

The role of oligomers in the synthesis of polysilanes by the Wurtz reductive coupling reaction

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Abstract

Size exclusion chromatography and ^{29}Si -NMR spectroscopy have been used to investigate the evolution of low-molecular weight molecules during the synthesis of poly(methylphenylsilane) by alkali metal-mediated reductive coupling in diethyl ether, tetrahydrofuran and toluene, revealing clear evidence for the important role played by a dimer. In addition, the distinct origins of the stable cyclic oligomers that are ubiquitous side products of these reactions have been established, cyclopentamers being formed through endbiting during chain growth and cyclohexamers by a degradative backbiting reaction.

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1. Introduction

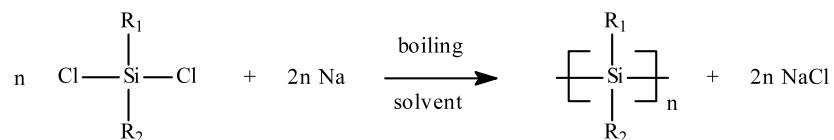
After the first tractable polysilanes were synthesised in the late 1970s and early 1980s [1–4] by the alkali metal-mediated coupling of diorganosilanes (see Scheme 1), there was a significant drive to understand the origins of the polymodal, usually trimodal, molecular weight distributions that invariably resulted. They were originally thought to arise from non-interacting polymerisation mechanisms but as evidence accumulated it was increasingly clear that this is not the case. A number of researchers have made significant contributions to the development of what is now an acceptable understanding validated by a mathematical model [5] (*vide infra*) but for a full historical description the reader is referred to a recent review [6].

A typical product molecular weight distribution from a Wurtz-type synthesis of poly(methylphenylsilane) (PMPS) as usually carried out in boiling toluene or xylene consists of three fractions: (i) an oligomeric fraction corresponding mainly to cyclic pentamers and hexamers, (ii) a broad and dominant fraction of inter-

mediate molecular weight corresponding to a degree of polymerisation of about 35–40 and (iii) a lesser amount of a narrow high-molecular weight fraction corresponding to a degree of polymerisation in the region of 50,000. The first of these is well understood to arise from endbiting and backbiting reactions that arise during the course of the polymerisation. However, until recently, why there should be two distinct polymeric fractions was an enigma. It is now understood that the polymer grows from the alkali metal surface in a random-coil conformation consisting of a mixture of irregular P- and M-helical segments, each separated from the next by reversal of the helix. These reversals diffuse rapidly within the chain, occasionally reaching the alkali metal surface, at which juncture the chain end can backbite with the elimination of a cyclic oligomer and concomitant disengagement of the growing chain from the surface. This is a polymerisation termination process, which is most probable when there is only one helix reversal present in the growing chain, and it is responsible for the formation of the intermediate-molecular weight fraction. Those chains that survive this possibility continue to grow and as their length increases, so does the number of helix reversals. The probability of adjacent reversals colliding and undergoing an inevitable mutual annihilation increases correspondingly. This increases the range of diffusion of the remaining

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Scheme 1.

reversals and in particular that nearest to the alkali metal surface and the probability of termination is accordingly reduced. The overall reaction increasingly assumes the characteristics of a living polymerisation and it is this that gives rise to the narrow high-molecular weight fraction. These processes are depicted in Fig. 1 in which the probability of termination is represented as P_i .

Viewed from the mechanistic as opposed to the molecular standpoint, it is clear that the polymerisation takes place in two stages [7,8]. The first of these occurs with the rapidity usually associated with a chain reaction polymerisation, and a satisfactory mechanism for such a process has been proposed [9]. Within 5 min, the parent dichlorosilane is consumed, all three molecular weight fractions are evident within the product mixture and about 60% conversion to polymer is achieved. The second stage, which takes place over the next 30 min, is characterised by about 50% reduction in the oligomeric fraction to the benefit of the two polymeric fractions. Given that cyclic pentamers and

hexamers are known to be thermodynamically stable end products of the overall process, it has been assumed that this stage is a condensation reaction in which linear oligomers are incorporated into the polymer at chain ends.

