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Rapid Photoactivated Hydrosilation Polymerization of Vinyldimethylsilane

Bryan E. Fry and D. C. Neckers*

Center for Photochemical Sciences, Bowling Green State University,
Bowling Green, Ohio 43403

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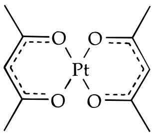
ABSTRACT: The complex bis(acetylacetonato)platinum(II) is inactive in the dark but forms a highly reactive hydrosilation catalyst upon irradiation with near-UV light. Vinyldimethylsilane is polymerized with it. Poly[(dimethyl)vinylsilane] is the major product; minor components consist of the dimers 1,1,2,3,3-pentamethyl-1,3-disilacyclopentane and 1,1,4,4-tetramethyl-1,4-disilacyclohexane and oligomers. After photoactivation the catalyst remains reactive for an indefinite period of time with hydride and vinyl polymer end-groups, thus the molecular weight of the major product increased from 5500 g/mol (M_w) shortly after irradiation to 12300 g/mol in six months due to end-linking of polymer chains. Photoactivation of the catalyst and the subsequent step polymerization reaction are unaffected by dissolved air.

Introduction

Bis(acetylacetonato)platinum(II), **1**, or Pt(acac)$_2$ was recently reported to serve as a photoactivated catalyst for hydrosilation addition of silanes to alkenes.[2] This catalyst is activated by near-UV irradiation which is thought to produce a homogeneous catalyst by loss of one bidentate ligand in the presence of silicon hydride or olefin.[2] The resulting complex **2** is the primary active catalyst, and once formed, **2** remains active such that the reaction proceeds without light. A less active heterogeneous catalyst, consisting of Pt^0 colloids, is also produced more slowly from **2** during and after irradiation.



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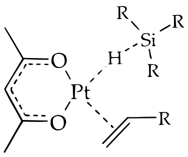

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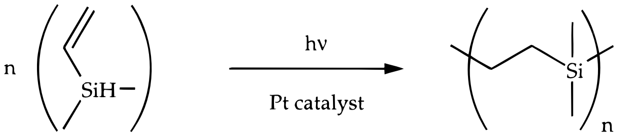
Other examples of catalysts which are activated by radiation for hydrosilation were also reported. (η^2-Cyclopentadienyl)trialkylplatinum forms colloidal platinum hydrosilation catalysts when irradiated in solutions containing silanes.[3] Silica-supported bis(trialkylphosphine) platinum oxalates lose the oxalate ligand under ultraviolet irradiation leading to a homogeneous catalyst.[4] A photocatalyst for addition of terminal alkenes to silanes under continuous irradiation is produced by photoinduced loss of a carbonyl from pentacarbonyliron[5] or chromium carbonyl.[6] Catalytic amounts of η^4-1,5-cyclooctadieneplatinum bis(4-methylphenyl) with ultraviolet irradiation produce gelation of mixtures of $H_2C{=}CHSiMe_2O(SiMe_2O)_{130}SiMe_2\text{-}CH{=}CH_2$ and $Me_3SiO(SiOMeH)_{35}SiMe_3$ oligomers.[7] Pt(acac)$_2$ is also patented as a catalyst for a similar siloxane coating system.[8]

These reports suggested the possibility of developing photoinitiated reactions for the polymerization of vinylsilanes as shown in Scheme 1 below. Thus we observed rapid polymerization of vinyldimethylsilane in the presence of Pt(acac)$_2$ when irradiated with near-UV light.

Scheme 1



The products are a low molecular weight polymer plus small amounts of dimers and oligomers. This polymer is nearly identical to the poly[(dimethyl)vinylsilane] (PDMVS) reported by Curry which was made using platinum on carbon powder[9] and by Corriu *et al.* made using chloroplatinic acid.[10]

Experimental Section

Materials. The following reagents and solvents were used as purchased: Vinyldimethylchlorosilane (United Chemical Tech.), Pt(acac)$_2$ (Alfa or Aldrich), LiAlH$_4$ (powder, Aldrich), dichloromethane (anhydrous, Aldrich), DMF (anhydrous, Aldrich), pyridine (Aldrich), 2,6-diisopropyl-*N*,*N*-dimethylaniline (Aldrich), decane (Aldrich), and tetrahydrofuran (HPLC grade, Aldrich). Dibutyl ether was either used as purchased (anhydrous, Aldrich) or distilled from sodium hydride. HPLC grade benzene (Baker), benzophenone (Fisher), and benzhydrol (Baker) were used as received for chemical actinometry.

Instruments and Equipment. The instruments used to collect data for the described experiments included an HP5890 gas chromatograph with flame ionization detector, an HP5880/5987A gas chromatograph/mass spectrometer, a Varian Gemini 200 NMR spectrometer, a Varian XL-200 NMR spectrometer, a Varian UnityPlus 400 NMR spectrometer, a Mattson Galaxy 6020 infrared spectrophotometer, and an HP8452A diode-array spectrophotometer. Gel permeation chromatography was performed with an HP 1050 series HPLC equipped with a diode array detector, an HP1047A refractive index detector, and a PLgel 5 μm mixed-C 300 × 7.5 mm column with a 5 μm guard column.

