

Polyethylene oxide—polysiloxane branched copolymers and networks

1. Hydrosilylation of vinyl ethers of oligoethylene glycols with polyhydridosiloxanes

B. A. Trofimov,^a T. A. Skotheim,^b L. N. Parshina,^{a*} M. Ya. Khil'ko,^a
L. A. Oparina,^a I. P. Kovalev,^b and A. B. Gavrilov^b

^aIrkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.

Fax: +7 (395 2) 35 6046. E-mail: bat@acer.irkutsk.su

^bMoltech Corporation,
9000 South Rita Road, Building 61, Tucson, Arizona, USA.
Fax: +1 (520) 799 7501

The hydrosilylation of vinyl methyl and divinyl ethers of oligoethylene glycols with polyhydridosiloxanes in the presence of chloroplatinic acid is accompanied by side processes, namely, polymerization of vinyl ethers and homodehydrocondensation of polyhydridosiloxanes. The electrical conductivity of ~1 M solutions of lithium triflate or bis(trifluoromethylsulfonyl) imide in the resulting hydrosilylation products is ~10⁻⁵ S cm⁻¹.

Key words: vinyl ethers of oligoethylene glycol, polyhydridosiloxanes, hydrosilylation; polyethylene oxide—polysiloxane copolymers; homodehydrocondensation of polyhydridosiloxanes.

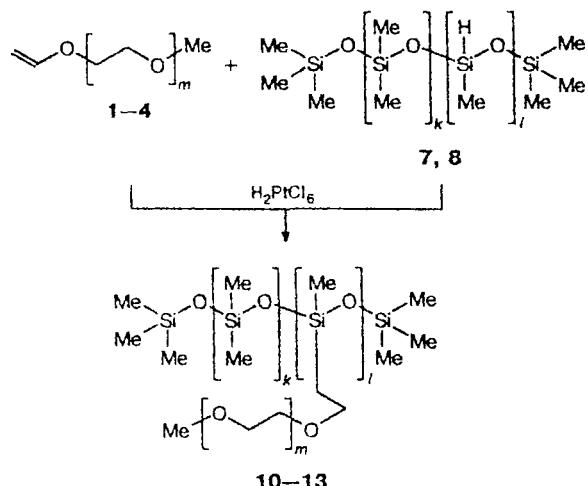
Despite the fact that a large number of publications dealing with hydrosilylation of vinyl ethers has been accumulated by now,^{1–3} data on hydrosilylation of these compounds by hydridosiloxanes are limited to those reported in patents,^{4,5} and the reactions with polyhydridosiloxanes have been considered only in one paper⁶ in which vinylglycidyl ether of ethylene glycol has been used as the vinyl ether. Meanwhile, the reaction of polyhydridosiloxanes with alkyl vinyl and divinyl ethers of ethylene glycols, especially oligomeric ethylene glycols, opens up a convenient way to the synthesis of promising polymeric electrolytes with a highly flexible polysiloxane backbone and oligooxyethylene side chains, favoring cation solvation and transport.^{7,8} These polymers can be of interest as hydrophilic materials for contact lenses.⁹

According to patents,^{4,5} in the presence of platinum supported on alumina or of a solution of chloroplatinic acid in propan-2-ol, hydridosiloxanes smoothly add to vinyl ethers to give β -adducts. However, in more recent publications^{1–3,10} devoted to hydrosilylation of alkyl vinyl ethers by various silanes, it has been invariably noted that the reaction is accompanied by side processes such as polymerization of vinyl ethers, replacement of the β -hydrogen atom in the vinyloxy group by a silyl group to give vinylsilanes, the formation of alkoxy silanes, reduction of vinyl ethers, etc.

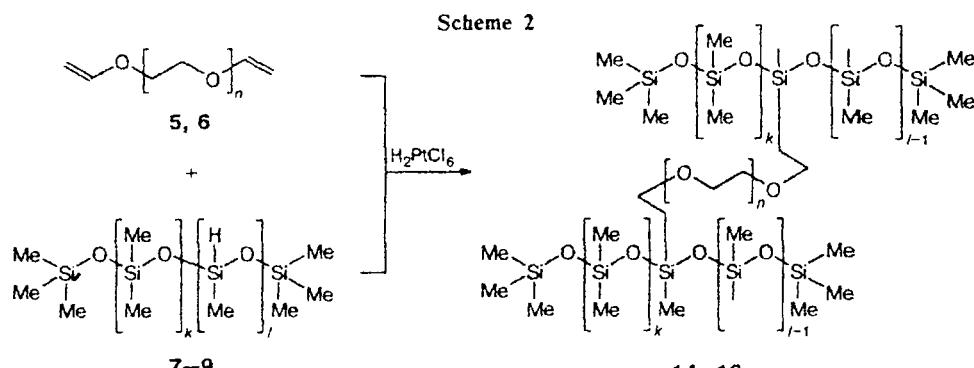
In order to verify the data on the route and selectivity of the reaction of simple vinyl ethers with hydridosiloxanes and to develop a convenient approach to the synthesis of polymers combining polysiloxane and

poly(ethylene oxide) chains, we studied the reactions of vinyl methyl (1–4) and divinyl (5, 6) ethers of oligoethylene glycols (Schemes 1 and 2, respectively), or mixtures of vinyl methyl ethers 1–4 with 5–20 mol.% of divinyl ethers 5, 6 as cross-linking agents with polyhydridosiloxanes 7–9 in the presence of chloroplatinic acid (a 0.1 N solution of $H_2PtCl_6 \cdot 6H_2O$ in

