A Novel Strategy for the Solid Phase Synthesis of Ultra Pure Organic Semiconductors

D. Turner[a], A. Spivey[a], D. Cupertino[b], P. Mackie[b], R. Anemian[b], S. Yeates[b],
a: Department of Chemistry,University of Sheffield, Brook Hill, Sheffield S3 7HF, U.K.
b: Avecia Ltd., Hexagon House, Blackley, Manchester M9 8ZS, U.K.

ABSTRACT

A new solid phase synthetic strategy for the production of organic semiconductors has been developed. The strategy uses a germanium-based linker and Suzuki-type cross-coupling protocols and has been demonstrated for the iterative synthesis of both a regio-regular oligo-3-alkyl-thiophene and an oligoarylamine. The process also incorporates a novel "double-coupling" after each iteration which minimizes deletion sequences. The key steps exploits the susceptibility of α-silyl- or α-silyloxy- but not germyl-substituted derivatives toward nucleophilic *ipso*-protodemetalation.

INTRODUCTION

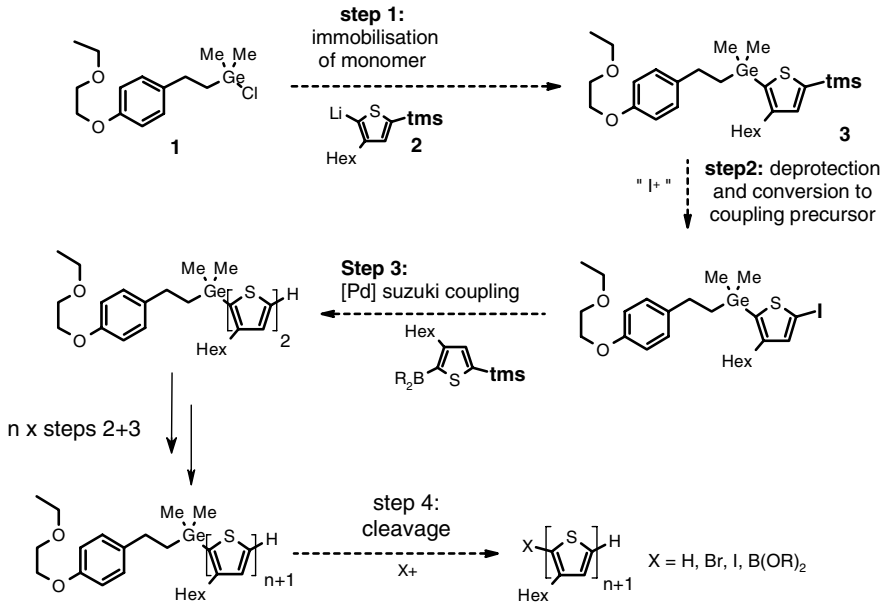
π-Conjugated heterocyclic oligomers are promising candidates for organic semiconductors but for these, high levels of purity are critical. Although solution phase chemistry may be used to target polyheterocycles and oligoheterocycles using repetitive transition metal catalyzed cross-coupling of the monomers in solution, the purification strategies required to meet the requisite levels of purity are inefficient requiring careful purification of chromatographically similar intermediates after each successive iteration; a process which is time-consuming, and inefficient [1]. Such methods are therefore of questionable commercial applicability. Moreover, conventional methods for preparing oligo-heterocycles (such as oligo-thiophenes) using solution phase cross-coupling (*e.g.* Suzuki, Kharasch, Stille or Negishi type processes) are plagued by undesirable side reactions such as homo-coupling and loss of functional groups again making purification arduous and inefficient.