Irradiation of monomer samples was accomplished with either a Rayonet photochemical reactor (8 W × 16, 300−400 nm) equipped with a merry-go-round, a jacketed beaker (Pyrex), and a magnetic stirrer or with an optical bench consisting of an Oriel 200 W mercury lamp with a focusing lens, a water filter, a bandpass filter (λ_{max} 366 nm, typically an Oriel 56531), an electric shutter, and a temperature-controlled cuvette holder with a magnetic stirrer. The temperature of the cuvette holder and jacketed beakers was kept at 25 °C with a Lauda circulating bath. A black box was used for dark experiments in which a jacketed beaker to maintain controlled temperatures and a magnetic stirrer were used. Quartz and Pyrex cuvettes were purchased from Spectrocell.

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1996.

Vinyldimethylsilane Synthesis. Vinyldimethylsilane was prepared by the method of Curry[9] with the addition of a 0 °C condenser to retain the volatile product (bp 36.7 °C) and without distillation prior to aqueous workup. The product mixture was chilled with an ice bath and 1 M HCl was added drop-by-drop. A total of 400 mL of acid was then introduced and the organic phase was separated after chilling with an ice bath. The aqueous phase was washed with three 50 mL portions of 2 °C toluene. The organic phases were combined and dried by adding silica gel. Fractional distillation under argon yielded 54.5 g (76.4%) of volatile product consisting of 97.8% vinyldimethylsilane and 2.2% impurity (predominately ethyldimethylsilane). ^{1}H NMR ($CDCl_3$): δ 0.14 (d, $J = 3.8$ Hz, 6H), δ 4.06 (m, 1H), δ 5.74 (dd, $J = 4.6$ Hz, 19.5 Hz, 1H), δ 5.97 (dd, $J = 4.6$ Hz, 14.6 Hz, 1H), δ 6.16 (ddd, $J = 2.34$ Hz, 19.5 Hz, 14.6 Hz, 1H); GC/MS: 88, 1%, $M + 2$; 87, 3%, $M + 1$; 86, 27%, M^+; 71, 58%; 59, 36%; 58, 100%; 45, 24%; 43, 29%.

General Procedures. Light sensitive samples were handled in a darkened room and/or in black-coated glassware. Most of the photoreactions were performed in cuvettes with 1 cm pathlength capped with septa on an optical bench. Capping was necessary to prevent evaporation. Typically, 2 mL samples were prepared with 0.5 M or 2 M monomer and dichloromethane.[11] The $Pt(acac)_2$ was finely ground before mixing and typically used at a concentration of 5×10^{-3} M. Decane was added to each sample as an internal GC standard. One of four types of treatments was conducted prior to irradiation, effecting the dissolved gases in the monomer solutions: (1) sample prepared in air, (2) sample deoxygenated by bubbling with dry argon for 10−15 min, (3) sample deoxygenated by three freeze/pump/thaw cycles, and (4) sample bubbled with oxygen for three minutes. The argon or oxygen was first bubbled through a solution of identical concentration and then bubbled through the sample to be irradiated to minimize changes in concentration of the monomer during bubbling. This was required because of the high volatility of the solvent and monomer. The vacuum line used for freeze/pump/thaw attained a pressure below 7×10^{-5} torr. The monomer mixtures were stirred by magnetic stir bars at 25 °C throughout irradiation and during subsequent dark holding periods. The optical bench light intensity at the cuvette was 20 mJ/s at 366 nm (3.7×10^{16} photons/s). The solutions were typically irradiated and then immediately placed in the dark. Gas chromatograms of each sample were obtained before and after irradiation and again following a dark holding time when applicable. The GC was calibrated for monomer. Detector response for dimeric and oligomeric products was assumed to be identical to that for monomer. Several attempts were made to detect platinum colloid growth during photolysis by taking absorption spectra and looking for base line increases. Quartz cuvettes were used for these experiments.

The resulting polymer was precipitated into methanol. Dimers and trimers remained soluble in the methanol which was filtered through 0.2 μm membranes. Solvent was then removed from the low molecular weight polymer using a Rotovap followed by drying under vacuum (<1 mmHg) at 25 to 45 °C for 15 min to several hours. Some solutions were aged at room temperature for up to several months after photolysis. In these cases polymer purification was done after aging. Brown color (attributed to platinum colloids) could not be separated from the polymer by filtration of dissolved polymer through a 0.2 μm membrane. Polystyrene calibration standards (Polysciences) were used for GPC molecular weight determination. Elemental analysis was performed by Quantitative Technologies Inc., NJ. ^{29}Si NMR was performed using a 50 s delay time and 880 transients. Oven-dried NaCl plates were used for IR samples.

The light intensity was determined by benzophenone/benzhydrol chemical actinometry according to the method of Moore and Ketchum.[12] Four repetitions were made and a value of $\Phi_{act}/\Phi_{sample} = 1.05$ was used in the calculations to correct for 35% conversion of benzophenone in our measurements.

Special Procedures. Large drops of mercury were added to some of the monomer/dichloromethane solutions (0.5 or 2 M) to test for inhibition of heterogeneous catalysis during photolysis. The level of inhibition was determined from the rate of consumption of monomer in the presence of mercury compared to the rate without mercury. The solutions compared were otherwise equal. Some additional inhibition experiments involved mixing DMF, pyridine, or 2,6-diisopropyl-*N*,*N*-dimethylaniline (DIDMA) with monomer and 0.01 M $Pt(acac)_2$. These were irradiated in borosilicate test tubes capped with septa using a Rayonet reactor.

