



Functionalization of polyhydromethylsiloxane with nitrogen-containing organic compounds

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Abstract

Linear polyhydromethylsiloxane (PHMS) was functionalized with nitrogen-containing organic compounds: *N*-allylaniline (Naa), *N*-allylcyclohexylamine (Nach), *N*-allylpiperidine (Nap) and 4-vinylpyridine (4VP) via hydrosilylation reaction in the presence of Pt⁰ complex (Karstedt's catalyst) under mild conditions. Reaction course was followed by FTIR spectroscopy and final hydrosilylation products were characterized by FTIR, ¹H, ²⁹Si NMR and ²⁹Si MAS-NMR spectroscopies as well as by elemental analysis. Results showed that functionalization of PHMS with *N*-allyl amines took place but in none of the systems it was complete. Hydrosilylation of Naa, Nach and Nap with PHMS led both, to the β and α addition products. ²⁹Si NMR spectroscopy showed unequivocally that the reaction of PHMS with 4VP did not occur and the only reactions in the systems were hydrolysis of Si–H groups of PHMS followed by condensation of the silanol groups resulting in cross-linking of the polymer. All the functionalized polymers studied in the work contained reactive amine moieties prone to further modifications, therefore exhibit a great potential for various applications.

Keywords Polysiloxanes · Polyhydromethylsiloxane · Hydrosilylation of amines · Hydrosilylation of pyridine

Introduction

Polyhydromethylsiloxane (PHMS) is an organosilicon polymer in which silicon atoms are linked via oxygen atoms and to each silicon atom in the polymer chain one methyl group and one hydrogen atom are attached (general formula: [–CH₃(H)SiO–]_n). The chain is terminated on one end with a trimethylsilyl group ((CH₃)₃Si–), on the other – with a trimethylsiloxyl group ((CH₃)₃SiO–). PHMS is non-toxic, inexpensive and commercially available as a colorless, free flowing liquid differing in the molecular mass range (supplier dependent), soluble in many organic solvents and fairly stable in air and moisture [1].

Because of the presence of reactive Si–H side groups, PHMS as well as its copolymers containing dimethylsiloxane

units in the backbone (PHMS-DMS) are widely applied in various fields of chemistry. For example, PHMS served as a safe and inexpensive source of hydride ions in reduction reactions of aldehydes, ketones, esters, imines, etc. [2–5] thus being a valuable reactant in synthetic organic chemistry. PHMS and PHMS-DMS copolymers offer also the possibility to modify chemical structure of polysiloxanes. This fact has a profound influence on both, physical and chemical properties and hence on the applications of this important group of polymeric materials applied as coatings, sealants, greases, medicinal materials or, after cross-linking, as precursors for SiCO ceramics [6–8]. Hence, PHMS and PHMS-DMS copolymers are important compounds in polymer, particularly in siloxane polymer chemistry.

Polysiloxanes functionalized by groups originating from organic compounds, often called organofunctional polysiloxanes are frequently synthesized by hydrosilylation. This reaction involves addition of Si–H groups to multiple carbon–carbon or carbon-heteroatom bonds in the presence of a catalyst [9]. In the hydrosilylation of carbon–carbon double bonds, most suitable for the preparation of organofunctional siloxanes [10, 11], two platinum compounds: H₂PtCl₆ and Pt₂[CH₂=CHSi(CH₃)₂O]₃ (complex of Pt⁰ and 1,1,3,3-tetramethyl-1,3-divinyldisiloxane), frequently

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referred to as Speier's and Karstedt's catalysts, respectively, are very efficient and mainly used [12, 13]. Survey of the literature shows that there are many organic moieties which can be incorporated into polysiloxanes by hydrosilylation. The most important are: epoxy and other oxygen-containing groups (e.g. acrylic and methacrylic ester or acid and polyether moieties), fluoroalkyl and other fluorine-containing groups as well as moieties originating from amines and other nitrogen-containing organic compounds [11].

Introduction of nitrogen-containing organic side groups to polysiloxanes results in the materials that show particularly attractive chemical and/or physical properties. Thus, presence of the nonbonding electron pairs on nitrogen atoms in amine groups allows for the formation of coordinate bonds. Therefore polysiloxanes functionalized by amine group-containing moieties can act as ligands for metal ions or particles and can be used, e.g. for extraction of toxic metal ions from waste water [14], as chemical membrane sensors for Fe^{3+} ions detection in water [15], as supports for metallic catalysts [16, 17] or as stabilizers for metal nanoparticles [18]. After transformation into quaternary ammonium salts (QAS) they exhibit antimicrobial properties [19]. Similarly, polysiloxanes modified by other nitrogen-containing organic moieties, e.g. imidazolyl or triazolyl groups, can be applied as carriers for metallic catalysts [20, 21]; the latter, in their salt forms, show biocidal activity [22].

Modification of polysiloxanes with aromatic *N*-containing heterocyclic organic moieties having specific electronic structure and hence interesting optical properties leads to the materials suitable for use in various optical devices [23, 24]. Polysiloxanes with introduced carbazolyl side groups, because of the influence of these moieties on the refractive index values and thermo-optical coefficient of the materials can exhibit tunable optical properties [25, 26]. Moreover, polysiloxanes functionalized by the carbazolyl and indolyl moieties were found to be good materials for photorefractive [27, 28] or nonlinear optical [29] applications. Among other nitrogen-containing organic side groups that were used to modify polysiloxanes providing them with interesting thermo-optical properties, phthalocyanine [30] can also be mentioned.

Importantly, direct hydrosilylation of amines and other *N*-containing organic compounds is associated with certain restrictions. Reactions with unsaturated amines in the presence of Pt catalyst may be accompanied by the undesired side processes that result in polymer cross-linking due to the reaction between Si–H and N–H groups [12] or catalyst poisoning [13]. Inhibiting effect of amines and aminated polymers on Speier's catalyst has been documented [31]. On the other hand, amines are known as additives that act as promoters for Pt hydrosilylation catalysts [13].

In the literature there are, however, also reports on successful hydrosilylation of amines by polymers with Si–H

groups in their structure. Kanjilal et al. [32] reported the reaction of PHMS with various amounts of *N*-allylcyclohexylamine, in the presence of H_2PtCl_6 as a catalyst (toluene, 70 °C). Using cyclohexylamine-functionalized polymers, membranes on porous polyethylene supports were fabricated and applied for pervaporative enrichment of 1,3-propanediol from binary aqueous mixtures. Guerra-Contreras et al. [33] and Lei et al. [19] hydrosilylated *N,N*-dimethylallylamine (DMAA), i.e. a tertiary amine, with PHMS-DMS in the presence of Karstedt's catalyst (anhydrous toluene, 90–100 °C) which afforded amine-substituted polysiloxanes. Then Lei et al. [19] introduced PDMS blocks at both termini of the modified copolymer to obtain PDMS/amine-modified PHMS-DMS/PDMS triblock copolymer. In both studies, the synthesized polysiloxanes with amine groups were converted to the QAS by treatment with 1-iodooctane [33] or benzyl chloride [19]. The prepared salts showed good solubility in polar organic solvents, such as ethanol [33] and high antibacterial activity [19]. Chen et al. [34, 35] reported successful hydrosilylation of 4-vinylpyridine (4VP) with PHMS-DMS copolymer using Karstedt's catalyst (toluene, 110 °C). Antibacterial polysiloxanes with pyridinium pendants were obtained by subsequent *N*-alkylation of pyridine ring with 1-bromohexane [34] or 6-perfluorooctyl-1-bromohexane [35].

