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# Synthesis and Characterization of Poly(tetramethyldisilylene-*co*-styrene)

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ABSTRACT: Dechlorination of dimethyldichlorosilane using sodium in toluene at 110 °C in the presence of styrene (for varying composition of the monomers) has resulted in copolymers which are soluble in common organic solvents. Characterization of these polymers by $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy, pyrolysis GC, and microstructural analysis reveals that they contain tetramethyldisilylene and styryl moieties as repeating units. Significantly, no monosilyl linkage was observed in these copolymers. In addition to the repeating units containing disilyl linkages, polysilyl linkages were observed at higher concentrations of DMDCS. Polystyrene blocks were observed when the styrene concentration was increased. GPC data reveal that the copolymers have a bimodal distribution and the low molecular weight fraction increases with an increase in the concentration of styrene. The present investigation strongly suggests that synthesis of polysilanes by dechlorination using sodium involves disilyl species as the probable reactive intermediates.

## Introduction

Soluble polydiorganosilanes have recently been shown to act as photoinitiators[1] for a variety of vinyl monomers such as styrene, methyl methacrylate, acrylic acid, etc. The vinyl polymers thus produced are in general typical of radical polymerized olefins but differ in one important respect, in that they contain short polysilane chains attached to the polyolefins.[2] Silyl and silylene radicals are postulated to be intermediates in the above photoinitiated polymerizations. However, the mechanism of the synthesis of polysilanes under Wurtz-type conditions also envisages the silicon-containing reactive intermediates such as silylenes, disilanes, silyl radicals, silyl anions and radical ions, etc. in the polymerization process.[3] Indeed, the polymerization of silane monomers containing olefin substituents has been used to justify the suggestion that silyl radicals are involved in the polymerization.[4] However, there seems to be no study on the copolymerization of a dichlorosilane and a vinyl monomer containing no silicon atom under dechlorination conditions. Such copolymers may have interesting properties, and a study of the microstructure of these polymers may provide a clue to the probable reactive intermediate in the copolymerization process and polysilane synthesis.

This paper deals with the synthesis of poly(tetramethyldisilylene-*co*-styrene) under dechlorination conditions from styrene and dimethyldichlorosilane in different mole proportions and their characterization by $^1$H, $^{13}$C, and $^{29}$Si NMR spectra and by SEC and TGA. The results suggest the involvement of disilyl species as reactive intermediates.

## Experimental Section

**Materials.** Dimethyldichlorosilane (DMDCS) was purified by distillation before use. Styrene was washed with 5% sodium hydroxide solution followed by water and dried over anhydrous sodium sulfate. It was then purified by vacuum distillation over calcium hydride. Toluene was refluxed over sodium and distilled.

**Synthesis of Copolymers.** In a typical experiment 7.35 g of freshly cut sodium was taken in 135 mL of toluene in a three-necked flask fitted with a stirrer mantle, condenser, inlet and outlet for nitrogen, and a calcium chloride guard tube. Sodium was melted under reflux conditions of toluene with stirring. To the finely divided molten sodium, a monomer mixture containing 19.7 g (0.153 mol) of DMDCS and 7.9 g (0.076 mol) of styrene was added using a pressure-equalizing funnel over a period of 5 min. The reaction mixture was allowed to reflux gently for 6 h. The unreacted sodium was neutralized with methanol, and the reaction mixture was poured into 1 L of methanol. The precipitate obtained was collected and dried in a vacuum oven at 60 °C for 3 h. The precipitate was dissolved in toluene and poured into a methanol–water mixture under stirring. The above reprecipitation was repeated twice, and finally, the polymer (P-I) was dried in a vacuum oven at 100 °C for 10 h. In a similar way polymers II (P-II) and III (P-III) were prepared using monomer mixtures containing DMDCS and styrene in the mole ratio 1:1 and 1:1.5, respectively.

**Characterization.** $^1$H, $^{13}$C, and $^{29}$Si NMR spectra were recorded at 90, 22.5, and 17.8 MHz, respectively, on a JEOL FX90Q spectrometer fitted with a tunable probe. $CDCl_3$ was used as a solvent, and tetramethylsilane was used as internal standard. For recording $^{29}$Si NMR spectra, a gated decoupling technique (decoupling frequency of 89.6 MHz for proton) was used in order to suppress the negative NOE and ferric acetylacetonate ($\sim 10^{-2}$ M) was used as the relaxation agent.

