

# Correlation of Structure and Molecular Weight Distributions during the Formation of Poly(methylphenylsilylene) by the Wurtz Reductive-Coupling Reaction

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Variations of yields and molecular weight parameters of poly(methylphenylsilylene) formed through sodium-mediated Wurtz-type reductive coupling of dichloromethylphenylsilane in refluxing toluene are described. The intermediate molecular weight fractions within the polymodal distributions that result from such syntheses are shown to correlate well with the length of *all-trans* sequences within the polymer as revealed through the near-ultraviolet spectra of the fractionated polymers. The origins of the polymodal distributions are explained as being the consequence of a competition between termination through a backbiting reaction and a continued growth reaction whenever additions in *gauche* conformation arise. The likelihoods of such additions are reasoned to increase with the lengths of the *all-trans* sequences that arise from the preceding additions, and the termination reaction is rationalized as having a maximum probability when the polymer consists of only one such sequence. The reasoning is shown to correlate with the polydispersities of the intermediate and high molecular weight fractions within the overall molecular weight distribution of the polymer. Reasoning from this explanation of the mechanism of the polymerization, it is shown that it is possible to obtain high molecular weight, monomodal poly(methylphenylsilylene) in high yield from syntheses conducted in refluxing tetrahydrofuran.

## Introduction

Despite much attention being given to the problem in recent years,<sup>1–14</sup> the origins of the polymodal molec-

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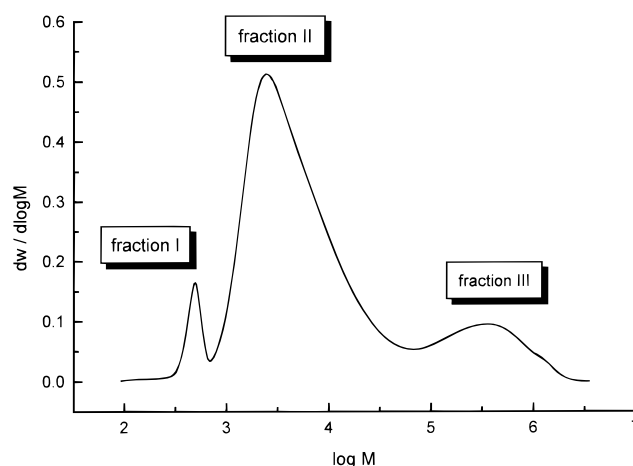
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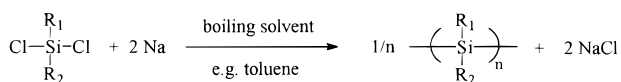


**Figure 1.** Representative molecular weight distribution of PMPS synthesized in refluxing toluene.

ular weight distributions, such as that depicted in Figure 1, that invariably result from the Wurtz-type reductive coupling of dichloroorganosilanes commonly used for the synthesis of polysilylenes (see Scheme 1)

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Scheme 1



have remained an enigma. The formation of the oligomeric fraction (I) through endbiting and backbiting reactions during the synthesis is not at issue, but there has been no satisfactory explanation as to why the majority of chains only grow to an intermediate molecular weight (fraction II) while others grow to quite high molecular weights (fraction III). If polysilylenes of a satisfactorily high molecular weight are ever to be routinely synthesized in high yield using this method (so far this is the most generally applicable and convenient synthetic procedure available), then it is important to know why. In recent publications,<sup>10,14</sup> we have attempted to rationalize the phenomenon. In the first of these,<sup>10</sup> based on observations of the synthesis of poly(methylphenylsilylene), PMPS, conducted in diethyl ether, it was concluded that the intermediate molecular weight fraction formed during the early stages of reaction was simply forced off the shrinking sodium surface and into solution until saturation was reached. Any chains then remaining attached to the sodium surface no longer had this option, so they grew to attain a maximum degree of polymerization. Such reasoning was flawed on at least two counts: (i) growing polymer molecules would still be forced to leave the shrinking sodium surface, if not into solution, then into the solid agglomerate, and (ii) for the reaction as normally conducted in boiling toluene, which is a much better solvent of the polymer, even in the early stages of reaction a significant proportion of the high molecular weight fraction is found in the solution phase. The later publication<sup>14</sup> followed from a more detailed consideration of the synthesis of PMPS under a wide range of reaction conditions. A correlation of the intermediate molecular weight fraction with the average length of  $\sigma$ -conjugated chain units in *all-trans* conformation was identified, and the formation of this fraction was attributed to a chain scission reaction occurring selectively at the ends of these wormlike sequences within polymer of high molecular weight formed earlier in the reaction. Subsequent experimentation and reconsideration confirm the correlation but disallow the detail of the interpretation. In this paper we present the relevant evidence together with an altogether more satisfactory explanation as to how the molecular weight distributions arise in these polymerization reactions. To that end, the essential arguments that were developed earlier<sup>14</sup> are outlined below.

