

SYNTHESIS OF ORGANOSILICON PEROXIDES AND A STUDY OF THEIR  
INITIATING ACTIVITIES IN RADICAL POLYMERIZATIONS

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The synthesis and an investigation of the properties of peroxides containing siloxane groups have been reported [1-5]. There is evidence of the successful use of siloxane peroxides as initiators of polymerization and vulcanization [6-9].

The organosilicon peroxides which we have synthesized (Table 1) are quite stable compounds and decompose at a noticeable rate only at 180-230°C. Judging from the observed values of the decomposition half-life, the stability of the peroxides increases upon the introduction of a siloxane group into the molecule. The most stable peroxides appeared to have branched structures (X), (XI), (XIII). Compared to the siloxane peroxides (II), (III), (IX), and (XII), they decompose three to four times slower at 230°C. The cumyl peroxides (IV), (V), (VI), (VIII), and (XIV) are less stable than the corresponding compounds with the tert-butylperoxyl group.

The synthetic peroxides were studied as initiators of polymerization and copolymerization of an oligoorganovinylsiloxane (OVS-1) obtained by the hydrolytic condensation of methylphenyl- and methylvinylchlorosilanes [10]. Upon the homopolymerization of OVS-1 (120-200°C), initiated by silicon-containing peroxides, a conversion constant corresponding to the formation of a solid polymer was not achieved, while in the presence of di-tert-butyl peroxide (DTBP) and dicumyl peroxide (CP), the solidification of the original oligomer was observed. From the data of Table 1 it is evident that quite a high degree of conversion (92%) may be achieved upon the copolymerization of OVS-1 with methyl acrylate (MA).

The copolymer thus synthesized is insoluble in organic solvents. Absorption bands characteristic of the CO group ( $1735\text{ cm}^{-1}$ ), and also bands corresponding to the fragments Si-O, Si-Ph, and Si-Me ( $1020-1090$ ,  $1110$ , and  $1260\text{ cm}^{-1}$ , respectively) are observed in the IR spectra.

The investigation of the thermal stability of the copolymers was conducted on samples previously purified of oligomers by extraction with  $\text{CCl}_4$  and dried to constant weight. Kinetic curves of weight loss of copolymers in a vacuum at 340°C (Fig. 1) show that upon polymerization in the presence of CP or DTBP the copolymers formed have inferior thermal stability to that of samples obtained with silicon-containing peroxides, in which the stability of the polymer increases with an increase in the number of siloxane groups in the initiator molecule. The most stable appeared to be the copolymers obtained with the branched peroxides (X) and (XI).

The peroxides  $\text{Me}_3\text{COOSiMe}_2\text{O}[\text{PhMeSiO}]_{2.33}[\text{Me}(\text{CH}=\text{CH}_2)\text{SiO}]_{1.00}\text{SiMe}_2\text{OOCMe}_3$  (XV) and  $\text{Me}_3\text{COOSiMe}_2\text{O}[\text{PhMeSiO}]_{2.33}[\text{Me}(\text{CH}=\text{CH}_2)\text{SiO}]_{1.00}\text{SiMe}_2\text{OSiMe}_2\text{OOCMe}_3$  (XVI), synthesized based on OVS-1, when used as original monomers are effective initiators of polymerization, and the polymer formed is close in thermal stability to the copolymer samples obtained in the presence of other organosilicon peroxides.

The diperoxides  $\text{Me}_3\text{COOSiMe}_2\text{OSiMe}_2\text{OOCMe}_3$  (XXII) and  $\text{Me}_3\text{SiOOCMe}_2\text{C}_6\text{H}_4\text{CMe}_2\text{OOSiMe}_3$  (XXIII) [2] enhance neither the conversion nor the thermal stability of the polymer formed compared with the monoperoxides. Cyclic polysiloxane peroxides  $(-\text{Me}_2\text{SiOO}-)_n$ , where  $n=3$  and greater, do not initiate the polymerization of OVS-1, which is related to the nonradical decomposition of the peroxide [11].

