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Sequential application of hydrothiolation and hydrosilylation reactions for the synthesis of new polyorganosiloxanes

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Abstract

This paper presents an approach for modifying silicones containing both Si-Vin and Si-H functional groups through the sequential application of hydrothiolation and hydrosilylation reactions. The advantages and limitations of this method for modifying multifunctional siloxanes are demonstrated. It has been established that this approach enables the targeted introduction of fragments of different natures into the polymer structure with good conversion.

Keywords functional polymers, modification, hydrothiolation, hydrosilylation

Introduction

The bottom-up approach in modern materials science involves the directed production of a polymer matrix with a strictly defined nature, architecture, and functionality. This allows for the predetermination of the material's desired properties at the synthesis stage[1]. The necessary components of this approach are deeply researched structure-property relationships and a wide range of synthetic methods that allow for flexible variation of the structure and distribution of functional groups in polymer substrates. Organosilicon chemistry is a very convenient platform for such research, as it can be used to create multifunctional compounds of various architectures. Different functional groups can combine both individual compounds (e.g., silanes [2], disiloxanes [3], stereoregular macrocycles [4]), and polymeric ones (e.g., siloxanes [5], nanogels [6], hyperbranched polymers [7]). It is most convenient to use vinyl- and hydride-silyl groups as the initial modifiable groups in such substrates. This is due to the fact that vinyl- and hydride-containing organochloro- and organoalkoxysilanes are large-scale products of the modern industry.

For example, methyldichlorosilane is one of the products of the direct synthesis of chlorosilanes [8], and vinylsilanes are obtained by hydrosilylation of alkynes [9] or the Grignard method [10]. The possibility of combining different functional groups within a single substrate leads to interest in developing synthetic approaches based on the sequential and selective performance of reactions with a single multifunctional substrate.

In [11] radical and nucleophilic hydrothiolation reactions were performed sequentially for the synthesis of carbosiloxane dendrimers. This turned out to be possible due to the high selectivity of these reactions toward conjugated and non-conjugated C-C double bonds. The multiple bond of acrylate reacted via a nucleophilic mechanism, whereas the double bond attached to silicon reacted via a radical one. The combination of Pierce-Rubinstein reactions with subsequent thiolation allows first for the creation of a nonpolar siloxane structure of a controlled shape, and then, using hydrothiolation, for the attachment of a polar fragment [12][13]. In this way, amphiphilic monomers with a strictly regulated siloxane nonpolar fragment can be obtained. A combination of Pierce-Rubinstein reactions and hydrosilylation has been used to synthesize comb-like polydimethylsiloxane polymers with a controlled architecture of side fragments [14] and dendrimers [15]. Another approach to producing high-molecular-weight hybrid polymers, based on the use of the different reactivity of double bonds in different environments, can be found in the works of the Drozdov group. They used sequential hydrosilylation and hydrothiolation to obtain organosilicon derivatives of limonene [16][17] and carvone [18]. Marchinets et al. also applied this reaction sequence

They performed an incomplete hydrosilylation of vinyl-functionalized polyhedral oligomeric silsesquioxane, followed by a hydrothiolation of the remaining double bonds on the same substrate [19]. Conducting different reactions on the same functional groups with incomplete conversion at the first stage is an approach that impresses with its simplicity; however, it has a limitation, namely, the inability to control the location of functional groups.

In our opinion, the most interesting approach is the one presented in [20], where the authors performed a hydrothiolation followed by a hydrosilylation of an organosilicon substrate containing Si-H and S-H functional groups. At the hydrothiolation stage, they attached aromatic fragments to regulate the refractive index, and at the hydrosilylation stage, crosslinked the resulting polymer with divinyl-disiloxane to obtain optical material.

Previously, we demonstrated the chemical stability of the Si-H group under the conditions of the hydrothiolation reaction [2] worked out the combined application of hydrothiolation and hydrosilylation reactions for low-molecular-weight and oligomeric substrates containing Si-H and Si-vinyl functional groups [3]. The purpose of this work is to apply this approach to the stepwise modification of a multifunctional PDMS containing Si-H and Si-vinyl groups.

Results and discussion

At the first stage, we obtained α,ω -vinyl-substituted polysiloxane with chain-distributed hydride groups (polymer **1**) and α,ω -hydride-substituted polysiloxane with chain-distributed vinyl groups (polymer **2**). The synthesis was carried out according to a well-known technique [22], using cationic copolymerization with the opening of siloxane cycles D₄ and D₄^H in the presence of

divinyltetramethyldisiloxane as a chain-growth terminator for polymer **1**, and the opening of D_4 and D_4^{Vin} in the presence of dihydrotetramethyldisiloxane for polymer **2** (**Figure 1**).