With appropriate activation, which might be either thermal or through the intermediation of a phase transfer agent such as a crown ether,<sup>15</sup> the formation of high molecular weight poly(methylphenylsilylene) corresponding to degrees of polymerization in the region of 50 000 is kinetically driven. However, it was argued that chain scissions that occur continuously throughout the synthesis reaction result in a reduction of the molecular weight of most of the polymer to a much lower

value corresponding to a degree of polymerization of about 50. Although the overall degradation of polysilylenes is to stable cyclic oligomers and is thermodynamically driven, the polymer at this intermediate degree of polymerization represents a metastable stage in the process. For reactions conducted under high-temperature conditions in a refluxing solvent such as toluene or xylene, the selective chain scissions were postulated to arise from electron transfer from the alkali metal to the LUMO of the polymer through adventitious contact of chain segments with the sodium surface during the polymerization process. They were further rationalized as occurring at strong turns (such as *gauche*), the positions of which within any one polymer molecule would be constantly changing, but which at any instant are statistically distributed among the extended sequences of silicon atoms which are in approximately *all-trans* conformation.<sup>16,17</sup> The bonds at these strong turns, which are considered to interrupt the  $\sigma$ -conjugation of the backbone, were identified as being the weakest bonds in the overall polymer structure, even though the difference in energy from that of a bond in an *all-trans* sequence would, at best, be slight.

## Experimental Section

**Materials.** Prior to use, toluene was distilled from sodium and tetrahydrofuran (THF) was distilled from sodium/potassium alloy. Dichloromethylphenylsilylene (Lancaster Synthesis) was also distilled before use and stored over magnesium turnings and 4 Å molecular sieves. Sodium (Fisons) was stored under paraffin oil and before use was cut and washed under toluene.

All glassware was flame dried. Sodium dispersions for use at temperatures below its melting point (98 °C), such as in the syntheses in refluxing THF, were prepared immediately prior to use by melting the freshly cut metal in mineral oil before dispersing it into a fine sand through the use of an homogenizer (Ultra-Turrax T 8, IKA Labortechnik, Staufen). The oil was removed by washing three times with diethyl ether. All volatiles were then removed under vacuum before the THF was added.

**Apparatus and Procedures.** Polymer structures were characterized as PMPS using NMR spectroscopy (JEOL GX-270), ultraviolet-visible spectroscopy (Shimadzu UV-240), and FTIR spectroscopy (ATI Mattson). Molecular weights of the polymers were measured as linear polystyrene equivalents in THF solution using size exclusion chromatographic (SEC) equipment supplied by Polymer Laboratories Ltd. and equipped with a mixed bed 5 mm PLgel column. A variable-wavelength UV detector set at 254 nm was used, and the calibration was over the molecular weight range 162 to  $1.03 \times 10^6$ . Relative amounts of the different fractions and their molecular weight parameters were determined by resolution of the individual chromatographic peaks using Peaksolve, a peak fitting package for Windows supplied by Galactic Industries Corp. The detector was not calibrated to compensate for absorbance differences between the monomeric, oligomeric, and polymeric fractions. However, it is the  $\pi\pi^*$  band of the phenyl substituents that are predominant in the determination of the absorbance at 254 nm, and these are common to all the species, but such discrepancies that might arise are of little consequence since the ensuing arguments only require consideration of trends and are not dependent on knowledge of absolute yields.

