Alternative Reducing Agents for the Wurtz Synthesis of Polysilanes

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Poly(methylphenylsilane) has been shown to be capable of formation from dichloromethylphenylsilane using metallic reducing agents other than the alkali metals that are invariably used in these Wurtz-type coupling reactions; for these preliminary studies yttrium and pyrophoric lead were chosen on the basis of electrochemical and mechanistic considerations, and their ready availability as powders of controlled particle size, and though these are far from ideal reagents for the purpose, they demonstrate the possibilities for tight control of these reactions being achieved through the use of alternatives to the alkali metals.

The synthesis and characterization of soluble polysilanes has been the focus of recent interest because of their potential applications as preceramic materials and as resists for microlithography.[1–4] The most common method for their synthesis is the reductive coupling of dichlorosilanes using alkali metals, most commonly sodium; traditionally this reaction has been considered to require forcing conditions, as it is usually carried out in refluxing toluene to ensure the ready dispersion of the alkali metal as a liquid [eqn. (1)].

$$n\ R_2SiCl_2 + 2n\ Na \rightarrow -[SiR_2]_n^- + 2n\ NaCl \qquad (1)$$

We have recently reported that these syntheses may be carried out at lower temperatures in refluxing diethyl ether[5] and indeed even at room temperature. This observation enabled detailed study of the nature of the blue coloration[6] that ubiquitously appears in these systems, and for us subsequently to draw significant conclusions about the mechanism of the reaction.[7] Though stoichiometrically it seems to resemble a step growth reaction, it is more reasonably explained in terms of a chain growth from an ionic centre on the alkali metal surface; the heterogeneity of the reaction being sufficient to explain the polymodal molecular weight distributions that invariably result.

Nonetheless, the synthesis of polysilanes by means of the Wurtz reaction, which to this day remains the most viable synthetic route, will continue to suffer from several disadvantages, which must be overcome if commercial applications of these materials are to be realised. These are (*i*) the highly exothermic nature of the alkali metal mediated reaction and the consequent problems of control which mean that large-scale synthesis is hazardous and impracticable; (*ii*) the difficulty of making the polymers with reproducible yields and molecular weight distributions, and hence of invariant quality; (*iii*) the ultimate and inevitable degradation of the polymers in media containing the highly reducing alkali metal,[4,7,8] so that high molecular weight polymers constitute only a proportion of the product material; and (*iv*) the limitation of the range of possible substituent groups on the silicon atoms to those which are resistant to reduction by the alkali metal.

Despite these disadvantages, there are no reports of viable alternatives to the alkali metals as chemical reducing agents for the synthesis of high molecular weight polysilanes by dechlorination of dichlorosilanes. Electrochemical methods, using sacrificial electrodes, have recently received considerable attention,[9–15] but in some cases only oligosilanes have been formed.[12,13] Although the electrochemical synthesis of poly(dimethylsilane) in up to 90% Faradaic yield has recently

been achieved,[11] this corresponded to a much lower degree of conversion when expressed in terms of the proportion of monomer consumed. We have therefore embarked upon a search for new, milder chemical reducing agents to improve the control and performance of the Wurtz synthesis of polysilanes. Here we report our preliminary results with two metallic reducing agents, yttrium and pyrophoric lead.

Yttrium was chosen for the following reasons. Firstly, its standard electrode potential (−2.372 V for the formation of tripositive cations) is less negative than those of sodium (−2.71 V) and potassium (−2.931 V); it is thus a milder reducing agent more closely matched in reducing power to the −1.3 to −2.1 V estimated to be required for reductive Si–Si bond formation from dichlorosilanes.[8,9] Secondly, yttrium is a mechanically hard metal, available in powdered form with a closely controlled particle size. Since the Wurtz synthesis is a heterogeneous reaction[2,7,16] occurring on the surface of the metal, it follows that the most important determinants of the reproducibility of these reactions are the reproducibility of the surface that is available for reaction sites and the number of metal atoms that are in the volume contained by that surface. These in turn will be determined by the initial surface to volume ratio and the cleanliness of the metal. It was from such considerations that it was reasoned that control of the reaction is unlikely to be achieved by employing dispersions of sodium or Na–K alloys, no matter how vigorous the reaction conditions.

