Polymerization by Hydrosilation. 1. Preparation of Poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene]. A Preliminary Report

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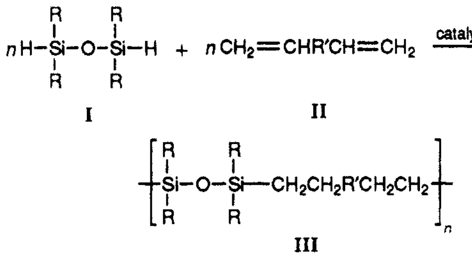
Introduction. Hydrosilation,[1] an addition reaction of Si-H compounds to π-unsaturated, vinyl, $CH_2{=}CH$, or allyl, $CH_2{=}CHCH_2$, groups, which can be represented by eq 1, has attracted considerable attention in silicon polymer

$$R_3SiH + CH_2{=}CHR' \xrightarrow{\text{catalyst}} R_3SiCH_2CH_2R' \qquad (1)$$

chemistry. Thus, in addition to its well-known applications for room-temperature vulcanization (RTV) processes for the preparation of siloxane elastomers,[2] this reaction has also been used for the synthesis of various siloxane-containing side-chain liquid-crystalline polymers[3] and, very recently, for Starburst dendrimers.[4]

However, this versatile reaction has not yet been successfully developed for the synthesis of truly high molecular weight linear polymers, although some attempts were made in this direction in the past, but all have resulted only in low molecular weight, oligomeric products.[5,6] These attempts can be classified into two major groups: (1) those in which various divinyl or diallyl compounds were reacted with dialkylsilanes in order to obtain polycarbosilanes[5] and (2) those in which 1,3-dihydridotetramethyldisiloxane (DHTMDS, **I**) was reacted with different comonomers containing two unsaturated groups, **II**, to yield polycarbosiloxanes,[6] **III** in eq 2, where R was CH_3, C_2H_5, C_6H_5, or $OSi(CH_3)_3$, R′ was $Si(R)_2[OSi(R)_2]_x$ (x = 3-5) or $CH_2Si(R)_2OSi(R)_2CH_2$, and n was 4-7, which corresponded to molecular weights of only 1000-2000.



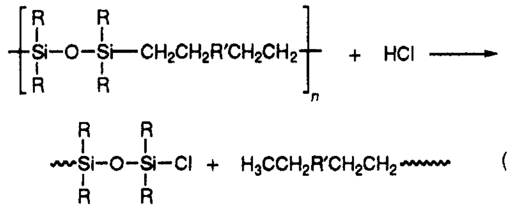
$$n\,\mathrm{H{-}SiR_2{-}O{-}SiR_2{-}H} + n\,\mathrm{CH_2{=}CHR'CH{=}CH_2} \xrightarrow{\text{catalyst}} \left[\mathrm{SiR_2{-}O{-}SiR_2{-}CH_2CH_2R'CH_2CH_2}\right]_n \qquad (2)$$

I **II** **III**

A common feature of all these previous attempts[6] was the use of hexachloroplatinic acid (H_2PtCl_6) in isopropyl alcohol, as the reaction catalyst. This was probably because this catalyst is the classic, most frequently used one for hydrosilation reactions in general[1] and because not enough significance was given to the finding that it can generate HCl after reduction, as shown by the following equation[7]

$$H_2PtCl_6 + (CH_3)_2CHOH \rightarrow H_2PtCl_4 + CH_3COCH_3 + 2HCl \qquad (3)$$

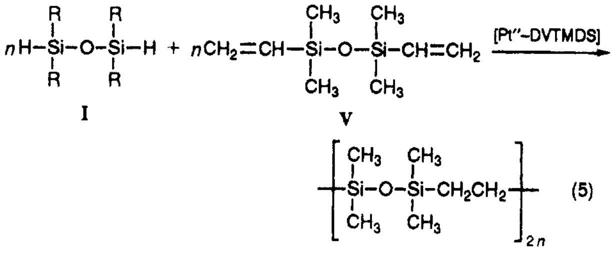
However, similar to the situation recently described for the silarylene-siloxane polymers,[9] HCl generated during the course of polymerization (such as in eq 2) may attack growing polymer molecules and cause desilylation at the Si-C bonds,[8] as shown by eq 4, which, if it becomes a competing side reaction to polymer formation, will result in the scission of polymer molecules and reduction in product molecular weight.



$$\left[\mathrm{SiR_2{-}O{-}SiR_2{-}CH_2CH_2R'CH_2CH_2}\right]_n + \mathrm{HCl} \longrightarrow \sim\mathrm{SiR_2{-}O{-}SiR_2{-}Cl} + \mathrm{H_3CCH_2R'CH_2CH_2}\sim \qquad (4)$$

If this were so, the main reason why previous attempts[5,6] failed to result in the high molecular weight products was not in the nature of the hydrosilation reaction itself but rather in the poor choice of reaction catalyst, implying that for polymerization purposes this reaction should be reexamined by using some more appropriate catalysts. Such catalysts should not generate HCl or, for that matter, any other ionic byproduct, and at present one potential choice would appear to be the recently described platinum-1,3-divinyltetramethyldisiloxane complex, [Pt-DVTMDS],[10] for example.