It should be noted that, up to our knowledge, in the literature there are no systematic studies on modification of siloxanes or polysiloxanes by hydrosilylation of various nitrogen-containing unsaturated organic compounds in the presence of Pt catalysts. Therefore we decided to conduct systematic investigations in which unsaturated *N*-containing compounds were hydrosilylated by a low-molecular-weight siloxane and a polysiloxane with Si–H groups in their structures, i.e. 1, 1, 3, 3-tetramethyldisiloxane (M_2^{H}) and PHMS, respectively. This work is a part of the larger scope of research conducted by our group aimed at evaluating feasibility of performing hydrosilylation of *N*-containing compounds in the presence of a Pt catalyst. It is a continuation of our earlier studies on the hydrosilylation of selected *N*-allyl compounds: *N*-allylaniline (Naa), *N*-allylcyclohexylamine (Nach), *N*-allylpiperidine (Nap) and vinyl nitrogen-containing compounds: 4-vinylpyridine (4VP), 2-vinylpyridine (2VP) by M_2^{H} catalyzed by Karstedt's catalyst [36]. In the present work, hydrosilylation of these *N*-containing compounds (except for 2VP) by PHMS is reported. The reactions with *N*-allyl amines were conducted using Karstedt's catalyst under mild conditions – in toluene at 60 °C, while in the case of 4VP, the reaction conditions were modified (with or without toluene, 110 °C).

The main aim of the work was to study functionalization of PHMS via hydrosilylation reaction with unsaturated *N*-containing compounds in the presence of Karstedt's catalyst. We performed the reactions with the polymer in an

analogous manner like in the case of M_2^H to find out the differences in both, the reaction course and products. We were interested in reactivity of *N*-allyl and vinyl compounds towards the polymer-in checking whether PHMS functionalization occurs in all of the systems, and in regioselectivity of the reactions, i.e. whether both types of regioisomeric linkages (α -according to Markovnikov's rule and β -anti-Markovnikov's rule) are formed, or only one of them. Additionally, comparison of the reactions of the selected *N*-containing compounds with PHMS and the previously studied M_2^H was of interest because it allowed drawing conclusions on the influence on the length of the hydrosiloxane molecule on the result of the process. Such comparison was particularly important in the case of 4VP since our studies showed that it does not react with M_2^H [36], whereas-as already mentioned-there are reports on its successful hydrosilylation with a high-molecular-weight compound, PHMS-DMS copolymer, catalyzed by Karstedt's catalyst [34, 35].

Experimental

Materials

PHMS (viscosity: 35–45 cSt, average molecular weight determined by ^{29}Si NMR spectrum of PHMS solution in CDCl_3 : 3800 g/mol) was purchased from ABCR (Germany) and vacuum-dried (pressure: $\sim 10^{-2}$ mbar) at 60 °C for 2 h before use. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) was supplied by Sigma-Aldrich (Poland) as the solution in xylene (2 wt.% of Pt) and used in the work without purification. 4VP, Naa and Nach were purchased from Sigma-Aldrich (Poland) and purified by vacuum distillation before use. Nap was synthesized using the procedure presented in Ref. [36]. Toluene was supplied by Avantor (Poland) and was distilled from sodium-benzophenone prior to use. Piperidine, sodium hydride 60% mixture in mineral oil and allyl bromide applied in the preparation of Nap, were purchased from ABCR (Germany), Sigma-Aldrich (Poland) and Avantor (Poland), respectively and used in the work without purification. Diethyl ether was purchased from Avantor (Poland) and, before use, dried using benzophenone and sodium, and then distilled under Ar.

Functionalization of PHMS with nitrogen-containing *N*-allyl compounds

PHMS was functionalized with *N*-allyl compounds by hydrosilylation performed in the presence of Karstedt's catalyst. Molar ratio of Si–H groups from the polymer to $\text{CH}_2=\text{CH}-\text{CH}_2$ -groups from the nitrogen-containing compound equal to 1:1.5 and 1:0.5 were applied.

In a typical run, 2.0 g (0.00089 mol; 0.032 mol of Si–H groups) of PHMS (previously dried on a vacuum line), the measured amount of selected *N*-allyl compound (Naa, Nach or Nap), toluene (4.0 ml) and Karstedt's catalyst solution ($0.17 \cdot 10^{-6}$ mol of Pt) were successively placed in the flowing Ar atmosphere in a Schlenk flask. Then the flask was closed, put in an oil bath, and its content, under magnetic stirring, heated to 60 °C. The reaction was carried out at this temperature for 48 h. FTIR spectra of the initial reaction mixture as well as the samples withdrawn after 24 and 48 h of the process were recorded to monitor the disappearance of the Si–H groups from the systems.

In the reactions carried out at Si–H: $\text{CH}_2=\text{CH}-\text{CH}_2$ -groups molar ratio equal to 1:1.5, 6.51 ml of Naa, 6.95 ml of Nach and 7.05 ml of Nap (0.048 mol) were applied. For the ratio 1:0.5 the amounts of *N*-allyl compounds were as follows: 2.17 ml of Naa, 2.32 ml of Nach and 2.35 ml of Nap (0.016 mol).

After the reactions, when liquid products were obtained, toluene was removed by rotary evaporation; then the remaining mixtures were dried on a vacuum line at 60 °C to distill off the unreacted *N*-containing compound. This method was sufficient to separate PHMS functionalized by Naa and Nach at the Si–H: $\text{CH}_2=\text{CH}-\text{CH}_2$ - group's molar ratio equal to 1:1.5 and Nap at both molar ratios. In the case of solid samples, i. e. PHMS treated with Naa and Nach at the molar ratio equal to 1:0.5, another procedure of purification was applied. Materials were washed few times with anhydrous toluene on a Büchner funnel in order to remove all unreacted *N*-containing compound from the sample. The presence of unreacted organic compounds in the collected filtrates was detected using gas chromatography (GC). Then the obtained products were dried on a vacuum line at 60 °C.

In the following parts of the paper, the symbols: PHMS_Naa_1.5, PHMS_Nach_1.5, PHMS_Nap_1.5 and PHMS_Naa_0.5, PHMS_Nach_0.5, PHMS_Nap_0.5 will be used to denote PHMS functionalized with the appropriate *N*-allylamine at the Si–H: $\text{CH}_2=\text{CH}-\text{CH}_2$ - groups molar ratios equal to 1:1.5 and 1:0.5, respectively.

Functionalization of PHMS with 4-vinylpyridine

Functionalization of PHMS with 4-vinylpyridine (4VP) was performed in an analogous manner to functionalization of the polymer with *N*-allyl compounds described in the previous section introducing, however, some modifications. The reactions were performed with and without solvent (toluene) and applying four different Si–H: $\text{CH}_2=\text{CH}-$ groups molar ratios equal to 1:1.5; 1:1; 1:0.5 or 1:0.25 using 5.20 ml (0.048 mol), 3.36 ml (0.032 mol), 1.73 ml (0.016 mol) or 0.84 ml (0.008 mol) of 4VP per 2 g of PHMS, respectively.

The reactions were carried out in an argon atmosphere at 110 °C for 48 h. FTIR spectra of the initial reaction mixture as well as the samples withdrawn after 24 and 48 h of the process served as the basis for establishing the disappearance of the Si–H groups from the systems. The obtained products (all of the samples were insoluble solids) were subjected to extraction using dry toluene in a Soxhlet apparatus for 24 h in order to remove the unreacted 4VP and then dried on a vacuum line at 60 °C.