It can be reasonably assumed that in the early stages of their growth, polymeric chains must grow more or less monotonically on the alkali metal surface through dimers, trimers, tetramers, pentamers, hexamers, etc. and that some ring closure is inevitable. However, little is understood on the role of oligomers in the overall process. In this paper, we present evidence that dimers play a more important role than has been formerly realised and the stable cyclic pentamers and hexamers have quite different origins.

2. Experimental

The present study involves the characterisation of the various species involved in the reductive coupling of

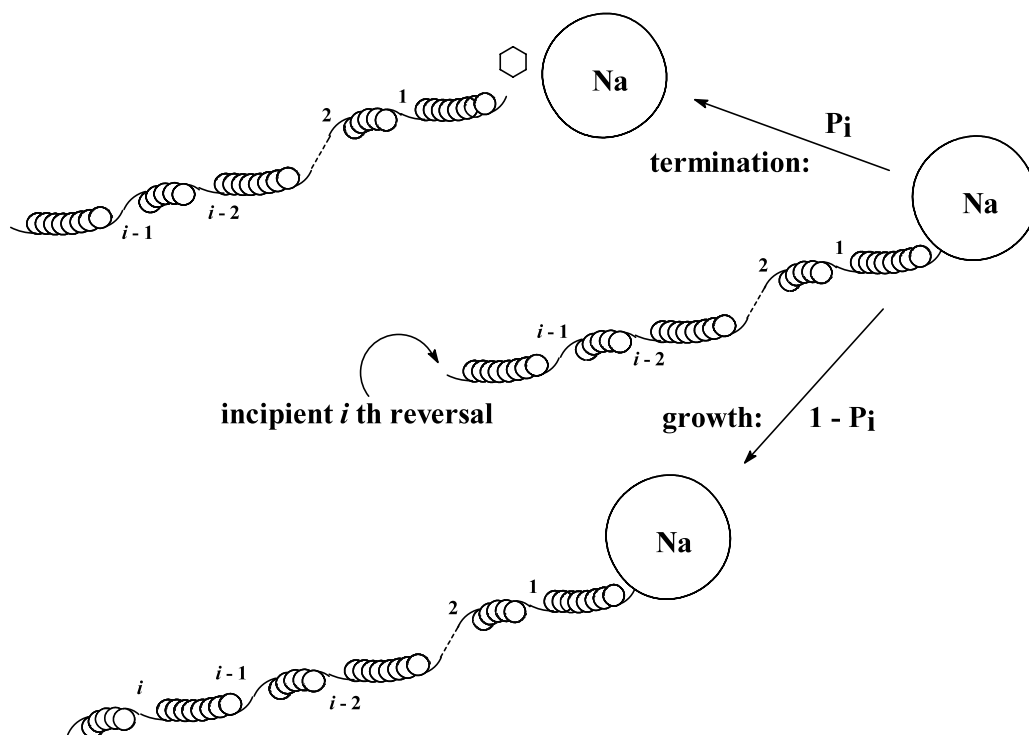


Fig. 1. Schematic of the progress of an alkali metal-mediated reductive coupling of a dihaloorganosilane.

dichloromethylphenylsilane by sodium metal in diethyl ether/15-crown-5 (DEE), tetrahydrofuran (THF) and toluene using size exclusion chromatography and NMR spectroscopy. The former technique was calibrated using polystyrene standards, dichloromethylphenylsilane, pentamethylpentaphenylcyclopentasilane and hexamethylhexaphenylcyclohexasilane. Extraction of the oligomers from the PMPS samples for ^{29}Si analysis was performed as follows.

2.1. Extraction from the product of the Wurtz reductive coupling polymerisation performed at 110 °C

After addition of excess methanol to the reaction mixture at the end of the polymerisation, the crude PMPS was filtered off. The filtrate was added dropwise to an excess of distilled water (500 ml) dropwise and the organic layer was isolated. The water phase was washed repeatedly with toluene (4×50 ml) and the organic layers were combined and dried over magnesium sulfate overnight. After filtration the solvent was removed in vacuo to give a thick viscous yellow oil (extract 1: $M_n = 840$, $M_w/M_n = 1.4$). The crude PMPS was redissolved in THF (~ 20 ml), the solution was filtered to remove insoluble material and then added dropwise to a large excess of stirred hexane (400 ml). The resulting polymer–solution mixture was stirred for a further 60 min after all of the polymer had been added. The mixture was filtered and the hexane solution dried over magnesium sulfate overnight. After removal of the hexane in vacuo a translucent whitish oil was isolated (extract 2: $M_n = 1460$, $M_w/M_n = 1.6$).