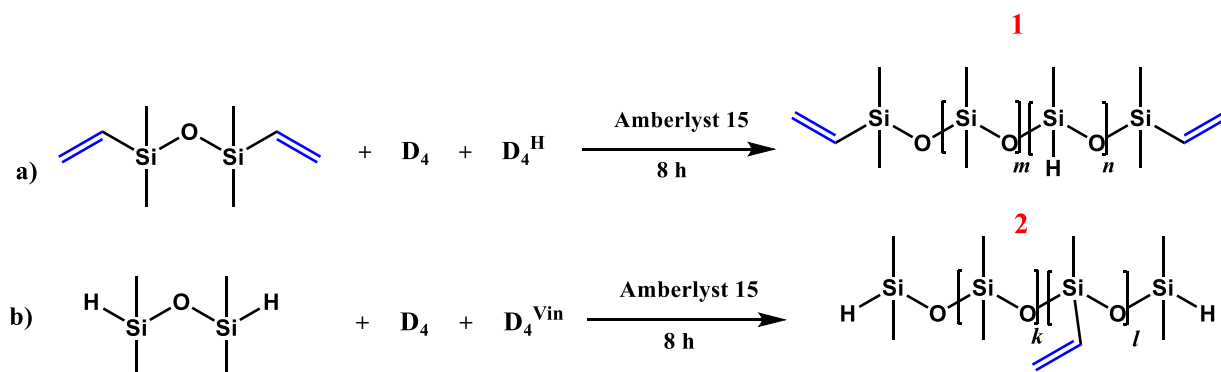


Figure 1. Scheme of synthesis of initial polymers **1** ($m = 22$; $n = 12$) and **2** ($k = 105$; $l = 31$)

As a result, polymer **1** (with chain-distributed hydride and terminal vinyl groups) and polymer **2** (with chain-distributed vinyl and terminal hydride groups) were obtained. The molecular weight characteristics are presented in **Table 1**.

Table 1. Molecular weight characteristics of the initial polymers **1** and **2**.

Polymer №	M_w (kDa)	M_n (kDa)	M_w/M_n
1	28,2	19,5	1,44
2	20,9	12,7	1,64

Hydrothiolation of polymers.

At the first stage of modification, we performed a hydrothiolation reaction on polymer **1** with terminal vinyl groups. The optimal reaction conditions depend on the nature of the thiol used. In the case of phenylthiol, the reaction proceeded under UV radiation without the use of photosensitizers and with an excess of 100–200% reagent. The activity of thiols depends on their substituents; electron-withdrawing substituents generally increase the activity of thiols in radical hydrothiolation reactions compared to alkyl thiols [23]. Consequently, under these conditions, there was practically no reaction with the less active mercaptopropyltrimethoxysilane. To achieve high conversion of the vinyl groups, initiation by photosensitizers or a thermal initiator (AIBN) must be used, along with a significant (300–400%) excess of thiol. The same principle holds true for the reaction with perfluorinated thiol (**Figure 2**).

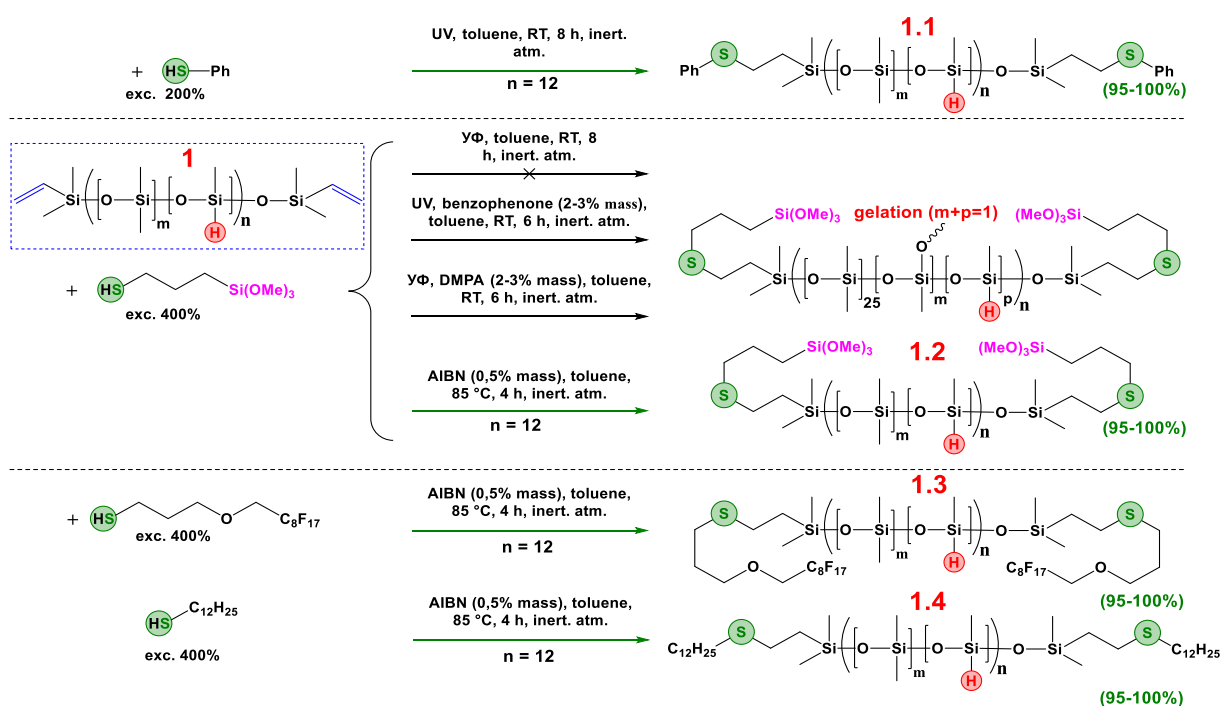


Figure 2. Scheme of modification of polymer **1** by hydrothiolation reaction with various thiols.

It should be noted that in the presence of photosensitizers (e.g., DMPA, benzophenone), a side reaction of hydrosilylation occurs, leading to the formation of insoluble polymer products. Thus, the most suitable conditions for using alkyl thiols are thermal initiation in the presence of AIBN (**Figure 3**).