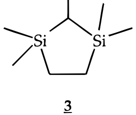
Polymer Data. Elemental analysis found: 55.7%C, 10.7%H; calculated: 55.7%C, 11.7%H.

Dimer Spectral Data. The cyclic dimers were analyzed together and were separated from polymeric products by fractional distillation. 1,1,2,3,3-Pentamethyl-1,3-disilacyclopentane ^{1}H NMR ($CDCl_3$): δ -0.25 (quart., $J = 7.7$ Hz, 1 H), δ −0.04 (s, 6 H), δ 0.00 (s, 6 H), δ 0.59 (d, $J = 1.4$ Hz, 4 H), δ 0.96 (d, $J = 7.8$ Hz, 3 H). GC/MS: 175, 0.4%, $M + 3$; 174, 3%, $M + 2$; 173, 9%, $M + 1$; 172, 45%, M^+; 157, 73%; 144, 23%; 129, 100%; 116, 13%; 97, 44%; 85, 21%; 73, 28%; 59, 41%; 43, 14%. 1,1,4,4-Tetramethyl-1,4-disilacyclohexane ^{1}H NMR ($CDCl_3$): δ −0.07 (s, 12 H), δ 0.67 (s, 8 H). GC/MS: 174, 5%, $M + 2$; 173, 11%, $M + 1$; 172, 62%, M^+; 157, 100%; 143, 14%; 129, 51%; 116, 84%; 97, 59%; 85, 30%; 73, 39%; 59, 52%; 43, 19%. 1,1,4,4-Tetramethyl-1,4-disilahex-5-ene (not isolated) GC/MS: 173, 0.3%, $M + 1$; 172, 1%, M^+; 171, 0.7%; 157, 31%; 144, 6%; 129, 14%; 116, 10%; 97, 18%; 85, 100%; 73, 14%; 59, 52%; 43, 11%.

Oligomer GC/MS Data. Oligomers were obtained after filtration and concentration of the methanol used to precipitate the polymer. Trimer 1: 260, 1%, $M + 2$; 259, 2%, $M + 1$; 258, 8%, M^+; 243, 84%; 215, 23%; 157, 19%; 143, 19%; 129, 18%; 85, 39%; 73, 100%; 59, 94%. Trimer 2: 260, 2%, $M + 2$; 259, 3%, $M + 1$; 258, 10%, M^+; 243, 15%; 157, 53%; 129, 26%; 86, 100%; 73, 87%; 59, 95%. Pentamer: 433, 0.3%, $M + 3$; 432, 2%, $M + 2$; 431, 3%, $M + 1$; 430, 6%, M^+; 258, 1%; 243, 7%; 157, 63%; 129, 16%; 97, 17%; 86, 47%; 73, 100%; 59, 54%.

Results

$Pt(acac)_2$ is soluble in neat vinyldimethylsilane only at very low concentrations, but when mixtures are irradiated with near-UV light, homogeneous solutions form rapidly. After a brief induction period, vigorous consumption of the silane monomer occurs resulting in complete conversion of the monomer to low molecular weight polymer and small amounts of dimers. Experiments conducted in this manner exhibited such vigorous exothermic reaction that the sealed reaction tubes burst. The dimers were identified[13] by ^{1}H NMR and GC/MS to be 1,1,2,3,3-pentamethyl-1,3-disilacyclopentane (**3**) and 1,1,4,4-tetramethyl-1,4-disilacyclohexane (**4**) (see below). In the absence of either $Pt(acac)_2$ or light, only minor amounts of monomer conversion occurred and negligible amounts of products resulted.



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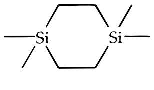

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Because of the difficulty of controlling the above reactions, most of the experiments were conducted at lower concentrations which slowed the reaction rates compared to neat monomer. Dichloromethane was used because it readily dissolves $Pt(acac)_2$ and does not inhibit platinum catalysis. Figure 1 shows the consumption of 2 M vinyldimethylsilane under irradiation and the concomitant production of dimers. An initial shoulder on the monomer consumption curve shows that there is an induction time of about 5 min. This is attributed to the photochemical formation of a homogeneous active catalyst consisting of a Pt(acac) and silicon hydride or olefin complex (**2**) which subsequently

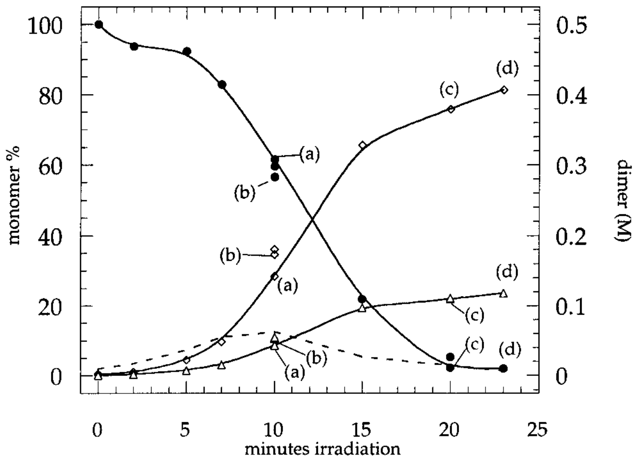


Figure 1. GC results of 366 nm irradiation of 2 ± 0.3 M vinyldimethylsilane in CH_2Cl_2 with 5×10^{-3} M $Pt(acac)_2$. Samples were prepared in air unless otherwise noted. Vinyldimethylsilane (left axis), ●; 1,1,2,3,3-pentamethyl-1,3-disilacyclopentane, ◇; 1,1,4,4-tetramethyl-1,4-disilacyclohexane, △; transient dimer, - - - - -. Argon bubbled, (a); oxygen bubbled, (b); freeze/pump/thaw degassed, (c); Hg drop added, (d).