GPC curves were recorded with a Waters ALC GPC 244 instrument using 100- and 500-$\mu$m styragel columns and tetrahydrofuran as the solvent. Pyrolysis studies of the polymers were carried out on Shimadzu GC equipment using an SE-50 GC column. TGA studies were made with a Dupont 990 thermal analyzer in conjunction with a 951 thermogravimetric analyzer in nitrogen atmosphere at a heating rate of 10 °C/min.

**Fractionation.** The solvent–nonsolvent precipitation method was used for the fractionation of P-III. Nonsolvent methanol (100 mL) was slowly added, with vigorous stirring, to a 10% solution of the polymer in toluene. When the solution turned milky, it was warmed till it became clear and allowed to settle (6 h) at room temperature. The precipitate was filtered off and dried. A total of three fractions were collected using 100 mL of methanol each time.

## Results and Discussion

**Composition and Molecular Weights.** The composition of P-I–P-III was evaluated from $^1$H NMR spectra on the basis of the relative intensities of the aromatic and aliphatic resonances. Molecular weights were determined by GPC using polystyrene standards. The results are given in Table I. All the polymers show a bimodal molecular weight distribution (Figure 1) in common with most of the polysilanes prepared by Wurtz-type polymerizations. It is interesting to note that the low molecular weight fraction increases with an increase in the amount of styrene in the feed, varying from 26% (by weight) in P-I to 70% in P-III, suggesting the involvement of styrene in the

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**Table I**
**Some Properties of Polymers I–III**

| sample | mole ratio of styrene to DMDCS in the feed | mole ratio of styrene to dimethylsilylene units in the copolymer[a] | high molecular weight fraction | | | low molecular weight fraction | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $10^{-4}M_n$ | $10^{-5}M_w$ | $M_w/M_n$ | $10^{-3}M_n$ | $10^{-3}M_w$ | $M_w/M_n$ | wt % |
| polymer I | 0.5 | 0.5 | 6.86 | 1.31 | 1.91 | 3.14 | 5.66 | 1.80 | 26 |
| polymer II | 1.0 | 0.8 | 6.92 | 1.19 | 1.72 | 2.54 | 5.52 | 2.17 | 39 |
| polymer III | 1.5 | 1.33 | 6.87 | 1.12 | 1.68 | 2.49 | 5.78 | 2.32 | 70 |

[a] Calculated from $^1$H NMR spectra.

