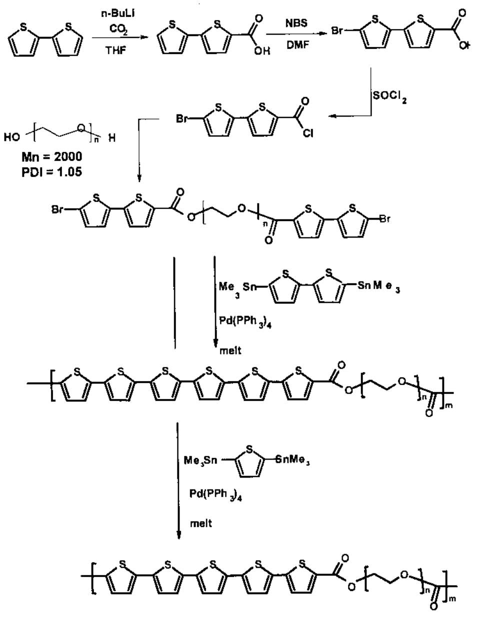

Figure 2. Schematic for the synthesis of copolymers of α,α-sexithiophene- and -pentathiophene-PEG copolymers, see reference 14 for experimental details.

Although the degrees of polymerisation attained are relatively low, the molecular weights are quite respectable because of the size of the PEO blocks incorporated and these polymers form films from solution or the melt; the **6T** polymer, for example, gives tough rubbery films.

Table: GPC ($CHCl_3$, PS standards) data for the oligothiphene-PEO block copolymers prepared by the routes indicated schematically in Figure 2; **2T**, **3T** etc indicates bi- tri- etc thiophene sequences.

	M_n	M_w	DP_n
2T polymer	13500	21100	6
3T polymer	14360	21780	2
4T polymer	14500	20700	6
5T polymer	9300	16900	4
6T polymer	13300	19000	5

Model compounds were prepared by a similar approach as show in Figure 3 for the sexithophene derivatives carrying monomethyl-PEG substituents of M_n 350 and 750. Higher molecular weight examples of this class and models carrying monodisperse chiral monomethyl PEG were also prepared and their characterisation by MALDI is shown in Figure 4.

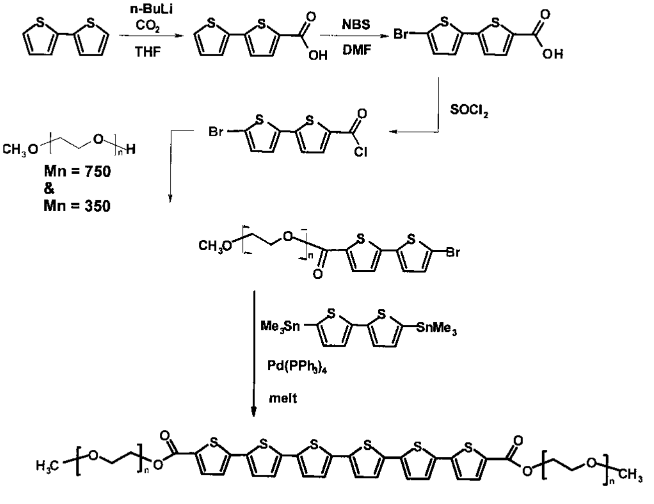

Figure 3. Schematic for the synthesis of a typical model α,α-sexithiophene carrying α,α- PEG substituents.