Table 1. Dimer Quantities after a Total of 20 Min[a]

hν (min)	dark (min)	**3** (mM)	**4** (mM)	**5** (mM)	% VDMS consumed
10	10	360	110	61	82
15	5	370	110	24	92
20	0	380	110	13	95

[a] From GC data with 2 M initial monomer concentration.

mediates hydrosilation.[2] Complete conversion of the monomer to polymer and dimers takes approximately 20 min at 2 M initial concentration. Lesser doses of irradiation result in only minor decreases in monomer conversion within a 20 min time period; see Table 1. The photolysis was not accompanied by a UV/visible absorption base line increase as would be expected if platinum colloid formation were taking place. The postirradiated mixtures turned brown after being stored overnight, however, which means that platinum colloids eventually formed.

A transient product was generated during the reaction which is postulated to be 1,1,4,4-tetramethyl-1,4-disilahex-5-ene (**5**). This dimer is the product of the initial addition of two monomers and parallels the formation of dimers in Figure 1 until 10 min irradiation after which it is gradually consumed. Dimer **5** is the building block of the major polymer product as well as the cyclic dimers. Measurable amounts of **5** (about 10 mM) are formed whenever the monomer and catalyst are mixed. In dark control experiments the transient is present but does not increase with time. The disilacyclopentane dimer, **3**, is probably produced from **5** by catalytic silicon hydride attack on the nonterminal vinyl site (α hydrosilation mode) and the disilacyclohexane dimer, **4**, by attack at the terminal site (*β* hydrosilation mode). Figure 1 shows **5** disappearing during the second half of the reaction under continuous irradiation. When shorter doses of light were given, however, elevated levels of **5** remained after a fixed time period (Table 1). This buildup of transient species indicates incomplete photoactivation of the catalyst and suggests that the activation photoprocess continues past the induction time. **5** was consumed eventually, given sufficient time in the dark (see Figure 2).

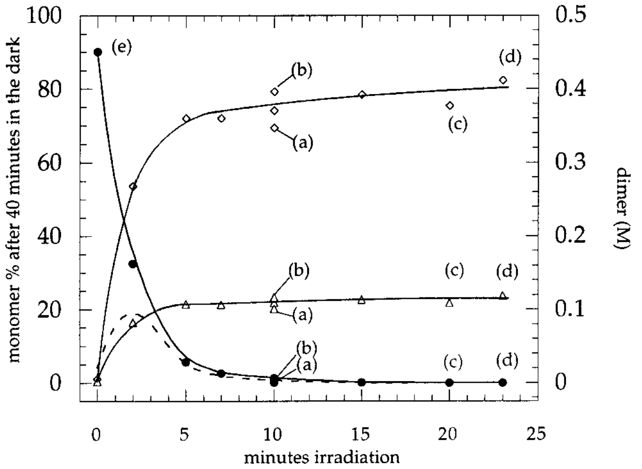
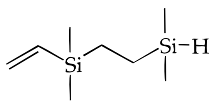


Figure 2. GC results of Figure 1 samples held in the dark 40 min at 25 °C after the specified irradiation time. Vinyldimethylsilane (left axis), ●; 1,1,2,3,3-pentamethyl-1,3-disilacyclopentane, ◇; 1,1,4,4-tetramethyl-1,4-disilacyclohexane, △; transient dimer, - - - - -. Argon bubbled, (a); oxygen bubbled, (b); freeze/pump/thaw degassed, (c); Hg drop added, (d), held 60 min in the dark, (e).

Table 2. Molecular Weight of PDMVS Prepared from 2 M Monomer

hν (min)	aged[a] (months)	M_w	PD	polym yield (%)
10	0	5500	2.5	61
10	6	12300	3.4	55
20	0	3700	2.1	74

[a] Each was held for 40 min in the dark at 25 °C postirradiation.



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After various doses of irradiation, the monomer solutions of Figure 1 were each held in the dark for 40 min to determine the course of the photoactivated reaction in the dark. The results are shown in Figure 2. The reaction of monomer takes place in the dark following as little as two minutes of irradiation. With a dose of five minutes (the induction time), the monomer was almost completely reacted during the allowed dark time.

Analysis of the methanol used for precipitation of the polymer revealed trace amounts of a variety of trimers, tetramers, and pentamers. The two most abundant of these are trimers present in quantities of about 24 mM ("trimer 1") and 60 mM ("trimer 2") in irradiated solutions of 2 M initial monomer. The mass spectra of these and one pentamer are reported.