The PHMS samples functionalized with 4VP at Si–H:CH₂=CH- groups molar ratios equal to 1:1.5; 1:1; 1:0.5 and 1:0.25 will be referred to as: PHMS_4VP_1.5, PHMS_4VP_1, PHMS_4VP_0.5 and PHMS_4VP_0.25, respectively.

Characterization methods

¹H NMR and ²⁹Si NMR spectra were recorded on a Bruker Avance III HD (400 MHz) Spectrometer, using CDCl₃ (δ = 7.26 ppm) as solvent. Fourier transform infrared (FTIR) spectra were recorded on a FTIR (BIO-RAD Excalibur) spectrometer, equipped with a horizontal zinc selenide (ZnSe) ATR sampling accessory. Spectra were obtained after collecting 32 scans in the 4000 to 550 cm⁻¹ range; incident beam angle was equal to 45°. Elemental analyses were taken on a Vario El III analyzer (Elementar Analysensysteme GmbH) after combustion of the analyzed sample in oxygen at 1150 °C. Contents of C, H, N in the samples reported in the work are the average values of two analyses. The contents of Si and O in the samples were calculated as the difference: 100% - ΣC,H,N. Gas chromatographic analyses were performed on a Shimadzu GC2010 chromatograph equipped with thermal conductivity detector (TCD) and Zebron ZB-1 capillary column (diameter 0.25 mm, length

30 m, liquid phase: polydimethylsiloxane) using helium as a carrier gas. The following temperature program was used in chromatographic analyses of the unreacted *N*-allyl compounds: detector temperature 250 °C, sample evaporation temperature 250 °C, working column temperature-initial 60 °C maintained for 3 min, then increased to 240 °C at the rate of 18 °C/min.

High resolution, solid state ²⁹Si MAS-NMR spectra were measured on a Tecmag APOLLO pulse NMR spectrometer at the magnetic field of 7.05 T generated by the Magnex wide bore superconducting magnet. A Bruker HP-WB high-speed MAS probe equipped with the 4 mm zirconia rotor and KEL-F cap was used to record the MAS spectra at the spinning speed of 4 kHz. The spectra were measured at 59.515 MHz, using a single 3 μs radio-frequency (rf) pulse, corresponding to π/2 flipping angle. The acquisition delay used in accumulation was 30 s, and 128–384 scans were acquired, depending on the signal strength. The spectra were normalized to the same mass and number of accumulations. The frequency scale in ppm was referenced to the ²⁹Si resonance of tetramethylsilane (TMS).

Results and discussion

In the work, hydrosilylation of carbon–carbon double bonds present in allyl groups of Naa, Nach and Nap as well as those occurring in vinyl group of 4VP with PHMS using Karstedt's catalyst was carried out. Conducted reactions are schematically depicted in Fig. 1. The scheme shows that as a result of the addition reaction both regioisomeric linkages, α (according to Markovnikov's rule) and β (anti-Markovnikov's rule), can be formed in the polymer molecule. In many hydrosilylation processes, however, the β addition prevails [12]. The purpose of the experiments was to check whether

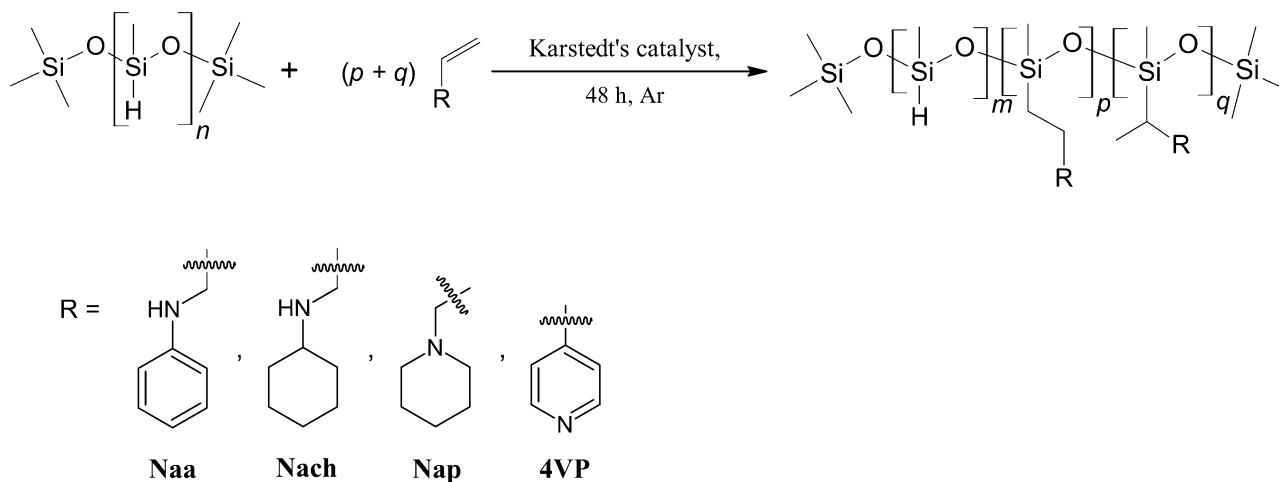


Fig. 1 Scheme of reactions of PHMS with the studied nitrogen-containing organic compounds

PHMS functionalization occurs in each of the systems and whether both types of linkages (α and β) are formed during the reaction, or only one of them.

Results of the investigations, separately for *N*-allyl compounds and 4VP, will be discussed in the following sections.

Functionalization of PHMS with *N*-allyl compounds

During the functionalization of PHMS with *N*-allyl compounds, the reaction progress was monitored by FTIR spectroscopy, analyzing the spectra of the initial reaction mixture, the sample withdrawn after 24 h of the process as well as the final reaction mixture (48 h of the process, Experimental Section).

FTIR spectra of all reaction mixtures show gradual lowering in the intensities of the bands corresponding to the Si–H groups, thus marking the progress of PHMS modification processes. This is illustrated by Fig. 2 in which the decrease in intensity of the band assigned to the stretching vibrations of the Si–H groups [37] at $\sim 2160\text{ cm}^{-1}$ in the spectra recorded during modification of PHMS with Nap is presented.

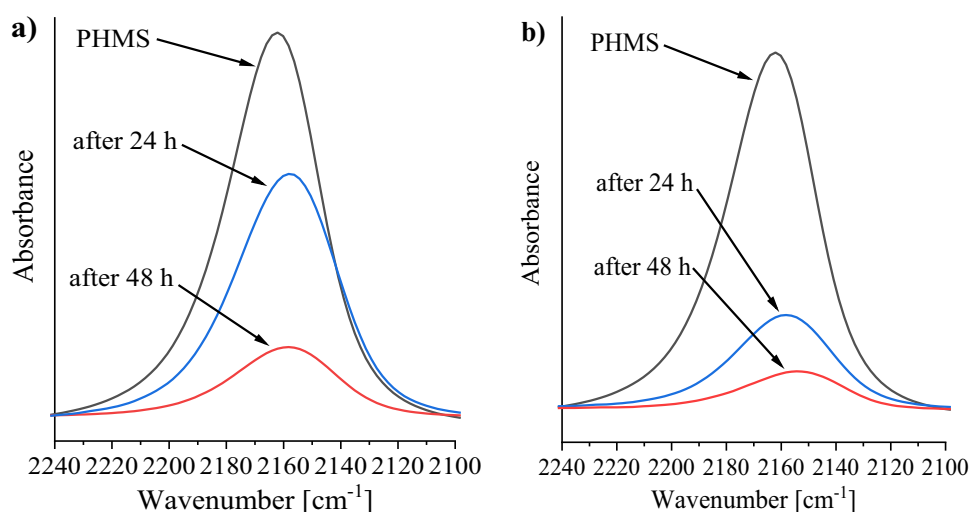
In none of the studied systems the disappearance of the band attributed to Si–H groups was complete, which indicates only partial functionalization of the polymer. This is understood in case of the reactions in which excessive amounts of Si–H groups with respect to allyl groups were applied (Si–H:CH₂=CH–CH₂– ratio equal to 1:0.5). In the reactions with the excess of allyl moieties (Si–H:CH₂=CH–CH₂– ratio equal to 1:1.5) preservation of some Si–H groups must have been due to steric limitations.