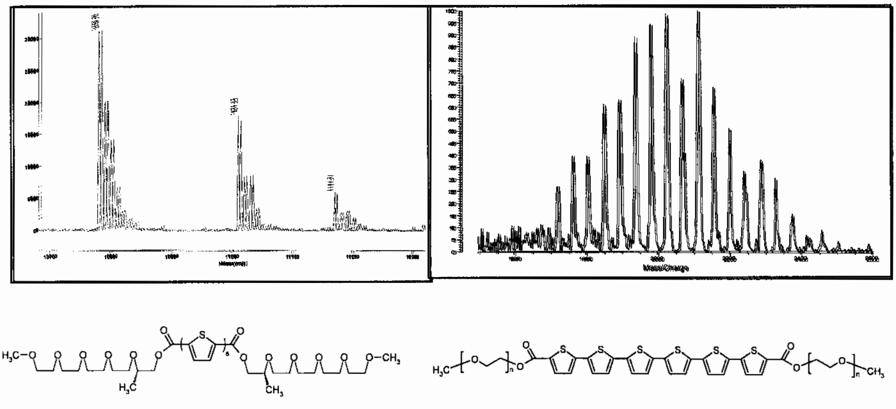

Figure 4. MALDI TOF spectra of model compounds. On the left the molecular ion of the chiral model compound with attached H$^+$, Na$^+$ and K$^+$ ions and appropriate isotopic abundances; on the right the spectrum of the sexithiophene with monomethylPEG 750 substituents; recorded using a KRATOS MALDI IV with hydroxycinnamic acid matrix.

Spectroscopic evidence for aggregation

The UV-vis absorption and emission spectra of chloroform and aqueous solutions (both 6.7 10^{-6} mol l^{-1}) of the polymers listed in the Table are shown in Figure 5.

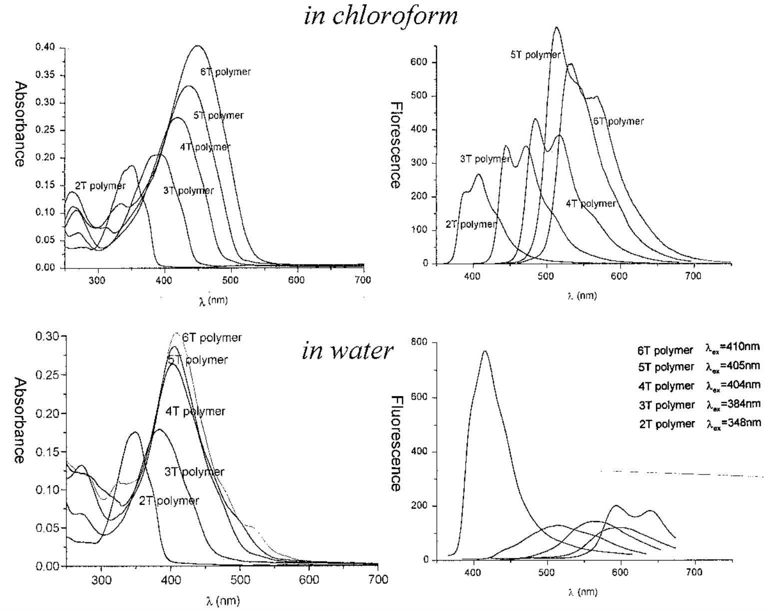

Figure 5. UV-vis absorption and emission spectra of chloroform and aqueous solutions (both 6.7 10^{-6} mol l^{-1}) of the polymers listed in the Table.

In chloroform the absorption spectra display structureless bands with the absorption maximum shifted towards the red for the longer oligothiophene sequences as expected for molecularly dissolved chromophores with increasing extents of conjugation. The fluorescence spectra show clearly three bands, which have been identified as the vibronic replicas of the 0-0 transition.

