

A New Insight into the Polymodal Molecular Mass Distributions Arising in the Wurtz Synthesis of Polysilanes

Richard G. Jones,* Robert E. Benfield, R. Harry Cragg and Anthony C. Swain

Centre for Materials Research, Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent CT2 7NH, UK

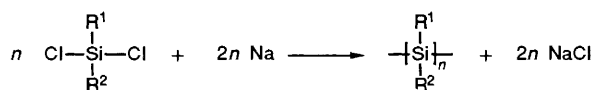
In the light of recent understanding of the role and ultimate fate of alkali metals used in Wurtz syntheses of polysilanes, the polymodal nature of the molecular weight distributions that arise in the formation of poly(methylphenylsilane) are shown to be entirely consistent with an anionic mechanism of polymerization and explicable solely in terms of the heterogeneity of the reaction medium.

Despite a considerable expenditure of effort in a search for alternatives, the sodium-mediated reductive-coupling (Wurtz coupling) of dichlorosilane monomers remains the most viable procedure for the synthesis of high molecular weight, linear polysilane homo- and co-polymers (Scheme 1).

Commonly conducted in boiling toluene, the reaction is difficult to reproduce and polymodal molecular weight distributions invariably result. A typical distribution is at least trimodal with M_w fractions (i) <1500 (consisting mainly of cyclic oligomers), (ii) 4000 to 3×10^4 (this fraction is commonly of two overlapping peaks) and (iii) 10^5 to several million. The cause of this is unclear and the mechanism of the reaction has remained an enigma, not the least reason being that a quite rapid reaction in a boiling medium containing molten alkali metal does not readily lend itself to detailed mechanistic investigation. It is a very complex, heterogeneous process that is generally accepted¹ to resemble more closely a chain growth rather than step growth polymerization, initiated and propagated at, or very close to, the sodium surface. It is thought that the overall polymerization may proceed by competing non-interactive mechanisms and it is this possibility that is generally invoked to rationalize the polymodal molecular weight distributions. However, there is evidence in some

cases, typically in the preparation of poly(methylphenylsilane),² that the heterogeneity of the reaction system might also be responsible. In this paper evidence is presented, at least for this particular system, that the polymodal molecular weight distributions can be entirely rationalized in terms of the heterogeneity of the reaction medium. The reasoning is quite general, however, and consequently there is no need to appeal to the possibility of competing mechanisms in any Wurtz syntheses of polysilanes.

We have recently reported³ studies of the formation of various polysilanes using the Wurtz condensation reaction mediated by sodium sand in the presence of 15-crown-5 in refluxing diethyl ether. Although agitation must be maintained, reflux conditions have subsequently been shown not to be essential. At these lower temperatures, the reaction is much slower but nonetheless goes to completion. Kinetic/mechanistic studies are more readily conducted, and using a simple adiabatic calorimeter it has been possible to follow the course of the formation of poly(methylphenylsilane) at room temperature. Following an induction period of about five minutes, the reaction of a 5% stoichiometric excess of sodium over dichloromethylphenylsilane obeys a first-order rate law ($t_{1/2} = 15$ min) for at least 97% of its subsequent course. After about 90 min, the ubiquitous blue colouration that characterizes these reactions appears in the gelatinous precipitate that is by then evident in the system. It might thus be reasonably concluded that the appearance of the colour is no more than the 'end marker' of a complete reaction. In the past it has been treated as such, and the colour, which is always



Scheme 1

destroyed in the process of isolation of the polymer, has been presumed to be that of a defect sodium chloride. However, studies⁴ of the precipitated solids separated from various Wurtz polymer forming reactions mediated by either sodium or potassium have shown that it is due to the formation of colloidal alkali metal. Consistent with the model of Zeigler and coworkers^{2,5} in which polymer growth occurs at the alkali metal-solvent interface, significant amounts of the product polymer are also found in these precipitates. The dry solids and their colours are surprisingly stable in air. Nonetheless, the colours are immediately destroyed if any attempt is made to dissolve either of the containing solids, *i.e.* the alkali metal halide in a protic solvent or the polymer in an aprotic solvent. Thus, rather than marking the complete consumption of the alkali metal, the colour reveals its continued presence in the reaction system, albeit in fine dispersion and stabilised within a solid polymer-alkali metal halide matrix. From scanning electron microscopy of the dry solid it is evident that, even in the dry state, it is an open porous material with a surface appearance not unlike that of a gel particle of the type used in size exclusion chromatography.⁶

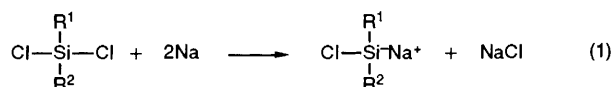
Following filtration, we found that polymer can be isolated not only from the blue precipitate, but also from the filtrate. Size exclusion chromatography (carried out relative to polystyrene standards) shows these two polymer samples to be in approximately equal amounts and to be essentially high and low molecular weight fractions of the total polymer that is formed. The polymer from the precipitate displays a symmetrical major peak centred at a molecular weight of about 24 000† and a very high molecular weight minor peak in a tail extending well into the millions. The chromatogram of the polymer isolated from the filtrate displays a symmetrical peak centred at a molecular weight of 4000 and a minor peak at about 500 associated with the cyclic oligomers. As indicated above, the chromatogram of the total polymer formed in a

typical polymerization would commonly display one or other of the two major peaks as a prominent shoulder on the side of the other.