Comparing the ratios of integral intensities of Si–H (at $\sim 2160\text{ cm}^{-1}$) and Si–CH₃ (at $\sim 1250\text{ cm}^{-1}$) bands in

the FTIR spectra of PHMS and final reaction mixtures, the final conversion degrees of the Si–H groups were estimated (as described in Ref. [38, 39]). They were equal to: 84.7% (PHMS_Naa_1.5), 62.8% (PHMS_Naa_0.5), 61.2% (PHMS_Nach_1.5), 46.5% (PHMS_Nach_0.5), 93.6% (PHMS_Nap_1.5), 59.9% (PHMS_Nap_0.5). Higher conversion degrees of the Si–H groups were found in all systems with the molar ratio of Si–H:CH₂=CH–CH₂– groups equal to 1:1.5 which suggests that the excess of *N*-allyl compound relative to the polymer allows achieving higher degrees of functionalization.

Additionally, it can be noticed that the conversion of Si–H groups determined on the basis of FTIR spectra in the reactions conducted with the excess of Naa and Nach is lower than in the respective systems in which M₂^H was the reagent (M₂^H/Naa–Si–H groups conversion rate = 98.6%, M₂^H/Nach–Si–H groups conversion rate = 97.0%, Ref. [36]). This can be explained by differences in molecular structure of PHMS and M₂^H: in the polymer chain the Si–H groups are adjacent and the reaction of *N*-allyl compounds with all Si–H groups is difficult. Linkages formed between silicon atoms in the polymer chain and carbon atoms from *N*-allyl compounds cause steric hindrance which limits the amount of organic moieties introduced into the system. This restriction does not occur in the case of M₂^H, where Si–H groups are located at the ends of the molecule. Moreover, the influence of the chain length on the reaction course can be considered. The polymer, whose chains are considerably longer than those of M₂^H, is a more viscous liquid than M₂^H. During functionalization, due to the increase in the molecular weight of the products with respect to those of the starting compounds, viscosity of the reaction medium grows. It must be higher in the reactions of PHMS than in those of M₂^H because of longer polymer chains and higher molecular weight of macromolecules with incorporated moieties of *N*-allyl amines as compared to the molecules of functionalized M₂^H. Although

Fig. 2 FTIR spectra showing the decrease of the Si–H stretching vibrational band during preparation of **a** PHMS_Nap_0.5 sample and **b** PHMS_Nap_1.5 sample



this problem has not been studied in the work (viscosity or diffusion rates were not measured), it can be supposed that increased viscosity results in slower rate of reactants' diffusion in the systems and this may lead to lower conversion of Si-H groups present in the polymer than those existing in M_2^H . Similar effect would be observed if PHMS contained a significant fraction of high-molecular-weight macromolecules. In practice, however, this seems unlikely owing to the known difficulties with the synthesis of PHMS showing high molecular weight.

Higher conversion degrees of Si-H groups in PHMS_Naa than in the corresponding PHMS_Nach systems prove in turn that the presence of a rigid and planar aromatic ring in the Naa molecule is beneficial for the functionalization of the polymer. M_2^H functionalization studies using Naa led to similar conclusion [36].

The highest conversion degrees of the Si-H groups in the PHMS_Nap_1.5 system in comparison with PHMS_Naa_1.5 and PHMS_Nach_1.5, as well as small differences in conversion degrees of the Si-H groups in the reactions of M_2^H and PHMS with the excess of Nap (M_2^H /Nap – conversion degree of the Si-H groups = 91.1%, Ref. [36]) indicate that the molecular structure of Nap – despite the non-planar, flexible aliphatic ring [40, 41] – does not constitute a significant obstacle for polymer functionalization.

All samples obtained by the reactions of PHMS with the excess of Naa, Nach and Nap (PHMS_Naa_1.5, PHMS_Nach_1.5 and PHMS_Nap_1.5) were liquid. Reactions of PHMS using deficient amount of an amine with respect to PHMS led to the formation of brittle and insoluble solids in case of Naa and Nach (PHMS_Naa_0.5 and PHMS_Nach_0.5) and to a liquid sample which solidified after storage for some time in air in case of Nap (PHMS_Nap_0.5). Only samples functionalized with Nach were colorless, the other ones were yellow.

Formation of liquid products was expected because PHMS is liquid and the *N*-allyl compounds used in the work for its modification contained only one reactive, allyl group in the molecules and could not act as PHMS cross-linking agents. Formation of solid, insoluble products during the reaction of PHMS with Naa and Nach at the molar ratio of Si-H:CH₂=CH-CH₂- groups equal to 1:0.5 proves, however, that hydrosilylation in these systems was accompanied by side processes that resulted in polymer cross-linking. Most probably, it was caused by condensation of silanol groups (Si-OH), resulting from hydrolysis of a fraction out of a large number of Si-H groups present in PHMS. Functionalization was carried out in an argon atmosphere (Experimental Section), but it cannot be excluded that during the 48-h process air got into the reaction flasks and water contained in it caused hydrolysis of some Si-H groups. The transformation of the initially liquid PHMS_Nap_0.5 sample after storage confirms the cross-linking of the polymer

in the air atmosphere. The fact that a solid sample was not formed in this case immediately after the reaction shows that hydrolysis of Si-H groups in PHMS_Nap_0.5 was slower than in PHMS_Naa_0.5 and PHMS_Nach_0.5 systems.

FTIR spectra of the final, purified products confirm that the reactions between PHMS and *N*-allyl compounds do occur but are not complete. In the spectra of all the studied samples (Fig. 3) the band at 2158 cm⁻¹ due to the unreacted Si-H groups is clearly visible. This band is more intensive in the spectra of the samples obtained with excessive amounts of Si-H groups with respect to allyl ones (Si-H:CH₂=CH-CH₂- equal to 1:0.5). Lower conversion degrees of Si-H groups, and therefore their higher content in the final samples obtained at the ratio to 1:0.5, were found, as already mentioned, on the basis of quantitative analysis of the spectra of the final reaction mixtures.