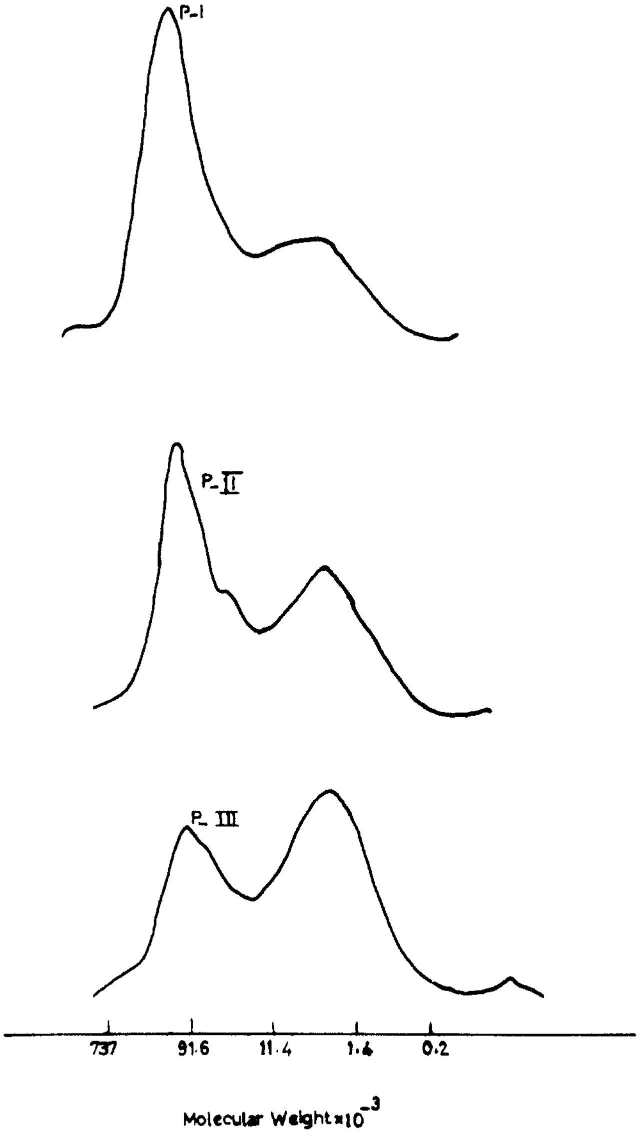


**Figure 1.** GPC curves of polymers I-III (P-I–P-III).

initiation reactions. As the concentration of styrene in the feed increases, the number of initiating radicals and consequently propagating chains increases resulting in a higher proportion of low molecular weight components.

**$^{29}$Si NMR Spectra.** The $^{29}$Si NMR spectra of P-I–III were recorded at 17.8 MHz in $CDCl_3$ solvent and the spectra of P-I and P-III are shown in Figures 2 and 3, respectively. All the three polymers show signals at $\delta$ = −11.42, −15.43, and −15.77 ppm. The relative intensities of the three signals are found to be the same in all the three polymers, suggesting that they originate from the same propagating unit. In addition, P-I shows signals at $\delta$ = −37.17 and −38.78 ppm and account for about 15% of the total Si atom.

Since the chemical shifts of $^{29}$Si in model compounds $RSi(Me)_2R$ and $RSi(Me)_2Si(Me)_2R$ (R = styryl, Me = methyl) are not available, the assignments of the observed resonances were based on the following considerations.

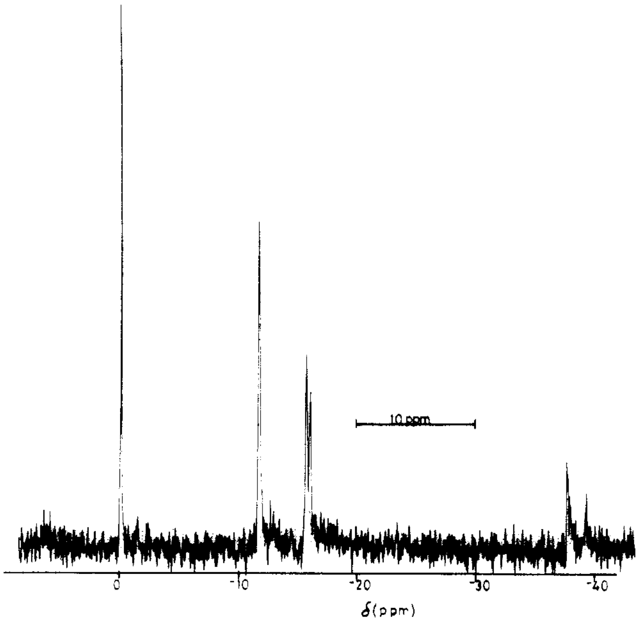


**Figure 2.** $^{29}$Si NMR spectrum of polymer I (P-I).

**(i) Substituent Effect.** The placement of the phenyl group $\alpha$ to a Si atom causes a small but downfield shift in the $^{29}$Si resonance as evidenced by the data for ($Me_3SiCH_2C_6H_5$ ($\delta$ = 1.16 ppm) and $Me_3SiCH_2CH_2C_6H_5$ ($\delta$ = 1.1 ppm).[5] Therefore it is quite reasonable to assume that the chemical shift of $^{29}$Si in $RSi(Me)_2R$ will not be far different from these values.