Table 2. Molecular weight characteristics of polymers after the hydrothiolation reaction.

Polymer №	M _w (kDa)	M _n (kDa)	M _w /M _n
1.1	25,97	17,87	1,45
1.2	33,3	21,5	1,54
1.3	28,9	20	1,45
1.4	26,1	18,4	1,42

A comparison of the molecular weight characteristics of the obtained polymers and the initial one (**Table 2**) shows that the polydispersity index of the modified polymers did not change significantly during modification by the hydrothiolation reaction. This indicates an absence of side processes and the high selectivity of the reaction. The modification of polymer **2**, which has vinyl groups distributed along the chain, was carried out under the conditions selected for polymer **1** with dodecyl thiol; however, the reaction required a longer time to proceed (**Figure 3**).

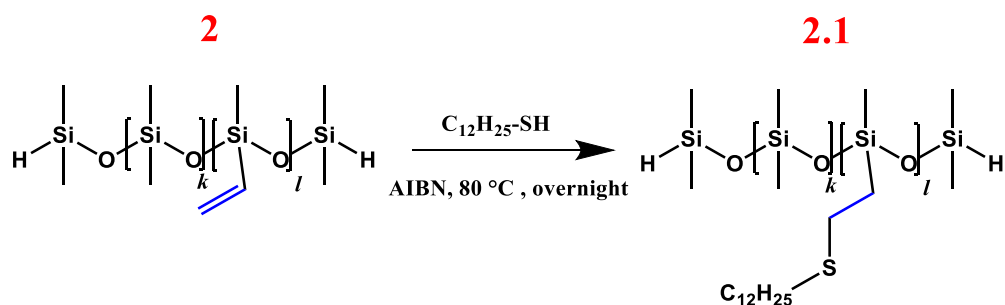


Figure 3. Scheme of modification of polymer **2** by hydrothiolation reaction with dodecylthiol.

An extremely important aspect of this approach is the thorough purification of hydrothiolation reaction products from residual thiols. The latter can completely deactivate organometallic catalysts, which is likely due to the formation of polymetallic complexes with bridging sulfide ligands [24]. Sulfur in organic sulfides is also capable of significantly reducing the catalytic activity of hydrosilylation catalysts or the yield of the desired product, often forcing researchers to change the catalyst's nature or increase its loading[25]. The quality of purification of the hydrothiolation product will determine the rate and necessary loading of the catalyst at the subsequent hydrosilylation stage. Evaporation of small amounts of thiols from the viscous medium of the first-stage products does not allow for achieving the required purity. The products were purified using multiple re-precipitations in a toluene-acetonitrile system (see SI).

Hydrosilylation of polymers.

The hydrosilylation of polymer **1**-based products obtained after the hydrothiolation reaction proceeds under approximately the same, rather mild conditions. The selected modifiers were allyl-trimethylsilyl ether, vinyltrimethoxysilane, a boron-containing organosilicon modifier with an ethylene glycol protecting group (obtained and described in [26] and [27]) and ethylene glycol.

Reactions were carried out with a molar ratio of modifiers equimolar to the number of Si-H groups in the polymer and with sufficient dilution of the reaction mass (5–10 wt.% in toluene). It should be noted that these conditions were chosen to evaluate the possibility of achieving high conversion (>90%) of Si-H groups at an equimolar ratio of reagents and low temperature. If necessary, the reaction can be intensified by using an excess of the modifier and increasing the temperature.