2.2. Extraction of product from Wurtz reductive coupling polymerisation at 60 °C

An identical extraction procedure was followed as for the high-temperature polymerisation. Extract 1 was isolated as a thin colourless liquid ($M_n = 785$, $M_w/M_n = 1.05$) and extract 2 was isolated as a yellowish oil ($M_n = 1230$, $M_w/M_n = 1.9$).

Otherwise, the materials used, the polymerisation and sampling methods, and the apparatus and analytical procedures have all been detailed previously [7,8].

3. Results and discussion

The reductive couplings of dichloromethylphenylsilane in refluxing DEE, THF (initially at ambient temperature) and toluene were chosen for investigation as both the reaction conditions and the molecular weight distributions of the polymeric products are quite different in these three systems. In refluxing DEE (b.p.: 35 °C), no high-molecular weight fraction is formed and the polymer is confined to average degrees of polymer-

isation of about 35–40 by a chain scission process that is unique to this system [7]. In THF (b.p.: 65 °C), again no high-molecular weight fraction is formed but the degree of polymerisation of the polymeric product increases linearly with conversion once reflux temperature is attained and can eventually exceed 100 [8]. This procedure thus appears to be free of termination. The reaction in toluene (b.p.: 111 °C) yields the familiar intermediate- and high-molecular weight fractions.

Of interest, here are low-molecular weight products found in these systems and Figs. 2–4 depict the variations with time of the this region of the size exclusion chromatograms of filtered samples taken from the above reaction mixtures. The superimposed numbers, 1, 5 and 6, indicate the positions at which dichloromethylphenylsilane, pentamethylpentaphenylcyclopentasilane and hexamethylhexaphenylcyclohexasilane elute whilst 2, 3 and 4 are the positions at which dimers, trimers and tetramers would be expected to elute, respectively. Taking account of the different rates at the various reaction temperatures, it is evident that in all three systems dichloromethylphenylsilane is converted quite rapidly to a dimeric species. This conversion is particularly well defined for the THF system in which the reaction is initiated at ambient temperature and only eventually achieves reflux as a consequence of the heat of reaction. Trimers and tetramers are also evident in all the systems, though in such small proportion that they can be viewed as transients in the overall conversion to high-molecular weight material. It is the dimeric species therefore that is the immediate precursor of all three fractions found in the product mixture. Although its structure has not been characterised (it is probably 1,2-

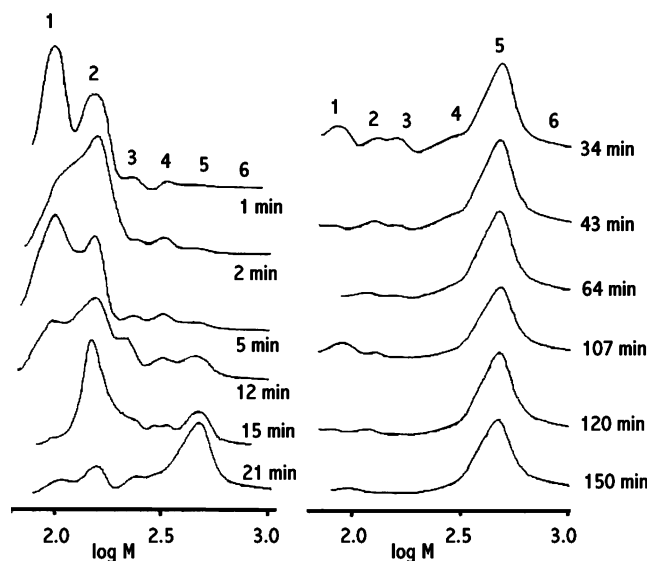


Fig. 2. Size exclusion chromatograms depicting the variations in the low-molecular weight region during the Wurtz-type synthesis of PMPS in refluxing diethyl ether containing $0.137 \text{ mmol dm}^{-3}$ of 15-crown-5.