**(ii) Monosilane Linkage.** A silicon atom bound to four $SP_3$ carbon atoms in compounds of the type $(Me)_3SiCH_2X$, $(Me)_3SiCH_2CH_2X$, and $XCH_2Si(Me)_2CH_2Y$, where X and Y are groups of widely differing electronegativities, resonates in a narrow range $\delta$ = −1.5 to +6 ppm, as shown by the compilation of $^{29}$Si chemical shifts data by Williams and Cargioli.[5]

**(iii) Disilane Linkage.** The chemical shifts of the silicon atom marked A in compounds of the type $(Me)_3Si^ASi(Me)_2X$ are in the range $\delta$ = −18 to −22.5 ppm when X = methyl, H, Cl, F, and CN, indicating that the substituents on an adjacent silicon atom do not greatly influence the chemical shifts of the Si atom.[5]

**(iv) Polysilane Linkage.** The chemical shifts of silicon atoms marked A and B in permethylated polysilanes of the structures $(Me)_3Si^ASi^B(Me)_2Si(Me)_2$ are in the range $\delta$ = −19.7 to −15.0 and −48 to −43 ppm, respectively.[6] This is also brought out by the data on other polysilanes.[7,8]

Thus the available literature data suggest that $^{29}$Si chemical shifts of mono- ($CH_2Si(Me)_2CH_2$), di- ($CH_2Si(Me)_2Si(Me)_2CH_2$), and trisilane ($CH_2Si(Me)_2Si(Me)_2Si(Me)_2$) linkages fall in three distinct regions and therefore can readily be distinguished from one another.

Hence the observed resonances in the region $\delta$ = −11 to −15 ppm can be assigned to disilane linkages, and the resonances at $\delta$ = −37.17 and −38.78 ppm can be assigned to trisilane linkages. Consequently, structural units of

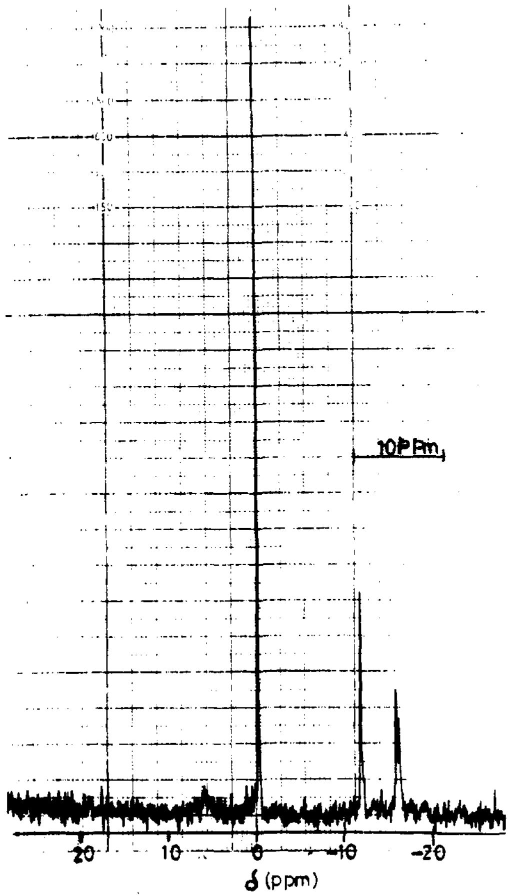
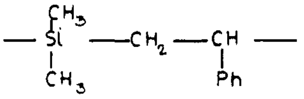
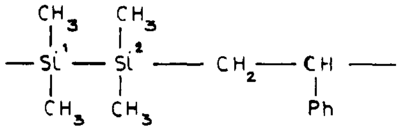


**Figure 3.** $^{29}$Si NMR spectrum of polymer III (P-III).

type A can be ruled out and the probable structural units of the copolymers can be represented by type B.

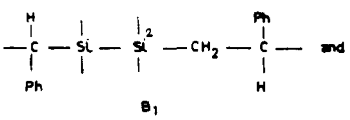

$$-Si(CH_3)_2-CH_2-CH(Ph)-$$

Type A

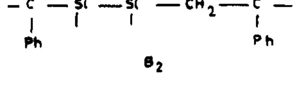

$$-\overset{1}{Si}(CH_3)_2-\overset{2}{Si}(CH_3)_2-CH_2-CH(Ph)-$$

Type B

The resonances at $\delta = -11.43$ ppm can then be assigned to Si$^1$ and the resonances at $\delta = -15.43$ and $-15.77$ ppm can be assigned to Si$^2$ in structure B. These assignments are based on the observation that branching at the $\alpha$-carbon atom deshields the Si atom whereas branching at the $\beta$-carbon has no effect.[5] The multiplicity of signals for Si$^2$ may arise from the two possible stereochemical arrangements B1 and B2. The equal intensities of the two signals in all the three polymers suggest that both arrangements are equally possible.