Dichloromethylphenylsilane was added to a stoichiometrically equivalent quantity of yttrium powder (particle size ≤ 420 μm, 99.9% purity) suspended in toluene, and the mixture was refluxed under a dinitrogen atmosphere in the usual way. Polysilane formation was indicated within a few hours by the solution becoming cloudy. Since metallic yttrium is passivated by a surface oxide layer,[17] it was found that the rate of the reaction could be greatly increased by its prior removal; this was readily achieved by cautiously adding aqueous HCl to the powdered yttrium followed by washing with diethyl ether and then drying *in vacuo*.

The reaction was monitored by size exclusion chromatography of aliquots of the supernatant liquor, using tetrahydrofuran (THF) as the mobile phase. Fig. 1 shows the molecular weight distributions (obtained relative to linear polystyrene equivalents, and hence subject to the usual degree of underestimation[2]) of polymer obtained from a reaction with activated yttrium powder after 7 and 30 days reflux. The yield and molecular weight of the poly(methylphenylsilane) increased steadily throughout the reaction. After 7 days, the weight-average molecular weight, $\overline{M}_{r,w}$ was ~9200; after 30 days, it had reached a value of ~31 000. It is significant that, in contrast to the usual experience with syntheses using alkali metals,[4,7,8] there was no evidence of degradation of the polymer over this prolonged reaction period. The eventual yield of poly(methylphenylsilane) was estimated to be only 5% but there was nothing to indicate that either this or the molecular weight of the polymer would not be increased by further maintaining the reaction conditions. A white precipitate of yttrium trichloride was also formed but the reaction was so slow that, consistent with the estimated conversion of monomer to polymer, the bulk of the yttrium remained. It will be recognised that these figures are not consistent with a step growth mechanism of polymerization. They can, however, be rationalized in terms of the previously accepted heterogeneous anionic mechanism of Gauthier and Worsfold[4,18] in which the initiation reaction and one stage of the two-stage propagation reaction would have to mount the high energy barrier associated with one electron transfers from yttrium atoms. These would be rate determining steps and would be expected to be very slow, but the powerful reducing properties of Y^+ should immediately secure two more monomer additions, possibly on chains growing on adjacent sites. The importance of the high surface area of the powdered yttrium was directly demonstrated by carrying out the reaction with acid-washed yttrium turnings; a much lower yield and average molecular weight for the product polymer were obtained, after an even more prologned reflux in toluene.

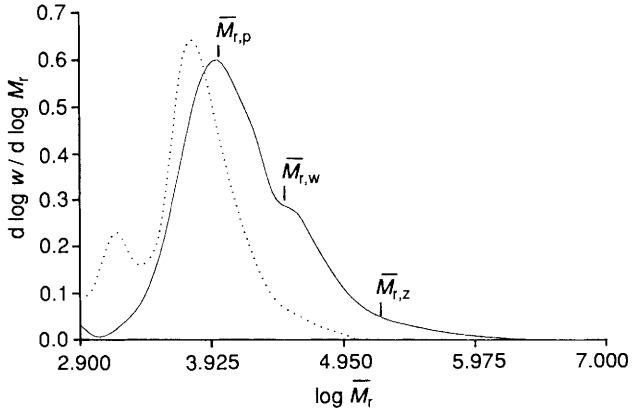

Fig. 1 Differential molecular weight plots of aliquots of poly(methylphenylsilane) formed in the reaction of dichloromethylphenylsilane with acid-activated yttrium powder in refluxing toluene. Molecular weights are quoted relative to polystyrene standards. ····· Reaction time 7 days; $\overline{M}_{r,p}$ = 5950, $\overline{M}_{r,n}$ = 4310, $\overline{M}_{r,w}$ = 9200, $\overline{M}_{r,z}$ = 25 500. —— Reaction time 30 days; $\overline{M}_{r,p}$ = 10 200, $\overline{M}_{r,n}$ = 9500, $\overline{M}_{r,w}$ = 31 000, $\overline{M}_{r,z}$ = 174 000.