(15) It was noted that these conditions are compatible with the stabilization of ionic intermediates, in particular anions in the chain propagation reaction.

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**General Procedure for the Syntheses of Poly(methylphenylsilylene).** All syntheses of PMPS used the following general procedure in one or the other of its modifications: Using Schlenk-line techniques, freshly cut sodium metal (0.75 g, 0.033 mol) was added under a nitrogen atmosphere to a two-necked round-bottom flask (100 mL) equipped with an egg-shaped PTFE (25 × 12 mm) stirring bar and a condenser. For reactions in THF the metal was transformed to a fine dispersion as outlined above. The 40 mL of the solvent of reaction (toluene or THF) was added, followed by 2.5 mL (0.015 mol) of dichloromethylphenylsilane. For reactions in toluene, the mixture was rapidly stirred under reflux for the duration of reaction. In contrast, for reactions in THF the mixture was rapidly stirred at ambient temperature. There followed an induction period of about 20 min as the polymerization got underway, during which time the temperature increased until the mixture started to reflux. Reaction was sustained at this temperature solely by the heat of polymerization, and thereafter the reaction mixture was allowed to cool to room temperature. For both the toluene and the THF systems, the reaction mixtures were then cooled in an ice bath while maintaining rapid stirring, and sufficient methanol was added to quench any unreacted sodium. A further 1 h of stirring at room temperature was allowed for complete termination before 50 mL of water was added. The organic layer was then decanted to stirred methanol (250 mL) at room temperature. The precipitated polymer was collected by filtration, washed with methanol, and dried in a vacuum oven prior to characterization. In the normal course of a polymer synthesis, it is usual to remove low molecular weight materials from the crude product by successive reprecipitations. Such procedures were not followed here, because as well as removing much of the oligomeric PMPS fraction (I) they also remove substantial amounts of the intermediate molecular weight fraction (II). The molecular weight distribution of this fraction is thus distorted which for the purposes of the present study was an undesirable effect that had to be kept to a minimum if not eliminated.

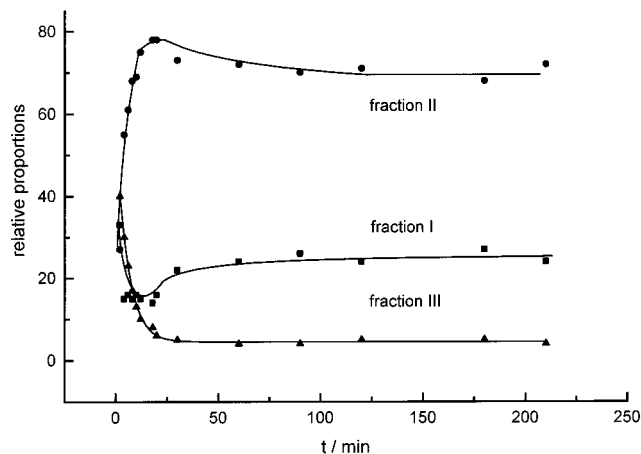
For following the course of the reactions in toluene, a reaction vessel was equipped with a serum cap to allow small aliquots of the liquid phase to be withdrawn at regular intervals using a syringe.<sup>18</sup> The syringe was equipped with a discharge filter to collect particulates that had inadvertently been withdrawn, after which the bulk of the toluene in the aliquots was removed under vacuum on a Schlenk line. The residues were immediately dissolved in THF and the concentration adjusted to a level suitable for analysis by SEC.

Fractionated PMPS samples for spectrophotometric studies were obtained by successive extractions of broad distribution samples using mixtures of the *n*-alkyl alcohols from ethanol to hexanol.