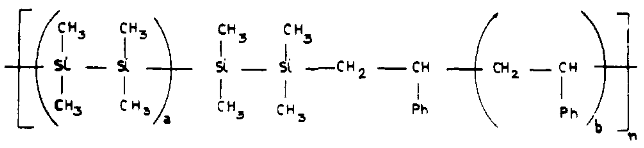

$$-\underset{Ph}{\overset{H}{C}}-Si-\overset{2}{Si}-CH_2-\underset{H}{\overset{Ph}{C}}- \text{ and}$$

$B_1$


$$-\underset{Ph}{\overset{H}{C}}-Si-Si^2-CH_2-\underset{Ph}{\overset{H}{C}}-$$

$B_2$

In addition, the presence of blocks of individual monomer units in the polymer chain has to be considered since the mole ratio of the two monomers varies from polymer I to III. Thus, a probable structure of the copolymer can be represented by C.


$$\left[\left(Si(CH_3)_2-Si(CH_3)_2\right)_a Si(CH_3)_2-Si(CH_3)_2-CH_2-CH(Ph)-\left(CH_2-CH(Ph)\right)_b\right]_n$$

Structure C

In the case of Polymer I, the value of $a$ is 0.2 as derived from the relative intensities of disilane ($\delta = -11$ to $-15$ ppm) and polysilane ($\delta = -37$ to $-38$ ppm) linkages in $^{29}$Si NMR spectra. For P-II and P-III, the value of $a$ is zero since no polysilane linkages are observed in their $^{29}$Si NMR spectra. The value of $b$ can be obtained from the mole ratio of the monomers using the relation

$$\frac{\text{mol of styryl units}}{\text{mol of silyl units}} = \frac{1+b}{2(1+a)} \tag{1}$$

The mole ratio can be obtained from $^1$H NMR data as indicated earlier. The computed value of $a$ and $b$ are given in Table II for P-I–P-III. Further confirmation of these structures was obtained by $^{13}$C NMR spectroscopy.

**$^{13}$C NMR Spectra.** The sensitivity of $^{13}$C chemical shifts to the neighboring groups enables one to distinguish readily carbons attached to Si (Si–CH$_2$–CH(Ph)–Si) from carbons in a block of styryl units (CH$_2$–CH(Ph))$_n$, where Ph denotes a phenyl group. Therefore, $^{13}$C NMR spectra of P-I to P-III were recorded and are shown in Figures 4 and 5 for P-I and P-III, respectively. The important observations that can be drawn from these spectra are as follows.

**(i) Methyl Group Resonances.** As expected, the methyl carbons show a large number of resonances in the region $\delta = -2$ to $-6$ ppm, and this can be attributed to the presence of different neighboring groups (CH and CH$_2$) as well as to the sensitivity to stereochemical environment (B1 and B2 structures). However, a prominent feature of this region is the presence of a line at $\delta = -3.80$ ppm in the spectrum of P-I (Figure 4, insert a) which is absent in the spectra of P-II and P-III. This can be attributed to the methyl groups attached to the two middle silicon atoms in a tetrasilane linkage (Si–Si–Si–Si). The intensity of this line is about 18% of the total methyl carbons and agrees with the value derived for polysilane linkages from $^{29}$Si NMR spectroscopy.

**(ii) Methylene and Methine Carbons.** Based on off-resonance decoupling experiments, the resonances at $\delta = 15.18$ and 30.4 ppm observed in all the three polymers were assigned to the methylene (SiCH$_2$) and methine (Si–CH) carbons, respectively. The chemical shifts of the methylene resonances are in agreement with the values reported for the SiCH$_2$ moiety in various polysilanes. These chemical shifts are quite different from those observed for similar carbons in polystyrene, unequivocally establishing the coupling of silane and styryl units. In addition, P-II and P-III show extra resonances in the region $\delta = 40$–44 ppm, which can be assigned to the methine and methylene carbons in blocks of styryl units.