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TABLE 1. Characteristics of Synthetic Organosilicon Peroxides

Compound	Formula	bp, °C (P, mm Hg)	$n_D^{20}$	$d_4^{20}$	MR		Composition, %				Formula	Calculated, %			Decom- position half-life, min (T, °C)	P*
					exp.	calc.	C	H	Si	Q <sub>ct</sub>		C	H	Si		
(I)	Me <sub>2</sub> COSiMe <sub>2</sub> OOCMe <sub>3</sub>		1,4010	0,8670	61,76	61,90	54,53	11,04	12,70	14,04	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub> Si	54,50	10,98	12,74	14,52	74
(II)	Me <sub>2</sub> COSiMe <sub>2</sub> OSiMe <sub>2</sub> O· ·OCMe <sub>3</sub>	62 (6)	1,4022							10,80	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> Si <sub>2</sub>				10,86	
(III)	Me <sub>2</sub> COSiMe <sub>2</sub> OSiMe <sub>2</sub> O· ·SiMe <sub>2</sub> OOCMe <sub>3</sub>		1,4040	0,9101	99,08	99,29	45,70	9,84	22,60	8,44	C <sub>14</sub> H <sub>18</sub> O <sub>4</sub> Si <sub>3</sub>	45,60	9,84	22,85	8,68	69
(IV)	Me <sub>2</sub> COSiMe <sub>2</sub> OOCMe <sub>3</sub> Ph		1,4675	0,9709	80,81	81,65	63,69	9,18	10,04	11,50	C <sub>15</sub> H <sub>18</sub> O <sub>3</sub> Si	63,78	9,28	9,94	11,33	56
(V)	Me <sub>2</sub> COSiMe <sub>2</sub> OSiMe <sub>2</sub> O· ·OCMe <sub>3</sub> Ph		1,4530	0,9665	99,75	100,34	57,05	9,26	15,40	8,85	C <sub>17</sub> H <sub>22</sub> O <sub>4</sub> Si <sub>2</sub>	57,25	9,05	15,75	8,97	54
(VI)	Me <sub>2</sub> COSiMe <sub>2</sub> OSiMe <sub>2</sub> O· ·SiMe <sub>2</sub> OOCMe <sub>3</sub> Ph		1,4430	0,9641	118,49	118,68	52,82	9,23	19,21	7,21	C <sub>18</sub> H <sub>20</sub> O <sub>4</sub> Si <sub>3</sub>	52,97	8,90	19,56	7,43	
(VII)	PhOMe <sub>2</sub> SiOOCMe <sub>3</sub>	31 (0,05)	1,4745	0,9940	68,02	67,71	59,34	8,15	12,03	13,02	C <sub>13</sub> H <sub>16</sub> O <sub>3</sub> Si	59,96	8,39	11,68	13,31	0
(VIII)	PhOMe <sub>2</sub> SiOOCMe <sub>3</sub> Ph		1,5106	1,0400	87,06	87,45	66,97	7,27	8,97	10,40	C <sub>17</sub> H <sub>22</sub> O <sub>3</sub> Si	67,51	7,33	9,29	10,58	39
(IX)	Me <sub>2</sub> SiOSiMe <sub>2</sub> OOCMe <sub>3</sub>		1,3952	0,8613	65,76	65,94	45,90	10,18	23,58	13,40	C <sub>8</sub> H <sub>12</sub> O <sub>3</sub> Si <sub>2</sub>	45,74	10,24	23,70	13,55	72
(X)	(Me <sub>2</sub> SiO) <sub>2</sub> MeSiOOCMe <sub>3</sub>	90 (20)	1,3951	0,8812	84,53	84,55	42,46	9,66	27,55	10,26	C <sub>11</sub> H <sub>16</sub> O <sub>3</sub> Si <sub>3</sub>	42,53	9,73	27,12	10,30	92
(XI)	(Me <sub>2</sub> SiO) <sub>2</sub> SiOOCMe <sub>3</sub>	96 (2,5)	1,3957	0,8921	103,56	103,23	40,26	9,60	29,34	8,34	C <sub>13</sub> H <sub>16</sub> O <sub>3</sub> Si <sub>4</sub>	40,58	9,43	29,20	8,32	82
(XII)	PhMe <sub>2</sub> SiOSiMe <sub>2</sub> OOCMe <sub>3</sub>	98 (0,05)	1,4610	0,9522	86,00	85,97	56,10	8,54	18,94	10,51	C <sub>14</sub> H <sub>18</sub> O <sub>3</sub> Si <sub>2</sub>	56,32	8,78	18,82	10,72	87
(XIII)	(PhMe <sub>2</sub> SiO) <sub>2</sub> MeSiO· ·OCMe <sub>3</sub>		1,4900	1,0090	124,57	124,80	58,08	7,90	19,22	7,08	C <sub>21</sub> H <sub>24</sub> O <sub>4</sub> Si <sub>3</sub>	58,01	7,88	19,38	7,36	81
(XIV)	Me <sub>2</sub> COOSiMe <sub>2</sub> OOCMe <sub>3</sub> Ph		1,4717	1,0020	83,37	83,85	56,99	8,32	9,45	21,02	C <sub>15</sub> H <sub>18</sub> O <sub>3</sub> Si	60,36	8,78	9,41	21,44	63

\*P is the initiating activity, which is determined by the percent conversion, %, during the copolymerization of OVS with MA in the presence of the corresponding peroxide. For the peroxides DTBP, CP, (XV), (XVI), (XXII), (XXIII), P has the following values: 88, 88, 82, 74, 73, 79%, respectively.