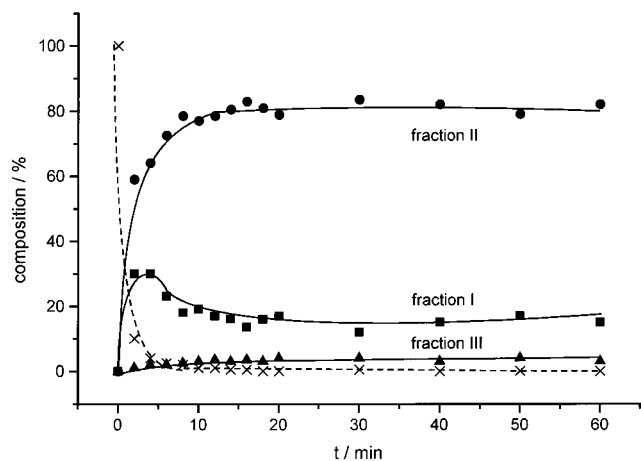
## Results and Discussion

In arriving at the understanding described above, undue emphasis was placed on a particular interpretation of the variation with time of the proportions of the low, intermediate and high molecular weight fractions of polymer isolated from the solution phase of the reaction mixture during a representative synthesis of PMPS. This plot is reproduced here as Figure 2, and it must be emphasized that, instead of representing variations in the absolute yields of the three product fractions, it depicts variations in their relative proportions,

(18) The point was made in ref 14 that, since toluene is a good solvent of the polymer, representative variations of the product molecular weight distributions with time could be obtained by monitoring the polymer isolated from the solution phase. It was also shown that less than 5% of the polymer remained associated with the solid phase at the end of reaction.



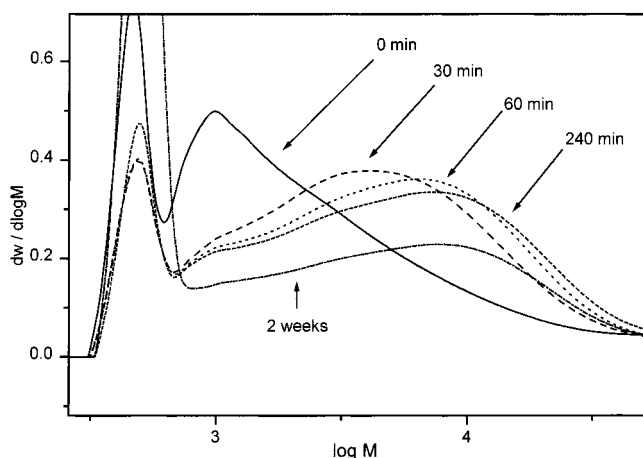
**Figure 2.** Variation with time of the proportions of the low (■), intermediate (●), and high (▲) molecular weight fractions of polymer isolated from the solution phase during a representative synthesis of PMPS in refluxing toluene.



**Figure 3.** Variation with time of the composition of the solution phase during a representative synthesis of PMPS in refluxing toluene: monomer (×) and low (■), intermediate (●), and high (▲) molecular weight polymer fractions.

no account having been taken of the extent of reaction. This is a representation that easily leads to the erroneous conclusion that the high molecular weight fraction is being converted to the intermediate molecular weight fraction. In contrast, Figure 3 is typical of the variation of the composition of such a reaction mixture, from which it is evident that the absolute yields of the high and intermediate molecular weight fractions both increase steadily with time.