Scheme 1



$m = 2$ (1, 10), $m = 3$ (2, 11), $m \approx 7$ (3, 12), $m \approx 12$ (4, 13);
 $k = 0$, $l = 15–20$ (7, 10), $k = l \approx 15$ (8, 11–13)



$n = 2$ (5, 14), $n \approx 6$ (6, 15, 16); $k = 0, l \approx 15-20$ (7, 14), $k = l \approx 15$ (8, 15), $k = 4-5, l \approx 25-30$ (9, 16)

propan-2-ol or tetrahydrofuran). According to the typical procedure, the catalyst was added to a stirred mixture of reactants; then the reaction mixture was allowed to stand with stirring at room temperature in a tightly stopped vessel or heated at intervals to 40–90 °C in an ampule. The course of the reaction was monitored by the disappearance of the absorption bands of the vinyloxy group (3110, 3080, 1635, 1620, 1200, 960, 840 cm^{-1} , etc.) and the Si–H bond (2160 cm^{-1}). The adducts of polymethylhydridosiloxanes 7–9 with vinyl methyl ethers 1–4 (Scheme 1, adducts 10–13), divinyl ethers 5 and 6 (Scheme 2, adducts 14–16), or their mixtures (adducts 17) were expected to form as the major reaction products.

Since the reactants are insoluble in each other, it may be expected² that in the absence of solvent, a polymer of

the vinyl ether used and the hydrosilylation product 10–17 would form in a low yield depending on the velocity of stirring. However, unexpectedly, the reaction of vinyl methyl ether of diethylene glycol 1 with polymethylhydridosiloxane with 100% content of hydridosiloxane units 7, taken in equivalent amounts regarding functional groups, at room temperature resulted in quantitative formation of a cross-linked, visually homogeneous polymer (Table 1, run 1). The use of a 50% excess of vinyl methyl ether 1 afforded a mixture of silylation product 10 and the polymer of the initial vinyl methyl ether (see Table 1, run 2). The latter can be identified in the reaction mixture by the appearance of an additional multiplet at ~1.70 ppm in the ^1H NMR spectrum, due to the $-\text{CH}_2-$ group. The amount of the polymer can be calculated from the ratio of the integral intensities.

Table 1. Products of hydrosilylation of vinyl methyl ether of diethylene glycol (1) by polymethylhydridosiloxane 7

Run	TBA /mL	Recovered 1 /mmol	Yield of 10 ^a (%)	Composition of the product mixture ^a (%)			Found Calculated (%)		
				10	Polymer of ether 1	7 + 18	C	H	Si
1 ^{b,c}	Not added	0	100 ^d	100 ^d	Traces	0	46.51 46.57	8.21 8.79	13.10 13.61
2 ^c	Not added	0	82	56	40	4	The mixture was not analyzed		
3	Not added	6.8	83	94	Traces	6	44.54 44.98	9.10 8.66	15.58 15.59
4	0.1	13.7	0	0	0	100	The mixture was not analyzed		
5 ^{e,f}	Not added	5.4	50	50	35	15	46.36 46.41	9.28 8.79	13.72 13.80
6 ^{e,g}	0.1	7.5	75	91	0	9	43.94 44.18	8.35 8.60	15.66 16.58

Note. Reaction conditions: benzene (1 mL) as the solvent, 20 °C, 24 h, 13.7 mmol of vinyl ether 1 and 8.3 mmol-equiv. of Si–H groups off siloxane 7, 0.1 mL of a 0.1 N solution of H_2PtCl_6 in Pr_2OH as the catalyst.

^a The yield of the hydrosilylation product 10 and the composition of the resulting product mixture were calculated based on the reacted ether 1 and the data of IR and ^1H NMR spectroscopy and elemental analysis.

^b The ratio 1 : 7 = 17 mol : 17 mmol-equiv. ^c Without a solvent.

^d The product was cross-linked as a result of homodehydrocondensation at the residual Si–H bonds.

^e At 80 °C. ^f Time 4 h. ^g Time 5 h.

A two-phase equimolar mixture of vinyl methyl ether of oligoethylene glycol **3** (lower layer) and polymethylhydridosiloxane with 50% content of the (SiHMeO) groups **8** (upper layer) reacts at room temperature without stirring in the presence of 0.25 mol.% H_2PtCl_6 to give a biphasic mixture consisting of a liquid polymer of vinyl ether **3** and a solid polymer of polysiloxane **8**. However, when the reaction mixture is heated or the amount of the catalyst decreases, hydrosilylation, resulting in a homogeneous reaction mixture, becomes the predominant process (see Experimental).

