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Organopolysilanes as photopolymerization initiators of polymethylvinylsiloxanes and polydimethylsiloxanes

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The organopolysilanes $Me(Me_2Si)_nMe$ (n = 4–6), $(Me_2Si)_6$ and $(Me_3Si)_2SiMePh$ are found to be effective photoinitiators for the polymerization of vinyl-containing siloxane rubbers. The trisilanes $Me(ME_2Si)_3Me$ and $Me_3SiSiMe_2SiMe_2Ph$ are slightly effective, while phenyldisilanes do not exhibit initiation activity in the process of photocuring. Polydimethylsiloxanes are cured at a slower rate under the same conditions than vinyl-containing derivatives. Two mechanisms of cross-linking are proposed: silylene–silirane–silanol and silylene–hydride–silanol.

Keywords: Organopolysilanes, organopolysiloxanes, photoinitiation, vulcanization, thin films

INTRODUCTION

Organopolysilanes with linear and cyclic structures are effective absorbers in the ultraviolet (UV) region of the spectrum, generating the silylenes and radicals.[1–3] Dodecamethylcyclohexasilane ($Me_{12}Si_6$), for example, under UV light generates dimethylsilylene (Me_2Si:) while linear organopolysilanes are also decomposed in parallel with formation of Me_2Si: and in this case also by a radical route (Scheme 1).[4,5]

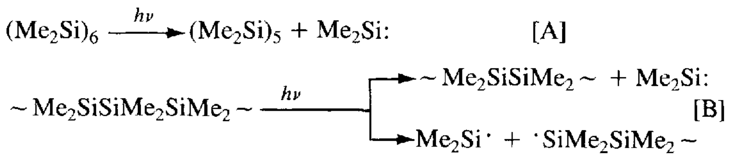
The ability of disilanyl Me, SiSiPh fragments statistically distributed among polydimethylsiloxane chains to generate radicals, and to carry out by their participation the cross-linking of siloxane chains, has been demonstrated.[6,7] West and co-workers[8–10] demonstrated the possibility of photocuring for styrene and acrylates through the use of polysilanes.

The authors of the present article use a set of organopolysilanes with linear and cyclic structure (see Table 1) as photoinitiators for curing polymethylvinylsiloxanes (PMVS) and polydimethylsiloxanes (PMS).[11,12]

EXPERIMENTAL

Analyses

Infrared (IR) spectra were recorded on a Perkin–Elmer 577 spectrophotometer between KBr plates. Gas chromatography (GC) analyses of reaction mixtures and individual compounds were carried out on a Tsvet-104 chromatograph, equipped with stainless steel columns 0.4 cm × 200 cm, packed with 5% SE-30 on Chromatone N-Super, with a thermoconductivity detector and with helium as carrier gas. Vinyl group content in PMVS was determined by the bromide–bromate method. Silanol group content was determined by the Chugaev–Tserevitinov method. The viscosity of PMVS and PMS was also determined with a U-tube capillary viscometer.



$$(Me_2Si)_6 \xrightarrow{h\nu} (Me_2Si)_5 + Me_2Si: \qquad [A]$$

$$\sim Me_2SiSiMe_2SiMe_2 \sim \xrightarrow{h\nu} \begin{cases} \sim Me_2SiSiMe_2 \sim + Me_2Si: \\ Me_2Si^{\cdot} + {}^{\cdot}SiMe_2SiMe_2 \sim \end{cases} \qquad [B]$$

Scheme 1

Initiators and inhibitors

Organopolysilanes were prepared according to procedures known from the chemistry of this class of compounds.[13,14] A mixture of linear permethylated polysilances $Me(Me_2Si)_nMe$, $n = 3-6$, was obtained by scission of dodecamethylcyclohexasilane ($Me_{12}Si_6$) by iodine[15] with subsequent methylation of the α, ω-di-iodopermethylpolysilanes formed with methylmagnesium iodide.

According to the iodometric analysis of the initiators di(t-butyl) peroxide and dicumyl peroxide, these two comprised up to 98% of the basic materials, which could therefore be used without extra purification.

Trimethylsilanol and phenyldimethylsilanol were obtained from corresponding disilazanes according to the known procedure;[16] n-butyldimethylsilanol was obtained by hydrolysis of n-butyldimethylchlorosilane in ether with ammonia.[17] n-Octanol was distilled prior to use; 2,4,6-tri(t-butyl)phenol was recrystallized from hexane.

Preparation of liquid silicone (siloxane) rubbers

PMVS-2

Octamethylcyclotetrasiloxane ($Me_8Si_4O_4$) (130 g, 0.438 mol), methylvinylcyclotetrasiloxane $(Me_2SiO)_3[Me(CH_2{=}CH)SiO]$ (30 g, 0.097 mol of $(Me_2SiO)_3(Me(CH_2{=}CH)SiO)$] and potassium hydroxide (KOH) in powder form (0.16 g, 2.9 mmol) were heated together for 3 h at a temperature of 120–130 °C with stirring. The reaction mixture was cooled and 200 cm^3 of hexane and 15 g of activated carbon were added with subsequent stirring for 4 h at a temperature of 20 °C; the solvent was then distilled off and the residue was evaporated under vacuum at 120 °C for 3 h. Polymethylvinylsiloxane (105 g) was obtained in the form of a transparent liquid with a viscosity value of 3000 centistokes (cSt) and a vinyl group content equal to 2%.