**(iii) Aromatic Carbons.** The distinct feature of the spectra in this region is the presence of two signals at $\delta = 124.45$ and 125.64 ppm, with the latter showing fine structure (Figure 5, insert b) as well as an increase in intensity from P-I to P-III. In comparison with polystyrene

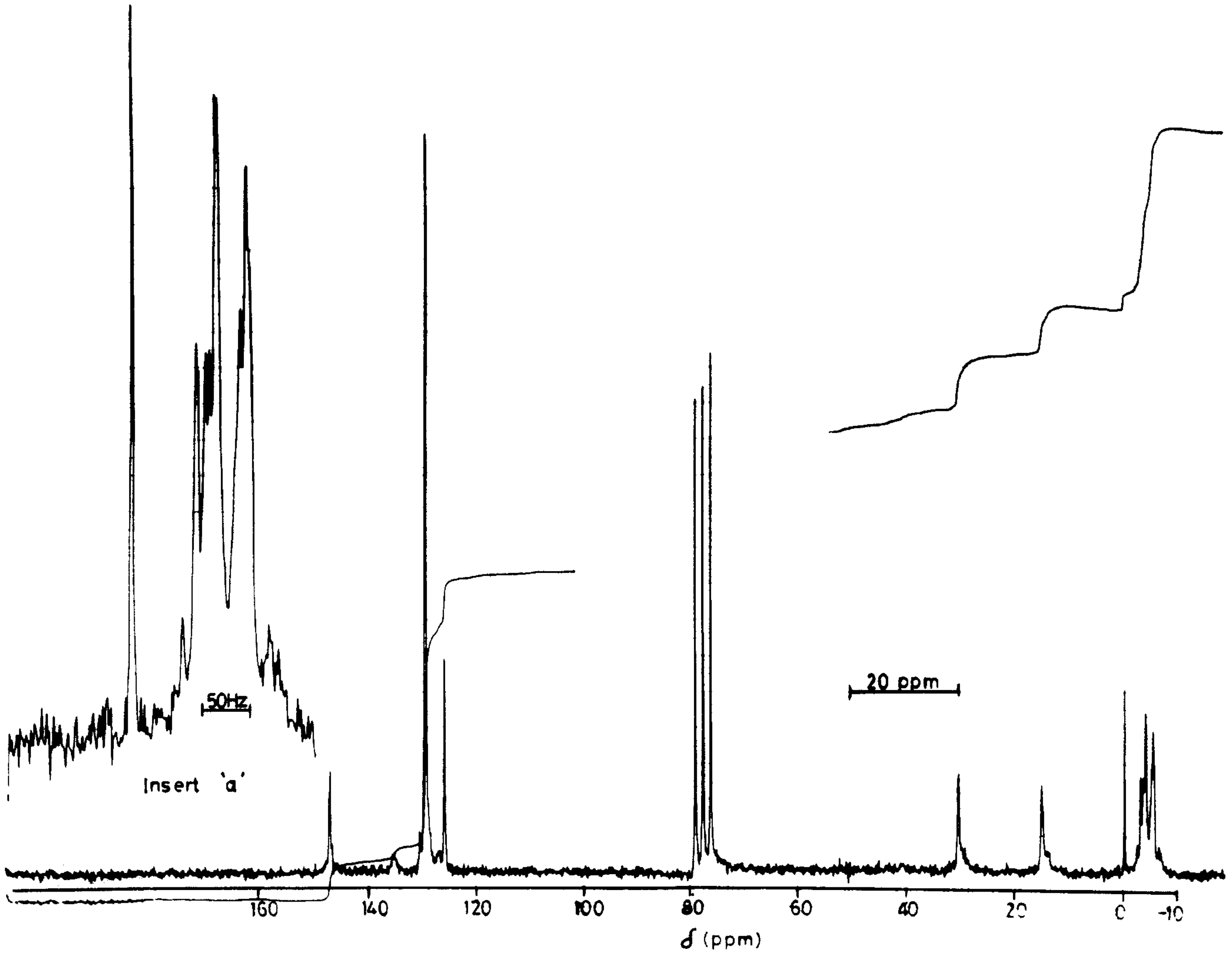


**Figure 4.** $^{13}$C NMR spectrum of polymer I (P-I).

Table II
Structural Parameters for Polymers I-III

| polymer | $a$ (based on $^{29}$Si NMR data) | $b$ based on eq 1 | $b$ based on $^{13}$C NMR data |
|---|---|---|---|
| P-I | 0.1 | 0.1 | 0.09 |
| P-II | 0 | 0.6 | 0.4 |
| P-III | 0 | 1.6 | 1.3 |