Poly[(dimethyl)vinylsilane] Analysis. This polymerization is a step reaction which takes place on the photogenerated platinum centers. The molecular weight of the polymer, shown in Table 2, is about 50% higher when produced with 10 min of irradiation than with 20 min. This is expected since fewer activated catalytic sites resulting from less complete photoactivation in a given concentration of monomer should produce longer polymer chains. These activated centers remain with the polymer after formation, producing chain growth linearly from vinyl and hydride end-groups even after the monomer is completely consumed. This apparently takes place by addition of polymer chains to one another. The molecular weight of polymer measured six months after irradiation of the monomer solution (Table 2) is more than two times the molecular weight immediately

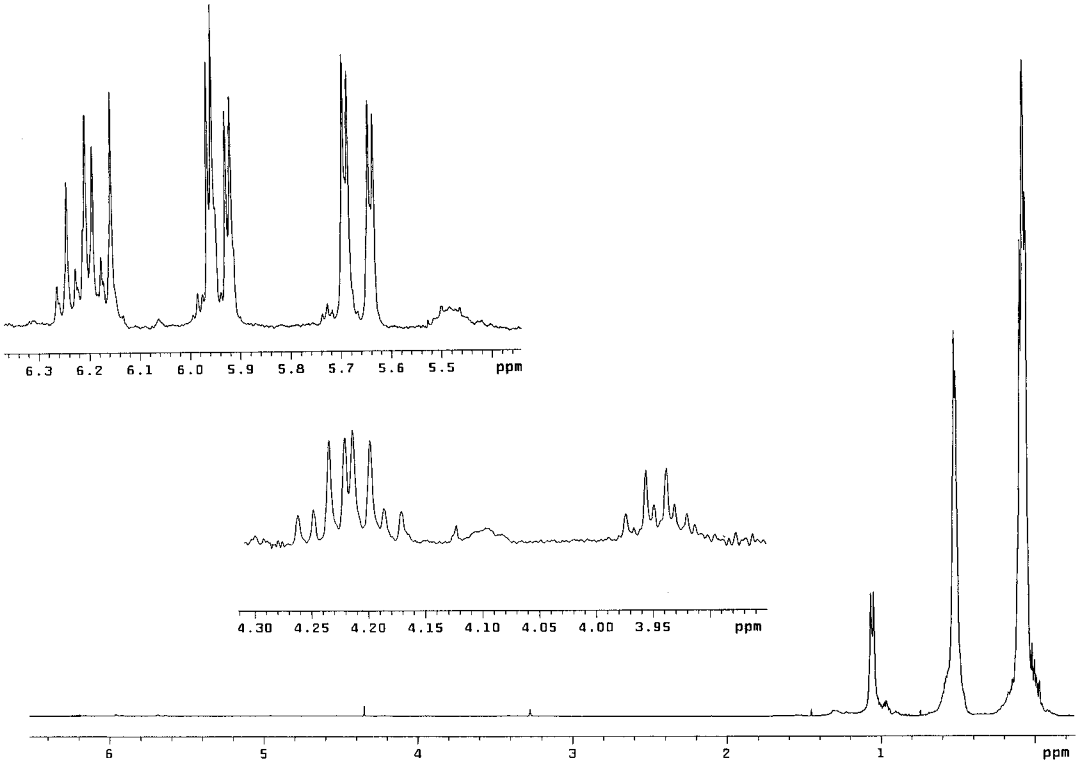
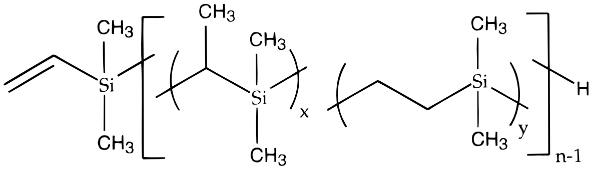


Figure 3. ^{1}H NMR (400 MHz, C_6D_6) of PDMVS produced by 366 nm irradiation of 2.0 M vinyldimethylsilane in CH_2Cl_2 with 5 × 10^{-3} M Pt(acac)$_2$. Chemical shift relative to residual protons in solvent.

after illumination. Brown color due to platinum colloids appears in the photoactivated solutions about one day after irradiation. The colloids could not be removed by filtration and are probably responsible for hydrosilation of the polymer during aging as discussed below.

A proton NMR of the low molecular weight polymer product aged about four months is shown in Figure 3. The polymer **6** consists of units x and y resulting from α and β hydrosilation modes, respectively.



x = 0.28, y = 0.72

6

The relative amounts of the units -Si(Me$_2$)CH$_2$CH$_2$-Si(Me$_2$)- and -Si(Me)$_2$CH(CH$_3$)Si(Me)$_2$- (y and x) are calculated from the integrated areas of the doublet centered at δ 1.06 (^3J = 7.6 Hz) arising from the methyl group of -CH(CH_3)- and the methylene singlets at about δ 0.52 attributed to -Si(CH_2)$_2$Si-. ^{1}H NMR peaks in the range of about δ 0.02 to 0.12 are due to -Si(CH_3)$_2$- functionality, and peaks due to the methine of -CH(CH$_3$)- are thought to be those at about δ 0.0. Vinyl peaks near δ 6 and silicon hydride peaks near δ 4.1 (Figure 3 inset) are also seen. These are assigned to polymer chain end-groups which enable chain growth after all of the monomer is consumed. The same ratio of y/x occurs for polymers produced in dichloromethane solution or neat monomer and is approximately equal to the ratio obtained using chloroplatinic acid as the catalyst.[10]