In our opinion, the formation of cross-linked products in the hydrosilylation of vinyl methyl ethers **1–4** by polymethylhydridosiloxanes **7, 8** can be explained by assuming that the initial polymethylhydridosiloxanes **7, 8** and their intermediate adducts with vinyl ethers, having residual Si—H bonds, undergo homodehydrocondensation induced by chloroplatinic acid. In this case, the overall outcome of the reaction of vinyl ethers with polymethylhydridosiloxanes is determined by the ratio of the rates of competing reactions, *viz.*, hydrosilylation, polymerization of vinyl ether **1–4** or **5, 6**, and homodehydrocondensation of polymethylhydridosiloxane **7–9** and the intermediate hydrosilylation adducts. Presumably, it is the latter process that has led to the above-described formation of a cross-linked product in the hydrosilylation of vinyl methyl ether **1** (see Table 1, run 1), taking into account the fact that siloxane **7** with the greatest (100%) content of hydridosiloxane units in the chain has served as the silylating reagent. More often, homodehydrocondensation of polyhydridosiloxanes **7–9** affords some quantity of insoluble solid particles in a liquid reaction mixture.

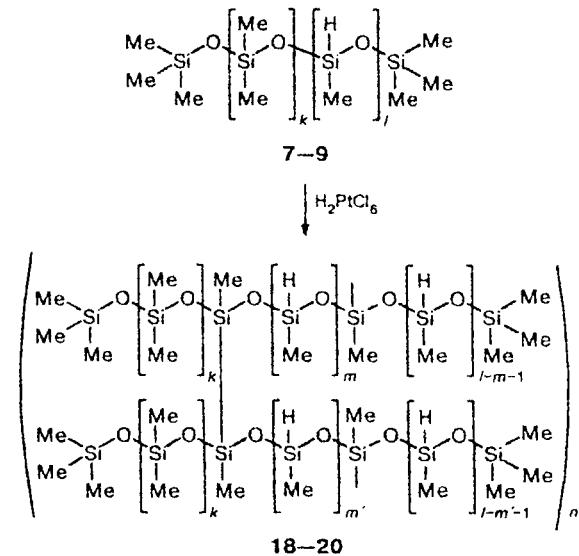
The use of an excess of vinyl methyl ethers of oligoethylene glycols **1–4** accelerates hydrosilylation and thus hampers homodehydrocondensation of siloxanes **7–9**; as noted above for ether **1**, this results in a mixture consisting mainly of two products, *viz.*, hydrosilylation product **10** formed according to Scheme 1 and the polymer of vinyl methyl ether (see Table 1, run 2). An increase in the temperature of the process or the amount of the catalyst accelerates all the competing reactions but to different degrees, thus changing the product ratio. If we also take into account the increase in the mutual solubility of the reactants on increasing temperature, it is quite natural that at elevated temperatures, hydrosilylation of vinyl methyl ether of oligoethylene glycol **3** predominates over the side process, and this leads to the homogenization of the reaction mixture described above.

When polymethylhydridosiloxanes **7–9** react with divinyl ethers **5, 6** (see Scheme 2), all three processes mentioned above are also possible; however, owing to the presence of two double bonds, the reaction gives visually homogeneous insoluble solid products.

It is of interest that, despite the observed ease of the side homodehydrocondensation of polymethylhydridosiloxanes **7–9** during hydrosilylation in the presence of

chloroplatinic acid (hydrogen evolution, formation of solid insoluble particles in the liquid silylation product), to the best of our knowledge, it has not been discussed in the literature so far. Among the numerous examples of coupling of organosilanes in the presence of various metal complexes (Ti, Zr, Hf, V, Nb, Cr, Mo, W, Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Zn, Hg, U, Th) presented in a review,¹¹ only one study¹² describing oligomerization of H_3SiHex (Hex is *n*-hexyl) induced by $H_2PtCl_6 \cdot 6H_2O$ and oxygen is mentioned (the product yields are not given). It was suggested¹¹ that this reaction could afford oligosiloxanes rather than oligosilanes. Only insignificant autodehydrocondensation of the initial Et_2SiH_2 during hydrosilylation of hex-1-ene in the presence of H_2PtCl_6 has been observed.¹³ Therefore, we checked whether autodehydrocondensation of the polymethylhydridosiloxanes **7–9** in the presence of 0.03–0.06 mol.% H_2PtCl_6 (a 0.1 *N* solution in THF or propan-2-ol) is possible (Scheme 3).

Scheme 3



$$k = 0, l \approx 15-20 \quad (7, 18), \quad k = l \approx 15 \quad (8, 19), \\ k = 4-5, l = 25-30 \quad (9, 20)$$

The addition of the catalyst to polymethylhydridosiloxanes **7–9** results immediately in the evolution of hydrogen. In the presence of 0.03 mol.% H_2PtCl_6 at room temperature, after approximately 1 h for **7** or 5 h for two other siloxanes with a lower density of Si—H groups in the chain, **8** and **9**, the viscosity markedly increases. After 4 h, the polyhydridosiloxane **7** with 100% content of (SiHMeO) groups is converted into a solid paraffin-like product, whereas the other two compounds remain thick liquids even after 12 h if the catalyst concentration is low (0.03 mol.%) or also form

solid paraffin-like products over this period of time if the catalyst concentration is higher (0.06 mol.%).