Recent publications applying solid phase organic synthesis (SPOS) to the preparation of oligo-3-alkyl-thiophenes demonstrate that SPOS offers an attractive solution to some of the purification issues [2]. However, the ultimate purity of the cleaved oligomer is critically dependent on the yields attained for each individual cross-coupling step. Incomplete cross-coupling results in deletions and leads to a distribution in the final oligomer length. We describe in this work the development of a novel and efficient strategy for the iterative solid phase preparation of oligo-β-3-alkyl-thiophenes) and also for an oligoarylamine organic semiconducting material of well-defined lengths and high purity involving a 'double-coupling' strategy. The method employs a germanium-based linker [3] and exploits the orthogonal susceptibility of α-silyl and α-germyl substituted thiophene-derivatives and α-silyloxy and α-germyl substituted arylamine-derivatives towards nucleophilic *ipso*-protodemetalation. The germanium-based linker also allows for final cleavage by electrophilic *ipso*-degermylation [3]. Cleavage with acid will yield α-H terminated oligomers, whereas cleavage with halonium ions will yield α-halo terminated oligomers [4]. Such α,ω- differentiated telechelic oligomers are valuable substrates for block co-oligomer preparation and for oligomer end-capping. The advantages of solid phase chemistry over solution phase chemistry include ease of purification, amenability to automation, the ability to use excess reagents to drive reactions to completion without the penalty of making purification tedious and dilution effects (site isolation) which prevent homo-coupling. For these reasons, solid phase synthesis is seen as an attractive alternative for preparing poly-and oligo- conjugated organic semiconductors on a large scale which as yet has undergone little investigation.

RESULTS AND DISCUSSION

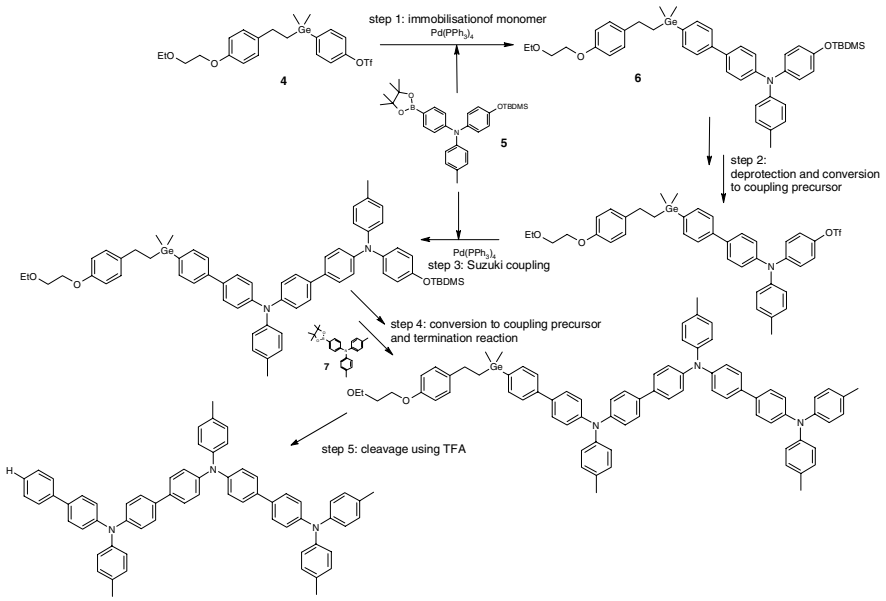
Initial studies for developing the SPOS system required the development of a solution phase model systems from the readily available chlorogermane. Two systems were investigated to give a regio-regular oligo-3-hexyl-thiophene and an oligoarylamine. Scheme 1. shows the a solution model synthesis of a regio-regular oligomer. Thiophene **3** was prepared by reaction of linker model **1** with lithiated thiophene **2**. The TMS protecting group ensures that none of the undesired alternate R-lithiated thiophene is formed and moreover, in the context of SPOS, would allow immobilization to be driven to completion by repeating the reaction steps (*double coupling*). The immobilized thiophene was then activated by removing the TMS blocking group and converting it to a reactive iodo species in a simple iodination reaction. This was followed by a second Suzuki coupling of a TMS protected monomer unit using $Pd(PPh_3)_4$ as the catalyst. Again the reaction was driven to completion by using a *"double coupling"* strategy by repeating steps 2 and 3 as shown in Scheme 1. Further monomer units were added by repeating the deprotection, iodination and Suzuki coupling. The final product was removed in a cleavage reaction using trifluoracetic acid TFA, in this case to give a H terminated group.