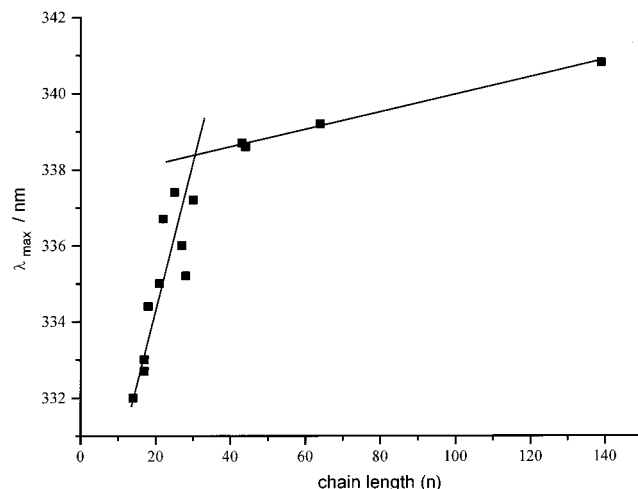
Figure 4 depicts the change in molecular weight distribution accompanying the reaction of a presynthesized PMPS with sodium in boiling toluene. In common with the earlier observation of Matyjaszewski and co-workers,<sup>13</sup> it is clear that the polymer does not degrade under these conditions unless reaction is prolonged, for there is an increase in molecular weight. A further feature of the synthetic procedure that is evident from Figures 2–4 is that a proportion of the oligomeric fraction which is formed in significant quantities in the early stages of reaction is later consumed in the polymer forming reaction. Conceivably these are linear oligomers which by virtue of their end groups are as readily involved in the coupling reaction as the dichloromethylphenylsilane precursor.



**Figure 4.** Variations in molecular weight distribution accompanying the reaction of a presynthesized PMPS with sodium in refluxing toluene.

All of these above observations deny the possibility of the intermediate molecular weight fraction being formed through the selective degradation of the high molecular weight fraction following adventitious contact of polymer segments with the sodium surface during the synthesis. Furthermore, although the earlier arguments explained the stability of the intermediate molecular weight fraction, it is not rational to assume that this fraction arises from what would appear to be chain scission, not just exclusively at the strong turns of a high molecular weight polymer molecule but at all of them simultaneously. If it was otherwise, the molecular weight distributions would be monomodal. It is therefore necessary to return to the notion that polysilylene chains, after growth to the polymerization degree of about 40, either depart to solution or stick to the sodium surface and grow by reaction with monomer, or with oligomeric or polymeric molecules with Si-Cl end groups. The following explanation is now advanced:

Central to the ensuing arguments are the  $\sigma$ -conjugation of the polymer backbone and the consequent pseudo-rigid-rod (wormlike) model of PMPS and many other polysilylenes. The delocalization of the  $\sigma$  electrons along the backbone results in a significant narrowing of the HOMO-LUMO bandgap of polysilylenes compared to that of the corresponding carbon-based polymers. This is evidenced by a remarkably strong absorption band in the near-UV spectra of polysilylenes. The maximum of absorption, and therefore the extent of conjugation, is strongly dependent on the nature of the organic substituents and the conformation of the polymer chain. Typically, poly(di-*n*-butylsilane) displays a  $\lambda_{\max}$  at 315 nm at room temperature at which the chain adopts a 7/3 helical conformation. However, this increases to 354 nm as the temperature is reduced, causing the chain to adopt an *all-trans* conformation.<sup>19</sup> PMPS displays a  $\lambda_{\max}$  at about 340 nm at room temperature. This value is substantially higher than that observed for poly(di-*n*-alkylsilane)s which in part is a consequence of the mixing of the phenyl  $\pi$ -orbitals with the molecular orbitals of the silicon backbone, but is also because PMPS in both solution and the solid phase consists of predominantly *all-trans* sequences separated



**Figure 5.** Variation of the position of the near-ultraviolet absorption maximum with chain length for solutions of PMPS in toluene.

