BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 2, pp. 393–398, 1995

0032-3861/95/$10.00 + 0.00

Chloromethylation of poly(methylphenylsilane)

R. G. Jones*, R. E. Benfield, A. C. Swain, S. J. Webb and M. J. Went
Centre for Materials Research, Chemical Laboratory, University of Kent at Canterbury, Kent, CT2 7NH, UK
(Received 11 April 1994; revised 5 August 1994)

The chloromethylation of poly(methylsilane) is readily achieved using chloromethyl methyl ether in a tin(IV) chloride-catalysed reaction in chloroform solution at 0°C. A convenient, less hazardous reaction, in which chloromethyl methyl ether is prepared *in situ*, is also reported. The accompanying variations of the polymer molecular-weight parameters are recorded for chloromethylations extending to 95% of the substituent phenyl groups, and discussed in terms of chain scissions arising at isolated siloxane linkages formed adventitiously during the isolation of the parent polymer.

(Keywords: chloromethylation; polysilanes; functionalization)

INTRODUCTION

In recent years much attention has been directed toward the synthesis of soluble linear polysilanes, otherwise called polysilylenes, which consist of catenated silicon atoms, each bearing two organic substituents[1]. The main approach has been via the *Wurtz* coupling of dichloroorganosilanes using molten sodium in a boiling aromatic solvent such as toluene. However, because these reaction conditions are highly reducing, reports of the direct synthesis of functionalized polysilane homopolymers have been sparse, functional groups that are resistant to the reaction conditions being restricted to aryl ethers[1,2], amino[2] and silyl[3] groups. The concept of protection has also been employed to introduce the phenolic moiety. In a multistage synthesis, the trimethylsilyl group was used to protect the hydroxy substituent of dichlorophenyl-[2-(3-hydroxyphenyl)propyl]silane prior to polymerization[4]. The modification of preformed polysilanes presents another possible approach to functionalization and has received some attention recently[5], though with mixed success since the reactions employed usually either lead to a large reduction in the molecular weight of the polymer, or result in the formation of a crosslinked network[6]. Perhaps the most useful chemical modifications so far reported are the Friedel–Crafts chloromethylations of poly(methylphenylsilane)[7] (*Scheme 1*) and poly(β-phenethylmethylsilane)[8] using chloromethyl methyl ether, and the mild Lewis acid, tin(IV) chloride, as a catalyst. Percentage chloromethylations of the phenyl groups are reported to be in excess of 95%. The former of these two reactions is by far the more attractive as the precursor polymer is so easily synthesized; and in view of the ease with which the chloromethyl group can undergo a host of other reactions, it is perhaps surprising that it has not been the subject of a detailed investigation. The attractions of this preparative route might be reduced somewhat by chloromethyl methyl ether being a potent carcinogen[9]. However, the use of *in situ* preparations of chloromethyl methyl ether has been documented for the chloromethylation of polystyrene[10] and here we report a similarly convenient procedure for the chloromethylation of poly(methylphenylsilane) and compare it with reactions that use chloromethyl methyl ether as an added reagent.

EXPERIMENTAL

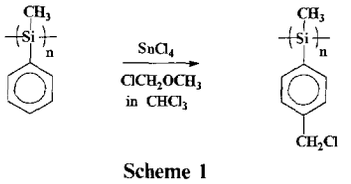
Materials

Dimethoxymethane, tin(IV) chloride, thionyl chloride, chloromethyl methyl ether, dichloromethylphenylsilane and phenyltrimethylsilane (PTMS) were supplied by the Aldrich Chemical Co. All other materials were supplied by Fisons.

SLR methanol, employed solely as a polymer precipitant, was used as supplied. Diethyl ether and tetrahydrofuran (THF) were distilled from Na/K alloy under dry nitrogen immediately prior to use. Dichloromethylphenylsilane was also distilled immediately prior to use, whilst sodium metal was stored under mineral oil until required. All glassware was oven-baked at 150°C.