spectra, the two signals can be assigned to the C$^4$ carbon, with the high field signal arising from styryl units flanked by disilyl moieties and the low field signal from a phenyl group in blocks of styryl units. Therefore, the relative intensities of these two signals could yield the fraction of blocks of styryl units (the value of $b$) in the proposed structure. The computed values of $b$ are shown in Table II. The approximate agreement between the values obtained from $^{29}$Si and $^{13}$C NMR spectroscopy validates the gross structural features of the copolymers.

**Thermal Analysis.** The copolymers P-I to P-III are stable up to 250 °C and undergo rapid degradation above this tempeature leaving behind 5–10% residue at 700 °C in nitrogen atmosphere. The poor thermal stability of the copolymers may be attributed to the presence of a weak Si–Si linkage in the copolymers.

**Pyrolysis GC.** About 0.5 mg of P-I–P-III was pyrolized at 500 °C and the resulting volatiles were separated on an SE-50 GC column. A typical pyrogram is shown in Figure 6 for P-II. A large number of components were observed, and no attempt was made to identify the components except styrene, which has a retention time of 3.84 min under the column conditions used. Polystyrene was also pyrolyzed under identical conditions and it was observed that 95% (by weight) was monomer styrene. If P-I–P-III were mixtures of homopolymers, the expected percentage of styrene in the pyrolyzates can be calculated assuming that polystyrene gives 95% monomer. The calculated and the observed values of styrene concentration in the pyrolyzates are given in Table III. The observed values are much lower than the calculated values indicating that P-I–P-III are indeed copolymers and not mixtures of homopolymers. Further, according to the repeating unit the silylene and styrene react in the mole ratio 2:1; the amount of styrene bonded to Si can be calculated, and the values are given in Table III. Thus, it is seen in the case of P-I where all the styrene is bonded to Si, the styrene produced is 50% compared to polystyrene. Assuming this, in the case of P-II and P-III in which styrene is bonded to Si as well to styrene, the percentage of styrene expected on pyrolysis can be calculated and the values thus obtained are given in Table III. These values agree satisfactorily with the observed values, thereby confirming the structures proposed from NMR studies.

**Fractionation of Polymers.** Since the polymers show a bimodal distribution, the fractionation of the polymers was undertaken to ascertain the variation of composition of the polymer with respect to molecular weight. Polymer P-III was chosen for this purpose because it provides the best chance to check the presence of monosilane linkages as well.