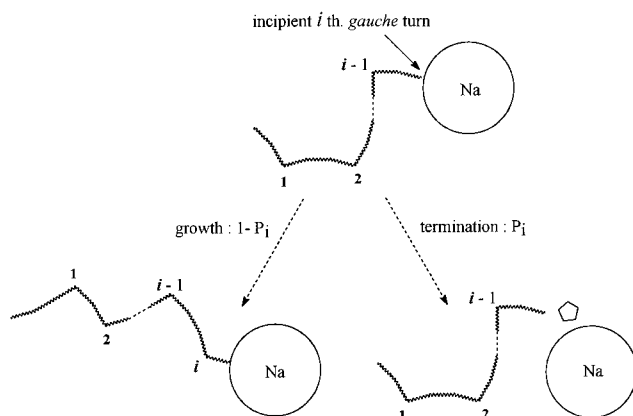
by segments of conformational disorder, i.e., the strong turns referred to above. This is not to describe PMPS as a rigid-rod polymer but a polymer of high molecular weight might well be visualized as a random coil of semirigid rods, i.e., a random coil of wormlike sequences. Values of 64 nm determined for the characteristic ratio,  $C_n$ , of PMPS using light-scattering photometry indicate a relatively stiff polymer chain.<sup>20</sup> The persistence lengths of PMPS, also determined from solution phase light-scattering studies, are in the range 7.0–8.0 nm which corresponds closely to 35–40 repeat units of the polymer chain<sup>21</sup> and correlates well with the effective conjugation lengths determined from UV and fluorescence spectrophotometry.<sup>16</sup>

The maximum conjugation lengths of polysilylenes are most readily discerned from plots of  $\lambda_{\max}$  against relative molecular weight. Such a plot is shown in Figure 5 for PMPS. It is reasonable to assume that the stabilization energy associated with the  $\sigma$ -conjugation varies in this way, and it shows that the greatest gains in stabilization energy (resonance stabilization) of the chain are achieved at an average degree of polymerization (DP) of about 35. Thus, a chain 35 units long is significantly more stable if the conjugation is uninterrupted than if its conjugation is broken at a strong turn after about 15 units (say). In contrast, a chain of length 100 units (say) would be no more stable if its conjugation was unbroken than if it was broken by strong turns into two, or even three, separately conjugated segments. It follows that a chain will grow to be on average 35 units long, gaining stabilization energy at every addition in *trans* conformation. However, eventually there is no energetic advantage in adding in *trans* rather *gauche* conformation (i.e. an incipient strong turn), and at the point in the growth at which such an addition does occur, then the defect is effectively held in this position since any attempt to transfer it back along the chain by conformational reorganization would lead to a reduction in the molecule's overall stability. It follows that the probability ( $P$ ) for the occurrence of a backbiting

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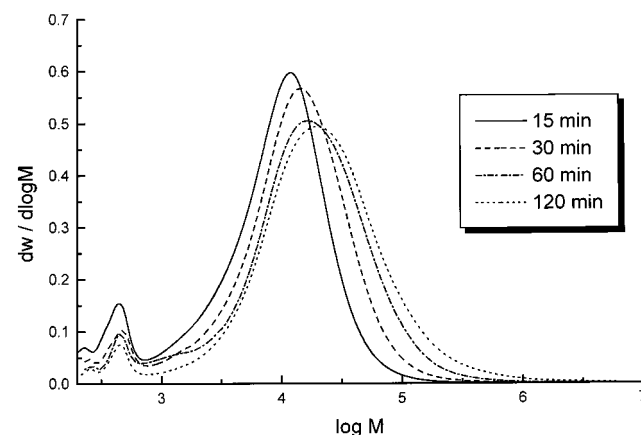
**Figure 6.** Schematic of the progress of the alkali metal mediated reductive coupling of a dihaloorganosilane.