The preparation of poly(methylphenylsilane) (PMPS)

To a three-necked round-bottomed flask (2000 ml) equipped with a reflux condenser, dropping funnel and mechanical stirrer was added freshly cut sodium (28.3 g, 1.23 mol) and mineral oil. A dispersion was prepared by



Scheme 1

* To whom correspondence should be addressed

melting the sodium whilst stirring rapidly. This was washed five times with portions (50 ml) of diethyl ether to remove all vestiges of the mineral oil. Diethyl ether (1300 ml) and 15-crown-5 (22.5 ml, 0.113 mol) were added to the flask and the mixture brought to reflux. Undiluted dichloromethylphenylsilane (100 ml, 0.651 mol) was carefully added from the dropping funnel over a 40 min period whilst stirring rapidly, the ubiquitous blue colour[11], which is characteristic of a Wurtz reaction, beginning to appear after complete addition of the reagent. The reaction mixture was rapidly stirred and held at reflux for 3 h, after which it was allowed to cool to room temperature. The reaction was quenched by the *very careful* addition of water (500 ml) and stirred until any unreacted sodium and/or dichlorosilane had been destroyed. The organic layer was decanted and added to stirred methanol (3000 ml), after which the precipitated polymer was collected in a Buchner funnel and air-dried (yield 82%). The oligomeric fraction was removed from the polymer by stirring with hexane (500 ml) for 2 h at room temperature followed by filtration and drying. The polymer was further purified by removing the intractable fraction from a solution in THF (600 ml) by centrifugation. The polymer that remained in solution was subsequently isolated by reprecipitation in methanol (2000 ml), and dried under vacuum (yield 16%).

The chloromethylation of poly(methylphenylsilane)

Method (a). PMPS (5 g, 0.0416 mol), chloroform (50 ml) and chloromethyl methyl ether (50 ml) (*extreme caution*: chloromethyl methyl ether is a formidable carcinogen[9]) were added to a Schlenk tube equipped with a magnetic stirring bar under an argon atmosphere. After complete dissolution of the polymer, the reaction mixture was cooled to 0°C and tin(IV) chloride (1.5 ml, 0.0128 mol) added dropwise whilst stirring. A dark yellow colour was immediately observed. The reaction mixture was stirred at 0°C for 3 h, after which it was carefully syringed into methanol (300 ml). The precipitated polymer was collected in a Buchner funnel, twice reprecipitated from toluene solution into an excess of methanol, filtered and air-dried.

Method (b). PMPS (5 g, 0.0416 mol), dimethoxymethane (40 ml, 0.452 mol) and chloroform (50 ml) were added to a Schlenk tube equipped with a magnetic stirring bar under an argon atmosphere. After complete dissolution of the polymer, the reaction mixture was cooled to 0°C and thionyl chloride (10 ml, 0.137 mol) added dropwise whilst stirring. *Extreme caution* should again be observed as chloromethyl methyl ether is generated *in situ*. The reaction mixture was allowed to warm to room temperature and stirred for a further 1 h. After again cooling the mixture to 0°C, tin(IV) chloride (1.5 ml, 0.0128 mol) was added dropwise whilst stirring. The characteristic dark yellow colour was again observed. The reaction was stirred for a further 2.5 h at 0°C, then syringed into methanol (300 ml). The precipitated polymer was isolated using the procedures described above.

Studies of the progress of the chloromethylation reaction was undertaken using the procedures described above on 5 ml aliquots that were removed from the reaction mixture at recorded intervals.

It must be emphasized that the reaction temperature is critical to the success of the chloromethylation reactions. The same reactions conducted at room temperature result in the degradation of the polymer to a mixture of oligomers.

The chloromethylation of phenyltrimethylsilane

The chloromethylation of PTMS (a simple model for PMPS) was carried out using both of the procedures described above except that reaction times of 18 h were employed. Water was added to destroy the tin(IV) chloride, after which the organic layer was decanted and the volatiles removed under reduced pressure. A mixture of chloromethylated products in 60% yield was obtained after reduced-pressure distillation (0.5 mmHg, 135°C). Column chromatography (Merck, silica gel 60 F_{254}) using heptane as the eluent effectively separated these into xylylidene dichloride and chloromethylphenyltrimethylsilane fractions as identified by ^{1}H n.m.r. The latter fraction was further purified by distillation under reduced pressure.