The UV-vis spectra of dioxane solutions of this set of five polymers with chromophore concentrations of $6.7\ 10^{-6}$ mol l^{-1} are the same as those shown above for chloroform solutions. Dilution of the dioxane solutions with water resulted in a progressive blue shift in the λ_{max} of the absorbtion spectra for all the polymers having thiophene block lengths greater than two. This shift increased with increasing water content and with thiophene block length and was most marked for the sexithiophene case where a 38nm shift was observed. Concomitant with these blue shifts the luminescence of the aqueous solutions of the polymers with thiophene block lengths greater than two was quenched. Both these phenomena are consistent with aggregation of the oligothiophene blocks in aqueous solution via face to face π-stacking. The spectra for the polymers in water:dioxane (83:17) solution are shown in the bottom half of Figure 5. This behaviour has been established for other oligothiophenes and we have recently reported the helical face to face π-stacking of the chiral di-substituted sexithiophene derivative shown in the left-hand side of Figure 4 (above) where analogous phenomena were observed and discussed in some detail.[15)] Furthermore we have shown that this tendency for sexithiphene aggregation is strong enough to allow the mass spectroscopic detection of aggregates up to the heptamer.[16)] Further evidence for aggregation in aqueous solution was obtained from ^{1}H NMR spectroscopy. In Figure 6 the lower spectrum, recorded in $CDCl_3$, displays the well resolved sharp signals characteristic of a molecularly dissolved species whereas the upper spectrum shows the broad lines reminiscent of the solid state and consistent with aggregation in aqueous solution.

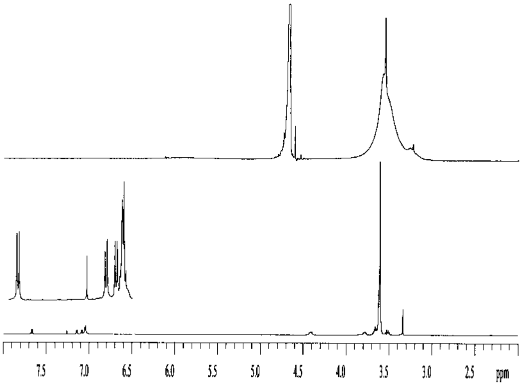

Figure 6. ^{1}H NMR spectroscopic evidence of aggregation of α,α-linked sexithiophene blocks carrying PEO substituents at the terminal α-positions; upper spectrum in D_2O, lower in $CDCl_3$ solution.

Organisation at the air-water interface

Ideally we would like to use these aggregating oligothiophenes as highly organised very thin films. To this end we have examined how the materials behave at the air-water interface on a Langmuir trough. The results for the sexithiophene-PEO block copolymer, and three model compounds containing sexithiophene units are shown in Figure 7. The model compounds carrying the chiral monomethylpentaethyleneglycol substituents (lower right-hand curve) and the model with the shorter achiral monomethylpolyethylene -glycol substituents (**n** = **8**, PEG 350, lower left-hand curve) both show classical amphiphile surface behaviour. Both these systems appear to give well organised monomolecular layers at the surface. By assuming that we are observing a monomolecular layer and extrapolating the steep parts of the pressure-area curves to the area axis, the surface area occupied by each sexithiophene unit is computed to be 56 Å^2. If true, this corresponds to the ideal situation where the conjugated units are lying on edge and face to face at the surface. When the PEG substituent is longer (**n** = **17**, PEG 750, lower left-hand curve) and the 6T-polymer (the spacer in the polymer was PEG 2000), the pressure-area curves show a break before entering the steep "pseudo solid" organisation stage. The pressure-area curves recorded for polymers with thiophene block lengths of less than six collapsed before reaching the "pseudo solid" organisation stage. Preliminary experiments indicate that the model compounds and the sexithiophene-PEO block copolymer undergo Langmuir-Blodgett transfer in a controlled well-defined manner.