reaction is at a maximum at this juncture (see Figure 6). If backbiting does occur, then a cyclic oligomer is clipped out at the chain end, and since the remnant chain end would now be remote from the alkali metal surface, the polymer molecule would enter solution. The more vigorous the reaction conditions, such as the high temperatures of refluxing toluene or xylene which are more than sufficient to maintain the alkali metal in a molten state, the more likely is this sequence of events. If the backbiting reaction does not occur, then the chain end remains anchored to the alkali metal surface where it continues to grow beyond the average of 35 units at which it attained its maximum stability as a single, approximately *all-trans* sequence. As it does so, the position of the strong turn changes continuously as conformational reorganization seeks to obtain the maximum overall stability for what are now two *all-trans* wormlike sequences. When another strong turn eventually arises, there is now the additional possibility of such a reorganization moving this new structural irregularity away from the chain end, and therefore from the alkali metal surface, as the longer chain seeks optimum stability for three *all-trans* sequences. The probability of a backbiting reaction is thereby reduced (i.e.  $P_2 < P_1$ ), and it follows that the probability of continued growth is increased. As each successive *gauche* turn arises in the ever extending chain, the probability of an immediate redistribution of these conformational defects to new positions away from the chain end further increases the probability of continued growth ( $1-P_i$ ) and decreases the probability of the backbiting reaction ( $P_i$ ) that is required to disengage the chain from the alkali metal surface. Thus it is that the product appears as two distinct fractions, one at  $DP \approx 35$  and the other at a very high degree of polymerization, and rather than the former representing a sole point of no return in the growth of the polymer molecule, it is simply the point at which the probability of that option is at its greatest.

To aid clarification it is perhaps worthwhile expressing these concepts in the following alternative way: At any instant during the growth of a polymer molecule it will contain a number of strong turns, the positions of which change rapidly such that they can effectively be viewed as traveling back and forth along the chain in a random fashion, but one in which the overall stability of the chain is maintained. The number of these turns will increase with chain length, and there would on

**Table 1. Molecular Weight Parameters for Resolved Intermediate and High Molecular Weight Fractions of Three Samples of PMPS Prepared in Accordance with the Standard Wurtz Methodology**

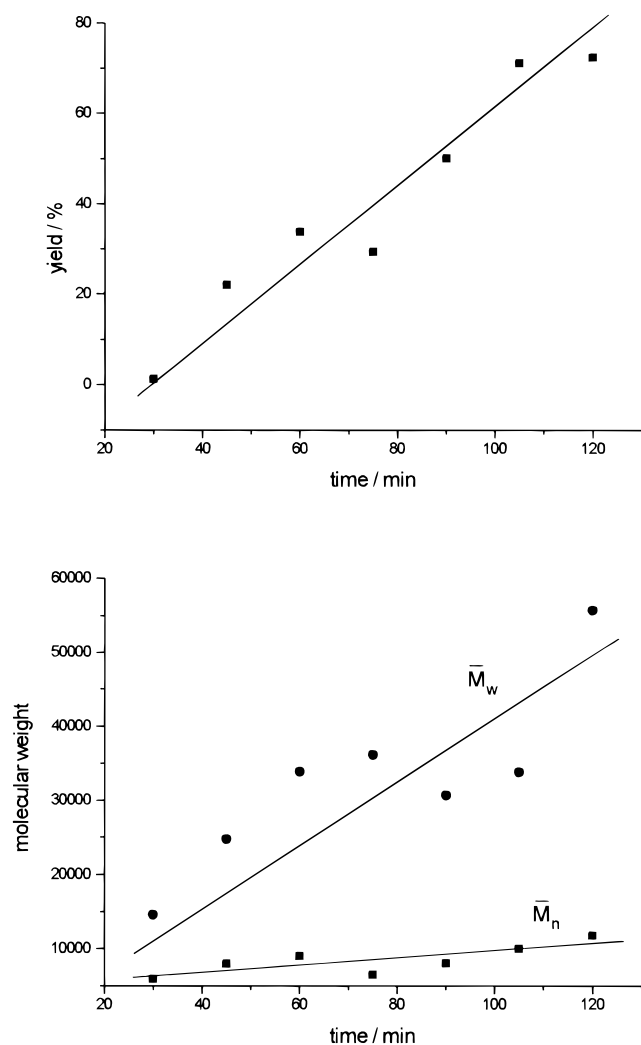
sample	intermediate MW fraction		high MW fraction	
	$10^3 M_n$	$M_w/M_n$	$10^5 M_n$	$M_w/M_n$
PMPS-1	4.62	8.1	4.65	1.7
PMPS-2	4.88	11.3	18.3	1.3
PMPS-3	4.37	8.8	17.7	1.3
$PD_8$		$9.84 \pm 2.5$		$1.55 \pm 0.35$