Apparatus and procedures

^{1}H and ^{13}C{NNE} n.m.r. spectra were recorded at probe temperature using a JEOL GX-270 spectrometer and ^{29}Si{DEPT} n.m.r. spectra were obtained on a Brucker ARX400 spectrometer. Chemical shifts were referenced to the solvent, $CDCl_3$. The extent of chloromethylation was readily established from the integrated n.m.r. spectra of the chloromethylated polymer. In the case of ^{13}C spectra, peak area measurements were achieved using inverse-gated decoupling with a 5 s pulse delay.

Gas chromatography was carried out using an Altech Econocap EC-30 silica column (30 m, 0.54 mm i.d.) on Pye Unicam PV4500 equipment.

Molecular weights were obtained as linear polystyrene equivalents in tetrahydrofuran solution using size exclusion chromatography equipment supplied by Polymer Laboratories Ltd and equipped with a mixed bed 5 μm PLgel column. The calibration was over the molecular weight range 162 to 1.03×10^6.

RESULTS AND DISCUSSION

The chloromethylation of PMPS was readily achieved using chloromethyl methyl ether in chloroform solution in the presence of tin(IV) chloride as the catalyst in a Friedel–Crafts reaction. The isolated polymers remained as tractable white powders over the whole chloromethylation range. N.m.r. spectroscopy revealed no evidence of either crosslinking or the CH_2OH groups that might conceivably be formed during the isolation procedures (see *Figure 1*). Elemental analyses confirmed that the polymers were free of hydroxyl groups. The n.m.r. spectra of these products and those prepared by the reaction in which the chloromethyl methyl ether was prepared *in situ* revealed that identical polymers are conveniently prepared using either procedure.

In order to ascertain the preferred site of substitution, the chloromethylation of the model compound PTMS was carried out under conditions essentially identical to those employed for the chloromethylation of the polymers. Under these conditions some substitution at the *ipso* position of PTMS occurs, as evidenced by the presence of benzyl chloride and xylylidene dichlorides in the product mixture. However, analysis of the chloromethyl region of

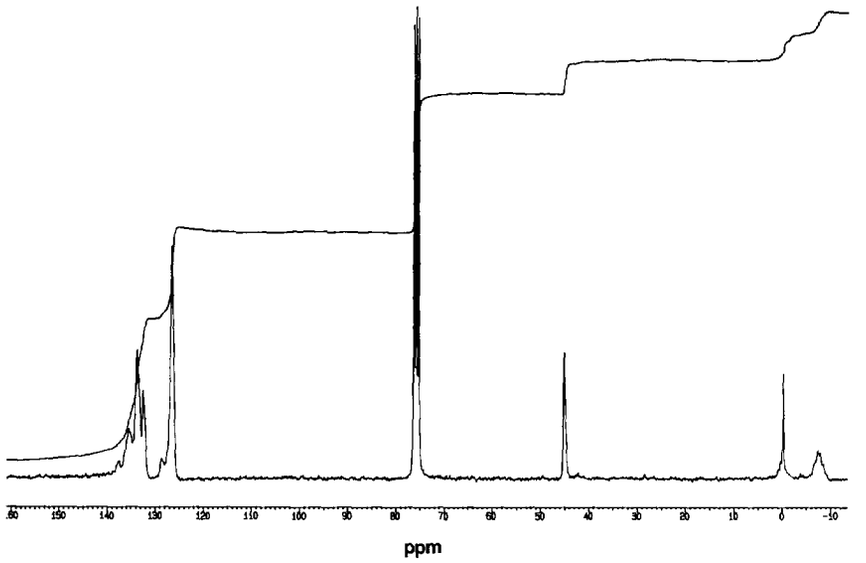


Figure 1 The $^{13}C\{NNE\}$ n.m.r. spectrum of a typical chloromethylated poly(methylphenylsilane) in chloroform solution