In the presence of H_2PtCl_6 , polymethylhydridosiloxanes 7–9 are gradually (within 1–3 days) converted into brittle solid polymers 18–20, which are colored gray, apparently, due to contamination by metallic platinum liberated upon reduction of the catalyst.¹⁴ As the amount of the catalyst increases, the reaction rate sharply increases. Thus in the presence of 0.06 mol.% H_2PtCl_6 with respect to siloxane 7, the reaction is completed over a period of 2–3 h, yielding a brittle solid polymer. The absorption band due to the Si–H bond at $\sim 2160\text{ cm}^{-1}$ in the IR spectrum of the product of homodehydrocondensation of polysiloxane 9 with 15% content of hydridosiloxane groups entirely disappears, whereas in the case of siloxanes 7 and 8, this band is partially retained and its intensity somewhat increases upon an increase in the content of the hydridosiloxane groups in the initial polymethylhydridosiloxane. Judging by the amount of the hydrogen evolved, homodehydrocondensation of polysiloxane 7 with 100% content of hydridosiloxane groups in the absence of a solvent occurs by no more than 10%. Evidently, further transformation is prevented by the formation of the huge cross-linked macromolecule.

When excess tributylamine (TBA) with respect to H_2PtCl_6 is added, the reaction rate substantially decreases. Since in the presence of HCl, homodehydrocondensation of siloxanes does not proceed, the "retardation" of the reaction by TBA cannot be attributed to neutralization of chloroplatinic acid or HCl produced from it.¹⁴

As noted above, the mutual solubility of methyl vinyl or divinyl ethers of oligoethylene glycols 1–6 and polyhydridosiloxanes 7–9 is limited; therefore, to avoid separation of the reaction mixture into layers and the formation of homopolymers, they were made to react in THF or benzene. Evidently, in this case, hydrosilylation is the prevailing process. However, the above-noted side reactions still do occur, which is indicated most clearly by the evolution of hydrogen. Monitoring of the composition of the reaction mixture by IR spectroscopy shows that the ratio of the rates of polymerization of vinyl ethers and homodehydrocondensation of polymethylhydridosiloxanes depends on the size and the structure of the reactant molecules, reaction temperature, and the reactant and catalyst concentrations. At room temperature, the rate of polymerization of vinyl ethers of oligomeric ethylene glycols 3, 4, and 6 is somewhat higher than the rate of homodehydrocondensation of polyhydridosiloxanes 8 and 9; consequently, with equivalent amounts of the vinyloxy groups and Si–H bonds, the absorption bands of the vinyloxy groups are the first to disappear from the IR spectrum; after that, the Si–H absorption band ($\sim 2160\text{ cm}^{-1}$) disappears as a result of homodehydrocondensation. The use of methyl vinyl ether of diethylene glycol 1 with a lower molecular weight and polyhydridosiloxane 7, having Si–H groups in each unit of the siloxane chain, results in the opposite ratio of the

rates: at room temperature, the rate of polysiloxane homodehydrocondensation is somewhat higher than the rate of polymerization of vinyl ether (see Table 1, run 3). When the temperature increases, the rate of polymerization of vinyl ether 1 increases more rapidly than the rate of homodehydrocondensation of siloxane 7. Having polymerized, ether 1 is removed from the reaction with polyhydridosiloxane 7, and this additionally increases the probability of homodehydrocondensation of the latter. Consequently, the selectivity of the reaction drops (see Table 1, run 5).

On dilution of the solutions, the rate of homodehydrocondensation increases. Thus during hydrosilylation of a mixture of vinyl methyl ether (1) and divinyl ether (5) of diethylene glycol (molar ratio 1 : 5 = 14.6 : 1) by polymethylhydridosiloxane 7 at room temperature in THF with a total reactant concentration of approximately 7.5 mol L^{-1} (H_2PtCl_6 = 0.03 mol.% in relation to the sum of the vinyl ethers), the amount of hydrogen evolved, which matches homodehydrocondensation, is ~4% of the maximum possible amount. When this solution is diluted tenfold, the amount of hydrogen evolved increases by a factor of almost 7 (27%).

A threefold increase in the amount of the catalyst results in approximately 1.5-fold increase in the amount of hydrogen evolved in both above-mentioned cases (6 and 43%, respectively).

For comparison, during hydrosilylation of divinyl ether of oligoethylene glycol (6) by polymethylhydridosiloxane with 50% content of hydridosiloxane groups 8 in THF (total concentration of the reactants $\sim 1.8\text{ mol L}^{-1}$, $[H_2PtCl_6] = 0.15\text{ mol.}\%$ in relation to the vinyl ether), only ~2% of the theoretically possible amount of hydrogen is evolved. Since the reactant and catalyst concentrations are close to those in the above examples, these results mean that the ratio of the main and side reaction rates depends on the molecular masses and the structure of reactants, most of all, on the closeness of the hydridosiloxane groups in the chain of polymethylhydridosiloxanes 7–9.