Following this reasoning and having found that hydrosilation of vinylsiloxanes by siloxanylsilanes can be carried out to sufficiently high conversions for the preparation of high molecular weight polymers by the step-growth polymerization mechanism,[11] we recently performed such an examination, and in this paper we report some preliminary results obtained from investigation of the reaction of 1,3-dihydridotetramethyldisiloxane (DHTMDS, **I**) and 1,3-divinyltetramethyldisiloxane (DVTMDS, **V**), which yields poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene] (PTMDSE, **IV**) as follows:



$$n\,\mathrm{H{-}SiR_2{-}O{-}SiR_2{-}H} + n\,\mathrm{CH_2{=}CH{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}CH{=}CH_2} \xrightarrow{[\mathrm{Pt''{-}DVTMDS}]} \left[\mathrm{Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}CH_2CH_2}\right]_{2n} \qquad (5)$$

I **V** **IV**

Experimental Section. Monomers **I** and **V** of eq 5 were purchased from ABCR GmbH and Co., Karlsruhe, Germany, and were used as received. [Pt-DVTMDS] catalyst was prepared from the commercial product (also from ABCR GmbH and Co.), in which [Pt-DVTMDS] complex was supplied in a xylene solution (3-3.5% by weight Pt), by adding 0.1 g of the commercial catalyst to 0.9 g of monomer **V** to obtain a 0.3% by weight Pt catalyst solution. Freshly distilled toluene was used as the reaction solvent, bp = 110-111 °C.

A typical polymerization reaction was performed in a 100-mL, three-neck, round-bottomed reaction flask, which was equipped with a Teflon-coated stirring bar and an air-cooled vertical condenser, and placed in a glycerine oil bath at 42 ± 1 °C. Toluene (40 mL) was charged to the reactor, followed by monomer **V** (14.0 mL, 11.35 g, 61.04 mmol) and a catalyst solution (1.5 mL, 3.65×10^{-3} g Pt), to yield a solution of 1.4×10^{-4} g atom Pt/mol of $CH_2{=}CH$ in the total of 66.93 mmol of monomer **V**.

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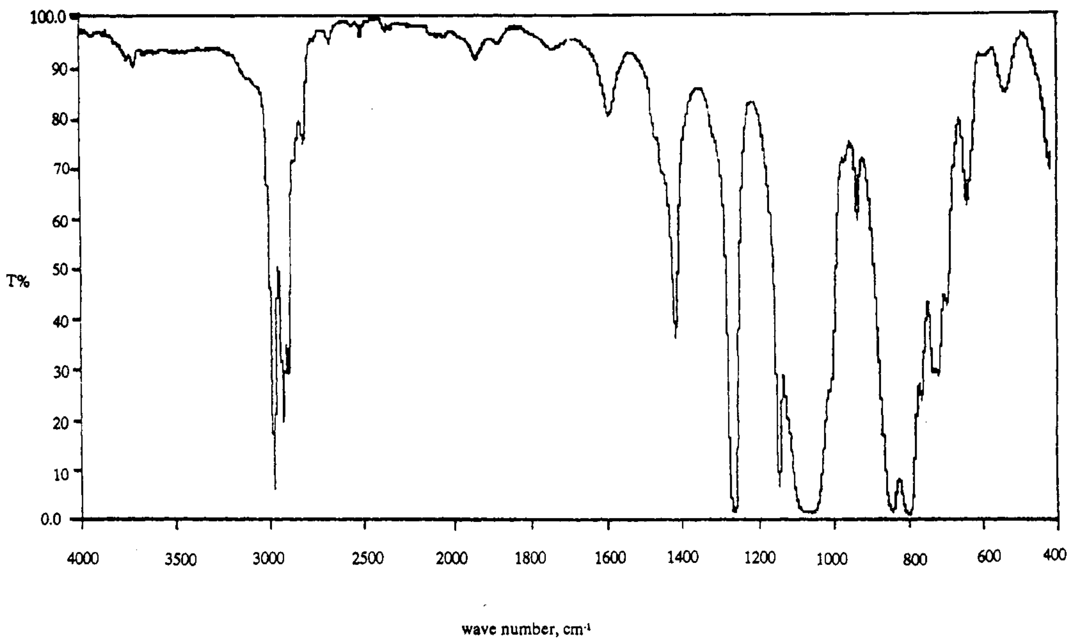

Figure 1. Fourier transform infrared spectrum of poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene] (PTMDSE).