PMVS-1 and PMVS-3 were obtained in a similar way.

PMVS-4

Trimethylchlorosilane (Me_3SiCl) (6 cm^3) and triethylamine (Et_3N) (6 cm^3) were added to a solution of PMVS-2 (20 g) in hexane (100 cm^3). The reaction mixture was boiled for 6 h, filtered, the volatile products were distilled off, and the residue was diluted with hexane and mixed with activated carbon for 3 h at 20 °C. The solution was filtered and hexane was first distilled at atmospheric pressure and then under vacuum. PMVS-**4** (16 g) was obtained in the form of a colourless transparent liquid, less viscous than the starting material.

PMS-1

Octamethylcyclotetrasiloxane ($Me_8Si_4O_4$) (100 g, 0.337 mol) and powdered KOH (0.1 g, 1.8 mmol) were heated for 4 h at 100–130 °C with stirring. The reaction mixture was cooled, hexane (150 cm^3) and activated carbon AG-3 (10 g) were added and the mixture was stirred for 4 h at 20 °C and filtered; the solvent was distilled off and the residue was evaporated under vacuum at 120 °C for 3 h. PMS-**1** (80 g) was obtained in the form of a colourless transparent liquid with a viscosity value of 2000 cSt.

PMS-2

PMS-**1** (5 g) was diluted in hexamethyldisilazane ($Me_3SiNHSiMe_3$) (10 cm^3) and heated for 7 h at 120 °C. Hexamethyldisilazane was distilled off under vacuum, then the residue was diluted in hexane (50 cm^3) and mixed for 4 h with activated carbon followed by filtration; the residue was evaporated for 3 h under vacuum at 120 °C. PMS-2 (3.2 g) was obtained in the form of a colourless, transparent, viscous liquid.

Polymerization

The initiator (0.01–0.02 g) was added to the liquid rubber (1 g), the mixture was stirred, a thin layer of the mixture (0.1–0.3 mm) was applied on the substrate (made of glass, procelain, metal, paper and plastic) which was then irradiated with the total light of a medium-pressure mercury-vapour lamp of the DRT type (220 W, 250 nm 26%, 365 nm 100%). The distance from the substrate to the lamp was 5–7 cm. The inhibitors were introduced at a quantity of 0.05–0.1 g per gram of the rubber.

To test the influence of atmospheric oxygen on the photopolymerization, the glass plate with the applied thin layer of composition (PMVS-**2** + $Me_3SiSiMePhSiMe_3$) was placed in the quartz tube, treated under vacuum for 1 h at 25 °C and irradiated under vacuum for 5 min. The composition was cured at the same rate as in the air. The rate of curing did not change in the presence of air.

Model reactions

Photoinitiated reaction of 2-phenylheptamethyltrisilane [$(Me_3Si)_2SiMePh$] with 3-vinylheptamethyltrisiloxane [$(Me_3SiO)_2SiMe(CH{=}CH_2)$] and trimethylsilanol ($Me_3SiOH$)

The mixture of $(Me_3SiO)_2SiMe(CH{=}CH_2)$ (1.4 g, 5.6 mmol) and $(Me_3Si)_2SiMePh$ (0.5 g, 1.8 mmol) was exposed to the total light of a DRT-220 mercury lamp in a quartz flask in an argon atmosphere when cooled to 10 °C. Me_3SiOH (0.2 g, 2.2 mmol) was added to the reaction mixture after 5 h of irradiation, and irradiation was then continued for another 2 h. Chromatographic analysis of the reaction mixture indicated the presence of the disilabutane $(Me_3SiO)_2MeSiCH_2{-}Ch_2SiMePh(OSiMe_3)$ in the quantity of 0.05 mol mol^{-1} of decomposed 2-phenylheptamethyltrisilane; after 10 h of irradiation this figure increased to 0.23 mol, and after 18 h it increased to 0.42 mol. In this time interval $(Me_3Si)_2SiMePh$ decomposed by 70%. The yield of $Me_3SiOSiMePhH$ after 18 h was equal to 0.19 mol. In addition, three unidentified products were present in the reaction mixture.

Photoinitiated reaction of dodecamethylcyclohexasilane $(Me_2Si)_6$ with 3-vinylheptamethyltrisiloxane $(Me_3SiO)_2SiMe(CH{=}CH_2)$ and trimethylsilanol (Me_3SiOh)

The mixture of $(Me_3SiO)_2SiMe(CH{=}CH_2)$ (1.24 g, 5 mmol), $(Me_2Si)_6$ (0.16 g, 0.5 mmol) and Me_3SiOH (0.2 g, 2.2 mmol) was irradiated for 20 h in a quartz flask in an argon atmosphere cooled to 5 °C. The presence of the disilabutane $(Me_3SiO)_2MeSiCH_2CH_2SiMe_2(OSiMe_3)$ was detected by the GC method with the yield equal to 0.26 mol mol^{-1} of the decomposed $(Me_2Si)_6$. Reaction products also included five more components which were not identified.