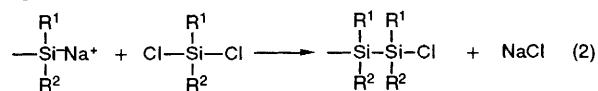
These observations can be rationalized in terms of the solubility of the polymer in the sustaining solvent. It is reasonable to assume that as the reaction proceeds, under conditions of agitation polymer is able to enter solution to the limit of its solubility in a given solvent and at a given temperature. In the early stages of reaction, only low molecular weight material will be present and it is this that would tend to saturate the solution. Although dissolution is an equilibrium process, the increasingly higher molecular weight polymer formed in the later stages of reaction, being of lesser solubility, would not displace the lower molecular weight material from solution. Instead, the higher molecular weight material would remain in the precipitate of alkali metal halide but, in accordance with the model of Zeigler and coworkers, with its chain ends remaining associated with the alkali metal surface at which they would continue to extend. The two fractions would thus appear to be 'non-interactive'. However, there is another significant and quite general point that should be made about the higher molecular weight polymer that is found in the solid phase. Even if the sustaining solvent is a good solvent of the polymer such as toluene, and the total amount of polymer present in the system is less than the amount required to saturate the solution, substantial quantities of the polymer are still to be found in the solid precipitate. It must, therefore, be concluded that the alkali metal halide plays an important role in determining the solubility of this fraction. One way in which it can do so is developed as follows: Various intermediates in the formation of polysilanes by Wurtz-type polymerization have been suggested. They include silyl radicals,² silyl anions^{7,8} and even radical anions polymerizing by a single-electron-transfer mechanism.⁹ However, EPR studies⁴ offer no evidence for the intermediacy of radicals or radical anions and the chain mechanism proposed by Gauthier and Worsfold^{7,8} reproduced in Scheme 2 is the most satisfactorily consistent with the body of mechanistic evidence available to date. The chain reaction proposed involves a two-stage propagation reaction through silyl anion active-centres. The growing chains are thus constantly switching between polar and covalent structures. In the polar form, the chain ends must prefer to remain associated with the medium of the alkali metal and its salt, and effectively remain insoluble. Only when it is in a covalent structure could a polymer molecule enter bulk solution and in so doing it would cease to participate in growth. As reaction proceeds, the particles of alkali metal will decrease in size and thus in surface area. Unless the alkali metal is in significant stoichiometric excess, growth sites are thus decreasing in number appreciably and the effect of this must be a driving force for dissolution of the polymer.

Whatever the mechanism that is represented, the polymer chain end that is remote from the active centre bears a halogen atom, which remains a potential site for reaction. Furthermore, if the Gauthier and Worsfold mechanism and the above reasoning are accepted, then the molecules of the low molecular weight fraction that enter solution (with the exception of the oligomers formed by the energetically favourable cyclization in the earliest stages of reaction) bear halogen atoms at both ends. Being of markedly lesser mobility than the dihalosilane monomer and thus with much lesser ability to penetrate the polymer/alkali metal halide barrier that surrounds the active centres in the vicinity of the alkali metal surface, the probability of these chain-end halogen atoms being involved in reaction is low. Nevertheless, just as polymer molecules diffuse into the pores of gel particles in size exclusion chromatography, so they will penetrate the expanded porous structure of these polymer-salt aggregates and some reaction will occur (Scheme 3). This will terminate growth at the active centre, but in so doing, very much higher

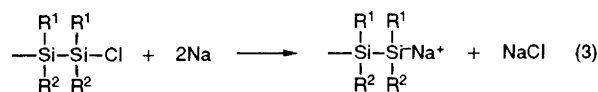
Initiation (slow)



Propagation (fast)