In a similar manner to that described for the synthesis of the RR-3-hexylthiophene, Scheme 2 shows a solution model synthesis of an oligomeric triarylamine. The germyl protected arylamine **6** was prepared by reaction of the germyl phenyltriflate linker **4** with the boronic ester derivatised –O-tributyldimethylsilyl (OTBDMS) protected monomer **5** using Suzuki cross-coupling conditions. The OTBDMS protecting group again allows the immobilization to be driven to completion by repeating the reaction steps (*double coupling*). The immobilized arylamine was then activated by removing the OTBDMS blocking group and converting it to a reactive triflate species by deprotecting with TFA and then reacting with triflic acid anhydride. A second unit of monomer **5** was then attached in a second Suzuki coupling.



Scheme 1

Step 1: Immobilization of monomer to Germyl linker group and deprotection of TMS group.
Step 2: Conversion to an R-iodide coupling precursor.
Step 3: Cross-coupling of a TMS blocked monomer.
Double-coupling: Repeat steps 2 and 3 and repeating to give build up of (n) repeat units
Step 4: Cleavage of final product

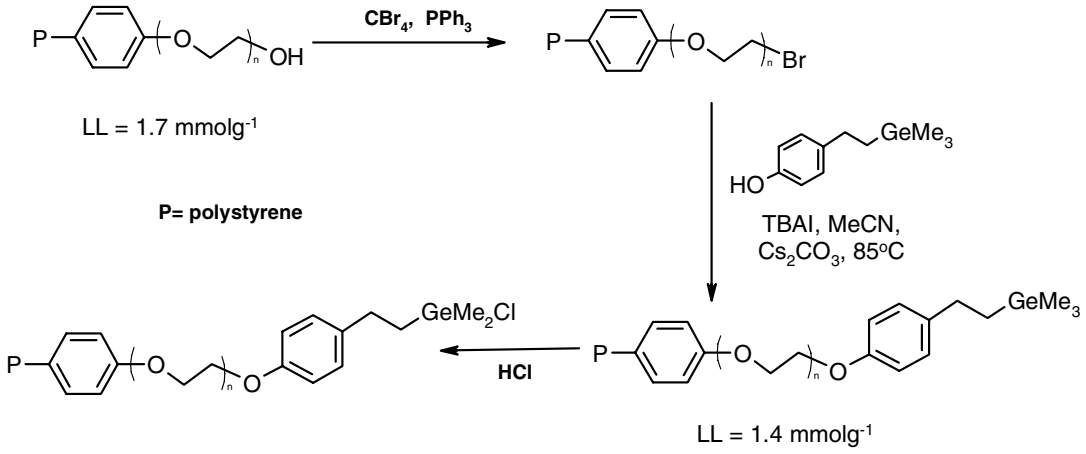


Scheme 2

Step 1: Immobilization of monomer to Germyl linker group.
Step 2: Deprotection of OTBDMS group and conversion to a triflate coupling precursor.
Step 3: Cross-coupling of an O-TBDMS protected boronic ester monomer.
Double-coupling: Repeat steps 2 and 3 and repeating to give build up of (n) repeat units
Step 4: Deprotection of OTBDMS group and conversion to a triflate coupling precursor and coupling to a terminal triarylamine unit.
Step 5: Cleavage of final product with TFA.

A second monomer units was then added by repeating the deprotection, triflation and Suzuki coupling. In the final coupling step, a terminal group **7** was added and the product was removed in a cleavage reaction using trifluoracetic acid TFA.