The solution was stirred continuously and allowed to warm up to polymerization temperature for about 30 min. Monomer I (11.62 mL, 8.52 g, 63.61 mmol) was then added to start the reaction at the molar ratio of the reacting functional groups, $r = [SiH]/[CH_2{=}CH]$, equal to 0.950. After about 2.5 h, an aliquot of 0.5 mL of the reaction mixture was taken for IR analysis which verified that all SiH groups (ν_{SiH} = 2126 cm^{-1}) had been consumed. Another aliquot of 1.5 mL was also withdrawn for intrinsic viscosity determination.

Additional monomer I (0.34 mL, 1.92 mmol) was then added to the reaction mixture to increase *r* to 0.98, and another pair of aliquots was withdrawn for analyses. This procedure was continued until *r* reached 1.01 when unreacted SiH units were detected and when intrinsic viscosity ceased to increase further. The reaction was stopped at that point, and the polymer product obtained was precipitated in methanol. The resulting viscous oil was separated from the methanolic layer and dried at 50 °C for 24 h under reduced pressure. The crude polymer product was dark brown and it was redissolved in chloroform (50 mL/1 g of polymer), the solution was treated with activated charcoal and filtered, and the polymer was isolated by solvent evaporation under reduced pressure to obtain a clear, slightly yellowish, viscous fluid.

Figures 1 and 2 show FTIR and ^{1}H NMR spectra of the polymer obtained. FTIR was recorded from film on a KBr pellet, while ^{1}H NMR was obtained from a 20% w/v polymer solution in $CDCl_3$.

Characteristic infrared peaks were observed at 2790–2956 (CH aliphatic), 1407 (SiMe asymmetric), 1255 (SiMe symmetric), 1133 ($SiCH_2CH_2Si$), and 1049 cm^{-1} (SiOSi asymmetric). The proton NMR spectrum exhibited signals at $\delta = 0.06$ ($SiCH_3$ singlet) and at $\delta = 0.42$ (CH_2 singlet) relative to TMS. The ratio of the integrals of two NMR peaks was 2.9 which corresponds well to the expected value of 3 for poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene] (**IV**).

Results and Discussion. In order to obtain high molecular weight products, the polymerization procedure utilized the one monomer deficient method.[12] It consisted of gradual addition of incremental portions of DHTMDS (I) into a solution containing an excessive amount of the comonomer (DVTMDS, V) in toluene, accompanied by monitoring molecular weight increase by dilute solution viscometry as the molar ratio of the reacting functional group concentrations, *r*, approached unity. This procedure allowed for monitoring the course of the polymerization reaction and determination of the equimolarity point at which the maximum polymer molecular weight was reached. The results obtained are shown in Figure 3.

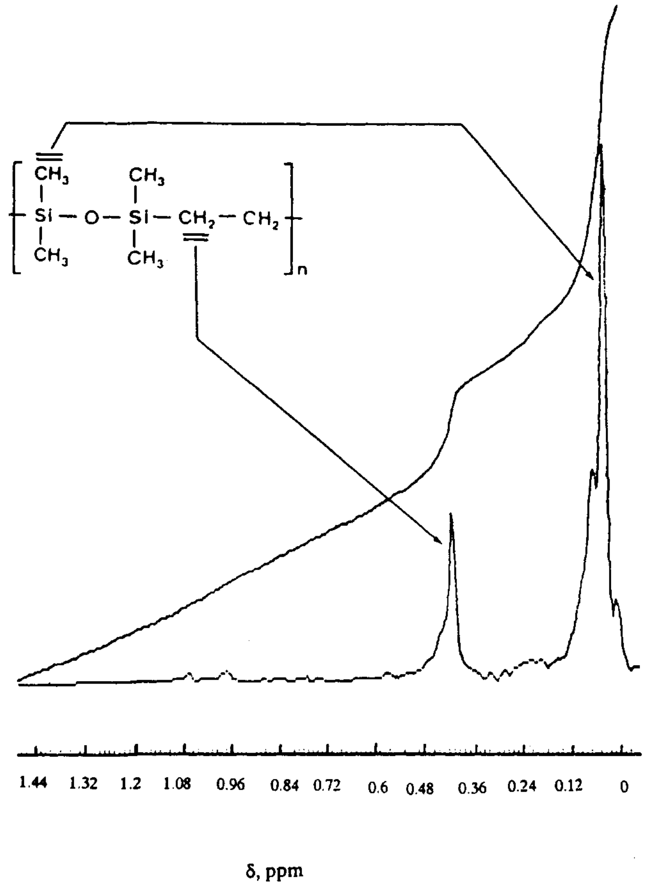

Figure 2. ^{1}H NMR spectrum of poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene] (PTMDSE).