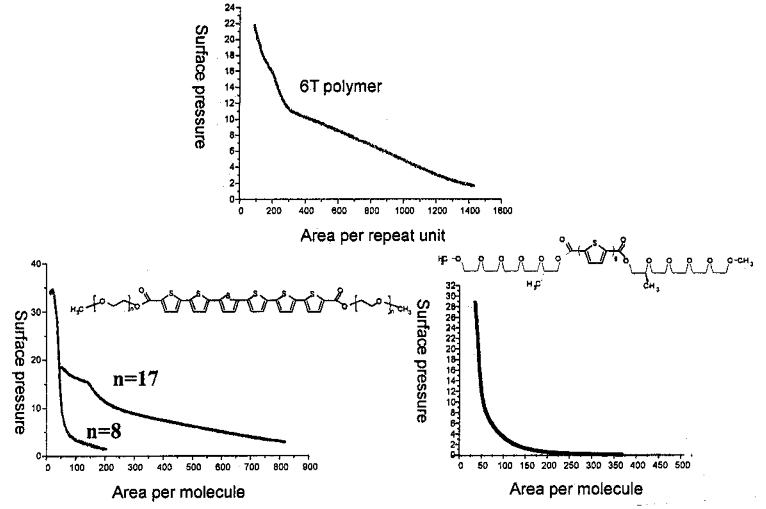

Figure 7. Pressure-area curves for the sexithiophene-PEO block copolymer and related model compounds. Surface pressures are in mN/m and areas are in Å^2.

Conclusions

A series of block copolymers and model compounds based on α,α-linked oligothiophene and polyethylene oxide subunits has been synthesised and characterised. These materials show a marked tendency to self-organisation that can be controlled by solvent selection and organised at an air-water interface. The manipulation of these types of structures along with their electrical and optical properties is the subject of ongoing work in our groups and elsewhere.

Acknowledgements

The authors wish to acknowledge the European Commission TMR Network SELOA (contract number ERBFMRX-CT960083) for financial support.

References

1. Horowitz, G.; Garnier, F.; Yassar, A.; Hajlaoui, R.; Kouki, F. *Adv. Mater.* **1996**, *8*, 52.
2 Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716-8721.
3. Wei, Y.; Yang, Y.; Yeh, J. M. *Chem. Mater.* **1996**, *8*, 2659-2666.
4. Katz, H. E.; Laquindanum, J. G.; Lovinger, A. J. *Chem. Mater.* **1998**, *10*, 633-638.
5. Katz, H. E.; Dodabalapur, A.; Torsi, L.; Elder, D. *Chem. Mater.* **1995**, *7*, 2238-2240.
6. Barbarella, G.; Zambianchi, M.; Bongini, A.; Antolini, L. *J. Org. Chem.* **1996**, *61*, 4708-4715.
7 Bidan, G.; DeNicola, A.; Enee, V.; Guillerez, S. *Chem. Mater.* **1998**, *10*, 1052-1058.
8. Tour, J. M.; Wu, R. L. *Macromolecules* **1992**, *25*, 1901-1907.
9. Goldoni, F.; Iarossi, D.; Mucci, A.; Schenetti, L. *J. Chem. Soc., Chem. Commun.* **1997**, 2175-2176.
10. Delabouglise, D.; Hmyene, M.; Horowitz, G.; Yassar, A.; Garnier, F. *Adv. Mater.* **1992**, *4*, 107-110.
11. Katz, H. E. *J. Mater. Chem.* **1997**, *7*, 369-376.
12. Stubb, H.; Punkka, E.; Paloheimo *J. Mater. Sci.* **1993**, *10*, 85.
13. Jarrett, C. P.; Friend, R. H.; Brown, A. R.; de Leeuw, D. M. *J. Appl. Phys.* **1995**, *77*, 6289.
14. Kilbinger, A.F.M and Feast, W.J. *J.Materials Chem.*, **2000,** *10*, 1777-1784.
15. Kilbinger, A.F.M., Schenning, A.P.H.J., Goldoni, F., Feast, W.J. and Meijer, E.W. *J. Amer.Chem.Soc*, **2000,** *122,* 1820-1821.
16. A. F. M. Kilbinger, A.F.M., Cooper, H.J., McDonnell, L.A., Feast, W.J., Derrick, P.J., Schenning, A.P.H.J. and Meijer, E.W. *Chemical Communications*, **2000**, 383-384.