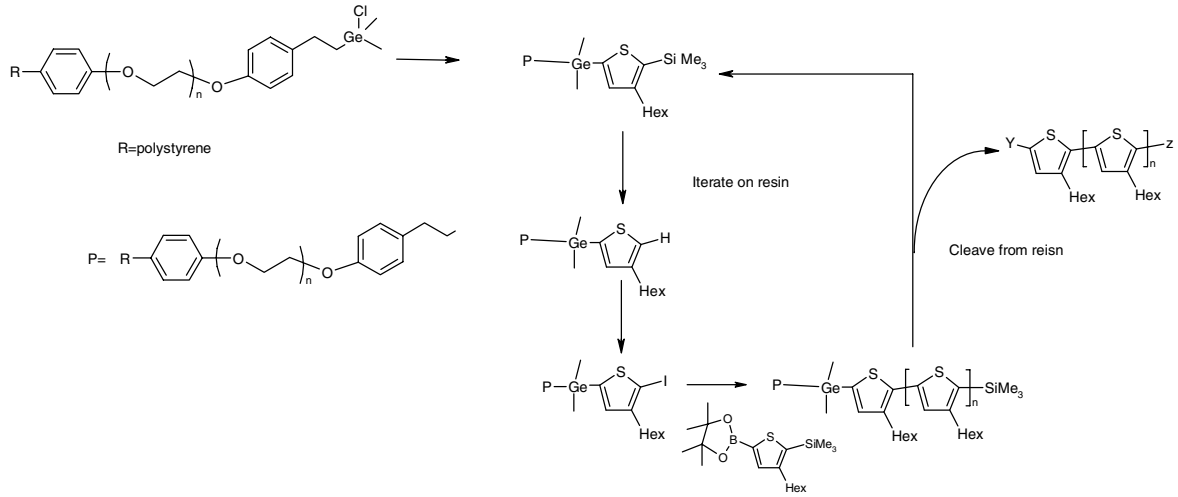
The solution phase chemistry was transferred to the solid phase resin for both the RR-thiophene and the triarylamine systems. The resin which was chosen as the solid support was based on Hypogel-200-OH which was purchased from Fluka Chemicals. Fictionalization of the resin to give the reactive germyl linker was achieved as shown in Scheme 3.