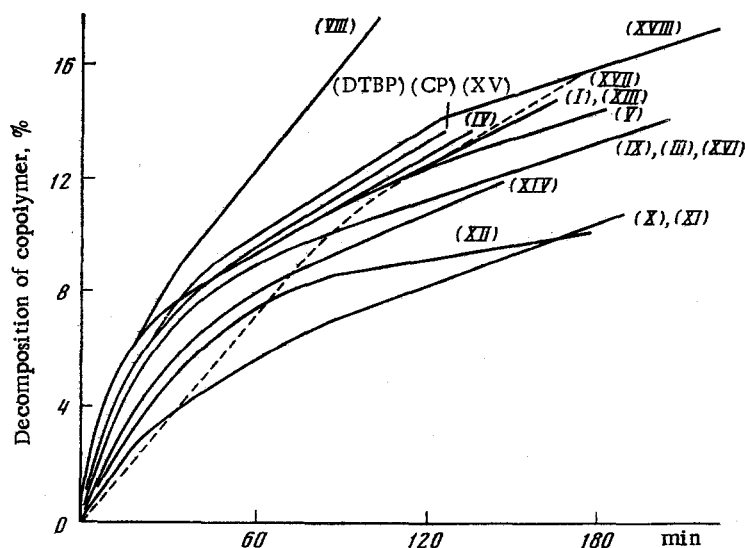


Fig. 1. Kinetic curves of thermal decomposition in vacuum of the copolymer of OVS-1 with MA, obtained with various organosilicon peroxides.

#### EXPERIMENTAL

tert-Butoxydimethyl(tert-butylperoxy)silane (I). A solution of 5.62 g of tert-butyl hydroperoxide in 20 ml ether was added dropwise with stirring and cooling (water-ice) to a solution of 10.42 g tert-butoxydimethylchlorosilane (XVIII) and 4.94 g pyridine in 50 ml ether. The mixture was stirred for 4 h at 20°, the ether solution was separated from the precipitate, and the filtrate was evaporated in a vacuum. Yield 9.26 g (67%) of the peroxide (I).

The peroxides (II)-(VIII), (X), and (XIII) were obtained analogously. Tert-butylperoxydimethyl(cumylperoxy)silane (XIV) was synthesized by an analogous method from tert-butylperoxydimethylchlorosilane [12], cumyl hydroperoxide, and pyridine.

tert-Butylperoxypentamethylidisiloxane (IX). To a cooled and stirred mixture of 6.21 g tert-butylperoxydimethylchlorosilane, 2.69 g pyridine, and 70 ml ether was added dropwise a solution of 0.034 mole trimethylsilanol in 30 ml ether. After filtration and evaporation of the ether in a vacuum the residue was distilled. Yield 5.02 g (62%) of the peroxide (IX).

Analogously, 1-phenyl-3-tert-butylperoxytetramethylidisiloxane (XII) was synthesized from phenyldimethylsilanol, tert-butylperoxydimethylchlorosilane, and pyridine.

Tris(trimethylsiloxy)tert-butylperoxysilane (XI). To a stirred solution of 21.84 g tris(trimethylsiloxy)silane (XX), 11.66 g pyridine, and 70 ml CCl<sub>4</sub> was added dropwise a solution of 11.78 g bromine in 20 ml CCl<sub>4</sub>. The mixture was stirred for 1.5 h, cooled (water-ice) and 6.63 g tert-butyl hydroperoxide in 20 ml CCl<sub>4</sub> was added dropwise. The mixture was stirred for an additional 4 h at 20° and filtered, the filtrate was evaporated under vacuum, and the residue was vacuum distilled. Yield 23.60 g (83%) of the peroxide (XI).

Oligoorganovinylsiloxane (OVS-1). HO(MePhSiO)<sub>2.33</sub>[Me(CH=CH<sub>2</sub>)SiO]<sub>1.00</sub>H, synthesized by the methods of [10], had the following properties: molecular weight 600 (cryoscopy), double-bond content 2.8·10<sup>-3</sup> mole/g, OH groups 4.42%, kinematic viscosity of a 10% solution in CCl<sub>4</sub> 1.272 cSt. Found: C 56.83; H 6.13; Si 23.67%.