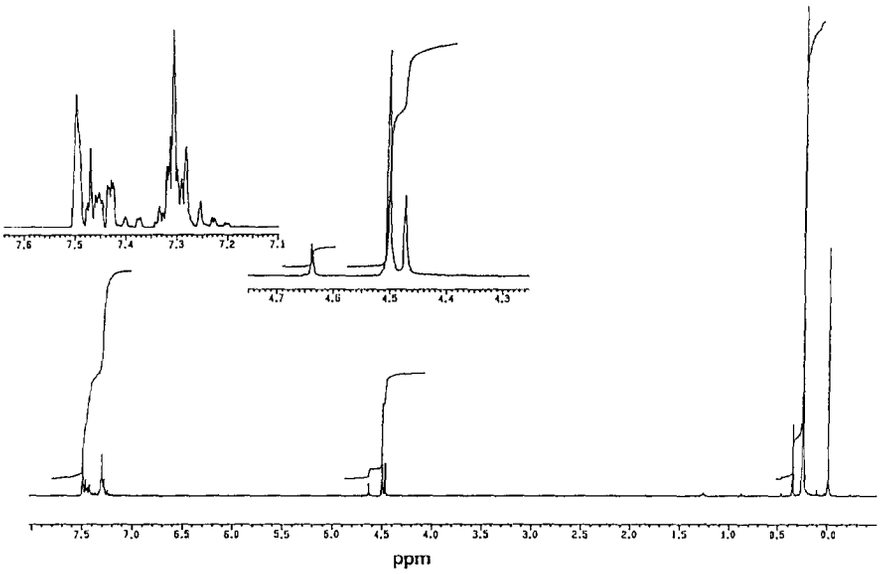


Figure 2 The ^{1}H n.m.r. spectrum of chloromethylated phenyltrimethylsilane in chloroform solution

the ^{1}H n.m.r. spectrum (see *Figure 2*) obtained for the chloromethylated PTMS shows the products of reaction to be a 67%/25%/8% mixture of isomers. G.c. analysis of the same sample gave 69%/22%/8%. These are assigned as the *para*, *meta* and *ortho* isomers respectively on the basis of partial rate factors[12] for the nitration of PTMS (ref. benzene) at the same positions being 3.1, 2.0 and 1.3. The first of these assignments is supported by the presence of four dominant peaks in the aromatic region of *Figure 2*, which display the AB splitting pattern characteristic of a *para*-substituted phenyl ring. Given the greater steric hindrance afforded by the adjacent silicon atoms in the polymer it is expected that the chloromethylation of PMPS results in a polymer containing a greater proportion of *para* substitution than that obtained in the model compound. For the same reason it is expected that little substitution at the *ipso* positions of the phenyl groups of the polymer would occur. Were this not the case, the polymer would be expected eventually to undergo total degradation.

The variation of the extent of chloromethylation with reaction time is shown in *Figure 3*. It can be seen that the plot can be divided into two regions: (1) an induction period, during which the rate of reaction is slow and which persists until approximately 15% chloromethylation has been achieved, followed by (2) a very much increased rate of reaction, which tends asymptotically to a limit at 100% chloromethylation (i.e. one chloromethyl group per repeat unit in the polymer chain). The same variation of the extent of chloromethylation with time is observed whether or not the chloromethyl methyl ether is generated *in situ*.

A comparison of the typical size exclusion chromatograms of a PMPS and the corresponding chloromethylated polymer depicted in *Figure 4* shows that the

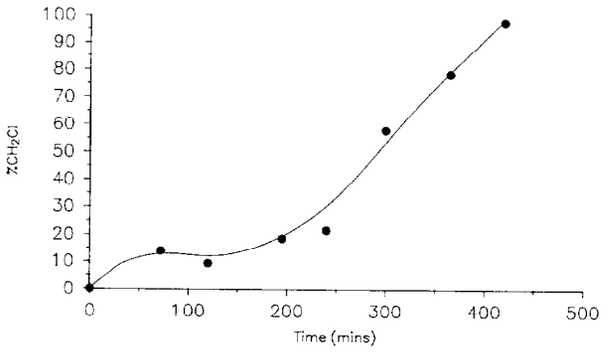


Figure 3 The variation of the extent of the chloromethylation of poly(methylphenylsilane) with time