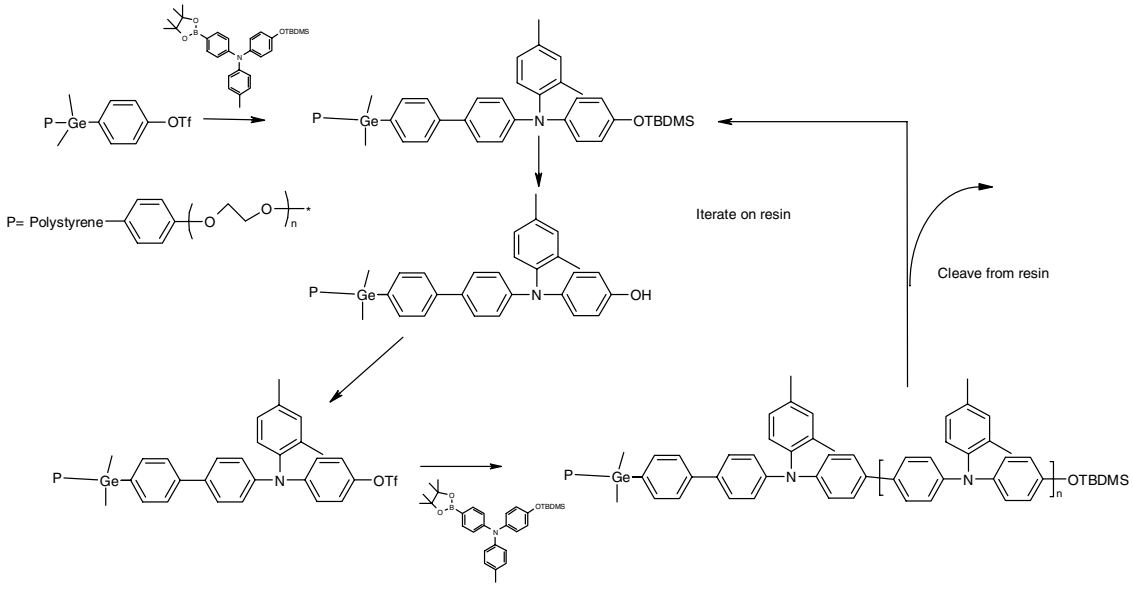
Scheme 3

To demonstrate the solid phase syntheses of the two semiconductors, trimers of each were prepared by iterative building on the solid support. All compounds were characterised by gel phase NMR spectroscopy and by elemental analysis and were found to be consistent with the expected structures. Scheme 4 shows the steps used to produce the RR-thiophene. The chlorogermyl functionalised resin was reacted with the first TMS protected thiophene monomer. The thiophene was deprotected and iodinated as before and reacted with the second monomer unit. The resin was then re-iodinated and the coupling reaction repeated to give high conversion of the second coupled thiophene. The steps were repeated to give a third unit on the resin.

In a similar approach, Scheme 5 shows the steps used to produce the triarylamine trimer. In this case, the chlorogermyl functionalised resin was reacted with the first OTBDMS protected arylamine monomer using Suzuki conditions.



Scheme 4.



Scheme 5

The arylamine was deprotected and converted to the precursor triflate which was then coupled to the second monomer unit $Pd(PPh_3)_4$ as the catalysts under Suzuki coupling conditions. Repeated triflation and coupling gave high conversion of the second coupled thiophene. The steps were then repeated to give a third unit on the resin which in this case was simultaneously deprotected and cleaved from the resin using TFA to give the H, H terminated triarlyamine trimer.

CONCLUSIONS

In summary, we have developed the key iterative steps of a new strategy for the synthesis of regioregular oligo-(β-hexylthiophenes) and triarlyamines that allows for double-coupling after each iteration to minimize deletion sequences and drive the reactions to high conversion. Model studies were carried in the solution phase utilising the significantly greater stability of (hetero)arylgermanes to nucleophilic conditions relative to the corresponding (hetero)-arylsilanes. This enhanced stability constitutes an important advantage that germanium-based "traceless" linker systems have for SPOS relative to their silicon-based counterparts. We have further demonstrated that the chemistry can be transferred to a solid phase supported resin to give trimers of the semi-conductor materials.

We are currently optimizing the strategy for the SPOS of high purity oligothiophenes and triarlyamines and adapting the concept for the preparation of other oligoheterocycles and derived block cooligomers.

REFERENCES

1. Bäuerle, P. In *Handbook of Oligo-Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 89 (1999).
2. (a) Malenfrant, P. R. L.; Fréchet, J. M. J.; *Chem. Commun*., 2657, (1998). (b) Briehn, C. A.; Kirschbaum, T.; Bäuerle, P. *J. Org. Chem.*, *65*, 352, (2000). (c) Kirschbaum, T., Briehn, C. A.; Bäuerle, P. *J. Chem. Soc., Perkin Trans. 1*, 1211, (2000). (d) Kirschbaum, T.; Bäuerle, P. *Synth. Met,* , *119*, 127, (2001). (e) Briehn, C. A.; Schiedel, M.-S.; Bonsen, E. M.; Schuhmann, W.; Bäuerle, P. *Angew. Chem. Int. Ed.*, *40*, 4680, (2001).
3. Spivey, A. C.; Diaper, Adams, H.;C. M.; Rudge, A. *J. Org. Chem.*, *65*, 5253, (2000).
4. Spivey, A. C.; Turner, D. J.; Turner M. L.; Yeates, S.; *Org. Lett.*, *4*, 1899, (2002).