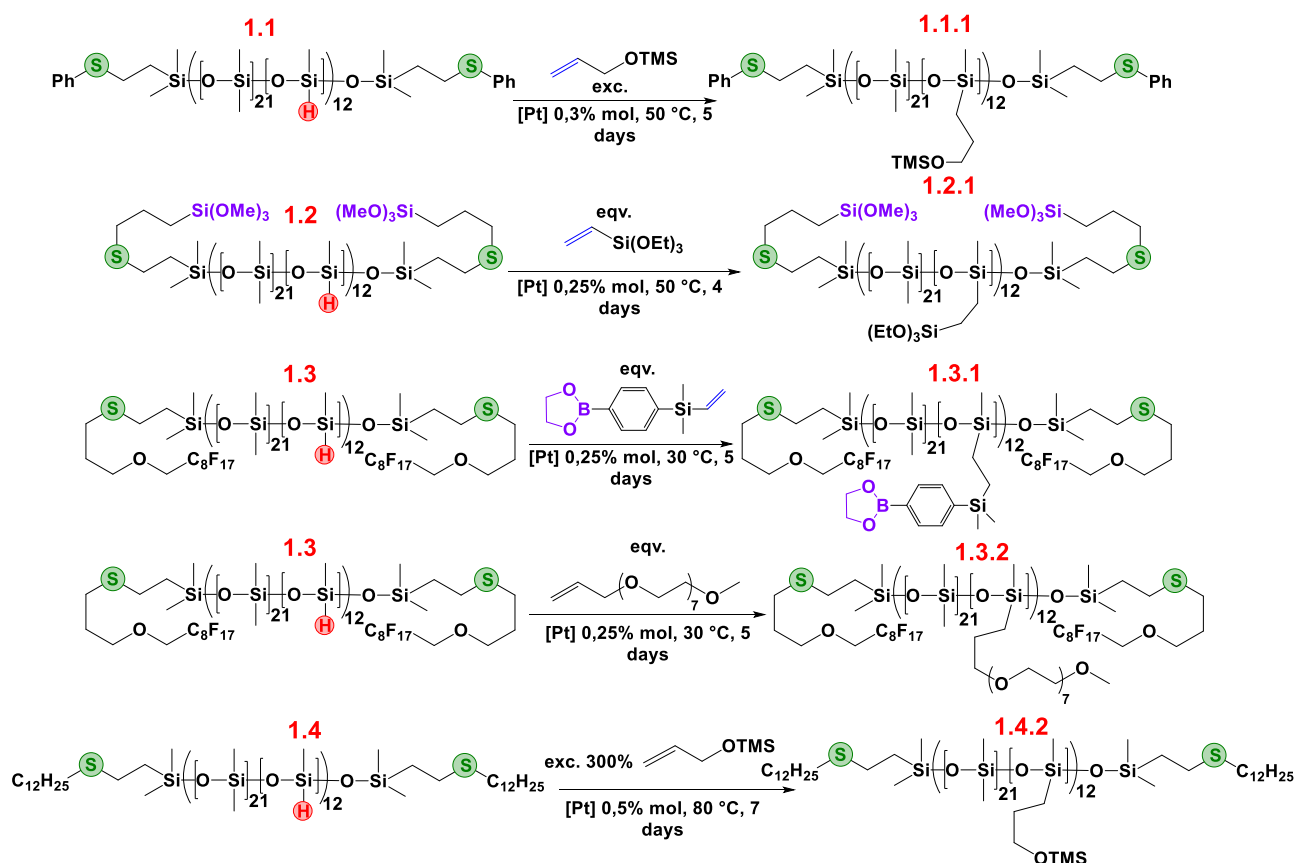


Figure 4. The scheme of modification of polymers by hydrosilylation reaction.

Thus, by sequential modification, we obtained siloxanes with different end and side substituents (**Figure 4**). The molecular weight characteristics of the polymers are presented in **Table 3**. As shown in **Table 3**, the PDI of the polymers increased slightly after the second stage of modification, which may indicate the occurrence of side processes or strong intermolecular interactions with the stationary phase of the column.

Table 3. Molecular weight characteristics of polymer 1-based products obtained by the hydrosilylation reaction and the conversion of Si-H groups.

Polymer	M_w (kDa)	M_n (kDa)	M_w/M_n	Si-H conversion (%), ^1H NMR
1.1.1	30,7	20,0	1,53	>95
1.1.2	33,2	20,5	1,62	>95
1.2.1	47,0	28,6	1,64	>95
1.3.2	46,6	27,7	1,68	>95
1.4.2	35,2	49,3	1,40	>95

All polymers were characterized by ^1H , ^{13}C , ^{19}F and ^{29}Si NMR spectroscopy as well as FTIR analysis (see SI). The degree of reaction was monitored by ^1H NMR (**Figure 4**) and FTIR (**Figure**

5); reactions were carried out until the signals corresponding to the Si-H groups had completely disappeared.