All the spectra contain also characteristic bands for siloxane fragments originating from: asymmetric stretching vibrations of Si-O-Si groups (1130–1000 cm⁻¹) as well as from C-H bond in Si-CH₃ groups vibrations: symmetric (1259 cm⁻¹) and asymmetric (1410 cm⁻¹) bending and symmetric (2927 cm⁻¹) and asymmetric (2962 cm⁻¹) stretching [37, 38, 42]. Besides the bands characteristic for the siloxane part of the molecule, in the FTIR spectra, the bands

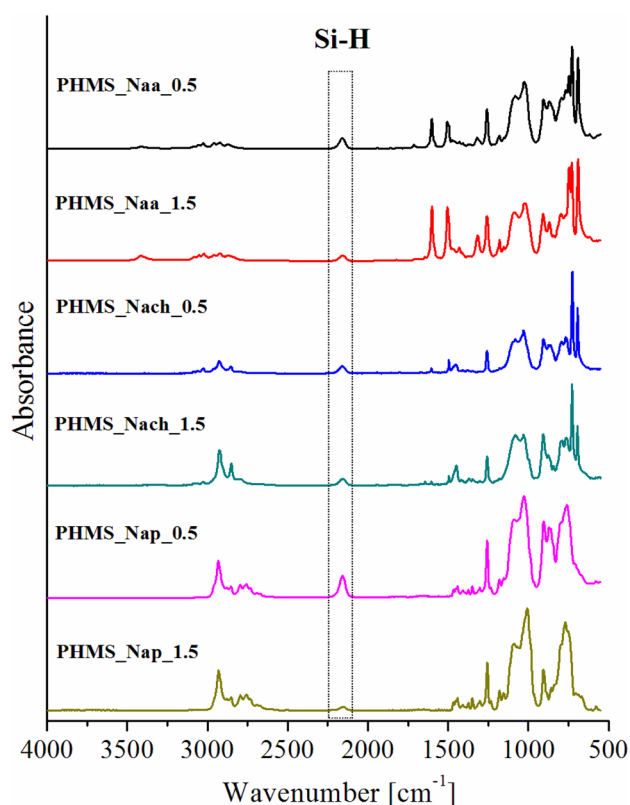


Fig. 3 FTIR spectra of the final, purified products of PHMS modification by *N*-allyl compounds

characteristic for nitrogen-containing compounds used for PHMS functionalization can be distinguished. The spectra of PHMS_Naa_1.5 and PHMS_Naa_0.5 contain the bands at 3024 cm^{-1} and 1505 cm^{-1} due to C-H and C=C stretching vibrations of aromatic ring, respectively and also the bands at 3414 cm^{-1} and 1602 cm^{-1} . The former can be unambiguously ascribed to N-H stretching vibrations [37], whereas the band at 1602 cm^{-1} is probably the superposition of a weak band due to C=C stretching vibrations of the aromatic ring and an intense band ascribed to N-H deformation vibrations [37]. Due to differences in their intensities, the latter band should be the predominant component in this spectral region. The weak band at 1180 cm^{-1} which is visible in the spectra of all samples, can be ascribed to C-N bond stretching vibrations in N-containing side groups in the final PHMS functionalization products [37].

Additionally, FTIR spectra of all the studied samples show the band at 2852 cm^{-1} attributed to $-\text{CH}_2-$ groups. The assignment of this band in the spectra is ambiguous. It may come from vibrations of C-H bonds in propylene bridges ($-\text{CH}_2\text{CH}_2\text{CH}_2-$) at silicon atoms resulting from hydrosilylation. In the spectra of PHMS functionalized by units originating from Nach or Nap, however, this band should be

considered as a combination of the bands originating from $\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}_2-$ groups present in the Nach and Nap rings (Fig. 1). In addition, possible existence of the unreacted *N*-allyl compounds in the final samples after purification step (Experimental Section) may be also the reason for the appearance of the band due to $-\text{CH}_2-$ groups in the spectra. Therefore, in the case of hydrosilylation of *N*-allyl compounds with PHMS, it was necessary to perform NMR spectroscopy investigations to corroborate unambiguously formation of polymer functionalization products.

Analysis of the ^1H NMR spectra of PHMS_Naa_1.5 (Fig. 4), PHMS_Nach_1.5 (Fig. 5), PHMS_Nap_1.5 and PHMS_Nap_0.5 materials (Fig. 6) corroborated that the reactions between PHMS and *N*-allyl compounds do occur. The proton signals seen in the spectra were assigned based on the experimental and simulated ^1H NMR spectra of the analogous modified disiloxane, M_2^{H} described in Ref. [36]. The measured spectra of the modified PHMS (Fig. 4 – Fig. 6) contain the lines at similar chemical shift values to those found in the spectra of the modified M_2^{H} . However, signals visible in the spectra of the polymer are broader than the ones occurring in the spectra of the functionalized disiloxane which is typical of polymeric materials due to