Photoinitiated reaction of 2-phenylheptamethyltrisilane $(Me_3Si)_2SiMePh$ with trimethylsilanol (Me_3SiOH)

The mixture of Me_3SiOH (1 g, 11 mmol) and $(Me_3Si)_2SiMePh$ (0.12 g, 0.45 mmol) was irradiated for 8 h in a quartz flask in an argon atmosphere at 10 °C. According to the GC data, the high-boiling reaction products comprised $Me_3SiOSiMePhH$, $(Me_3SiO)_2SiMePh$, $(Me_3Si)_2SiMePh$ in molar ratio 47.2:2.1:50.7. The IR spectrum of the reaction mixture had intensive absorption bands at 3000–3700 cm^{-1} (O—H), 2120 cm^{-1} (Si—H) and 1060 cm^{-1} (Si—O).

Model compopunds

3-Vinylheptamethyltrisiloxane ($(Me_3SiO)_2SiMe(CH{=}CH_2)$)

A mixture of Me_3SiCl (97.65 g, 0.9 mol) and $Me(CH_2{=}CH)SiCl_2$ (43.3 g, 0.3 mol), with stirring and cooling, was dropped into the distilled water (200 cm^3). The organic layer was separated, diluted with hexane, washed with distilled water until neutral and dried with calcium chloride. The hexane was distilled off and the residue was distilled under vacuum. The liquid (20.5 g) was separated and, according to GC and spectrometry data, comprised the main product $(Me_3SiO)_2SiMe(CH{=}CH_2)$ (90.5%) mixed with the silanol $Me_3SiOSiMe(CH_2{=}CH)OH$ (9.5%). The liquid so obtained was dissolved in hexane (70 cm^3) followed by addition of triethylamine (1.2 g, 11 mmol). Trimethylchlorosilane (1.1 g, 10 mmol), diluted in hexane (10 cm^3), was added to this mixture with stirring. The mixture was stirred for 2 h at boiling temperature, filtered and the hexane was distilled off. Distillation under vacuum gave 3-vinylheptamethyltrisiloxane (14.3 g, 58 mmol, 19%) with b.p. 56 °C/14 torr, n_D^{20} 1.3960 (Ref. 18, b.p. 48 °C/8.8 torr, n_D^{25} 1.3947).

1,1,4-Trichloro-1,4-dimethyl-4-phenyl-1,4-disilabutane ($Cl_2MeSiCH_2CH_2SiMePhCl$)

A solution of PhMgBr (300 cm^3) obtained from 5 g (0.21 mol) of magnesium and 31.4 g (0.2 mol) of bromobenzene was dropped slowly into a solution of $Cl_2MeSiCH_2CH_2SiMeCl_2$ (37.9 g, 0.148 mol) in ether (200 cm^3) with stirring and cooling. The reaction mixture was boiled for 8 h, filtered, the ether was distilled off and the residue was distilled under vacuum. $Cl_2MeSiCH_2CH_2SiMePhCl$ (18.5 g, 0.062 mol, 42%) was obtained with b.p. 128–130 °C/1 torr, n_D^{20} 1.5286 (Ref. 19, b.p. 135–136 °C/3 torr).

1,1,4-Tris-trimethylsiloxo)-1,4-dimethyl-4-phenyl-1,4-disilabutane $(Me_3SiO)_2MeSiCH_2CH_2SiMePh(Me_3SiO)$

A solution of $Cl_2MeSiCH_2CH_2SiMePhCl$ (13.5 g, 0.045 mol) in hexane (25 cm^3) was dropped into the solution of Me_3SiOH (12.25 g, 0.136 mol) and triethylamine (13.74 g, 0.136 mol) in 75 cm^3 of hexane with vigorous stirring. An abundant white precipitate separated from the solution. The reaction mixture was stirred for 4 h without heating and for 7 h at boiling temperature. The precipitate was filtered off and hexane was distilled off from the organic fraction. The liquid (10.8 g) with b.p. 160–165 °C/3 torr was distilled under vacuum and comprised, according to GC data, the main product and an unidentified admixture. We did not succeed in purification of the main product by vacuum distillation. (There were two products.)

The mixture of $(Me_3SiO)_2MeSi(CH{=}CH_2)$ (1.24 g, 5 mmol) and $Me_3SiOSiMePhH$ (1 g, 5 mmol) was heated for 3 h at 60 °C in the presence of a catalytic quantity of a Speier catalyst. Vacuum distillation yielded disilabutane $(Me_3SiO)_2MeSiCH_2CH_2SiMePh(Me_3SiO)$ (1.23 g, 2.7 nnol, 55%), with b.p. 154–155 °C/1 torr, n_D^{20} 1.4475, d_4^{20} 0.9085 MR_D

$$\left(\text{molecular refraction} - MR_D = \frac{n^2 - 1}{n^2 + 2}\frac{M}{d}\right)$$

134.60 (calcd 133.90). Analysis: found: C, 49.95; H, 9.44; Si, 30.39. Calcd for $C_{19}H_{42}O_3Si_5$; C, 49.72; H, 9.22; Si, 30.60%.