In order to prevent polymerization of the vinyl ether in the presence of chloroplatinic acid, hydrosilylation of vinyl methyl ethers of oligoethylene glycols 1–4 was carried out in the presence of TBA taken in an excess with respect to H_2PtCl_6 . It has been reported² that hydrosilylation of divinyl ethers of glycols by monomeric silanes accelerates when pyridine is added to the Speier catalyst. However, in our case, TBA additives markedly retarded the reaction. Thus hydrosilylation of vinyl methyl ether of diethylene glycol 1 by polymethylhydridosiloxane 7 in benzene in the presence of chloroplatinic acid and TBA at room temperature for 24 h virtually does not give the adduct (see Table 1, run 4), whereas under the same conditions but without TBA, the product is formed in ~80% yield (see Table 1, run 3). However, on heating to 80 °C, when polymerization of vinyl ether 1 is suppressed and homodehydrocondensation of siloxane 7 is substantially re-

tarded, the use of amine considerably increases both the yield and the purity of hydrosilylation product **10** (see Table 1, runs 5 and 6).

Mention should be made of yet another feature of the hydrosilylation studied here, which is manifested most clearly in hydrosilylation of vinyl methyl ethers of oligoethylene glycols **1–4** with cross-linking of products induced by the addition of small amounts (5–20 mol.%) of divinyl ethers of oligoethylene glycol **5** and **6**. In the absence of a solvent, cross-linked solid polymers **17** are formed. When the process is carried out in THF (total concentrations of vinyl ethers 0.4–1.5 mol L⁻¹), no solid products are obtained after removal of the solvent. In this case, the ¹H NMR spectrum exhibits a clear-cut additional triplet at ~1.30 ppm, while the triplet at ~1.0 ppm (SiCH₂) is less intense than the signal corresponding to the hydrosilylation product. Apparently, the evolution of hydrogen, which is enhanced by dilution, and the presence of platinum catalysts, including metallic platinum formed from H₂PtCl₆,¹⁴ result in partial hydrogenation of vinyl ethers **1–6**. The triplet at 1.30 ppm in the ¹H NMR spectrum corresponds to the methyl protons in the ethoxy group formed. Thus, in these systems, in which the reactant concentration is initially low and, besides, the siloxane is efficiently consumed in homodehydrocondensation and the vinyl ether is hydrogenated and polymerizes, virtually no hydrosilylation products, especially cross-linked ones, are produced.

The products of hydrosilylation **10–13** of vinyl methyl ethers of oligoethylene glycol **1–4** by polymethylhydridosiloxanes **7, 8** or the hydrosilylation products obtained in solution from ethers **1–4** with addition of 5–20 mol.% of divinyl ethers **5, 6** are moderately thick dark liquids (apparently, the color is due to the reduction of platinum), soluble in most organic solvents. Hydrosilylation of divinyl ethers of oligoethylene glycols **5, 6**, both in a solvent and without one, or vinyl methyl ethers of oligoethylene glycol **1–4** containing 5–20 mol.% divinyl ethers **5, 6** without a solvent yields cross-linked insoluble paraffin-like polymers **14–17**.

The ¹H NMR spectrum confirms the formation of hydrosilylation products, most of all, by the triplet at 1.0 ppm (CH₂Si). If hydrosilylation is accompanied by polymerization of vinyl methyl ethers **1–4**, multiplets due to —CH₂—CHO— groups appear at 1.60–1.70 and 3.80 ppm in the ¹H NMR spectrum of the reaction products. The latter signal falls in the region of the signal due to the OCH₂ group, which becomes a multiplet. The reduction of vinyl methyl and divinyl ethers of oligomeric ethylene glycols results in the appearance of an additional signal at 1.32–1.35 (t, CH₃CH₂—).

Some of the obtained products (e.g., **3** and **17**) were tested as polymeric electrolytes. For this purpose, lithium triflate, readily soluble in THF, was added to the final product (Table 2, run 1) or to the solution of reactants before the synthesis (see Table 2, runs 2–6). It had been known that this salt by itself (in a dry chamber) does not affect either vinyl ethers **1–6** or poly-

Table 2. Electrical conductivity of solutions of lithium triflate in the products of hydrosilylation of vinyl ethers of oligoethylene glycol by polymethylhydridosiloxane **8**^a

Run	Reagents (molar ratio)	C_{Σ}^b mol L ⁻¹	C_1^c mol L ⁻¹	γ^d
1	3 : 8 (1 : 1)	1.87	0.75	3.8
2	3 : 6 : 8 (0.9 : 0.1 : 1)	0.68	0.81	3.0
3	3 : 6 : 8 (0.8 : 0.2 : 1)	0.60	0.77	2.1
4	3 : 6 : 8 (0.8 : 0.2 : 1)	0.62	0.80 ^e	3.5
5	4 : 6 : 8 (0.8 : 0.2 : 1)	0.40	0.91	2.3
6	4 : 6 : 8 (0.7 : 0.7 : 1)	0.35	0.89	3.1

^a The products were obtained at an equivalent ratio of the vinyloxy groups and the Si—H bonds: run 1 was carried out without a solvent, and runs 2–6 were performed in THF; the concentration of H₂PtCl₆ was 0.7–2.7 mmol L⁻¹; 20 °C; 48 h.

^b C_{Σ} is the total concentration of vinyl ethers.

^c C_1 is the concentration of CF₃SO₂Li.

^d γ/S (cm 10⁵)⁻¹ is the electrical conductivity.