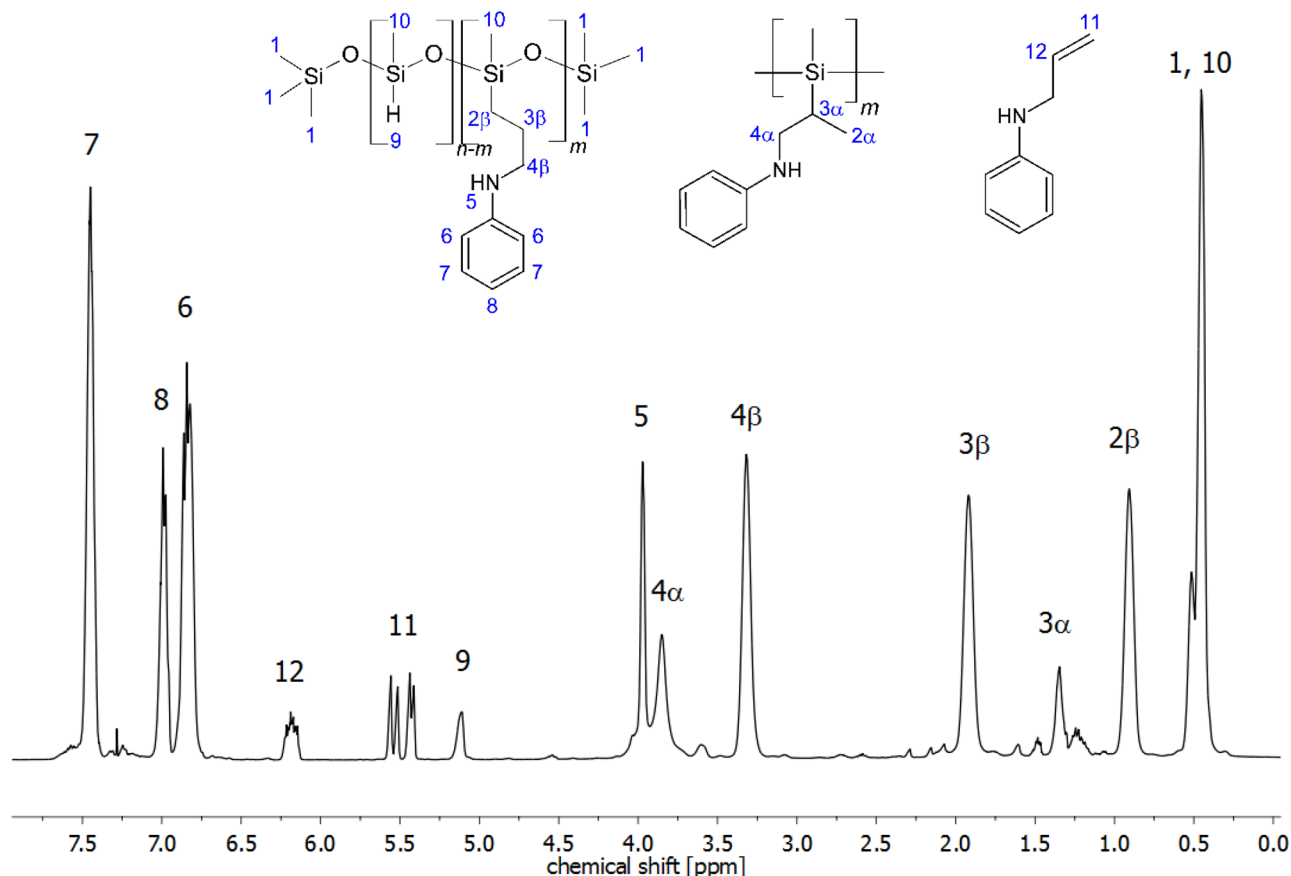


Fig. 4. ^1H NMR spectrum of PHMS_Naa_1.5 in CDCl_3

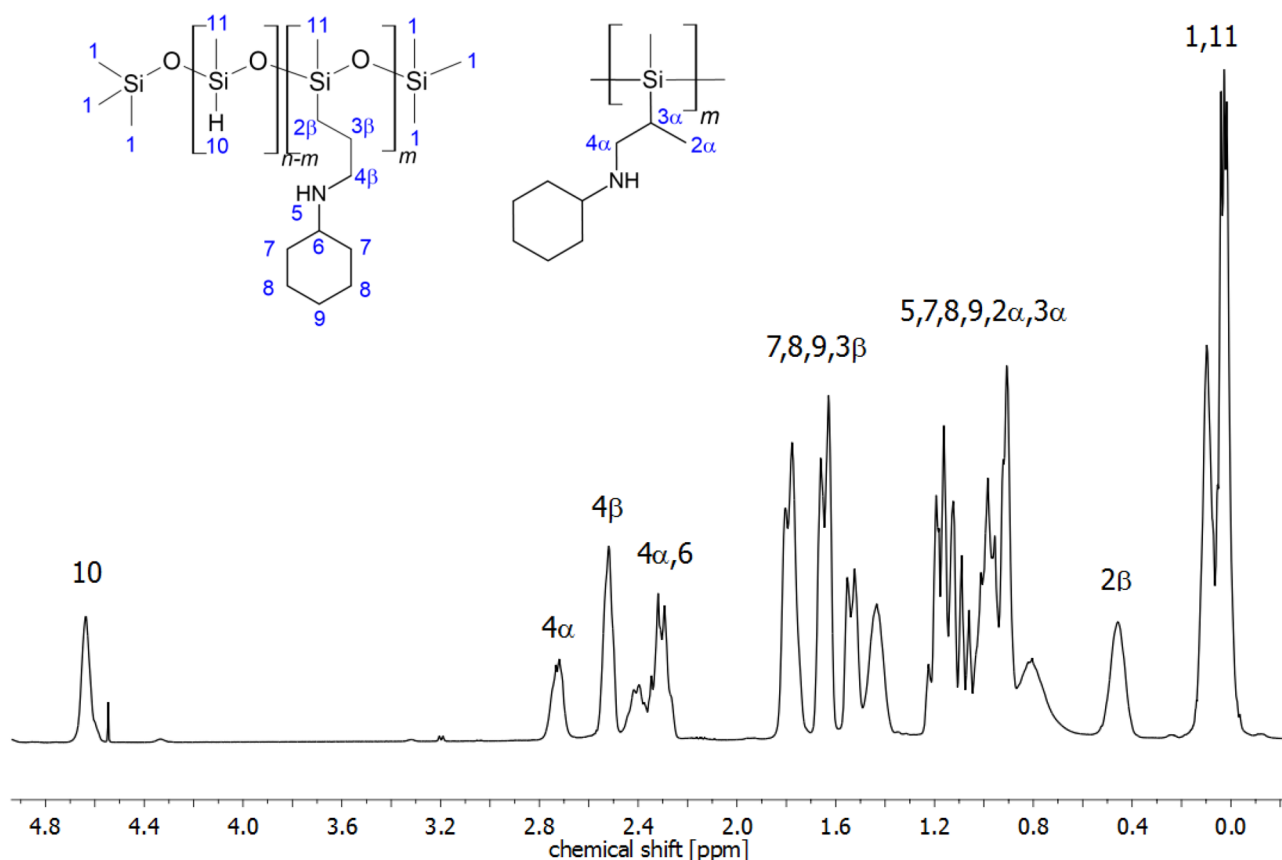


Fig. 5. ^1H NMR spectrum of PHMS_Nach_1.5 in CDCl_3

increased correlation time of the higher molecular weight entities [43].

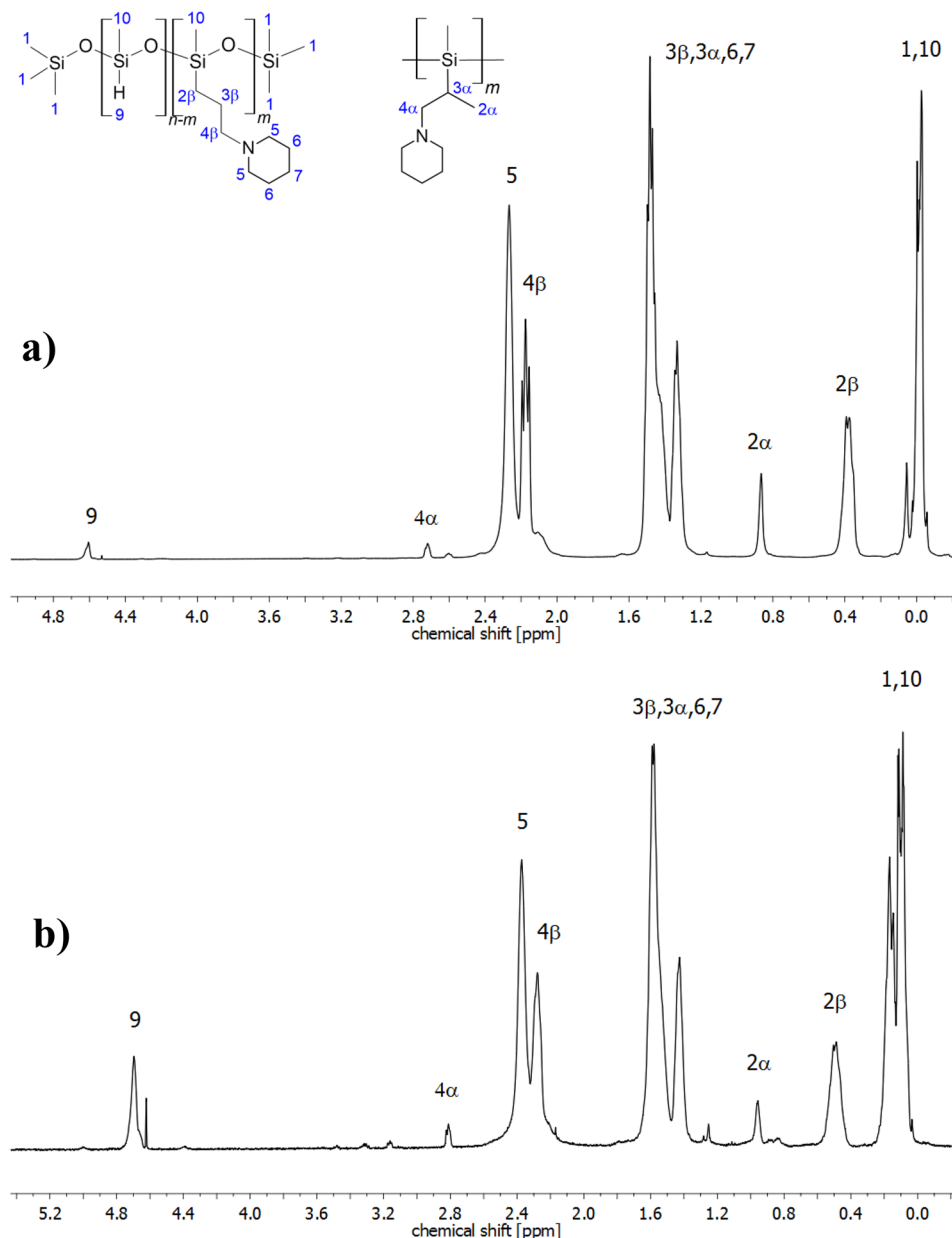
As can be seen in all spectra, signals of the H2β, H3β and H4β protons at $\delta = 0.88, 1.89, 3.29$ ppm (PHMS_Naa_1.5, Fig. 4), $\delta = 0.46, 1.43\text{--}1.80, 4.52$ ppm (PHMS_Nach_1.5, Fig. 5) and $\delta = 0.39, 1.33\text{--}1.48, 2.18$ ppm (PHMS_Nap_1.5 and PHMS_Nap_0.5, Fig. 6) prove that β-products (Fig. 1) are formed in the hydrosilylation of Naa, Nach and Nap with PHMS.