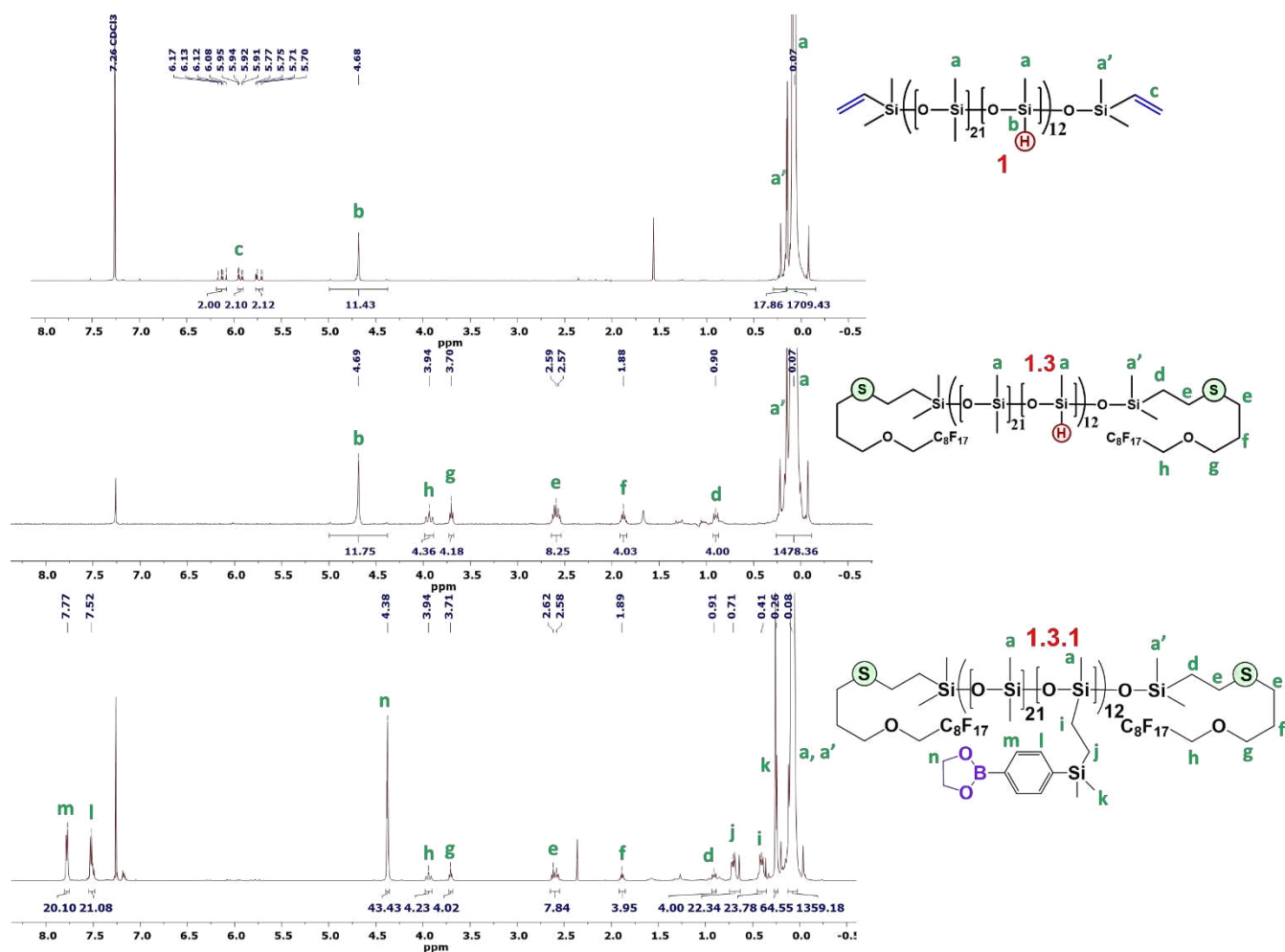


Figure 5. ^1H NMR spectra of one of the polymers at different stages of modification.

Analysis of ^1H NMR spectra (**Figure 5**) of polysiloxane after the hydrothiolation stage showed the disappearance of vinyl group signals (signal **c** in the range of 5.70–6.17 ppm), while maintaining the integral intensity of the Si-H group signal (signal **b**, 4.69 ppm). New methylene proton signals from the attached thiol also appeared (signals **d**, **e**, **f**, **g**, **h** at 0.90, 2.57–2.59, 1.88, 3.70, and 3.94 ppm, respectively). After the hydrosilylation stage, the disappearance of silicon-bound hydride groups was observed, along with the appearance of new proton signals: bridging methylenes (signals **i** and **j** at 0.41 and 0.71 ppm, respectively), protons of the boroxalane protecting group (signal **n**, 4.38 ppm), and phenyl groups (signals **l**, **m** at 7.52 and 7.77 ppm) in an amount similar to the calculated value. These results indicate a quantitative and selective process without adverse reactions.

The qualitative analysis of polymers was carried out using IR spectroscopy (**Figure 6**). The polymer spectrum after the hydrothiolation stage shows the appearance of an absorption band for the C-F bond (1217 cm^{-1}) and the preservation of the characteristic oscillation frequency of the Si-H bond (2157 cm^{-1}), which confirms the ^1H NMR results. Conversely, the IR spectrum of the

compound obtained after the hydrosilylation reaction is characterized by the presence of B-O bonds ($1341\text{--}1399\text{ cm}^{-1}$) and aromatic C-H bands ($802\text{--}860$ and 3062 cm^{-1}) and the absence of the Si-H band.