Peroxide Oligomer Me<sub>3</sub>COOSiMe<sub>2</sub>O(PhMeSiO)<sub>2.33</sub>[(CH=CH<sub>2</sub>)MeSiO]<sub>1.00</sub>SiMe<sub>2</sub>OOCMe<sub>3</sub> (XV). To a solution of 1.65 g OVS-1 and 0.34 g pyridine in 10 ml ether was added dropwise with stirring and cooling 0.75 g tert-butylperoxydimethylchlorosilane in 5 ml ether. Stirring continued at 20° until complete gellation of the residue (7-8 h).

The mixture was filtered, the residue was washed with ether, dried in a vacuum desiccator, and weighed. The filtrate was washed with distilled water and dried with Na<sub>2</sub>SO<sub>4</sub>. The ether was evaporated under vacuum. Yield 1.66 g (74%) of a viscous yellow liquid containing 11.20% tert-butylperoxy groups.

Peroxide Oligomer  $\text{Me}_3\text{COOSiMe}_2\text{OSiMe}_2\text{O}(\text{SiMePhO})_{2.33}[\text{SiMe}(\text{CH}=\text{CH}_2)\text{O}]_{1.00}\text{SiMe}_2\text{OSiMe}_2\text{OOCMe}_3$  (XVI). By the reaction of OVS-1 with tert-butylperoxy-3-chlorotetramethylsiloxane (XVII) in the presence of pyridine, the peroxide (XVI) was synthesized, and contained 9.3% tert-butylperoxy groups.

1-tert-Butylperoxy-3-chlorotetramethylsiloxane (XVII). To a stirred and cooled mixture of 29.48 g 1,3-dichlorotetramethylsiloxane, 5.54 g pyridine, and 100 ml ether was added dropwise 6.30 g tert-butyl hydroperoxide in 50 ml ether. The reaction mixture was stirred for 3 h and filtered, the ether was evaporated from the filtrate under vacuum, and the residue was distilled. Yield 10.80 g (60%) of the peroxide (XVII), bp  $67^\circ$  (10 mm);  $n_D^{20}$  1.4070;  $d_4^{20}$  0.9609. Found: C 37.47; H 8.54; Cl 13.75;  $O_{\text{act}}$  12.29, Si 21.30%.  $\text{C}_8\text{H}_{21}\text{ClO}_3\text{Si}_2$ . Calculated: C 37.41; H 8.24; Cl 13.80;  $O_{\text{act}}$  12.45, Si 21.87%.

Analogously obtained were:

1-tert-Butylperoxy-5-chlorohexamethyltrisiloxane, bp  $78^\circ$  (5 mm);  $n_D^{20}$  1.4061;  $d_4^{20}$  0.9601. Found: C 35.86; H 8.15; Cl 10.94;  $O_{\text{act}}$  9.73, Si 25.59%.  $\text{C}_{10}\text{H}_{27}\text{ClO}_4\text{Si}_3$ . Calculated: C 36.28; H 8.22; Cl 10.71;  $O_{\text{act}}$  9.67, Si 25.45%.

tert-Butoxydimethylchlorosilane (XVIII), bp  $122^\circ$ ;  $n_D^{20}$  1.4030;  $d_4^{20}$  0.9118. Found: C 42.93; H 8.97; Cl 21.94; Si 16.69%.  $\text{C}_6\text{H}_{15}\text{ClO}_2\text{Si}$ . Calculated: C 43.22; H 9.07; Cl 21.26; Si 16.90%.

1-tert-Butoxy-3-chlorotetramethylsiloxane, bp  $170^\circ$ ;  $n_D^{20}$  1.4025;  $d_4^{20}$  0.9282. Found: C 39.75; H 9.04; Cl 15.01; Si 22.95%.  $\text{C}_8\text{H}_{21}\text{ClO}_2\text{Si}_2$ . Calculated: C 39.89; H 8.79; Cl 14.72; Si 23.32%.

1-tert-Butoxy-5-chlorohexamethyltrisiloxane, bp  $97^\circ$  (18 mm);  $n_D^{20}$  1.4033;  $d_4^{20}$  0.9369. Found: C 37.88; H 8.77; Cl 11.18; Si 26.94%.  $\text{C}_{10}\text{H}_{27}\text{ClO}_3\text{Si}_3$ . Calculated: C 38.12; H 8.64; Cl 11.25; Si 26.75%.