Importantly, in the proton spectra of the samples, signals ascribed to the α-products (Fig. 1) are also detected. The signals of the H3α, H4α protons are visible at $\delta = 1.32, 3.83$ ppm (PHMS_Naa_1.5, Fig. 4), $\delta = 0.80\text{--}1.22, 2.73$ and 2.32 (PHMS_Nach_1.5, Fig. 5) and $\delta = 1.33\text{--}1.48, 2.72$ ppm (PHMS_Nap_1.5 and PHMS_Nap_0.5, Fig. 6). The signals of the H2α protons are clearly visible in the spectra of PHMS_Nach_1.5 ($\delta = 0.81\text{--}1.19$ ppm, Fig. 5), PHMS_Nap_1.5 and PHMS_Nap_0.5 ($\delta = 0.87$ ppm, Fig. 6) while in the spectrum of PHMS_Naa_1.5 (Fig. 4) this signal is not distinguished probably because of low intensity. Lower intensities of the signals ascribed to the α-products in all the spectra (Fig. 4–6) than the signals assigned to

protons in β-products indicate that the β-products (anti-Markovnikov's) were formed predominantly in hydrosilylation of *N*-allyl amines with PHMS. Integration values of the signals due to the H2β and H4α protons (selected for quantitative analysis because they are well resolved in the spectra and each of them corresponds to two protons, Fig. 4, Fig. 6) in the ^1H NMR spectra showed that molar ratios of β to α isomers were equal to 2/1, 2/0.17 and 2/0.14 for PHMS_Naa_1.5, PHMS_Nap_1.5 and PHMS_Nap_0.5, respectively (Table 1). This means that the β adduct constituted ca. 67, 93 and 92 mol % in the respective product mixtures. Unfortunately, the ^1H NMR spectrum of PHMS_Nach_1.5 (Fig. 5) was complex. Strict determination of the β/α isomer molar ratio was not possible in this case because of coincidence of the Hβ and Hα signals resulting in the lack of well separated signals ascribed to the α-isomer.

Thus, NMR analysis clearly shows that hydrosilylation reactions of Naa, Nach and Nap with PHMS lead both to the β and α-products, however β addition prevails. It is worth mentioning here that hydrosilylation of Naa and Nap with M_2^{H} was very selective: it led exclusively to the β product. Only in the case of Nach, α addition also took place [36].

Fig. 6. ^1H NMR spectra in CDCl_3 : **a** PHMS_Nap_1.5, **b** PHMS_Nap_0.5



Thus, hydrosilylation of *N*-allyl amines with the polymer are less regioselective than analogous reactions with a small molecule of M_2^{H} .

^1H NMR-like FTIR-spectra of PHMS functionalized by all studied *N*-allyl amines contain the signals of protons in Si–H groups ($\delta = \sim 4.8$ ppm [44]) which corroborates partial functionalization of the polymer. In the spectra of PHMS_Nap_1.5 and PHMS_Nap_0.5 the difference in intensity of this signal (proton H9, Fig. 6a, b) is clearly visible. In the case of the sample prepared with the excess of amine the intensity of the signal is lower than in the case when the deficient amount of Nap was used in the process. This finding is also in accordance with FTIR results.

The ^1H NMR spectrum of PHMS_Naa_1.5 (Fig. 4) contains characteristic signals at $\delta = 5.54$, 5.42 and 6.17 ppm corresponding to protons of the allyl group in Naa (H11 and H12). The presence of these signals in the spectrum indicates contamination of the sample with unreacted Naa. The signals assigned to allyl groups are not observed in the spectra of the other investigated systems. Thus, the separation of the functionalized polymer from the unreacted *N*-allylamine was insufficient only in the case of PHMS_Naa_1.5.

Chemical structure of the obtained samples has been also investigated by ^{29}Si NMR (liquid samples) and ^{29}Si MAS-NMR (solid samples) spectroscopy. All the spectra of the final products (Fig. 7) show the signals in the ranges of -22.6

Table 1 Results of ^1H NMR, ^{29}Si NMR and ^{29}Si MAS-NMR spectra analysis

Sample	^1H NMR			^{29}Si NMR and ^{29}Si MAS-NMR		
	Proton ^a	δ [ppm]	Integration	Unit	δ [ppm]	Relative contribution of each signal in the spectrum [%]
PHMS_Naa_0.5	- ^b			D	-21.0	45
				D ^H	-34.5	23
					-38.5	23
				T	-66.0	9
PHMS_Naa_1.5	H2 β	0.88	2H	D	-19.2	9
					-20.6	22
	H4 α	3.83	1H		-21.9	41
				D ^H	-35.8	10
PHMS_Nach_0.5	- ^b				-36.7	18
				D	-20.8	37
				D ^H	-34.9	29
					-39.0	23
PHMS_Nach_1.5	H2 β	0.46	2H	T	-65.7	11
				D	-21.5	67 ^d
	H4 α	2.73, 2.42–2.22	- ^c	D ^H	-37.5	33 ^d
PHMS_Nap_0.5	H2 β	0.40	2H	D	-20.6	45
				D ^H	-34.8	22
	H4 α	2.72	0.14H		-38.9	23
				T	-65.8	10
PHMS_Nap_1.5	H2 β	0.39	2H	D	-21.3	28
					-22.6	58
	H4 α	2.72	0.17H	D ^H	-37.8	14

^aProtons denoted as in Fig. 4–6^b ^1H NMR spectra were measured for liquid samples only^cA great number of overlapping lines in this region of the spectrum (Fig. 5) hinder accurate signal integration^dThe result may not be accurate due to poor spectrum quality

to -19.2 ppm and -38.5 to -32.2 ppm. Moreover, in the spectra of the samples prepared using the deficient amount of the amine ($\text{Si-H:CH}_2=\text{CH-CH}_2$ - equal to 1:0.5), additional signal at about -66.0 ppm occurs (Fig. 7).

The signals in the range of -22.6 to -19.2 ppm can be ascribed to the $[\text{SiO}_2(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_2)]$ units since they are located in the region characteristic for the D (i.e. $[\text{SiO}_2\text{C}_2]$) units occurring in linear polysiloxanes (-20.5 to -22.0 ppm [45]). This is a further proof that functionalization of PHMS by Naa, Nach and Nap does occur in the studied systems. It should be noted that in this spectral region, in the case of liquid samples, three (PHMS_Naa_1.5) or two (PHMS_Nap_1.5) separated signals occur (Fig. 7, Table 1). Because of the poor quality of the spectrum of PHMS_Nach_1.5 (Fig. 7), which was also a liquid sample, signal due to D units is broad and has low intensity. The shape of the signal indicates, however, that it is composed of several lines. Broad and complex signals originating from

D units in the ^{29}Si MAS-NMR spectra of solid samples (PHMS_Naa_0.5; PHMS_Nach_0.5; PHMS_Nap_0.5) are also observed. Thus, it can be assumed that the presence of several signals and their complexity in the range corresponding to D units in the spectra of liquid and solid products of PHMS modified with *N*-allyl compounds, is due to the existence of α and β linkages in different chemical environment in the polymer structure. This is consistent with the results of the ^1H NMR analysis of liquid products of PHMS functionalization and also with our previously reported results concerning functionalization of M_2^{H} by Nach [36]. The ^{29}Si NMR measurements prove, however, that during modification of the polymer with *N*-allyl compounds, both α and β linkages are formed in all studied systems.