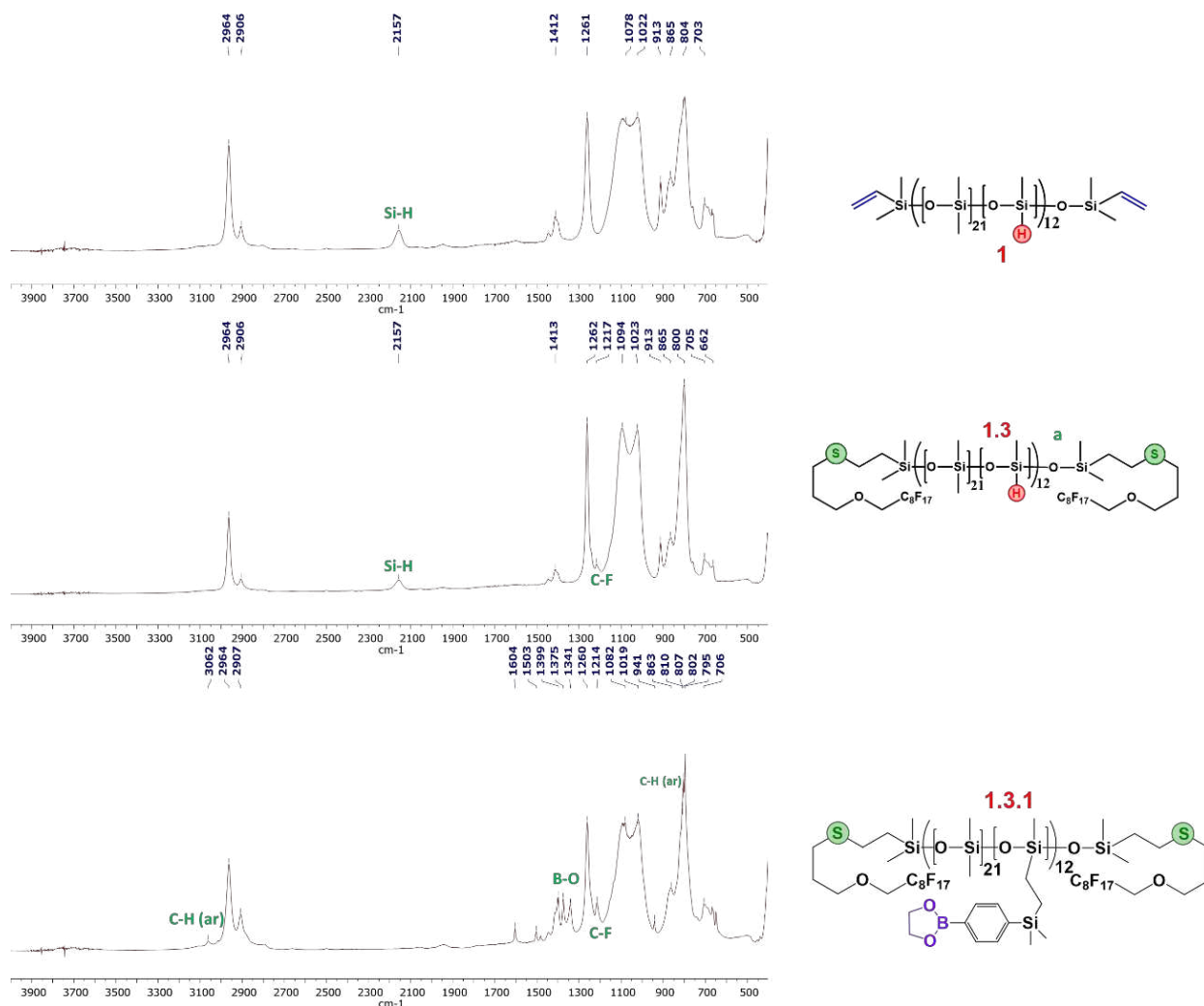


Figure 6. IR spectra of one of the polymers at different stages of modification.

Next, we investigated the hydrosilylation of vinyltriethoxysilane with a polymer containing terminal hydride groups and found that no reaction occurred over a wide range of modifier concentrations, temperatures, catalyst loadings, and process durations (**Figure 7**).

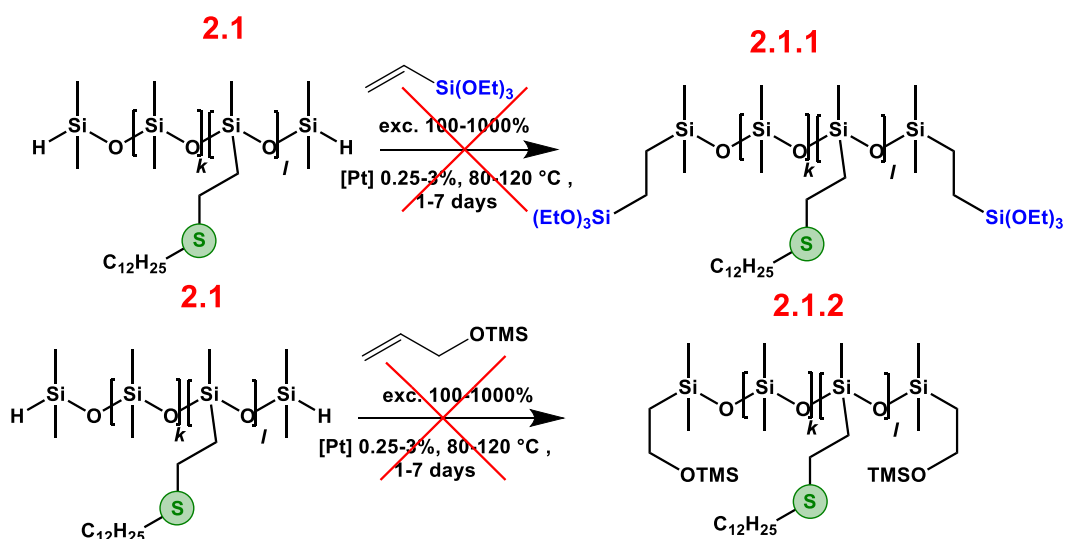


Figure 7. Scheme of modification of polymer **2** by hydrosilylation reaction with vinyltriethoxysilane and trimethylsilyl ether of allyl alcohol.

Analysis of the ^1H NMR spectrum of polymer **2** (**Figure 8**) after hydrothiolation with dodecyl thiol showed complete conversion of vinyl groups, evidenced by the disappearance of their signal in the 5.7–6.0 ppm region. The signal for terminal hydride groups at 4.7 ppm was retained. New signals corresponding to bridging methylene groups appeared at 0.88 and 1.38 ppm, as well as those related to alkyl chains at 0.88, 1.26, 1.57, 2.50, and 2.56 ppm.