**Figure 7.** Variation in the molecular weight distribution with time during the Wurtz-type synthesis of PMPS in refluxing THF.

average be about one per 35 chain segments. However, the longer the chain the lesser the probability that at a given instant any of these turns will be found in the vicinity of a chain end and in particular, the chain end located at the alkali metal surface, i.e., there will be an ever increasing probability of them being found at points between the chain ends such that the chain should be divided so as to obtain maximum stability by containing all of the chain atoms within extended *all-trans* sequences. Thus, the highest probability of a strong turn being found at a chain end is for when there is only one such turn, and the chain is of insufficient length to stabilize two *all-trans* sequences, i.e., when it is less than about 35 chain units long. It is in this situation that backbiting and concomitant disengagement of the residual polymer chain from the alkali metal surface would have the highest probability.

On the basis of the above reasoning, the molecular weight distribution of the intermediate molecular weight fraction can be modeled as a series of overlapping normal distributions of decreasing amplitude which give rise to an overall polydispersity that is significantly greater than 2. In contrast, the polydispersity of the high molecular weight fraction should be a much lower value since in this region  $P_i$  is disappearingly small and the growth reaction then approximates to that of a "living" polymerization limited only by the availability of reactants. Table 1, which lists the polydispersities of the intermediate and high molecular weight fractions of three representative samples of PMPS determined following the resolution of the peaks in their size exclusion chromatograms, shows that this is indeed the case. The average polydispersities of the intermediate and high molecular weight fractions for a total of eight samples are also shown.



**Figure 8.** Variation of the yield and molecular weight parameters with time during the Wurtz-type synthesis of PMPS in refluxing THF.

It is also reasoned that if polymerizations are carried out at a lower temperature, then all values of  $P_i$  would fall because thermal activation is probably the most important factor determining the values of these parameters. Overall yields would be lower, but the result should be a more dominant high molecular weight fraction. For the reaction in toluene at 65 °C, Miller et al.<sup>22</sup> report a 10% yield of PMPS with  $M_w = 1\,073\,000$  and  $M_n = 377\,000$  without any intermediate molecular

weight fraction. It follows, that with careful choice of temperature to keep  $P_i$  as low as possible, and a suitable solvent capable of stabilizing the anionic intermediates, it should be possible to conduct syntheses which are close to living polymerizations. Among the criteria for identifying living polymerizations are linear variations of  $M_n$  and yield with time. Figures 7 and 8, for a Wurtz-type synthesis of PMPS in refluxing THF, depict reasonably linear correlations of these types, and although there is progressive broadening of the molecular weight distribution because termination cannot be prevented, they do show that the idea is not unreasonable.

### Conclusion

The above reasoning makes no appeal to reaction mechanism. The nature of the chain ends at the point at which backbiting occurs and whether the propagation reaction is sustained through radicals, anions, or any other intermediate are of no consequence. The stability that is described is that associated with the electronic structure of the catenated silicon atoms that constitute the backbone of the polymer. This is simply the stability arising from electron delocalization within the  $\sigma$ -conjugated HOMO of the polymer during its formation. The nodes within the HOMO are to be found at the strong turns in the backbone which therefore divide a polysilylene chain into segments, the stabilities of which can be considered individually. The overall stability of a growing polymer molecule is the sum of the stabilities of the individual segments. Within a solvent medium, this is maintained at its optimum by the constant repositioning of the sharp turns as the molecule seeks to maximize its complexions through conformational reorganization. On the basis of such a picture of the solution phase structure of PMPS, it has proved possible to rationalize the Wurtz-type synthesis in terms of a simple competition between termination and propagation reactions, the probabilities of which vary continuously during the growth of a molecule.

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