^e (CF₃SO₂)₂NLi was used instead of lithium triflate.

methylhydridosiloxanes **7–9**. However, later it was found that lithium triflate promotes polymerization of vinyl ethers in the presence of chloroplatinic acid. Thus polymerization of divinyl ether of diethylene glycol **5** at 56 °C in tetraglyme (~3 mol L⁻¹ of **5** and 0.04 mol.% H₂PtCl₆ relative to **5**) occurs over a period of 4–5 h, whereas the same process in the presence of ~1 mol L⁻¹ of CF₃SO₂Li in the reaction mixture occurs over a period of 8 min. However, at room temperature the time of polymerization of the same mixture increases to 3 h (if the mixture is diluted with siloxane, it should be even longer), and judging by the rate of disappearance of the absorption band of vinyloxy group from the IR spectrum, it does not affect significantly the course of hydrosilylation. This is also indicated by the fact that dissolution of the salt in the final reaction product (see Table 2, run 1) and in the initial reaction mixture (see Table 2, runs 2–5) results in close electrical conductivity values equal to ~10⁻⁵ S cm⁻¹.

Experimental

¹H NMR spectra were recorded on a Jeol FX-90Q spectrometer. IR spectra were measured on Specord IR-75 and Mattson Galaxy 5020 instruments in thin film or in KBr.

The electrical conductivity of electrolytes was measured by the impedance method using an SI 1260 frequency analyzer (Solartron company) conjugated with the electrochemical SI 1280 interface. The impedance spectra were recorded in a glass cell with platinum electrodes in the frequency range of 200 kHz

to 500 Hz at an exciting signal amplitude of 10 mW. The cell was preliminarily calibrated against standard aqueous solutions of KCl with known conductivity. The cell constant was 0.812 cm⁻¹.

Vinyl methyl (1–4) and divinyl (5, 6) ethers of oligoethylene glycols were prepared by vinylation of the corresponding oligoethylene glycols and their monomethyl ethers by acetylene in the superbasic KOH–DMSO system.

Polymethylhydridosiloxanes 7–9 used were commercial products manufactured by the Huls Petrarch Systems company.

The IR spectra of hydrosilylation products 10–17 exhibit the following bands, ν/cm^{-1} : 800–805, 845–847 (for 17), 911–915, 1025–1035, 1070–1105, 1260–1261, 1350–1351 (for 12, 15), 1450–1460, 2865–2873, 2958–2972 (a shoulder in the case of 12, 13). The ¹H NMR spectra of the hydrosilylation products 10–17 contain the following bands, δ : 0.16–0.17 (s, 3 H, CH_3Si); 0.94–1.0 (t, 2 H, CH_2Si); 3.30–3.38 (s, 3 H, CH_3O); 3.53–3.63 (t, 10–50 H, CH_2O).

Hydrosilylation of vinyl methyl ether of diethylene glycol (1) by polymethylhydridosiloxane 7 (see Table 1, run 3). A 0.1 N solution of H_2PtCl_6 (0.1 mL) in propan-2-ol (0.036 mol.% H_2PtCl_6 relative to ether 1) was added to a solution of ether 1 (2.0 g, 13.7 mmol) and polymethylhydridosiloxane with 100% content of (SiHMeO) groups 7 (0.5 g, 8.3 mmol-equiv. of Si–H groups) in 1 mL of benzene. The mixture warmed up to 26–27 °C. Then it was allowed to stand for 24 h at ~20 °C. The benzene and unreacted vinyl ether 1 (1.0 g) were evaporated *in vacuo* (2 Torr). The residue (1.5 g) was a thick liquid, soluble in ether, acetone, alcohol, benzene, chloroform, and DMSO. The IR spectrum of the residue did not exhibit absorption bands due to vinyloxy groups but contained a weak absorption band corresponding to the Si–H group in hydridosiloxane at 2160 cm^{-1} . The ¹H NMR spectrum of the residue corresponded to the hydrosilylation product. The yield of hydrosilylation product 10 was 1.4 g (89% of the theoretical yield based on the consumed ether 1); the content of 10 in the product was 93%. Found (%): C, 44.54; H, 9.10; Si, 15.58. Calculated for a mixture of 93% hydrosilylation product 10 and 7% initial polymethylhydridosiloxane 7 (%): C, 44.71; H, 8.64; Si, 15.93.

Runs 1, 2, and 4–6 presented in Table 1 were carried out in a similar way.

Hydrosilylation of vinyl methyl ether of triethylene glycol (2) by polymethylhydridosiloxane 8. A 0.1 N solution of H_2PtCl_6 (0.1 mL) in THF (0.07 mol.% H_2PtCl_6 relative to ether 2) was added to a solution of ether 2 (1.14 g, 6.0 mmol) and polymethylhydridosiloxane with 50% content of (SiHMeO) groups 8 (0.94 g, 7.0 mmol-equiv. of Si–H groups) in 10 mL of THF. The reaction mixture was allowed to stand at ~20 °C; at intervals, IR spectra were recorded. After 2 days, the absorption bands due to the vinyloxy and Si–H groups disappeared. The THF was removed *in vacuo* (5 Torr) to give 2.08 g (100%) of a moderately thick dark liquid, soluble in conventional organic solvents, whose IR and ¹H NMR spectra corresponded to hydrosilylation product 11.