It can be seen from this figure that the observed intrinsic viscosity increase during the course of this polymerization reaction showed the typical trend for a step-growth process.[12] Thus, while very little change in intrinsic

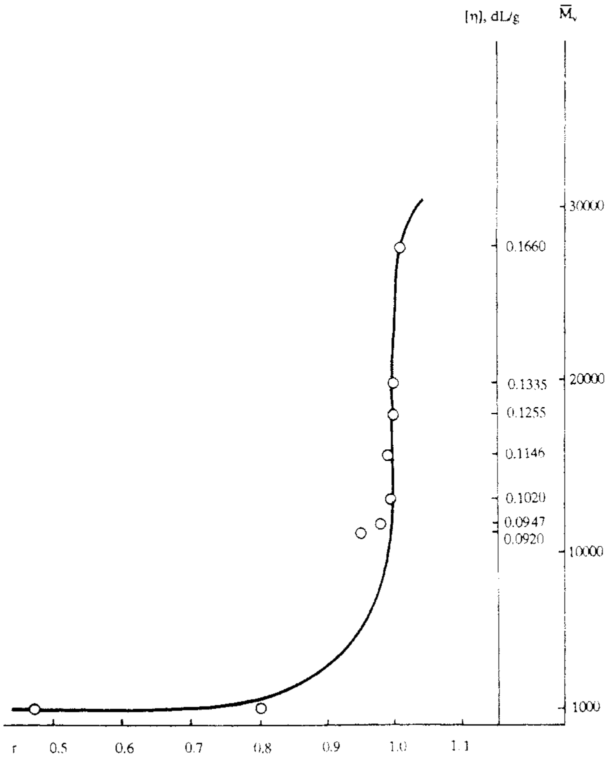

Figure 3. Monitoring of the hydrosilation polymerization reaction of dihydriodotetramethyldisiloxane (DHTMDS) and 1,3-divinyltetramethyldisiloxane (DVTMDS) catalyzed by platinum–1,3-divinyltetramethylsiloxane ([Pt–DVTMDS]) by intrinsic viscosity.

viscosity occurred until the value of r equaled about 0.9, indicating that only low molecular weight oligomers formed during that stage of the reaction process, a sharp increase in intrinsic viscosity followed, until r reached 1.01, when the intrinsic viscosity leveled off, indicating that equimolarity of the reacting functional group concentrations was attained. Because this value of r was close to unity, this also suggests that no significant side reactions occurred in this polymerization reaction system.[12]

However, the molecular weight values given in Figure 3 should only be taken approximately. Namely, because appropriate constants are not yet available for poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene] (**IV**), the $\bar{M}_v$ values were calculated from intrinsic viscosities by using a Mark–Houwink type equation with K and a for closely related poly(dimethylsiloxane) (PDMS).[13] However, since the PDMS main-chain backbone is expected to be more flexible than that of polycarbosiloxanes, including polymer **IV**, the use of PDMS constants for this purpose should result in lower $\bar{M}_v$ values for polymer **IV** than if its own constants were available. Thus, it should be expected that true $\bar{M}_v$ values of polymer **IV** obtained in this work were higher than those indicated in Figure 3.

In addition to this, since critical molecular weights of PDMS and poly(dimethylsilyloctylene) ($-[Si(CH_3)_2-(CH_2)_8]_n-$) were recently found to be 34 500[14] and about 15 000,[15] respectively, and because inherent conformational flexibility of the main-chain backbone of polymer **IV** should be between those of the above-mentioned polymers, and considering that critical polymer molecular weight generally increases with chain flexibility, the critical molecular weight of polymer **IV** should be between the above values. Hence, we conclude not only that polymers prepared in this work had considerably higher molecular weights than the products obtained by the previous workers ($\overline{DP}$s of about 180 vs $\overline{DP}$s of only 4–7, respectively) but also that these molecular weights were high enough to consider the obtained products as truly high molecular weight polycarbosiloxanes.

Thus, the results presented clearly show that hydrosilation reactions of difunctional siloxanylsilanes and vinylsiloxanes, such as that shown by eq 5, can be used for the preparation of high molecular weight polycarbosiloxanes if only appropriate catalyst and preparative methods are selected for use. The selection of catalyst seems to be the key factor, and it must take into account possible undesirable side reactions, if during the polymerization catalyst can produce ionic byproducts. Hence, in contrast to hexachloroplatinic acid utilized by the previous workers, the use of the [Pt–DVTMDS] complex enables hydrosilation polymerization reaction to proceed unobstructed and to yield high molecular weight polymers. This ranks this reaction with only a few other addition polymerization reactions known. Further investigations of the reaction kinetics and of the properties of the polycarbosiloxanes are in progress in our laboratories.

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