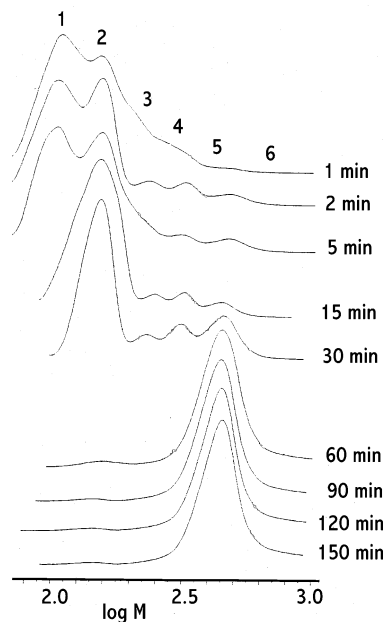


Fig. 3. Size exclusion chromatograms depicting the variations in the low-molecular weight region during the Wurtz-type synthesis of PMPS in THF initially at ambient temperature.

dichloro-1,2-dimethyl-1,2-diphenyldisilane), it is nevertheless reasonable to associate it with the chain reaction phase of the overall polymerisation, playing a role analogous to that of a monomer in a vinyl chain polymerisation. It cannot be a disilene, although it is conceivable that on the alkali metal it is converted to such a structure, stabilised on adjacent surface sites in a configuration not unlike that of the masked disilene precursor in the anionic synthesis of polysilanes developed by Sakurai and coworkers [10]. Tameo and coworker [11,12] have previously advanced the hypothesis that dimers may play an important role in polysilane syntheses and self-condensation of the alkali metal halomethylphenylsilane, XR_2M , forming a β -halodisilanyl metal species, $\text{XR}_2\text{SiSiR}_2\text{M}$. Whilst our results do not confirm the hypothesis, they lend considerable support.

The most notable difference between these sets of chromatograms is that only pentamers are seen amongst the final products for the DEE and THF systems, whilst in the toluene system hexamers are also seen. It is difficult to associate this difference with the nature of the solvent, so it more likely arises from a temperature effect. It is only at the elevated temperature of the reaction in toluene that the high-molecular weight polymer fraction is formed. It is therefore reasonable to assume that cyclic pentamers and cyclic hexamers are formed through distinctly different processes. Furthermore, if termination of polymerisation occurs by chain disengagement from the alkali metal surface with a

concomitant elimination of a cyclic oligomer as postulated, since this will be an activated process, it is consistent with all of the foregoing [6]. Thus, it can be reasoned that endbiting in the early stages of the overall reaction is common to all three systems and gives rise to cyclic pentamers, whilst it is only at elevated temperatures that terminating disengagement with backbiting occurs and that this gives rise to the cyclic hexamer.

In order to check that this salient difference in the size exclusion chromatograms is associated solely with the temperature of reaction, the low-molecular weight products of reactions conducted in toluene under reflux conditions and at 60°C were separated from the polymer for further analysis. The ^{29}Si DEPT-NMR spectra for fraction 1 are shown in Fig. 5. The characteristic quartet of the cyclic pentamer [13] centred just below -30 ppm is evident in both spectra, together with another strong resonance at about -33 ppm. However, the characteristic multiplet associated with the cyclic hexamer [13,14] between -40.7 and -41.6 ppm only appears in the spectrum of the products of the high-temperature reaction. Also evident in this spectrum, between -38 and -40 ppm, are the resonances that can be associated with the various stereosequences of the linear oligomers. These can just be discerned in the spectrum of the products from the low-temperature reaction but their intensity is so low that the observation simply confirms the prominence of the cyclic pentamer as an end product of this system. Similarly, fraction 2 isolated from the low-temperature polymerisation only showed resonances for the pentamer (with no hexamer evident) and fraction 2 from the high-temperature reaction only showed resonances for the hexamer (in addition to oligomeric species).