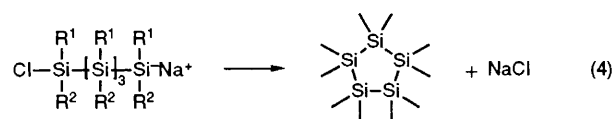


Rate determining

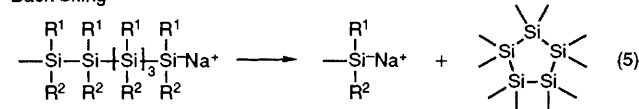


Cyclization

fast

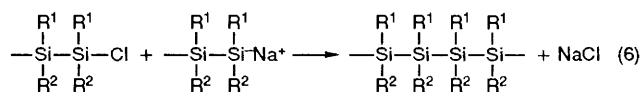


Back-biting



Scheme 2

† Molecular weights of polysilanes are recognized to be at least twice those quoted here, obtained using polystyrene standards.¹



Scheme 3

molecular weight polymer will be produced as it is a polymer-polymer coupling reaction. Furthermore, the resulting molecule will still be available to undergo the same process again. It is in this way that it is possible to rationalize the formation of the very high molecular weight fraction that is invariably formed in any of these polymerizations. It is clear that different reaction media, methods and conditions of agitation, and different polymer structures will all influence the permeability of the solid agglomerate by preformed polymer chains and, therefore, the extent to which high molecular weight material will form in this way from the lower molecular weight fractions.

Two other phenomena are commonplace at the apparent end of a Wurtz polymerization as characterized by the appearance of the blue colour and are worthy of consideration in this paper: (i) if reaction conditions are maintained for a period, a slow increase in the high molecular weight fraction of the product polymer, at the expense of the lower molecular weight fractions can occur, even in those systems that do not contain an excess of sodium, and (ii) if the reaction conditions are maintained for too long, all the polymer will inevitably degrade to oligomer. It is possible that the presence of colloidal alkali metal at this stage of reaction is sufficient to explain the first of these effects, for even in the colloidal state it is still available for reaction as described above. The second effect, however, almost certainly arises through the back-biting chain mechanism proposed by Gauthier and Worsfold. From a simple kinetic analysis applied to the unified reaction mechanism of Schemes 2 and 3, eqn. (7) can be derived. It shows that as the monomer and shorter polymer molecules are progressively consumed, so the lifetime (τ) of the remaining silyl anion active ends will increase. The rate constants are numbered in accordance with the reactions of Schemes 2 and 3, and P*, M and P represent polymer with active chain ends, monomer, and polymer with chlorine chain ends, respectively.

$$1/\tau = k_2[\text{P}^*][\text{M}] + k_6[\text{P}^*][\text{P}] + k_5[\text{P}^*] \quad (7)$$

A critical point is reached at which this competitive first-order reaction of active chain ends (back-biting) dominates over the combined effects of the second-order propagation and polymer-polymer reactions. It is thus essential that reaction conditions are not prolonged in the vain hope that chain extension will result. If alkali metal is used in considerable excess over monomer, such a condition will be reached at much lower degrees of polymerization.

A single heterogeneous anionic polymerization mechanism can thus explain the observed polymodal molecular weight distributions resulting from the sodium-mediated reductive coupling of dichlorosilanes. The bulk of the product will commonly be of two intermediate molecular weight fractions, and though a small amount of very high molecular weight material will usually be formed, along with the other fractions this will in due course degrade to cyclic oligomer if reaction conditions are maintained.

We gratefully acknowledge the Royal Society's support for R. E. B. through the award of a University Research Fellowship, and the SERC for a Postdoctoral Research Fellowship for A. C. S. We also thank a final year undergraduate student, Sidney McIntosh, and a visiting student under the Erasmus scheme, Beatrice Albert of Ecole Nationale Supérieure de Chimie de Montpellier, for their valuable experimental assistance.

Received, 10th September 1991; Com. 1104709D

References

- 1 R. D. Miller and J. Michl, *Chem. Rev.*, 1989, **89**, 1359.
- 2 J. M. Zeigler, *Polym. Prep.*, 1986, **27**, 109.
- 3 R. H. Cragg, R. G. Jones, A. C. Swain and S. J. Webb, *J. Chem. Soc., Chem. Commun.*, 1990, 1147.
- 4 R. E. Benfield, R. H. Cragg, R. G. Jones and A. C. Swain, *Nature*, 1991, **353**, 340.
- 5 J. M. Zeigler, L. A. Harrah and A. W. Johnson, *Polym. Prep.*, 1987, **28**, 424.
- 6 E. A. Collins, J. Bareš and F. W. Billmeyer, Jr., *Experiments in Polymer Science*. Wiley, New York, 1973, pp. 155-157.
- 7 S. Gauthier and D. J. Worsfold, *Macromolecules*, 1989, **22**, 2213.
- 8 S. Gauthier and D. J. Worsfold, *Adv. Chem. Ser.*, 1990, **224**, 299.
- 9 W. Heitz, *Macromol. Chem. Macromol. Symp.*, 1986, **4**, 35.