The H^1 decoupled ^{13}C NMR peak assignments were reported.[10] The three methyl carbon (SiCH_3) peaks in

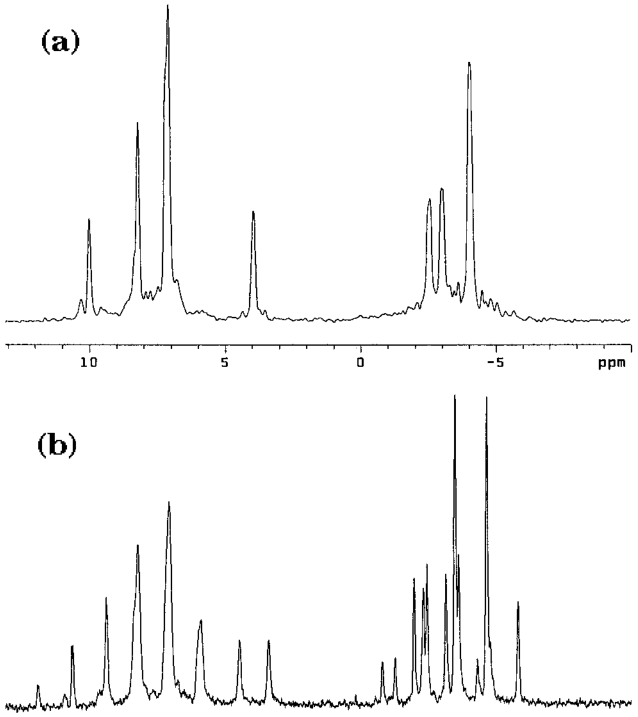


Figure 4. ^{13}C NMR (100.6 MHz, C_6D_6) of PDMVS produced by 366 nm irradiation of 2.0 M vinyldimethylsilane in CH_2Cl_2 with 5 × 10^{-3} M Pt(acac)$_2$. ^{1}H decoupled, (a); ^{1}H coupled, (b). Chemical shift relative to solvent.

Figure 4 at δ −4.0, −3.0, and −2.6 are split into quartets (^1J = 119−118 Hz) in the coupled spectrum. The methine carbon (SiCHSi) peak at δ 3.9 ppm is split into a doublet (^1J = 108 Hz), and the methylene peaks at δ 7.1 and 8.2 produce overlapping triplets ($^1J \approx 117$ Hz). The methyl peak from -CH(CH_3)- at δ 10.0 ppm is split into a quartet (^1J = 127 Hz). These NMR results

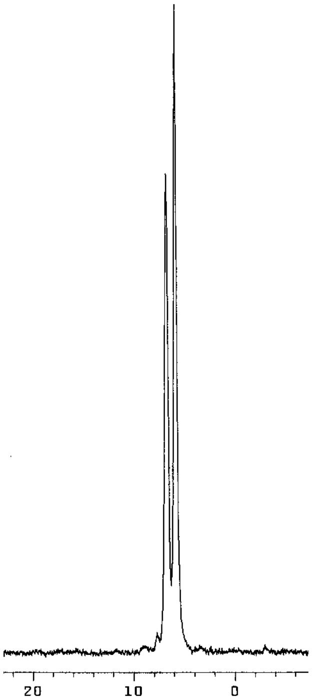


Figure 5. ^{29}Si NMR {^{1}H} (79.5 MHz, C_6D_6) of PDMVS produced by 366 nm irradiation of 2.0 M vinyldimethylsilane in CH_2Cl_2 with 5 × 10^{-3} M Pt(acac)$_2$. Chemical shift relative to external tetramethylsilane.

indicate that the PDMVS produced with photoactivated Pt(acac)$_2$ is a linear polymer and is virtually identical to the polymer produced using chloroplatinic acid.[10]

Assuming that no two x-type links are adjacent to one another (since they are less abundant than y-type) two silicon moieties exist in the polymer chain: silicon atoms attached to both y and x links, $-CH_2CH_2Si(Me_2)CH(CH_3)-$, (xy) and those attached to two y links, $-CH_2CH_2Si(Me_2)CH_2CH_2-$, (yy). The ratio of xy to yy silicons is 1.27 to 1 based on the fractions for x and y units given above from ^{1}H NMR. Two ^{29}Si NMR peaks arise from **6**; see Figure 5. The integrated area of the larger silicon peak (δ 5.9) is 1.17 times the area of the smaller (δ 6.7) in fair agreement with the expected ratio above. The upfield peak, therefore, is attributed to xy-type silicon atoms and the downfield peak to yy-type. This is opposite of the assignment reported.[10]

The IR spectrum of **6**, Figure 6, contains bands attributed to both x- and y-type units of PDMVS.[10] The spectrum of the polymer taken shortly after photopolymerization (Figure 6a) includes a weak band from silicon hydride end-groups (2109 cm^{-1}). This peak is not present in the spectrum of polymer aged for four months (Figure 6b) as a result of end-group consumption by hydrosilation during aging. Vinyl functionality is not discernible by IR in either of these cases, although both end-group functionalities are visible in the ^{1}H NMR spectra of aged polymers.