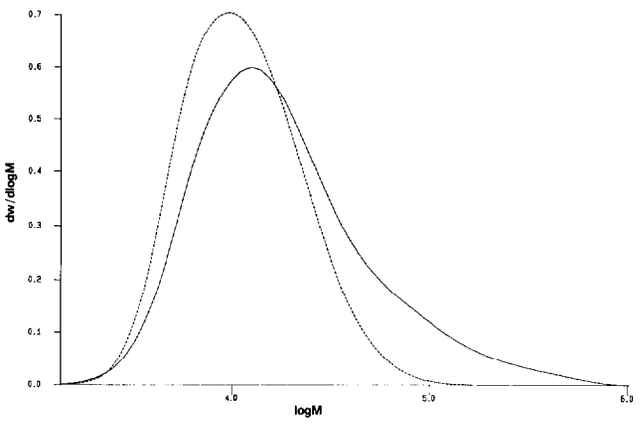


Figure 4 A comparison of the size exclusion chromatograms of a poly(methylphenylsilane) before (——) and after (----) chloromethylation

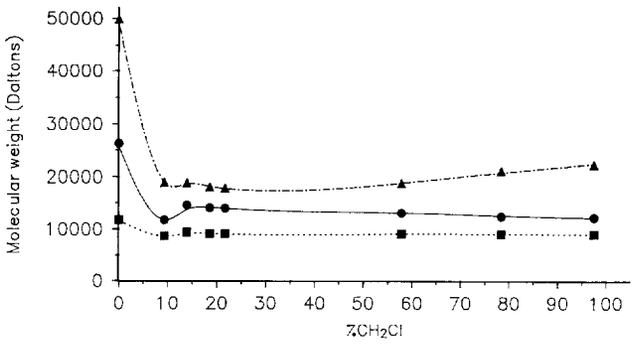


Figure 5 Variation of peak (●), number-average (■) and weight-average (▲) molecular weights with percentage chloromethylation of poly(methylphenylsilane) in chloroform solution at 0°C

chloromethylation is accompanied by a reduction in molecular weight. In particular, it is the high-molecular-weight fraction of the initial PMPS that seems to react preferentially, thereby giving rise to a polymer with lower molecular-weight parameters and of a narrower distribution. Furthermore, the period of time over which this occurs correlates sensibly with the duration of the induction period of the chloromethylation. A plot showing the variation of the number-average (M_n), the weight-average (M_w) and the peak (M_p) molecular weights with percentage chloromethylation is shown in *Figure 5*. There is a rapid decrease in both M_n and M_w whilst approximately 15% chloromethylation is being achieved, the dispersity index taking on a value close to that corresponding to a normal distribution. Thereafter M_n remains essentially constant for the duration of the reaction whilst M_w increases steadily again over the time that it takes to achieve complete chloromethylation. This increase is not unexpected since an increase in the percentage chloromethylation increases the average size of the polymer repeat unit accordingly. It is evident that the period of slow chloromethylation (the apparent induction period of *Figure 3*) corresponds to the chloromethylation range over which the greatest reduction in the molecular-weight parameters of the polymer is observed. However, *Figures 6* and *7* for the reaction of another PMPS with tin(IV) chloride in chloroform solution depict a similarly rapid initial decrease in the molecular-weight parameters. Chloromethyl methyl ether was not included in this reaction but otherwise the conditions were identical to those used for chloromethylations. Although an almost linear reduction in molecular weight with reaction time is observed to persist over what would be the duration of a chloromethylation reaction, the magnitude of this change is negligible when compared to the sharp initial reduction.

Since, when the chloromethylation is conducted at higher temperatures, the PMPS is degraded to oligomers, it might be reasoned that the initial sharp reduction in

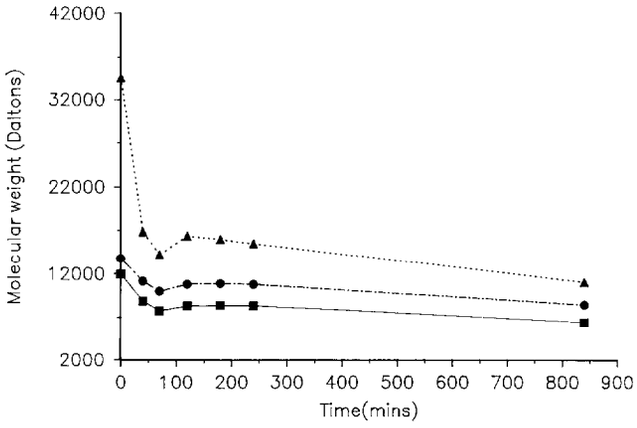


Figure 6 Variation of the molecular-weight parameters for the reaction between poly(methylphenylsilane) and $SnCl_4$ in chloroform solution at 0°C. The notation is consistent with that of *Figure 5*