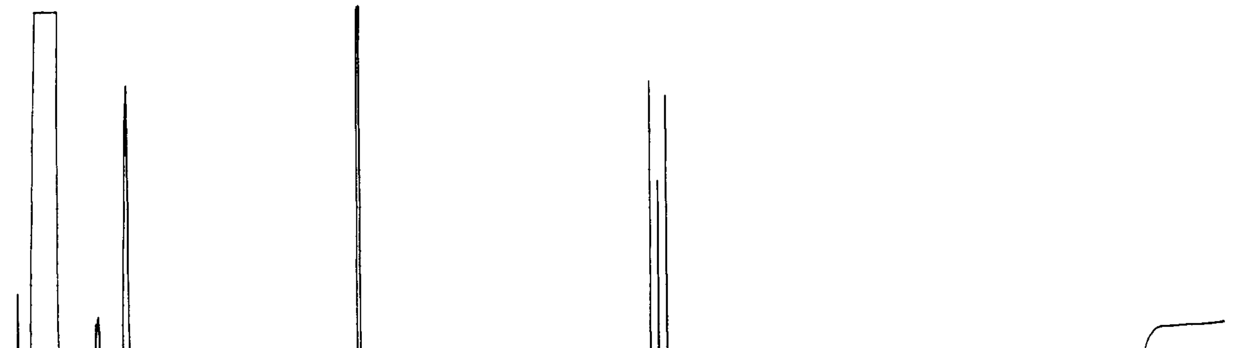


**Figure 5.** $^{13}C$ NMR spectrum of polymer III (P-III).

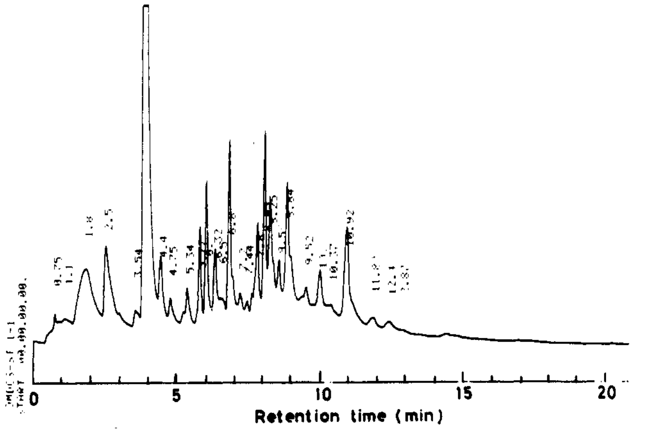


**Figure 6.** Pyrolysis GC of polymer II (P-II).

Toluene–methanol was used as the solvent and nonsolvent, and three fractions were collected. The molecular weights of the fractions were determined by SEC, and the composition was obtained from $^{1}H$ NMR spectra. The results are shown in Table IV and clearly indicate that the composition of the polymers varies with molecular weight, the silyl content decreasing with decreasing molecular weight. This is in agreement with the observation that the low molecular weight fraction increases with increasing styrene content in the feed (cf. Table I). Moreover, the $^{29}Si$ NMR spectrum of even the lowest molecular weight fraction is identical to the spectrum of the unfractionated sample and does not show the presence of any monosilyl linkages. These results strongly suggest the involvement of disilyl species as the reactive intermediates and also that the reactivities of the silyl radical are greater than those of styryl radicals.

**Table III**
**Pyrolysis Data for Polymers I–III**

| | wt % styrene in the copolymer | | wt % styrene in pyrolyzate | | |
|---|---|---|---|---|---|
| sample | total | bound[a] | obs | calc 1[b] | calc 2[c] |
| polymer I | 47.3 | 47.3 | 20.1 | 44.5 | |
| polymer II | 56.4 | 39.1 | 33.3 | 53.0 | 32.9 |
| polymer III | 70.5 | 26.5 | 57.2 | 66.3 | 52.7 |

[a] Calculated assuming structure C. [b] Calculated assuming physical mixtures (total styrene × 0.95). [c] Calculated assuming structure C (20.1/47.3) × % bound styrene.

**Table IV**
**Fractionation of Polymer P-III**

| fraction | $\bar{M}_n$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | [styryl]/[dimethylsilyl] |
|---|---|---|---|---|
| 1 | $1.05 \times 10^5$ | $1.47 \times 10^5$ | 1.40 | 0.65 |
| 2 | $2.88 \times 10^4$ | $5.92 \times 10^4$ | 2.05 | 0.97 |
| 3 | $4.27 \times 10^9$ | $2.39 \times 10^4$ | 5.60 | 1.81 |

**Probable Mechanism.** Any mechanism that is proposed should satisfy the following observations: (a) In all three polymers only disilyl linkages are present and no monosilyl linkages are observed. (b) With the increase in the molar concentration of styrene the low molecular weight fraction increases and polystyrene blocks are observed in the copolymer. (c) When the mole ratio of DMDCS to styrene is 2, polysilyl linkages are observed.

However, an unambiguous mechanism which satisfactorily explains the above observations cannot be arrived at with the present experimental data. But it can be stated with reasonable certainty that the disilyl species (radicals, radical anions, or anions)[9,10] are reactive intermediates under dechlorination conditions.

## Conclusions

Microstructural analysis of the copolymers obtained by the dechlorination of dimethyldichlorosilane in the presence of styrene reveals that the repeating units contain disilyl linkages. The absence of monosilyl linkage and the presence of disilyl linkage in the copolymers offers the valuable information that during dechlorination of dimethyldichlorosilane, disilyl intermediates are mainly formed.

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**Registry No.** DMDCS, 75-78-5; St, 100-42-5; (DMDCS)(St) (copolymer), 30328-26-8.