1,1,1,3-tetramethyl-3-phenyldisiloxane ($Me_3SiOSiMePh$)

A mixture of $Me_3SiOSiMe_3$ (8.1 g, 0.05 mol), $MePhHSiOSiMePhH$ (12.9 g, 0.05 mol) and concentrated sulphuric acid 98% (3 cm^3) was heated for 2 h with stirring at 100 °C. Hexane (100 cm^3) was added to the reaction mixture. The acid layer was separated, the organic layer was washed with distilled water until neutral and it was then dried above calcium chloride. The hexane was distilled off and the residue was distilled. $Me_3SiOSiMePhH$ (12.8 g, 0.061 mol, 61%) was obtained, b.p. 180–182 °C/740 torr, n_4^{20} 1.4620, d_4^{20} 0.8912, MR_D 65.09 (calcd 65.67). Analysis: found: C, 56.80; H, 8.52; Si, 27.30 calcd for $C_{10}H_{18}OSi_2$: C, 57.08; H, 8.62; Si, 26.70%.

Polymethyl-1,4-disilacarbosesquioxane ($(Me_3Si_2CH_2CH_2O_{1.5})_n$)

Ice (200 g) and 400 cm^3 of distilled water were placed into a vessel of capacity 1 dm^3. $Cl_2MeSiCH_2CH_2SiMe_2Cl$ (30.35 g, 0.13 mol) was added over a 20-minute period with stirring followed by further stirring for the next hour. The solid polymer was filtered, washed on the filter with distilled water, dried for 3 days in the air at 20 °C and for 5 h under vacuum at 120–150 °C. $(Me_3Si_2CH_2CH_2O_{1.5})_n$ (14.1 g) was obtained in the form of a hydrophobic, white, lightweight powder.

1,1,4-Tris(trimethylsiloxy)-1,4,4-trimethyl-1,4-disilabutane

The sesquioxane polymer $(Si_2Me_2CH_2CH_2O_{1.5})_n$ (3.5 g) powdered in a mortar, hexamethyldisiloxane $(Me_3Si)_2O$ (40 cm^3) and concentrated sulphuric acid (4 cm^3) were mixed at 20 °C until complete dissolution of the polymer had occurred. The organic layer was washed with distilled water until neutral and dried with calcium chloride. Hexamethyldisiloxane was distilled off and the residue was distilled in vacuum. The disilabutane $(Me_3SiO)_2MeSiCH_2CH_2SiMe_2(OSiMe_3)$ (2.4 g, 6.1 mmol, 26.5%) was obtained with b.p. 99–100 °C/4 torr, n_D^{20} 1.4080 (Ref. 20, b.p. 106 °C/5 torr, $n_D^{20} = 1.4070$).

RESULTS AND DISCUSSION

Liquid silicone rubbers

PMVS (polymethylvinylsiloxane) with terminal, statistical (i.e. chain) and statistically-terminal (i.e. chain and terminal) positions of vinyl groups were used as curing liquid rubbers.[21] The best results in the curing rate were found for the last two PMVS types with a total vinyl group content of 2%. At a vinyl group content within the range 0.2–1.0 % the curing proceeded slowly.

PMVS with a terminal position of the vinyl groups (PMVS-1) (0.2%) was obtained by the catalytic rearrangement of octamethylcyclotetrasiloxane (**D$_4$**) and 1,3-dimethyltetravinyldisiloxane mixture (Eqn [1]).

PMVS with a statistical position of the vinyl groups (PMVS-2) (2%) was obtained in a similar way from **D$_4$** and methylvinylcyclotetrasiloxane (Eqn [2]).

PMVS with statistically-terminal positions of the vinyl groups (PMVS-3) (2%) was obtained from **D$_4$** and methylvinylcyclotetrasiloxane and 1,3-dimethyltetravinyldisiloxane (Eqn [3]). Reactions [1]–[3] are shown in Scheme 2.

Polydimethylsiloxane was synthesized by the catalytic rearrangement of **D$_4$** (Eqn [4]).

$$\underset{\mathbf{D_4}}{(Me_2SiO)_4} + [(CH_2{=}CH)_2MeSi]_2)O \xrightarrow[140\ °C]{KOH} \underset{\textbf{PMVS-1}}{(CH_2{=}CH)MeSi(OSiMe_2)_nOSiMe(CH{=}CH_2)_2} \quad [1]$$

$$\underset{\mathbf{D_4}}{(Me_2SiO)_4} + (Me_2SiO)_3[Me(CH_2{=}CH)SiO] \xrightarrow[140\ °C]{KOH} \underset{\textbf{PMVS-2}}{HO(Me_2SiO)_m[Me(CH_2{=}CH)SiO]_nH} \quad [2]$$

$$\underset{\mathbf{D_4}}{(Me_2SiO)_4} + (Me_2SiO)_3[Me(CH_2{=}CH)SiO] + [(CH_2{=}CH)_2MeSi]_2O \xrightarrow[140\ °C]{KOH}$$

$$\underset{\textbf{PMVS-3}}{(CH_2{=}CH)_2MeSi(OSiMe_2)_m[OSiMe(CH{=}CH_7)]_nOSiMe(CH{=}CH_2)_2}$$