Bis(trimethylsiloxy)methylsilane (XIX). To a solution of 0.106 mole  $\text{Me}_3\text{SiONa}$  in 1 liter of ether was added dropwise a solution of 60.70 g  $\text{MeSiCl}_2\text{H}$  in 100 ml ether. The mixture was stirred for 10 h with heating, and then filtered. The filtrate was washed with distilled water and dried with  $\text{CaCl}_2$ , the ether was evaporated, and the residue was vacuum distilled. Yield 70 g (59%) of the siloxane (XIX), bp  $77^\circ$  (69 mm);  $n_D^{20}$  1.3820, compare [13].

Tris(trimethylsiloxy)silane (XX). From  $\text{Cl}_3\text{SiH}$  and  $\text{Me}_3\text{SiONa}$ , (XX) was synthesized, bp  $112^\circ$  (80 mm);  $n_D^{20}$  1.3870, compare [14].

Bis(phenyldimethylsiloxy)methylsilane (XXI). From sodium phenyldimethylsilanolate and  $\text{MeSiHCl}_2$ , (XXI) was synthesized, bp  $156^\circ$  (3.5 mm);  $n_D^{20}$  1.5000;  $d_4^{20}$  0.9890. Found: C 59.03; H 7.74; Si 24.23%.  $\text{C}_{17}\text{H}_{26}\text{O}_2\text{Si}_3$ . Calculated: C 58.90; H 7.56; Si 24.30%.

Bis(trimethylsiloxy)methylbromosilane. a. To a stirred mixture of 60.6 g of the silane (XIX), 18 g pyridine, and 100 ml  $\text{CCl}_4$  was added dropwise a solution of 36.8 g bromine in 50 ml  $\text{CCl}_4$ . The mixture was filtered, the solvent was evaporated from the filtrate, and the residue was fractionated under vacuum. Yield 48.2 g (70%) of the siloxane, bp  $82^\circ$  (28 mm),  $n_D^{20}$  1.4110;  $d_4^{20}$  1.0685. Hydrolyzable bromine found 26.63%, calculated 26.51%.

b. Bromine (33.2 g) was added dropwise to 65.4 g bis(trimethylsiloxy)phenylmethylsilane [15]. The mixture was heated at 4 h at  $110^\circ$  and then vacuum distilled. The fraction of bp  $70\text{--}87^\circ$  (30 mm) was distilled again in a fractionating column. Yield 26.2 g (42%) bis(trimethylsiloxy)methylbromosilane.

Bis(phenyldimethylsiloxy)methylbromosilane. This was synthesized by method a from the silane (XXI), bp  $162^\circ$  (2.5 mm);  $n_D^{20}$  1.5090;  $d_4^{20}$  1.1520. Found: C 48.31; H 6.17; Br 18.82; Si 19.58%.  $\text{C}_{17}\text{H}_{25}\text{BrO}_2\text{Si}_3$ . Calculated: C 47.98; H 5.92; Br 18.78; Si 19.80%.

The decomposition half-life of the peroxides in nonane solution was determined by an ampul method. The initial concentrations were 0.2–0.4 mole/liter.

The copolymerization of OVS-1 with MA was carried out in sealed, previously evacuated ampuls with a gradual increase of the temperature from  $120$  to  $220^\circ$ . The original ratio of components was 1 mole MA per mole of double bond in OVS-1. The polymer samples obtained were extracted with  $\text{CCl}_4$  in a Soxhlet extractor for 8 h. The polymers were dried in a vacuum desiccator at  $100^\circ$  to constant weight. The polymerization conversion was determined by the weight of the polymer sample after extraction, since it is known [16] that the polymer is insoluble, and the unreacted OVS is extracted from the polymer.

The weight loss during thermal decomposition of the polymer was studied in a high vacuum apparatus of the McBain weight [17], equipped with a quartz spring. The residual pressure in the system was  $2 \cdot 10^{-5}$  tor.

#### CONCLUSIONS

1. A series of organosilicon peroxides  $R^1O(SiMe_2O)_nSiMe_2OOR^2$  and  $(R^3Me_2SiO)_mSiMe_2-m-OOCMe_3$ , where  $R^1 = Me_3C, Me_3Si, \text{ or } Ph$ ;  $R^2 = Me_3C, Me_2PhC$ ;  $R^3 = Me, Ph$ ;  $n = 0, 1, 2$ ; and  $m = 1, 2, 3$ , were synthesized by reactions of the corresponding chlorosiloxane with tert-butyl or cumyl hydroperoxide in the presence of pyridine.
2. Siloxane peroxides are effective initiators of the copolymerization of oligoorganovinylsiloxanes and methyl acrylate.
3. The copolymer formed is more thermally stable than samples obtained in the presence of tert-butyl or dicumyl peroxide.

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