Pyrophoric lead is a mild heterogeneous reducing agent with a high surface area, which has been reported in the organic chemical literature as being effective for forming C–C bonds by the Wurtz reaction,[19] despite the low reduction potential for Pb [$E^\ominus(Pb^{2+}/Pb)$ = −0.126 V at 298 K]. This was prepared by thermally decomposing lead(II) tartrate under a dinitrogen atmosphere[20] prior to reaction with a stoichiometrically equivalent amount of dichloromethylphenylsilane in refluxing toluene. Again, the solution became cloudy after a few hours, indicating that a reaction was taking place. The reaction was terminated after 33 days by the addition of methanol. Size exclusion chromatographic analysis showed that only oligomers up to a molecular weight of about 850, corresponding to heptamers, had been formed and the yield was estimated to be about 5%. Although the yield was again very low, it is noteworthy that any Si–Si bond formation occurred at all with such a mild reducing agent. According to standard electrode potentials, the reducing power of metallic lead is more than a volt short of that required for the reductive coupling of dichloromethylphenylsilane. Standard electrode potentials refer to conditions in which the metal cations and chloride anions have unit activity. In the present reaction systems, however, this is far from the case for metal chloride salts are almost completely insoluble in toluene and the other solvents commonly employed for Wurtz reactions. The effect of this is the promotion of the reductive formation of the Si–Si bonds through the precipitation of the metal chloride, almost to the extent that it is the sole driving force for the reaction. We have demonstrated the thermodynamic favourability of polysilane formation under these conditions by considering appropriate Born–Haber cycles. The fact that we have achieved Si–Si bond formation with a metal of such mild reducing power as lead means that a far wider range of candidate reducing agents than has previously been realised can be considered for the Wurtz synthesis of polysilanes.

Another important consequence follows from the work with pyrophoric lead. With sodium as the reducing agent, the addition of a crown ether to the reaction mixture greatly enhances the yields of polysilanes both in refluxing toluene[4,21] and diethyl ether.[5] We believe that this effect arises because the crown ether solubilises the sodium chloride formed in the reaction, so assisting the polymerisation by the removal of NaCl from the growth sites on the sodium surface. The reducing power of sodium is sufficiently great that the reverse

depropagation reaction† does not occur, despite the complexed sodium ions in solution. However, where much less powerful reducing agents are used, so that the necessary driving force for the polymerisation comes from the precipitation of the metal chloride, a different behaviour is to be expected. In these cases, the addition of crown ethers or similar metal-ion-solubilising agents will not promote Si–Si bond formation, but may instead inhibit it.

In conclusion, we have demonstrated that the Wurtz synthesis of poly(methylphenylsilane) can be carried out with alternative metallic reducing agents. The reactions using yttrium and pyrophoric lead are slow, and the yields are low. However, the yields are comparable with those of the electrochemical methods which have recently received considerable attention but in sharp contrast with these methods, in the case of yttrium a polymer of favourably high molecular weight has been obtained. Furthermore, the problem of polymer degradation that is always encountered with the alkali metals at prolonged reaction times, appears to have been overcome. If the reaction can be carried out at a more moderate rate than that which obtains using alkali metals in boiling toluene, the possibilities for achieving tight control of the molecular weight of the product are evident. In addition, if the initial quality of the reducing agent that is used to mediate these reactions is consistent, then reproducibility of the reaction will also be realised. We acknowledge that neither yttrium nor pyrophoric lead are suited to these purposes but their investigation has demonstrated the potential and we are therefore continuing our search for alternative mediating agents for these syntheses.

† Not to be confused with the polymer degradation through the backbiting mechanism that invariably results if the reaction conditions are prolonged.[7]

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