Scheme 2

Table 1 Photocuring of polysiloxanes

Polysiloxane	Percentage of vinyl in PMVS by weight	Initiator	λ_{max} (nm)[a]	$\epsilon \times 10^{-3}$ ($dm^3\ mol^{-1}\ cm^{-1}$)	Inhibitor	Time of curing (min)	Result obtained[b]
PMVS-1	0.2	$Me(Me_2Si)_nMe$[c]			–	60	nc
PMVS-2	0.2	$Me(Me_2Si)_nMe$			–	60	nc
PMVS-2	2.0	$Me_3COOCMe_3$			–	60	nc
PMVS-2	2.0	$PhMe_2COOCMe_2Ph$			–	60	nc
PMVS-2	2.0	$Me(Me_2Si)_nMe$			–	4	hp
PMVS-2	2.0	$(Me_2Si)_6$	255	2.0	–	3	hp
			232	5.8			
PMVS-2	2.0	$(Me_3Si)_2SiMePh$	243	13.0	–	5	hp
PMVS-2	2.0	$Me_3SiSiMe_2Me_2SiMe_2Ph$	240	15.4	–	15	tp
			221	13.0			
PMVS-2	2.0	$Me(Me_2Si)_4Me$	235	14.7	–	5	hp
PMVS-2	2.0	$Me(Me_2Si)_3Me$	215	9.02	–	30	tp
PMVS-2	2.0	$Me_3SiSiBu_2Ph$			–	20	nc
PMVS-2	2.0	$Me_3SiSiMePh_2$	230	16.5	–	20	nc
PMVS-2	2.0	$Ph_2MeSiSiMePh_2$	237	21.3	–	20	nc
PMVS-3	2.0	$Me(Me_2Si)_nMe$			–	4	hp
PMVS-4	2.0	$(Me_3Si)_2SiMePh$			–	15	tp
PMVS-2	2.0	$Me(Me_2Si)_nMe$			Me_3SiOH	20	tp
PMVS-2	2.0	$Me(Me_2Si)_nMe$			$BuMe_2SiOH$	20	tp
PMVS-2	2.0	$Me(Me_2Si)_nMe$			$PhMe_2SiOH$	30	tp
PMVS-2	2.0	$(Me_3Si)_2SiMePh$			$PhMe_2SiOH$	15	tp
PMVS-2	2.0	$Me(Me_2Si)_nMe$			$H(CH_2)_8OH$	15	tp
PMS-1	–	$(Me_2Si)_6$			–	30	hp
PMS-1	–	$(Me_3Si)_2SiMePh$			–	30	hp
PMS-2	–	$(Me_3Si)_2SiMePh$			–	30	nc

[a] λ and ϵ values are taken from Ref. 22. [b] nc, Uncured; hp, hard polymer; tp, tacky polymer. [c] Mixture of permethylpolysilanes with $n = 3–6$.

$$\underset{\mathbf{D_4}}{(Me_2SiO)_4} \xrightarrow[140\ °C]{KOH} \underset{\text{PMS-1}}{HOMe_2Si(OSiMe_2)_nOSiMe_2OH} \quad [4]$$

The rubbers obtained are colourless transparent liquids with viscosities from 2000 to 3000 cSt (molar masses 100,000–120,000). They are stable under prolonged storage at room temperature. Throughout the year no changes were observed in respect to turbulence, colour or viscosity.

The composition containing PMVS or PMS and organopolysilane is cured only under UV light. The initiator was added in a proportion of quantity 1–2%. A thin layer of substrate was applied to a glass plate and irradiated by a medium-pressure mercury lamp. For comparison an experiment on photoinitiation in the presence of peroxide initiators was carried out. The results obtained are presented in Table 1.

Mechanism of initiation and cross-linking

It follows from Table 1 that linear permethylated polysilanes [$\mathrm{Me(Me_2Si)_{\mathit{n}}Me}$, $n = 4-6$], dodecamethylcyclohexasilane and 2-phenylheptamethyltrisilane provide effective initiators of solidification. The phenyldisilanes $\mathrm{Me_3SiSiBu_2Ph}$, $\mathrm{Me_3SiSiMePh_2}$ and $\mathrm{Ph_2MeSiSiMePh_2}$, in spite of fairly high extinction coefficients (ϵ), do not initiate photopolymerization of PMVS and PMS. The addition of di-t-butyl peroxide and dicumyl peroxide also did not bring about the solidification of siloxane rubbers even with prolonged irradiation. From the data obtained one cannot make a conclusion about any dependence between the wavelength of the silane absorption and the coefficient of absorption and initiation activity. For example, dodecamethylcyclohexasilane has a lower ϵ value than the tetrasilane $\mathrm{Me(Me_2Si)_4Me}$ or phenyltrisilanes $\mathrm{(Me_3Si)_2SiMePh}$, $\mathrm{Me_3SiSiMe_2SiMe_2Ph}$, but exhibits very high initiation activity. At the same time tetraphenyldimethyldisilane, with the highest ϵ value among the compounds studied, does not initiate polymerization. Analysis of the data from Table 1 reveals that in all cases the active initiators are only those compounds that effectively generate silylenes under irradiation.

The initiation activity of linear permethylated polysilanes [$\mathrm{Me(Me_2Si)_{\mathit{n}}Me}$,$n \geq 4$] can be explained by their ability to generate radicals.[5] However, such compounds as dodecamethylcyclohexasilane and 2-phenylheptamethyltrisilane, as is known,[1–3] provide a very good source of silylenes, but not radical intermediates. In principle, radicals are formed under photolysis of $\mathrm{(Me_2Si)_6}$, but only at prolonged exposure and with a low yield.