When the amount of the solvent decreased 4-fold (2.5 mL of THF) and the amount of the catalyst increased simultaneously 2-fold (0.2 mL), polymerization of vinyl ether 2 occurred faster than hydrosilylation (the band for the vinyloxy group was the first to disappear from the IR spectrum; after that, the Si–H band disappeared as a result of homodehydrocondensation). Evaporation of the solvent gave a moderately thick dark liquid, turbid due to the presence of particles of cross-linked polysiloxane.

Hydrosilylation of vinyl methyl ether of oligoethylene glycol 3 by polymethylhydridosiloxane 8. A 0.1 N solution (0.2 mL) of H_2PtCl_6 in THF (0.25 mol.% of H_2PtCl_6 relative to

ether 3) was added to a two-phase system consisting of oligoethylene glycol ether 3 (1.50 g, 4.0 mmol) (lower layer) and polymethylhydridosiloxane with 50% content of (SiHMeO) groups 8 (0.54 g, 4.0 mmol-equiv. of Si–H groups) (upper layer). The mixture warmed up to 33 °C. It was allowed to stand at ~20 °C and shaken at intervals. After 2 days, the lower layer was a moderately thick liquid whose IR spectrum did not contain bands for the vinyloxy group (homopolymer of vinyl ether 3). The upper layer consisted of a solid, slightly frothed homopolymer of polymethylhydridosiloxane 19 containing, according to the IR spectrum, some Si–H groups.

B. When the reaction mixture described in the previous procedure was heated to 50 °C over a period of 1.5 h, a homogeneous thick liquid was obtained; the IR and ¹H NMR spectra of this product corresponded to hydrosilylation product 11.

C. When the amount of the catalyst decreased twofold (to 0.1 mL) relative to its amount used in the previous experiment, even though the mixture was not efficiently stirred, the reaction also gave hydrosilylation product 11. Lithium triflate (0.25 g, 1.6 mmol) was dissolved in this product upon prolonged stirring. The concentration of the resulting solution was 0.78 mol L⁻¹; its electrical conductivity was $3.8 \cdot 10^{-3}$ S cm⁻¹ (see Table 2, run 1).

Hydrosilylation of vinyl methyl ether of oligoethylene glycol 4 by polymethylhydridosiloxane 8. A 0.1 N solution (0.1 mL) of H_2PtCl_6 in THF was added to a solution of oligoethylene glycol ether 4 (1.44 g, 2.5 mmol) and polymethylhydridosiloxane with 50% content of (SiHMeO) groups 8 (0.33 g, 2.5 mmol-equiv. of Si–H groups) in 4 mL of THF. The reaction mixture was allowed to stand at ~20 °C with stirring; at intervals, IR spectra were recorded. After 24 h, noticeable bands due to the vinyloxy and Si–H groups still remained in the spectrum. An additional 0.1 mL of the catalyst was added (totally, 0.4 mol.% H_2PtCl_6 relative to ether 4). After 2 days, the IR spectrum virtually did not contain bands for the vinyloxy and Si–H groups. The THF was evaporated *in vacuo* (5 Torr) to give 1.77 g (100%) of a moderately thick dark liquid, soluble in conventional solvents; the IR and ¹H NMR spectra of this product corresponded to hydrosilylation product 13.

Hydrosilylation of divinyl ether of oligoethylene glycol 6 by polymethylhydridosiloxane 8. **A.** A 0.1 N solution of H_2PtCl_6 (0.15 mL) in THF (0.25 mol.% H_2PtCl_6 relative to ether 6) was added to a solution of oligoethylene glycol ether 6 (1.06 g, 3.0 mmol) and polymethylhydridosiloxane with 50% content of (SiHMeO) groups 8 (0.80 g, 6.0 mmol-equiv. of Si–H groups) in 3 mL of THF. The reaction mixture was allowed to stand at ~20 °C with stirring; at intervals, IR spectra were recorded. After 24 h, the reaction mixture was an almost solid gel including the solvent. The spectrum of this product still exhibited noticeable bands for the vinyloxy and Si–H groups. THF was evaporated in air until the weight of the residue became equal to the weight of reactants taken (1.86 g), to give a light brown insoluble, brittle solid polymer, whose spectrum contained no absorption bands for the initial compounds.

B. When the amount of the solvent was increased to 25 mL and the amount of the catalyst was increased to 0.8 mL (1.33 mol.% H_2PtCl_6 relative to ether 6), polymerization of divinyl ether 6 accelerated most of all: after 20 h, the IR spectrum did not contain bands for the vinyloxy group but did contain a noticeable band at 2160 cm^{-1} (Si–H). Polymethylhydridosiloxane 8, which thus became excessive, underwent homodehydrocondensation to give 4.0 mL of hydrogen after a period of 20 h (the degree of conversion of siloxane into homopolymer 19 was 6%); after 2 days, the IR spectrum did not contain the hydridosiloxane absorption band. Evaporation of the THF in air gave a dark insoluble, brittle polymer.