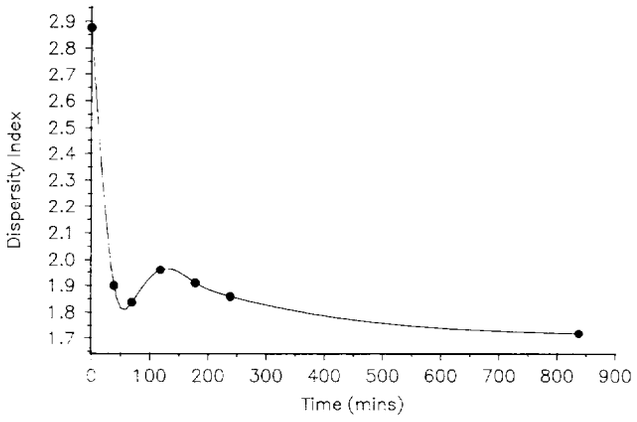


Figure 7 Variation of the dispersity index during the reaction between poly(methylphenylsilane) and $SnCl_4$ at 0°C in chloroform solution

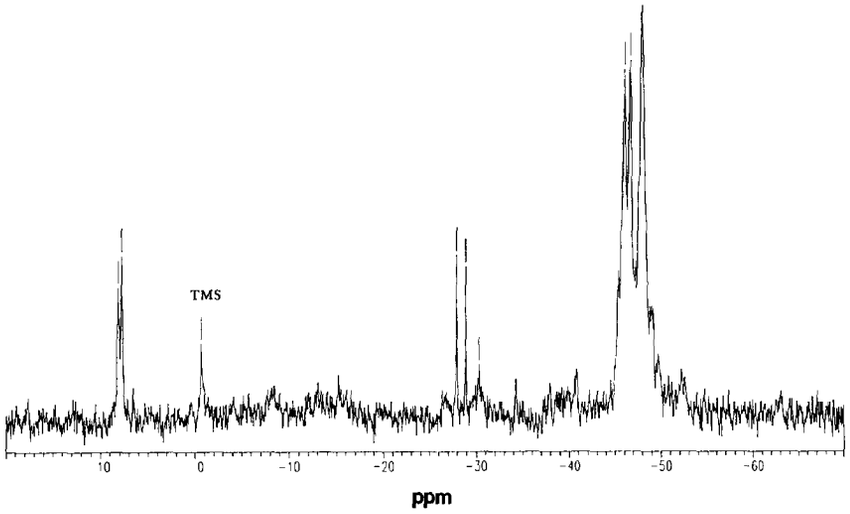


Figure 8 The $^{29}Si\{DEPT\}$ n.m.r. spectrum of a poly(methylphenylsilane) prepared by the Wurtz reaction after removal of both insoluble material and low-molecular-weight hydrolysis products. The signals due to the silicon atoms of poly(methylphenylsilane) are centred on -46 ppm, whilst those at lower field are assigned to siloxy moieties