Inhibition. Bubbling the solutions with oxygen or argon prior to irradiation had no significant effect on the reaction rates or product distributions of the hydrosilations (see marked data points in Figures 1 and 2) compared to samples prepared in air. This was the case both at 2 M and 0.5 M vinyldimethylsilane concentrations. Rigorous removal of dissolved gases by freeze/pump/thaw prior to irradiation did not significantly alter the course of the reaction either. These results demonstrate that oxygen does not function as a reactant, cocatalyst, or significant inhibitor of this polymerization reaction.

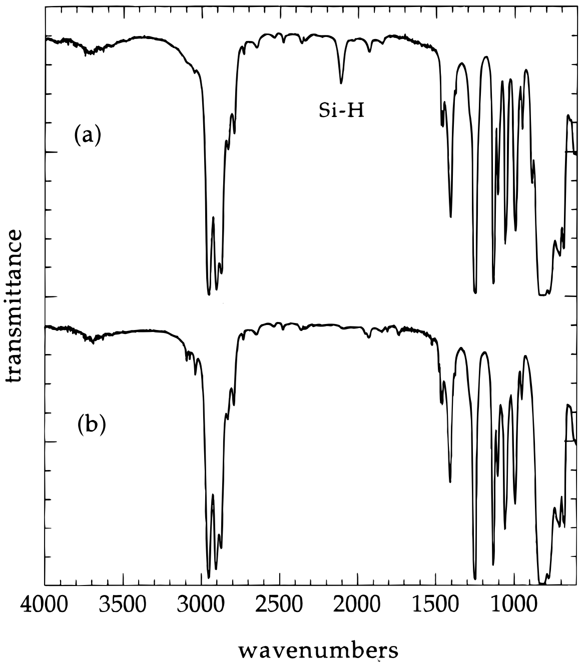


Figure 6. Infrared spectrum of PDMVS produced by 366 nm irradiation of 2.0 M vinyldimethylsilane in CH_2Cl_2 with 5 × 10^{-3} M Pt(acac)$_2$. Freshly photopolymerized, (a); aged four months, (b).

Table 3. Inhibition of Photoactivated Polymerization by Complexing Solvents

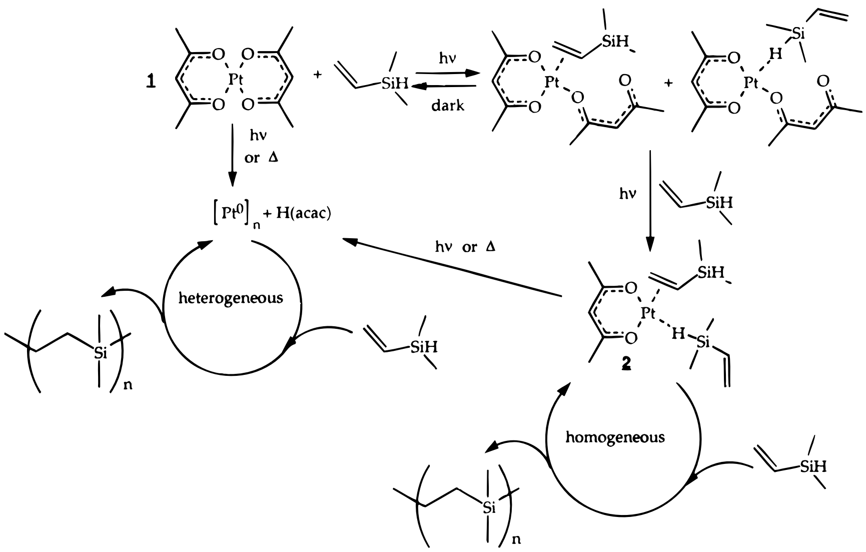
additive	monomer consumption time	polymer yield (%)	solvent polarity[a]	solvent donicity[b]
DMF (0.6 M)	2.5 h	94	404	0.69
pyridine (0.6 M)	15 min[c]	–	302	0.85
DIDMA (0.2 M)	3.5 min[c]	–	(0.179)[d]	(0.82)[e]
none	1.5–3.5 min[c]	–	(0)[f]	–

[a] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: New York, 1988, pp 365–371. [b] Ibid. pp 20–21. [c] Sample tubes burst after this time. [d] Value for aniline. [e] Value for triethylamine. [f] Value for TMS.

Metallic mercury is known to inhibit heterogeneous platinum-catalyzed hydrosilation reactions, but not homogeneous reactions.[4,14] An added drop of mercury did not inhibit the reaction of 2 M vinyldimethylsilane with 0.005 M Pt(acac)$_2$ noticeably. However, at reduced concentrations of 0.5 M vinyldimethylsilane and 5 × 10^{-4} M Pt(acac)$_2$ mercury inhibited the reaction resulting in 40% longer time for reaction of half of the monomer.