Hydrosilylation of divinyl ether of oligoethylene glycol 6 by polymethylhydridosiloxane 9 was carried out as described above in procedure **A** using oligoethylene glycol ether **6** (1.06 g, 3.0 mmol) and polymethylhydridosiloxane with 15% content of (SiHMeO) groups **9** (2.63 g, 6.0 mmol-equiv. of Si—H bonds) in 5 mL of THF. The reaction gave 3.69 g of a light brown cross-linked polymer, whose IR spectrum did not exhibit absorption bands of the initial compounds.

Hydrosilylation of vinyl methyl ether of diethylene glycol (1) and 5 mol.% divinyl ether of diethylene glycol 5 by polymethylhydridosiloxane 7. A 0.1 N solution of H_2PtCl_6 (0.1 mL) in $PrOH$ (0.033 mol.% of H_2PtCl_6 relative to ether **1**) was added to an intensely stirred emulsion of polymethylhydridosiloxane with 100% content of (SiHMeO) groups **7** (1.0 g, 16.6 mmol-equiv. of Si—H groups), ether **1** (2.19 g, 15.0 mmol), and ether **5** (0.13 g, 0.8 mmol). The reaction mixture frothed and rapidly warmed up to 31 °C and, after about 1 h, to 70 °C. The reaction mixture was allowed to stand for 24 h at ~20 °C to give a paraffin-like grayish polymer insoluble in ether, acetone, benzene, or chloroform; the IR spectrum of this product did not contain absorption bands due to vinyloxy and Si—H groups.

Hydrosilylation of a mixture of vinyl methyl ether of triethylene glycol **2** (1.14 g, 6.0 mmol) and divinyl ether of oligoethylene glycol **6** (0.18 g, 0.5 mmol) by polymethylhydridosiloxane **8** (0.94 g, 7.0 mmol-equiv. of Si—H bonds) in the presence of 0.1 mL of a 0.1 N solution of H_2PtCl_6 in THF under similar conditions occurred much more slowly and was completed over a period of 2 days giving a solid cross-linked polymer.

When the latter reaction was carried out with the same amounts of the reactants and the catalyst dissolved in 2.3 or 10 mL of THF, it was completed over a period of 24 h or 2 days, respectively, to give a moderately thick dark liquid rather than a solid polymer.

Hydrosilylation of vinyl methyl ethers of oligoethylene glycol **3** and **4** with 5–20 mol.% divinyl ether of oligoethylene glycol **6**, added as a cross-linking agent, by a stoichiometric amount of polymethylhydridosiloxane **8** in THF occurred in a similar way. With the solution concentrations (0.4–0.8 mol L^{-1} for vinyl methyl ethers **3** and **4**) and the catalyst amounts (0.1–0.7 mol.% relative to the sum of vinyl ethers **3** or **4** and **6**) used, the reactions always gave liquid non-cross-linked products.

When CF_3SO_3Li (0.27 g) was added before the synthesis to a solution of oligoethylene glycol vinyl methyl ether **3** (1.44 g, 2.5 mmol), oligoethylene glycol divinyl ether **6** (0.09 g, 0.25 mmol), polymethylhydridosiloxane **8** (0.40 g, 3.0 mmol-equiv. of Si—H groups), and 0.2 mL of the catalyst in 5 mL of THF, then after stirring of the reaction mixture at ~20 °C for 2 days and evaporation of THF, the electrical conductivity of the resulting solution of lithium triflate in the reaction product (concentration of $CF_3SO_3Li \approx 0.91 \text{ mol } L^{-1}$) was $2.3 \cdot 10^{-5} \text{ S } cm^{-1}$ (see Table 2, run 5).

Homodehydrocondensation of polymethylhydridosiloxane 7 in the presence of chloroplatinic acid. **A.** Polymethylhydridosiloxane **7** (3 g) was placed in a flask connected to a gas meter, and a 0.1 N solution of H_2PtCl_6 (0.3 mL) in THF (0.03 mol.% H_2PtCl_6 relative to siloxane **7**) was added. Vigorous hydrogen evolution and frothing of the reaction mixture was immediately observed. After 1 h, the liquid appreciably thickened becoming almost solid and the gas evolution virtually ceased. After 4 h, the siloxane was a paraffin-like polymer; after 12 h, it was a solid grayish polymer. During the first 4 h (mainly during 1 h), 33 mL of hydrogen was collected (5.9% of the

maximum possible amount). The IR spectrum of the product contained an absorption band at 2157 cm^{-1} (Si—H).

B. When tributylamine (0.3 mL) was added in the above-described reaction mixture, hydrogen evolution was slower: 19 mL of the gas (3.4%) was collected over a period of 5 h; after that, virtually no gas evolution occurred. The substantial increase in the viscosity of polymethylhydridosiloxane **7** was observed only after 24 h, and a solid gel-like polymer formed after approximately 36–40 h.

C. When the amount of the catalyst was increased twofold compared to that given in clause **A** (0.06 mol.% H_2PtCl_6 relative to siloxane **7**), homodehydrocondensation of this siloxane was approximately twice as fast: curing of the siloxane occurred over a period of 2 h; 50 mL of hydrogen (8.9% of the maximum possible amount) evolved during 0.5 h; after that, gas evolution virtually ceased.

For siloxanes **8**, **9**, the process occurred similarly but at a lower rate.

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