Thus, prolonged irradiation of dodecamethylcyclohexasilane in cyclohexane solution finally leads to the formation of octamethylcyclotetrasilane and octamethyl-1,4-dihydrotetrasilane. The latter is formed as a result of the scission of $\mathrm{(Me_2Si)_4}$ with formation of a biradical and subsequent break-off of the hydrogen atoms (Eqn (5]).

The non-radical character of vulcanization is attested by the absence of any influence of atmospheric oxygen or inhibitor (2,4,6-tri(t-butyl)phenol addition) on the time of solidification.

Characteristically, known silylenes sources of low effectiveness such as octamethyltrisilane and 1-phenylheptamethyltrisilane at the same time exhibit lower initiation activity as well. the first of these for a short period of time does not solidify PMVS, while the second one solidifies it considerably more slowly compared with $\mathrm{(Me_2Si)_6}$ and $\mathrm{(Me_3Si)_2SiMePh}$.

None of the phenyldisilanes tested exhibited even minimal initiation activity, despite their fairly effective absorbance in the UV region. Evidently, this is explained by the fact that disilanes are unable to generate silylenes under UV irradiation.

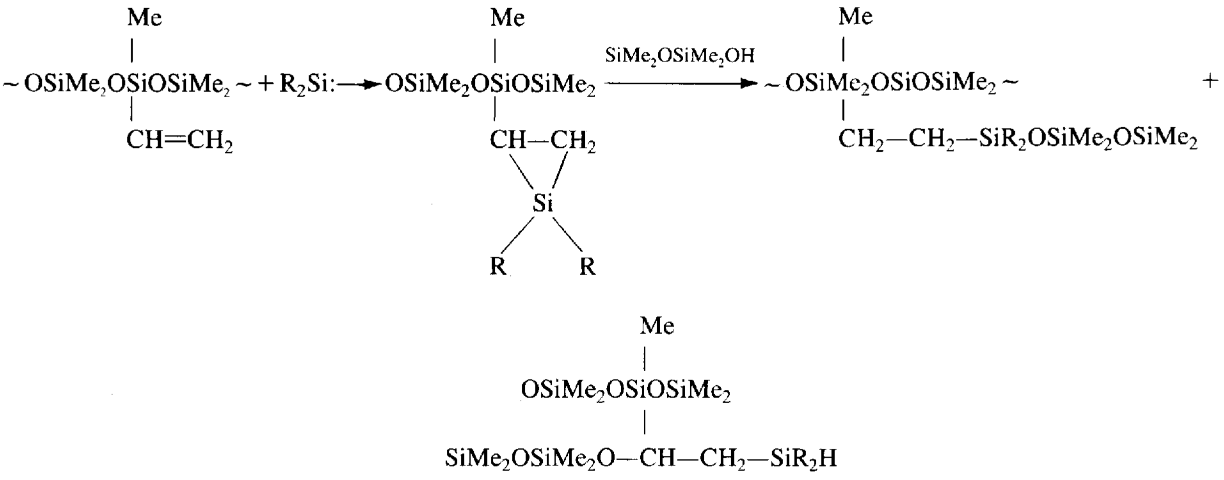
Proceeding from the premise mentioned above, it should be expected that initiation of polymerization should be able to be accomplished by silylenes, which have been obtained with good yield already at the initial stages of organopolysilane photolysis. It is known that dimethylsilylene is incorporated into the silicon–oxygen bond.[2] However, this reaction proceeds only in the case when hexamethylcyclotrisiloxane (**D**$_3$ and 1,1,3,3,-tetramethyl-1,3-disila-2-oxacyclopentane were used as traps for $\mathrm{Me_2Si}$: radicals. Hexamethyldisiloxane and octamethylcyclotetrasiloxane do not interact with dimethylsilylene, while methylphenylsilylene does not react with **D**$_3$ as well.[2] Obviously the silicon–oxygen (Si–O) bond in PMS and PMVS cannot be used as an effective trap of silylenes.

Silylenes are readily added to a multiple carbon–carbon bond with formation of siliranes.[1–3] In principle there are factors that would interfere with such a process of photosolidification of PMVS in the presence of organopolysilanes. The cross-linking of siloxane chains can be carried out through the interaction of the silanol part of the polysiloxane molecule with the silirane fragment obtained as a result of silylene reaction with the vinyl group (Scheme 3).

It is known that siliranes, especially those not having bulky substituents at the carbon and silicon atoms, are

$$\mathrm{(Me_2Si)_6} \xrightarrow[-\mathrm{Me_2Si:}]{h\nu} \mathrm{(Me_2Si)_5} \xrightarrow[-\mathrm{Me_2Si:}]{h\nu} \mathrm{SiMe_2SiMe_2SiMe_2SiMe_2^{1}} \xrightarrow{\mathrm{SH}} \mathrm{H(Me_2Si)_4H} \qquad [5]$$

(SH = hydrocarbon solvent)



Scheme 3

readily scissioned by alcohols. Formation of unstable (i.e. lacking sterical protection) siliranes is traditionally proven by their reaction with methanol.[23,24] Silicoorganic alcohols (silanols), as is known,[25] enter into almost the same reaction as aliphatic ones. Thus, it is not improbable that they can enter the reaction with silirane fragments, thereby providing the cross-linking of siloxane chains. The problem whether this cross-linking mechanism is realized or not may be checked. It comprises the following:

(1) When silanol terminal groups of the polymer molecules are 'closed' completely or partially, the solidification should not be observed, or it should proceed at a slower rate.

