polymer communication

## The formation of polysilanes from homogeneous reagents in tetrahydrofuran solution at low temperatures

**Richard G. Jones*, Robert E. Benfield, R. Harry Cragg, Philip J. Evans and Anthony C. Swain**
*Centre for Materials Research, Chemical Laboratory, University of Kent, Canterbury CT2 7NH, UK*
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Poly(methylphenylsilane) has been synthesized through homogeneous reductive dechlorination of dichloromethylphenylsilane using sodium/electron-acceptor complexes in tetrahydrofuran solution at $-79°C$. The optimization of product molecular weights is considered through analogy to a step-growth polymerization.

**(Keywords: polysilanes; synthesis; homogeneous Wurtz coupling)**

In spite of synthetic developments in recent years[1–4], the alkali-metal-mediated heterogeneous Wurtz-type reductive dechlorination of dichloroorganosilanes, shown in *Scheme 1*, remains the most viable method for the synthesis of polysilanes.

$$R_2SiCl_2 + 2Na \rightarrow 1/n \left( SiR_2 \right)_n + 2NaCl$$

**Scheme 1**

The reaction is most commonly carried out using sodium in 'inert' solvents that boil at temperatures above the melting point of the metal, though recent studies have shown that the reaction can be carried out successfully at lower temperatures, particularly in the presence of additives such as diglyme, cryptands or crown ethers[5,6]. Another low-temperature synthetic strategy has involved the use of high intensity ultrasonic activation of the reaction[7,8]. However, by whatever method the heterogeneous reaction is conducted, the polymer molecular weight distributions are usually complex, the yields are often low and cyclic oligosilanes are major by-products. Various arguments concerning the heterogeneous nature of the reaction mixture[9–11] and/or the relative importance of anions and radicals as chain carriers in the propagation reaction[12–15] have been advanced to explain these experimental observations. It is now generally accepted that the polymodal molecular weight distributions arise from the heterogeneity of the reaction medium, and since each step in the chain growth requires the transfer of two electrons from the alkali metal, that the propagating centres must in turn progress from covalent structures through anion-radical and radical structures to anionic structures, immediately prior to monomer incorporation.

A modification of the synthetic strategy that might be pursued to further clarify the nature of the propagation reaction would follow from the achievement of the reductive dechlorination of dichlorosilanes homogeneously in solution. It is generally accepted that this is not possible, the stated reason being the importance of the metal solution interface in the determination of the polymerization reaction. The isolation of only oligomeric products from the reaction of dichloromethylphenylsilane and the sodium/biphenyl complex in glyme at ambient temperature[9] is usually presented in support of this conclusion[16]. In this paper, however, we show that it is possible to form poly(methylphenylsilane) using homogeneous reagents in tetrahydrofuran (THF) solution at $-79°C$ in accordance with *Scheme 2*, in which A represents an electron-acceptor molecule such as biphenyl, naphthalene or anthracene.

$$Na + A \rightarrow Na^+ + A^{-\bullet}$$
$$R_2SiCl_2 + 2A^{-\bullet} \rightarrow 1/n \left( SiR_2 \right)_n + 2Cl^- + 2A$$

**Scheme 2**

Sodium/acceptor complexes were prepared under an inert atmosphere, as they would be for use as 'living polymerization' initiators[17], by dissolving sodium in a solution of about 5% stoichiometric excess of the electron acceptor in THF which had been predried over Na/K alloy. This solution and a solution of the monomer in THF were allowed to equilibrate at the desired temperature prior to mixing in stoichiometric ratio. Both 'normal' addition reactions, in which the monomer solution is added to that of the acceptor anion radical, and 'inverse' addition reactions were investigated. In all cases, the mixing of reagents was accompanied by an immediate discharge of the characteristic colour of the anion radical, the precipitation of sodium chloride causing the medium to assume the consistency and appearance of paste, and a significant generation of heat which, for reactions at $-79°C$, was evidenced by a marked increase in the discharge of carbon dioxide from the dry ice/acetone coolant mixture. Shortly afterwards, the product polymers were isolated using standard procedures[11]. Their $^1H$ and $^{13}C$ n.m.r. spectra, i.r. and u.v.–vis. spectra, and elemental analyses were consistent with the structure of poly(methylphenylsilane), confirming that no electron transfer reagents were incorporated in the polymer chain.