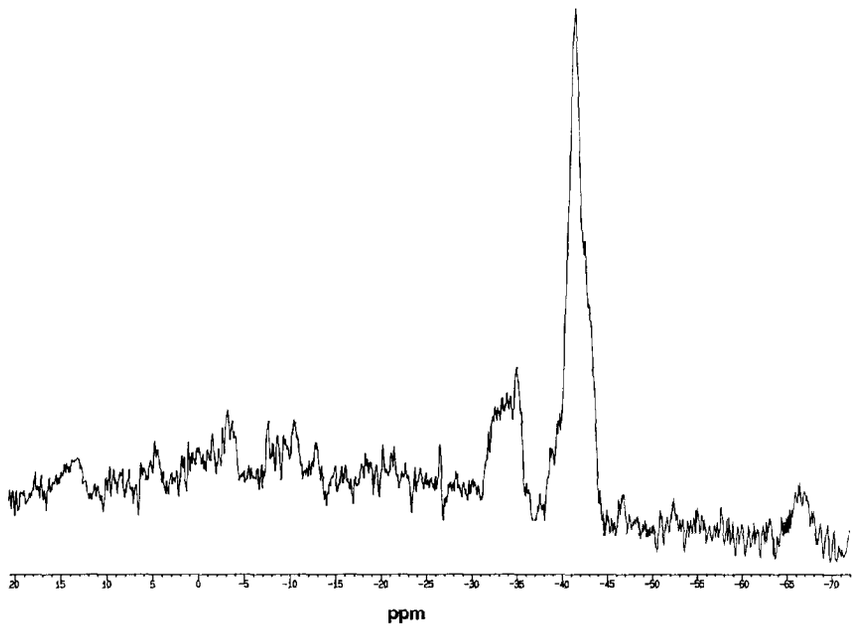
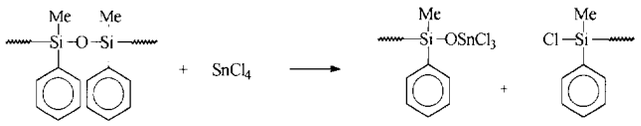
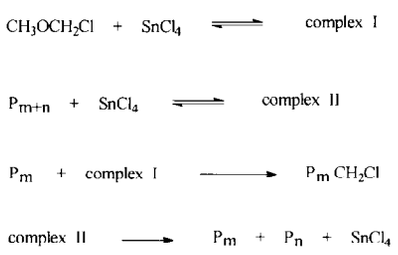


Figure 9 The $^{29}Si\{DEPT\}$ n.m.r. spectrum of a typical sample of a partially ($\sim 50\%$) chloromethylated poly(methylphenylsilane)

molecular weight can be explained as being a reagent-induced chain degradation that is a commonplace reaction of polysilanes. However, such a degradation, rather than apparently ceasing after some given time during which the degree of polymerization has approximately halved, would be expected to continue inexorably until all of the polymer had been consumed. It seems that the reaction that in this instance is responsible for the molecular-weight reduction is either limited by some main-chain structural feature or arises only at such a feature. The latter seems more probable, for it has been reported[13] that, if exclusively aqueous conditions are employed at the first stage in product isolation, then the average molecular weight of a Wurtz-synthesized polysilane is higher than if alcoholic conditions are utilized. This is explained as resulting from the formation of small but significant numbers of siloxane linkages through the hydrolysis of terminal Si–Cl bonds[13,14]. Furthermore, Sakurai *et al.*[15] have observed strong infra-red bands, which accord with the presence of siloxane linkages, within the structures of polysilanes prepared using the Wurtz reaction, and Matyjaszewski[16], using ^{29}Si n.m.r., has also observed siloxane linkages. *Figure 8* depicts the $^{29}Si\{DEPT\}$ n.m.r. spectrum of a PMPS that has been isolated using exclusively aqueous procedures. Low-field signals that can be assigned to Si–O-based species are evident at about -28 ppm. However, following chloromethylation, only signals that can reasonably be assigned to the silicon atoms of a polysilane (< -40 ppm) are observed (*Figure 9*). It is proposed that a siloxane linkage behaves as a Lewis base and as such represents a site of reaction with tin(IV) chloride and that it is this reaction



Scheme 2



Scheme 3

that results in the marked reduction in the molecular weight of the polymer that is observed in the early stages of reaction. A possible reaction, shown in *Scheme 2*, is in competition with the chloromethylation of PMPS at the onset of reaction. It is presumed to be complete when approximately 15% chloromethylation has been achieved, after which only chloromethylation is observed.

Friedel–Crafts reactions require the initial formation of a complex of the catalyst and the reagent; in this case it would be a simple adduct of chloromethyl methyl ether and tin(IV) chloride. It might reasonably be assumed that a similar complexation of the catalyst with the siloxane linkage would be required as a precursor to the chain scission. In the reactions depicted in *Scheme 3*, complex I represents the chloromethylation complex whilst complex II represents the siloxane complex. Dependent upon the relative stabilities of these complexes, the extent of formation of one would be suppressed by the formation of the other. It is postulated that in these chloromethylation reactions it is the siloxane complex that is the more readily formed. The concentration of the chloromethylation complex is accordingly suppressed and remains so until chain scissions are complete, after which its concentration increases and with it the rate of chloromethylation. Although it is not represented in *Scheme 2*, it is assumed that tin(IV) chloride behaves as a true catalyst and through some subsequent reaction is released following chain scission as depicted in *Scheme 3*.