(2) Addition of silanols (R_3SiOH), and probably of alcohols ROH as well, should also inhibit curing, by virtue of the fact that they would compete with polyorganosiloxanols in the reaction of the three-membered silacyclopropane ring opening.

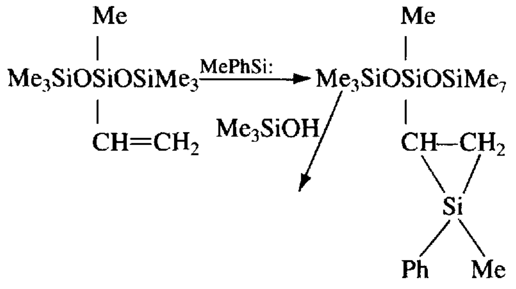
The test demonstrated that both the above-mentioned mechanisms of cross-linking inhibition take place. The elimination of the silanol terminal groups was carried out with the help of the PMVS-2 reaction in excess of trimethylchlorosilane and triethylamine. The hydroyl group was controlled by the IR spectroscopy method according to the intensity of the silicon hydroxyl (SiO—H) absorption band in the region of 3600–3800 cm^{-1}. It was found that the number of Si—OH groups reduced by a factor of 4–5. Polymethylvinylsiloxane (PMVS-4) obtained by that method, with trimethylsiloxy groups on the chain terminal positions, loses the tendency towards rapid curing. The increase of exposure time from 3–5 to 15–20 min leads only to partial vulcanization. The film obtained remains sticky and flimsy and easily decomposed on pressing.

Addition of silanols RMe_2SiOH (R = Me, Bu, Ph) to PMVS-**2** was found to be even more effective in the retardation of cross-linking. Trimethylsilanol and *n*-butyldimethylsilanol, added in a quantity of 10 mol mol^{-1} of the initiator, strongly inhibit curing and do not allow one to obtain the firm with a good quality even after prolonged exposure. Phenyldimethylsilanol is a still more effective agent for inhibition of PMVS-**2** solidification. In its presence the composition remained uncured after 20 min of irradiation.

In connection with the results obtained, it is necessary to investigate the influence of alcohols as well as to clarify the effect of PMVS-**2** dilution with inert compounds. Methanol, conventionally used for investigation of siliranes,[23,24] did not mix with PMVS-**2**; ethanol did not dissolve in silico-organic oligomers as well. *N*-Octyl alcohol mixed with PMVS-**2** fairly well, but exhibited a somewhat lower cross-linking inhibition effect than silanols. Dilution of PMVS-**2** prior to exposure with a small portion of dodecane brought about a film of the same quality as that without a solvent.

The silylene–silirane–silanol cross-linking mechanism was also confirmed with the use of model compounds. 3-Vinylheptamethyltrisiloxane can be used

$$(M_3Si)_2SiMePh \xrightarrow{h\nu} MePhSi: + Me_3SiSiMe_3$$



$$(Me_3SiO)_2MeSiCH_2CH_2SiMePh(OSiMe_3)$$

Scheme 4

as the simplest model for PMVS, whilst trimethylsilanol may be used as a model of the polymeric silanol. If the supposed mechanism is valid, then on irradiation of 3-vinylheptamethyltrisiloxane, trimethylsilanol and the organopolysilane mixture, Me_3SiO-substituted 1,4-disilabutane should be obtained. In fact, photoinitiated reaction of 2-phenylheptamethyltrisilane with Me_3SiOH and $(Me_3SiO)_2MeSiCH{=}CH_2$ led to the formation of 1,1,4-tris(trimethylsiloxy)-1,4-dimethyl-4-phenyl-1, 4-disilabutane with a yield of 42% calculated on the basis of decomposed 2-phenylheptamethyltrisilane (Scheme 4).

Methylphenylsilylene is also introduced on the SiO—H link of trimethylsilanol. As a result 1,1,1,3-trimethyl-3-phenyldisiloxane was formed with a yield of 19% (Eqn [6]).

$$Me_3SiOH + MePhSi: \rightarrow Me_3SiOSiMePhH \quad [6]$$

The photoinitiated reaction of dodecamethylcyclohexasilane with 3-vinylheptamethyltrisiloxane and trimethylsilanol also led to the formation of the scission product of silirane by silanol. The yield of 1,1,4-tris(trimethylsiloxy)-1,4,4-trimethyl-1,4-disilabutane was calculated at 26% (Scheme 5).

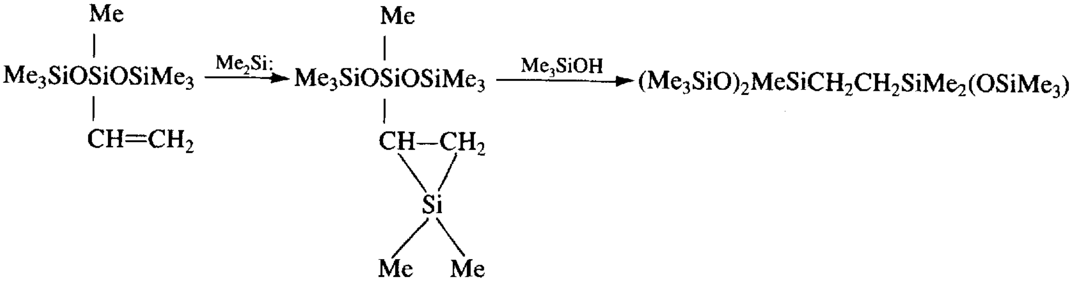
Examples of polydimethylsiloxane photocuring are presented in Table 1. PMS-1 vulcanization proceeds markedly more slowly compared with vinyl-containing rubbers and requires 30 min for irradiation. The elucidation of the cross-linking mechanism was carried out with the use of model compounds, inhibitors and via elimination of silanol terminal groups of PMS-1 molecules.