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* To whom correspondence should be addressed

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**Table 1** Yields and molecular weight parameters of polymeric products from the reaction of electron acceptor anion radicals with dichloromethylphenylsilane at −79°C in THF solution

| Electron acceptor | Addition mode | Yield (%) | $M_{r,n}$ | $M_{r,w}$ | $M_{r,w}/M_{r,n}$ |
|---|---|---|---|---|---|
| Naphthalene | Normal | 16 | 3280 | 4800 | 1.46 |
| Naphthalene | Inverse | 24 | 3940 | 7350 | 1.87 |
| Naphthalene[a] | Normal | 4 | 4040 | 8680 | 2.15 |
| Anthracene | Normal | 6 | 3100 | 4750 | 1.53 |
| Biphenyl | Normal | 23 | 3470 | 9500 | 2.73 |
| Tetraphenylethene | Normal | 6 | 12000 | 24500 | 2.04 |

[a] In the preparation of sodium naphthalide for this reaction naphthalene was used in 50% molar excess over sodium

Yields and product qualities were found to be more difficult to reproduce than for the reaction as it is normally carried out under heterogeneous conditions. In all instances, much of the product is oligomeric; however, as stated in the introductory paragraph, the same is true of the products of the heterogeneous reaction. *Table 1* lists the best yields and molecular weight parameters (as linear polystyrene equivalents) of polymeric products isolated from a selection of the reactions carried out at −79°C. Molecular weights of polysilanes are recognized to be at least twice those of linear polystyrene equivalents[16], so applying a factor of 2, the degrees of polymerization of the polymers depicted in the table range from about 50 to 200. Generally, as is apparent from the table, number average molecular weights of about 3500 could be achieved without difficulty, and the much higher value recorded for the tetraphenylethylene system is regarded as being fortuitous for reasons outlined below. In contrast, when the reactions were conducted at ambient temperature, much lower molecular weight products were obtained. For most of the systems these could truly be described as consisting only of oligomers and as such were lost during the normal isolation procedures. We have confirmed that it is only such low molecular weight products ($M_{r,n}=500$, $M_{r,w}=750$) that are formed in the dichloromethylphenylsilane/sodium–biphenyl/glyme system at ambient temperature described earlier by Zeigler[9].

The polydispersities given in *Table 1* are much lower than those obtained using the standard heterogeneous Wurtz synthesis of polysilanes, which, as a consequence of their polymodal distributions[11], are commonly greater than 5 even after removal of the oligomeric fractions. The size exclusion chromatograms of the products of the homogeneous reaction are monomodal and correspond closely to normal distributions. It follows that only one mechanism of propagation is involved and from the nature of the initiating species it can be concluded that the chain carrier is a silyl anion. These observations lend strength to the postulate that the complex distributions obtained from the reaction as it is normally carried out on an alkali metal surface, arise from the heterogeneous nature of the reaction medium.

Furthermore, we have established that the sodium-naphthalide-induced degradation of preformed poly(methylphenylsilane) to cyclic oligomers in THF solution at ambient temperature is completed in less than 30 min. For this reason alone it might be concluded that it is important to ensure stoichiometric proportioning of the reagents in these homogeneous reactions, for if any acceptor anion radical were to remain at the end of reaction, degradation would surely ensue. However, this consideration conceivably distracts from a more important point. Though the Wurtz polymerization propagates through a chain mechanism, from the stoichiometric standpoint it bears a close resemblance to a step-growth reaction. The only significant difference when it is conducted under homogeneous conditions, is that one reagent (essentially the electron), instead of being partly incorporated into the polymer as would be the case in a normal step-growth polymerization, is removed completely in the eliminated species as the charge on the halide ion. It is well known that for step-growth reactions, in order to obtain maximum molecular weights, it is essential that the reagents be mixed in stoichiometric proportion. Thus, leaving aside the consequences of the thermodynamically favoured cyclization of pentamers and hexamers, if either the dichlorosilane monomer or the acceptor anion radical were in stoichiometric excess at the instant of mixing, polymer chains could only grow until the reaction centres of the lesser reagent had been consumed. It is assumed that the difficulty in ensuring the stoichiometric proportion of these two reagents, both of which are extremely sensitive to adventitious impurities such as moisture, is the main reason for the difficulties encountered in reproducing the reactions. Only by preparing the reagents and conducting the reactions under the most stringent experimental conditions is it possible that higher molecular weight products might be obtained.

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