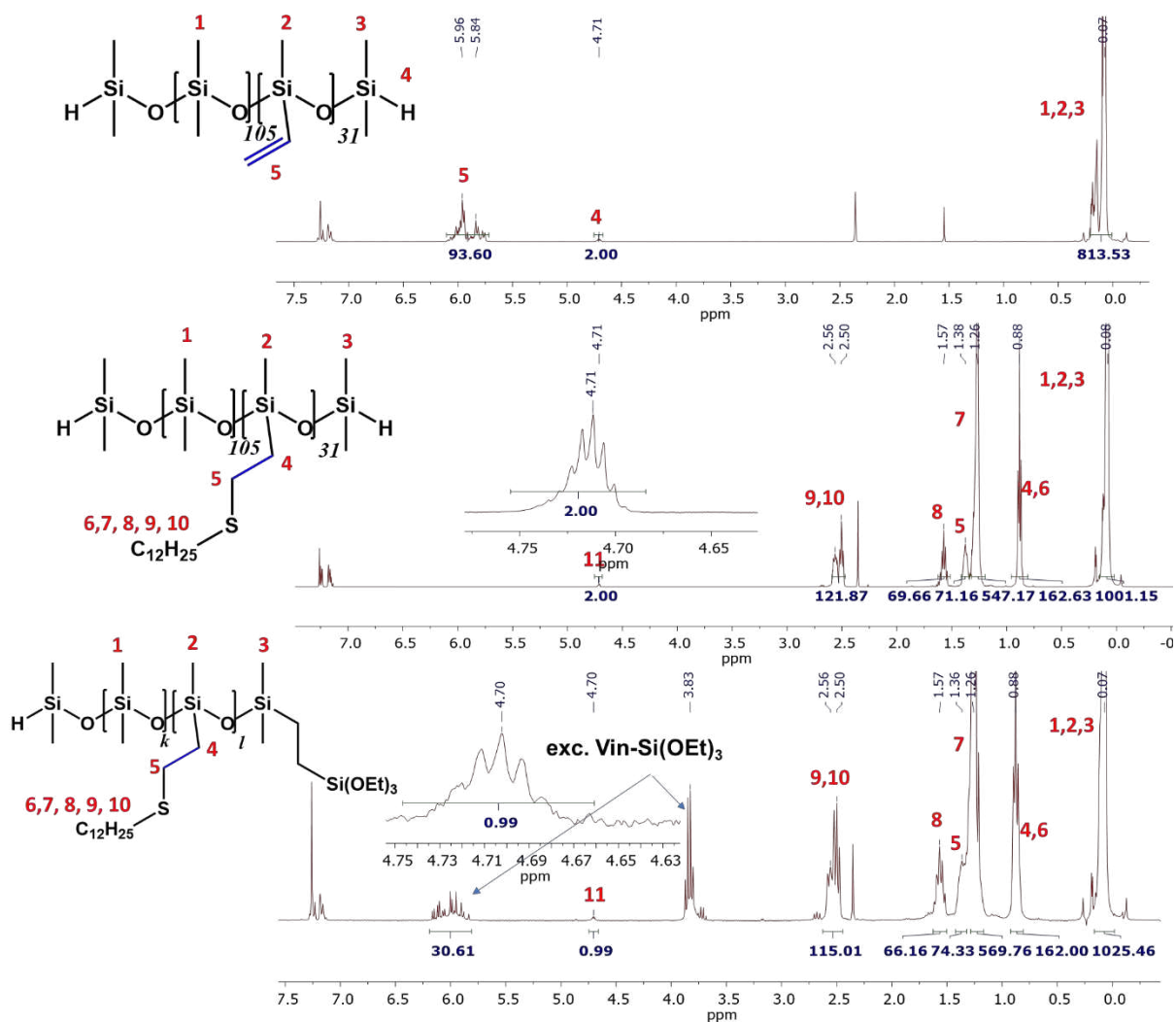


Figure 8. ^1H NMR spectra of polymer **2** at different stages of modification.

Analysis of the polymer spectrum after the hydrosilylation reaction showed that even with a large excess of vinyltriethoxysilane (1000 %), a high temperature of 120 °C, and a long reaction time (7 days), the reaction did not take place.

Thermal properties of the obtained polymers.

The thermal stability of all obtained samples based on polymer **1** was evaluated by thermogravimetric analysis (TGA) in air and argon atmospheres. The analysis was performed over a temperature range of 50-800 °C at a heating rate of 10 °C/min.

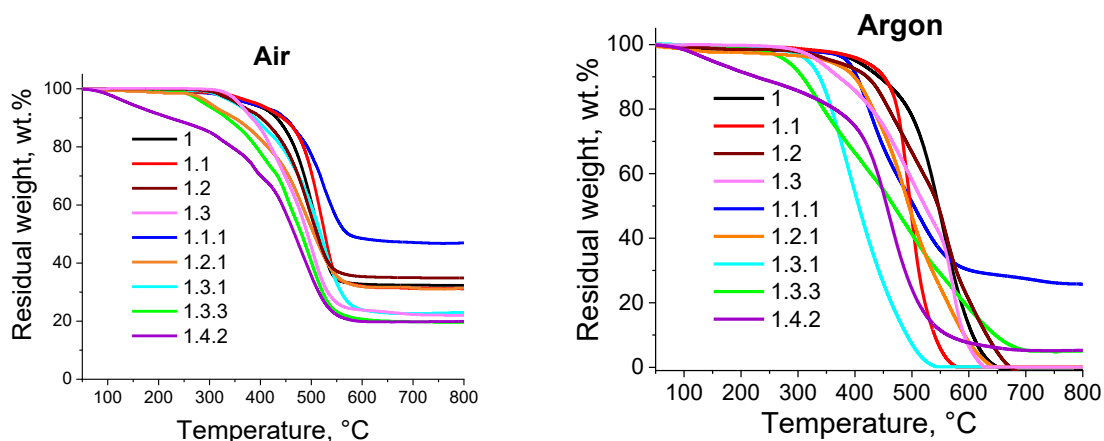


Figure 9. TGA curves of polymers obtained in air and argon.