The addition of Lewis bases to neat monomer inhibits the reaction as shown in Table 3. The DMF appears to be consumed during the reaction based on GC data and is not incorporated into the polymer in significant amounts. The polymers produced with added DMF, pyridine, 2,6-diisopropyl-*N*,*N*-dimethylaniline (DIDMA) and from neat monomer had virtually identical NMR spectra. The lack of inhibition by DIDMA may be caused by an inability of the compound to complex with platinum active sites due to steric interference. Pyridine might be expected to display greater inhibition than DMF because of its stronger electron-donating ability but this proved not to be the case. The higher polarity of DMF may enhance its contact with Pt(acac)$_2$ compared to the other additives thus increasing inhibition.

Scheme 2



Discussion

Photoactivated Pt(acac)$_2$ polymerizes vinyldimethylsilane yielding a linear polymer which has a similar molecular weight to the polymer reported by Corriu *et al.*[10] and is produced in about the same reaction time. Based on this observation and from comparison of the NMR results, the photogenerated polymer appears to be equivalent to polymer formed with chloroplatinic acid, a standard hydrosilation catalyst. The polymerization of vinyldimethylsilane using platinum/carbon[9] required more severe reaction conditions than the current system to produce a polymer of about the same molecular weight (based on M_n) as **6**. One cyclic dimer was reported as a minor product in the work by Curry,[9] but no mention of dimers was made by Corriu *et al.*

The approximate doubling of molecular weight which occurred during aging (Table 2) is postulated to arise from an average of one additional hydrosilation reaction per molecule during that time period. Polymer chain end-groups consisting of silicon hydride and vinyl provide the points of connection of the chains leading to the molecular weight growth. This chain end-linking can theoretically continue as long as reactive end-groups remain and active catalyst is present, leading to high molecular weight polymer. We did not experiment with higher reaction temperatures to determine what molecular weights are attainable. The thermal behavior of PDMVS and its utility as a preceramic polymer has been reported.[10]

Pt(acac)$_2$ is reported to function as a photoactivated hydrosilation catalyst via a secondary photoproduct.[2] Absorption of near-UV light is thought to induce ligand localized $\pi-\pi^*$ transitions which lead to sequential breaking of the four Pt−O bonds.[15] Active platinum sites are thus produced which complex with olefin and silicon hydride moieties and facilitate hydrosilation. Continued photolysis and/or thermolysis of the secondary photoproduct ultimately leads to Pt^0 which, according to this report, apparently grows colloids that scatter light as hydrosilation progresses. Scheme 2 shows the mechanism proposed by Lewis *et al.* extended to the current polymerization system.[2] In this mechanism, absorption of two photons is required to cleave a ligand from **1** and produce the secondary photoproduct **2** which is believed to be a homogeneous catalyst. Further absorption of light by **2** leads to destruction of the homogeneous catalyst and formation of a heterogeneous hydrosilation catalyst (Pt^0). Platinum colloid growth during addition reactions was reported as a result of the latter process.[2] This was determined from increases in the absorption base lines of the solutions. In our experiments colloid growth was detected only after the complete consumption of monomer. Heterogeneous catalysis, therefore, may be responsible for the increase in our polymer molecular weight during aging, while homogeneous catalysis by **2** is probably active during the initial reaction of the monomer.

The presence or absence of oxygen seems to play no role in the polymerization reaction. This is in contrast to the findings of Lewis *et al.* who determined that hydrosilation addition reactions catalyzed by the secondary photoproduct were inhibited by oxygen.[2] The secondary photoproduct (homogeneous catalyst) was said to catalyze hydrosilation faster than the ultimate photoproduct, Pt^0 colloids, in simple addition reactions. Our observation of mercury inhibition at low concentrations of monomer and catalyst indicates that heterogeneous catalysis plays some role (perhaps minor) in the early polymerization reaction. If **2** is the main catalyst during monomer consumption, the absence of oxygen inhibition in our reactions might mean that the polymerization of vinyldimethylsilane is competitive with oxygen coordination at the catalytic surfaces. Alternatively, if **2** is not a major player and instead our reaction is primarily heterogeneous, early polymerization may take place before Pt^0 colloids large enough to scatter light (and be detected by absorption) are formed. Platinum colloids of this small size are likely to produce relatively fast hydrosilation reactions. Chloroplatinic acid or Speier's catalyst is said to catalyze hydrosilation via a heterogeneous route stemming from platinum colloid formation.[16]

In a study of platinum-catalyzed hydrosilation with Karstedt's catalyst for addition of alkenes to silanes, oxygen was found to be necessary for the reaction.[17] Diatomic oxygen was postulated to function as a cocatalyst with platinum by coordinating with the active catalyst thus hindering colloid growth. This report is dissimilar to our observation since the removal of oxygen did not appear to inhibit polymerization with Pt(acac)$_2$.

Conclusion

The photoactivation of Pt(acac)$_2$ in vinyldimethylsilane promotes rapid hydrosilation polymerization which forms poly[(dimethyl)vinylsilane], dimers and oligomers. This reaction is not inhibited by the presence or absence of oxygen, but is inhibited by DMF. The mechanism includes heterogeneous platinum catalysis to some degree, but a homogeneous component may be involved as well. The polymer doubles in molecular weight during aging by chain end-linking at residual vinyl and hydride groups. This is apparently catalyzed by platinum colloids formed after photolysis. Photoactivated Pt(acac)$_2$ appears to be as reactive as chloroplatinic acid for the polymerization of vinyldimethylsilane.

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