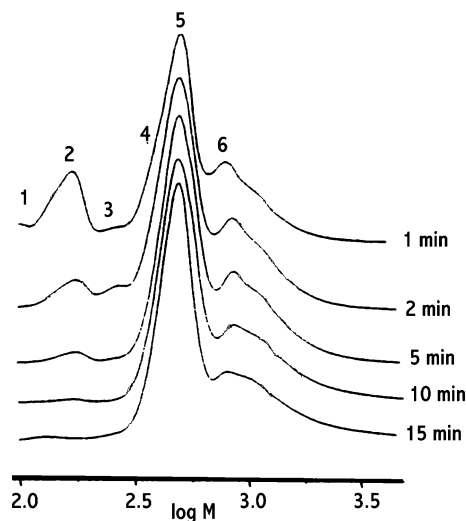


Fig. 4. Size exclusion chromatograms depicting the variations in the low-molecular weight region during the Wurtz-type synthesis of PMPS in refluxing toluene.

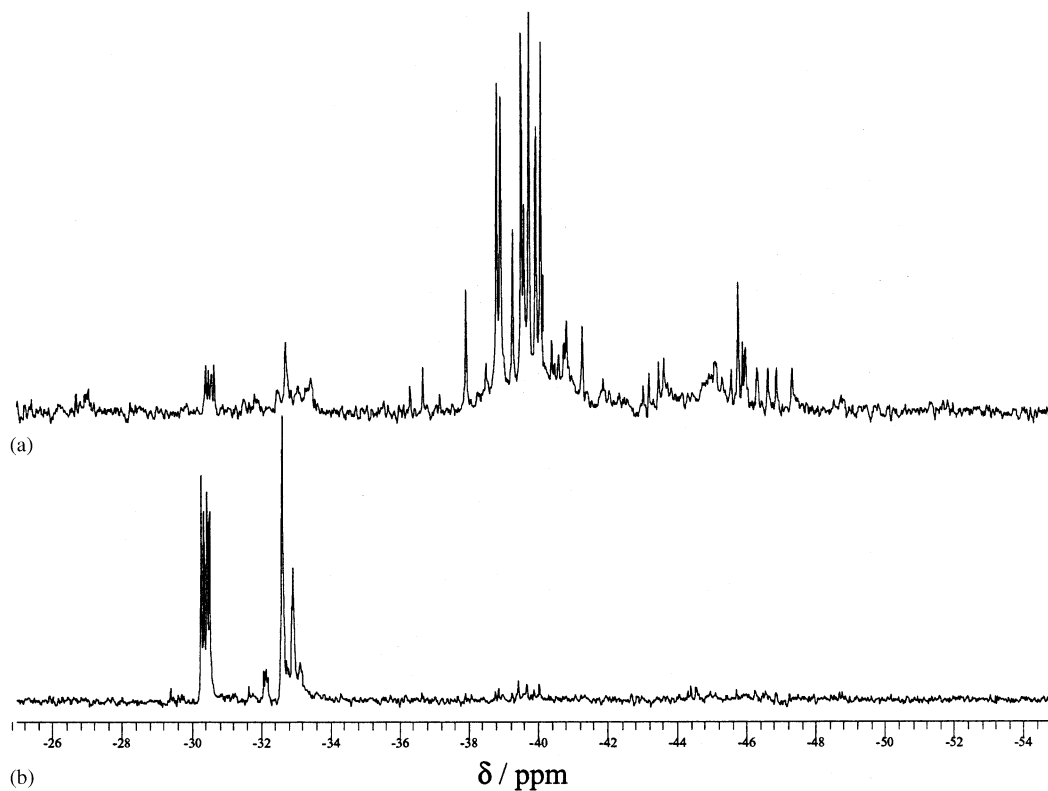


Fig. 5. ^{29}Si DEPT-NMR spectra of low-molecular weight products extracted from Wurtz-type synthesis of PMPS in toluene at (a) reflux temperature and (b) $60\text{ }^\circ\text{C}$.

The NMR results can thus be rationalised in a manner consistent with the observations and deductions from the size exclusion chromatograms. In addition, although cyclic pentamers and hexamers have long been known to be formed in Wurtz-type syntheses of polysilanes by endbiting and backbiting reactions, these have now been unequivocally proven to have distinctly different origins. The endbiting reaction always occurs and is simply the consequence of ring closure competing with chain extension. In contrast, cyclic hexamers are not formed in the early stages of chain growth and only arise as a consequence of a single thermally activated backbiting reaction that simultaneously terminates polymerisation in a way that is entirely consistent with the representation of Fig. 1.

Acknowledgements

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