The substitution of silanol groups in PMS-1 for Me_3SiO— groups was carried out by prolonged heating of polydimethylsiloxane solution in hexamethyldisilazane (Eqn [7]).

The rubber obtained (PMS-2) is not cured on exposure to UV light in the presence of 2-phenylheptamethyltrisilane.

The addition of RMe_2SiOH (R = Me, Bu, Ph) to PMS-1 also resulted in a loss of the composition's ability to photocure. Thus, the process of polydimethylsiloxane vulcanization proceeds through silanol groups. The cross-linking mechanism consists in the introduction of silylene into SiO—H bonds and condensation of the silicon-hydride group with the silanol terminal group of the other PMS-1 molecule (Eqn [8]).

$$\begin{gathered} {\sim}OSiMe_2OH + R_2Si: \rightarrow {\sim}OSiMe_2OSiR_2H \\ OSiMe_2OSiR_2H + HOSiMe_2O{\sim} \rightarrow \\ {\sim}OSiMe_2OSiR_2OSiMe_2{\sim} + H_2 \end{gathered} \quad [8]$$



Scheme 5

$$HOSiMe_2O{\sim}SiMe_2OH + (Me_3Si)_2NH \quad Me_3SiOSiMe_2O \quad SiMe_2OSiMe_3 + NH_3$$

PMS-2 [7]

$$\mathrm{Me_3SiOH + (Me_3Si)_2SiMePh \xrightarrow{h\nu} \underset{96\%}{Me_3SiOSiMePhH} + \underset{4\%}{(Me_3SiO)_2SiMePh}} \qquad [9]$$

It is known[26] that such a conversion proceeds quickly only in the presence of catalysts, whilst verification with model compounds indicated that under conditions of photoinitiation reactions, the resulting hydride is condensed with the silanol without any catalyst. Thus, the exposure of 2-phenylheptamethyltrisilane solution in trimethylsilanol led to the formation of 1,1,1,3-tetramethyl-3-phenyldisiloxane and 3-phenylheptamethyltrisiloxane (Eqn [9]).

Though 3-phenylheptamethyltrisiloxane yield is slight, its presence in the mixture supports the possibility of a condensation of silicone-hydride and silanol groups (Eqns [10]).

$$\mathrm{Me_3SiOH + MePhSi\colon \rightarrow Me_3SiOSiMePhH}$$

$$\mathrm{Me_3SiOSiMePhH + Me_3SiOH \rightarrow (Me_3SiO)_2SiMePh + 0.5\,H_2} \qquad [10]$$

Photolytic decomposition of 2-phenylheptamethyltrisilane was also carried out in a medium of α, ω-oligodimethylsiloxanediols [$\mathrm{H(OSiMe_2)_nOH}$, n = 2–6]. After a 4 h exposure the transparent mixture of diols became turbid, and the disintegration of the initiator ceased due to strong light scattering. It was found by the GC that 2-phenylheptamethyltrisilane was decomposed only by 10%. In the IR spectra of the reaction products the ν(Si—H) absorption band at 2150 $\mathrm{cm^{-1}}$ was absent. A thin silicone film appeared on the vessel wall and, also, on the side of the irradiation source. The absence of the ν(Si—H) band can be explained by rapid and complete condensation of the resulting silicon-hydride groups with $\equiv$SiOH groups. However, the silicone film formation and turbidity of the mixture took place without any addition of organopolysilane. Thus, diol condensation with the release of water occurs under conditions of exposure to UV light.

Based upon the data obtained, one can expect that PMS photocuring would proceed without any addition of organopolysilane only through condensation of the terminal silanol groups. At the same time the test revealed that prolonged irradiation (40–50 min) of the PMS thin layer without addition of organopolysilane does not lead to vulcanization of the liquid rubber, while with addition the photocuring occurs after 30 min of exposure. Thus $\equiv$SiOH group condensation proceeds under conditions of PMS irradiation, if it proceeds at all, and is insufficient to bring about the rubber curing.

Polydimethylsiloxane vulcanization appears to be carried out via the following mechanism: silylene–hydride–silanol. The cross-linking by participation of silicon-hydride and silanol groups proceeds also at PMVS vulcanization as well, i.e. two types of cross-linking are realized for vinyl-containing polysiloxanes: silylene–silirane–silanol and silylene–hydride–silanol.

The PMVS and PMS films (after curing of the rubber) are transparent, thermally stable and insoluble in organic solvents, and have a good adhesion to glass. Their heating at 280–300 °C for 4 h in air does not result in turbidity, darkening, decomposition or peeling from the base. Non-illuminated parts of the silicone composition are not cured and can be washed with an organic solvent, after which the relief image of an object on the plate remains.

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