The above arguments are advanced as only part of the possible explanation of the apparent induction period of the chloromethylation reaction. The reaction sequence is clearly more complicated than that represented in *Scheme 3*, for bearing in mind the incidence of siloxane linkages, it is acknowledged that complexation with them alone would not be sufficient to reduce significantly the concentration of the chloromethylation complex, and that the involvement of other equilibria that effectively reduce the availability of tin(IV) chloride for complexation would be required. Other sites on the polymer chain may serve such a purpose and conceivably these are the sites from which total degradation ensues when the chloromethylation is conducted at higher temperatures.

CONCLUSION

Poly(methylphenylsilane) is one of the easiest polysilanes to prepare in high yield from relatively cheap starting materials. Whereas, in common with all polysilanes, it is readily degraded in reactions that employ strongly acidic or basic conditions, it is apparent that it is relatively resilient under Freidel–Crafts conditions at low temperatures. Thus, the dominantly *para* selective chloromethylation of PMPS can be undertaken in a controlled fashion with only minor modification to the molecular-weight distribution; those changes that do occur are attributable to the scission of siloxane bonds formed adventitiously during the isolation of the precursor polymer. The product is a functionalized polysilane, the chloromethyl groups of which are reactive sites allowing access to a host of structures that would otherwise be either too difficult or impossible to prepare. Such reactions and the structural characterization of their products will be the subjects of a following publication.

ACKNOWLEDGEMENTS

We gratefully acknowledge the Royal Society's support for R.E.B. through the award of a University Research Fellowship, the SERC for a Postdoctoral Research Fellowship for A.C.S. and British Telecom for a CASE award for S.J.W. We would also like to thank Brucker Spectra Spin for their help in obtaining the high-field $^{29}Si\{DEPT\}$ n.m.r. spectra.

REFERENCES

1 Miller, R. D. and Michl, J. *Chem. Rev.* 1989, **89**, 1359
2 Ho Yi, S., Maeda, N., Suzuki, T. and Sato, H. *Polym. J.* 1992, **24**, 865
3 Harrah, L. A. and Zeigler, J. M. *Macromolecules* 1987, **20**, 2037
4 Horiguchi, R., Onishi, Y. and Hayase, S. *Macromolecules* 1988, **21**, 304
5 West. R. *J. Organomet. Chem.* 1986, **300**, 327
6 Wolff, A. R. Ph.D. Thesis, University of Wisconsin, 1984
7 Ban, H., Sukegawa, K. and Tagawa, S. *Macromolecules* 1987, **21**, 304
8 Seki, T., Tamaki, T. and Ueno, K. *Macromolecules* 1992, **25**, 3825
9 Van Duisen, B. L., Sivak, A., Goldschmidt, B. M., Katz, C. and Melchionne, S. *J. Natl. Cancer Inst.* 1969, **43**, 481
10 Wright, M. E., Toplikar, E. G. and Svejda, S. A. *Macromolecules* 1991, **24**, 5879
11 Benfield, R. E., Cragg, R. H., Jones, R. G. and Swain, A. C. *Nature* 1991, **353**, 340
12 Speier, J. L., *J. Am. Chem. Soc.* 1953, **75**, 2930
13 Worsfold, D. J. in 'Inorganic and Organometallic Polymers', ACS Symp. Ser. 360 (Eds. M. Zeldin, K. J. Wynne and H. R. Allcock), American Chemical Society, Washington, DC, 1988, Ch. 8
14 Jones, R. G., Benfield, R. E., Cragg, R. H. and Swain, A. C. *J. Chem. Soc., Chem. Commun.* 1992, 112
15 Sakurai, H. personal communication
16 Kim, H. K. and Matyjaszewski, K. *J. Polym. Sci. (A) Polym. Chem.* 1993, **31**, 299