The thermograms obtained are shown in **Figure 9**. For all samples, mass loss was observed in the temperature range of 290-392 °C (Air) and 281-413 °C (Ar). The general decomposition profile is comparable to that of linear PDMS. The products of the double bond addition reaction exhibit slightly lower thermal stability (355-359 °C) or remain close to that of the initial polymer **1** (379 °C). As can be seen, the addition of terminal groups does not significantly contribute to changes in the thermal properties of the polymers. In contrast, addition at the silicon atom makes

a visible contribution to these changes. These addition products reduce both the thermal and thermo-oxidative stability of the initial polymer 1 and polymers 2-9 (290-352 °C).

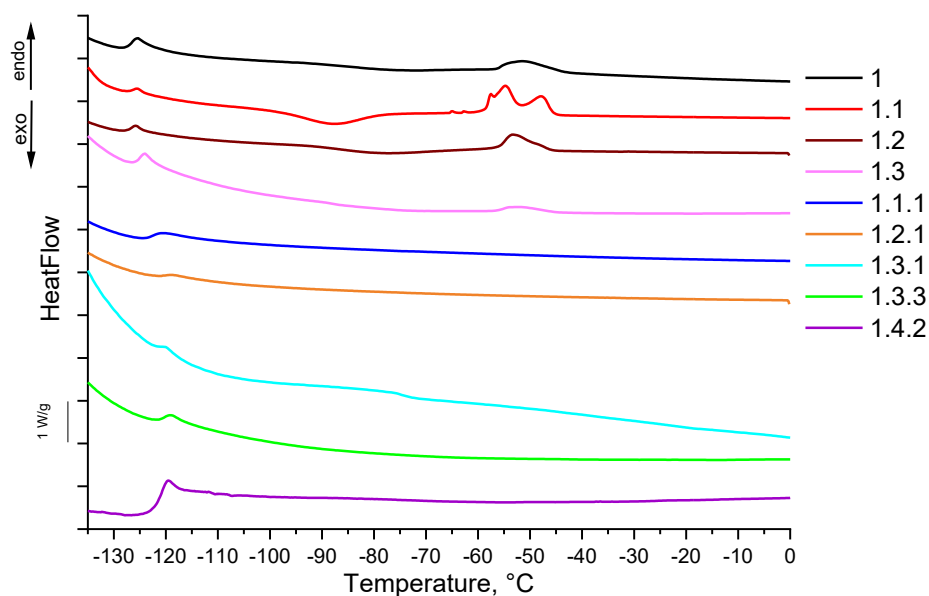


Figure 10. DSC of the obtained polymers.

The DSC analysis showed that all samples have a glass transition temperature (T_g) in the range of -117 to -129 °C, which is typical for linear PDMS. At the same time, samples that underwent both stages of modification exhibited suppressed crystallization ability (see **Table 4** and **Figure 10**). This is explained by the molar fraction of modified links being sufficient for such suppression (1/25 – 4 mol %) and is described in detail in the literature [28].

Table 4. Thermal properties of polymers 1-9.

№ of polymer	T_g (°C)	T_{cr} (°C)	T_m (°C)	ΔH_g (J/g)	ΔH_m (J/g)	$T_d^{5\%}$ (°C)		Residual weight after destruction, %	
						(Air)	(Ar)		
1	-127	-	-51	-	3.24	379	402	32	0
1.1	-129	-88	-55	28.05	27.23	392	413	31	0
1.2	-127	-92	-53	14.88	11.54	355	360	35	0
1.3	-125	-	-52	-	2.29	359	336	22	0
1.1.1	-122	-	-	-	-	380	386	47	26
1.2.1	-125	-	-	-	-	301	353	32	0
1.3.1	-120	-	-	-	-	352	318	23	0
1.3.3	-123	-	-	-	-	290	281	20	5
1.4.2	-122					142	148	20	5

Conclusion

In this paper, we demonstrate for the first time the possibility of modifying a siloxane copolymer containing Si-H and Si-vinyl groups using our previously developed technique for the sequential application of hydrothiolation and hydrosilylation reactions. This approach allows for the targeted and high-yield introduction into a polymer structure - containing hydride and terminal vinyl groups distributed along the chain - of fragments of various natures: perfluorinated alkyls, ethylene oxides, methoxysilyl, alcohol, phenylboronic acid derivatives, and phenyls. All aspects of the synthesis and isolation of target polymers and intermediates are described in detail.

The study of polymers by DSC showed that all samples have a glass transition temperature (T_g) in the range of -117 to -129 °C, which is typical for linear PDMS. At the same time, samples that underwent both stages of modification exhibited suppressed crystallization ability. A synthetic limitation of this approach is shown using an example of a polymer containing vinyl groups distributed along a chain and terminal hydride groups. The hydrothiolation reaction proceeds with quantitative conversion of the vinyl groups; however, the large number of sulfide groups formed along the siloxane chain inhibits the Karstedt catalyst, and the subsequent hydrosilylation reaction does not occur.

The developed approach is an effective tool for the targeted modification of siloxane polymers and opens up opportunities for obtaining new silicone materials.

Author Contributions Frank Inga, Krizhanovskiy Ilia, Tiulkin Andrey: Writing—original draft, Methodology, Investigation, Formal analysis, Data curation. Ratnikov Andrey: Methodology, Investigation. Manokhina Elizaveta: Supervision, Methodology. Anisimov Anton and Temnikov Maxim: Supervision, Funding acquisition, Conceptualization, Writing review & editing.

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Data Availability No datasets were generated or analyzed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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