Additionally, ^{29}Si NMR spectroscopy, like other spectroscopic methods, clearly shows that functionalization of PHMS in our systems was not complete and in the polymer chain unreacted Si-H groups still remained after

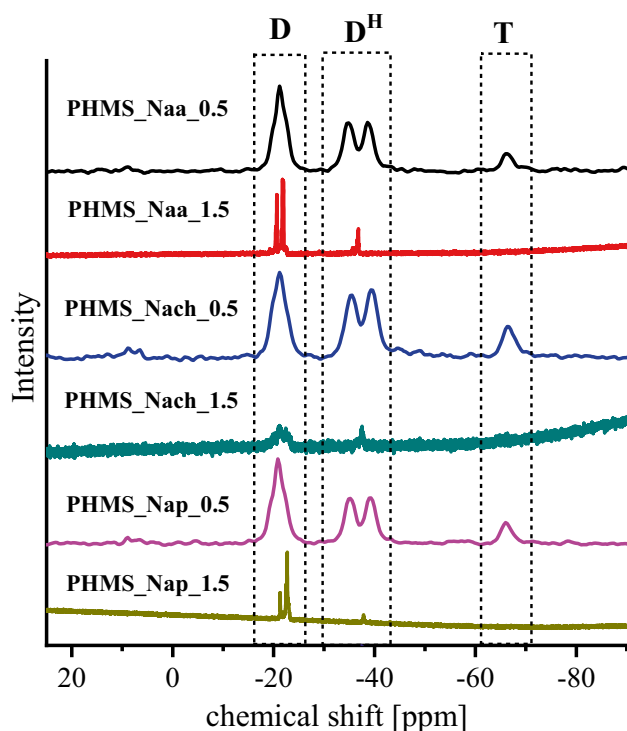


Fig. 7 ^{29}Si NMR (samples PHMS_Naa_1.5; PHMS_Nach_1.5; PHMS_Nap_1.5) and ^{29}Si MAS-NMR spectra (samples PHMS_Naa_0.5; PHMS_Nach_0.5; PHMS_Nap_0.5) of PHMS functionalized with *N*-allyl compounds

hydrosilylation; in the spectra the broad signals in the range of -38.5 to -32.2 ppm associated with the Si units containing H atoms [$\text{SiO}_2(\text{CH}_3)\text{H}$], referred to as D^{H} (Fig. 7, Table 1), in different chemical environments, are observed [45].

^{29}Si MAS-NMR spectra also contain the signal at about -66.0 ppm related to the presence of the T ($[\text{SiO}_3\text{C}]$) units in the polymer structure (Fig. 7) [45]. The fact that these signals are visible only in the spectra of solid, insoluble samples (prepared during the reaction of PHMS with *N*-allyl amines at molar ratio of $\text{Si-H}:\text{CH}_2=\text{CH-CH}_2$ groups equal to 1:0.5), unambiguously confirms, postulated previously, crosslinking of the polymer caused by the condensation of Si-OH groups, resulting from hydrolysis of a part of a large number of Si-H groups in these systems.

According to quantitative analysis of ^{29}Si NMR spectra, relative contributions of the signals of D units, originating in the investigated systems from hydrosilylation of *N*-allyl compounds with PHMS, constitute 37% for PHMS_Nach_0.5 and 45% for PHMS_Naa_0.5 and PHMS_Nap_0.5, respectively (Table 1). The relative contributions of the signals of D units in the spectra of the samples obtained with the excess of the *N*-allyl compounds are significantly higher: 72% and 86% for PHMS_Naa_1.5 and PHMS_Nap_1.5, respectively (Table 1). This means that the degrees of polymer functionalization in these samples are higher. Simultaneously,

Table 2 Results of elemental analysis of PHMS functionalized by *N*-allyl compounds

Sample	Contents of elements [wt.%]		C	H	SiO ^c
	N				
	calc. ^a	found ^b			
PHMS_Naa_0.5	5.42	5.17 (95.4)	50.60	7.71	36.52
PHMS _Naa_1.5	7.15 (8.70)	6.84 (95.7)	56.86	9.94	26.36
PHMS _Nach_0.5	5.30	4.53 (85.5)	46.76	9.93	38.78
PHMS _Nach_1.5	6.94 (8.24)	4.95 (71.3)	48.30	10.13	36.62
PHMS _Nap_0.5	5.60	5.87 (104.8)	47.79	12.61	33.73
PHMS _Nap_1.5	7.45 (9.15)	7.50 (100.7)	55.31	12.57	24.62

^a Without brackets-the maximum possible nitrogen content [%] resulting from the stoichiometry of the reaction are given; in brackets – resulting from the amount of the *N*-allyl compound used in the reaction;

^b In brackets fractions of N incorporated into the polymer, calculated as $(N_{\text{found}}/N_{\text{calc}}) \cdot 100\%$ are given;

^c $\% \text{SiO} = 100\% - \Sigma \% \text{C}, \% \text{H}, \% \text{N}$

in the spectra of the systems obtained at the molar ratio of $\text{Si-H}:\text{CH}_2=\text{CH-CH}_2$ groups equal to 1:1.5, the relative contributions of D^{H} units are lower (28%-PHMS_Naa_1.5 and 14%-PHMS_Nap_1.5, Table 1) than in the spectra of the samples obtained at the molar ratio of $\text{Si-H}:\text{CH}_2=\text{CH-CH}_2$ equal to 1:0.5 (46%-PHMS_Naa_0.5, 52%-PHMS_Nach_0.5 and 46%-PHMS_Nap_0.5, Table 1), which clearly shows that the samples obtained with the deficiency of the *N*-allyl compound contained higher amounts of unreacted Si-H groups than those obtained with its excess. These findings are fully consistent with the results of FTIR studies.

Moreover, the relative contributions of T units in the ^{29}Si MAS-NMR spectra of the samples obtained using deficient amounts of amines, are relatively low-equal to 9–11% (Table 1). This indicates that in these systems crosslinking of PHMS accompanying the hydrosilylation process occurred to a low degree.

Elemental analysis proved that moieties originating from *N*-allyl amines (Naa, Nach and Nap) were introduced into the polymer chain. All the samples contained nitrogen (Table 2). As expected, the amount of nitrogen introduced into PHMS increased with increasing amount of the *N*-allyl compound used in the reaction. However, considering the obvious discrepancies observed for the samples modified by Nap (overestimated nitrogen contents, Table 2) and the presence of unreacted Naa in the final PHMS_Naa_1.5 sample,

which was proven by ^1H NMR studies, the elemental analysis results should be interpreted with caution.

To summarize, results of the conducted experiments show that direct hydrosilylation of *N*-allyl amines with PHMS in the presence of a Pt catalyst is possible. Functionalization, however, in all the systems is not complete; after the reaction unreacted Si–H groups still exist in the polymer structure even if the excess of *N*-allyl compound is used. For the samples with higher amount of unreacted Si–H groups crosslinking of the polymer is observed. It should be noted that the applied *N*-allyl amines differed in nucleophilicity and molecular structure [36]. Their influence on reactivity of these compounds in hydrosilylation reaction with PHMS appears to be rather complex. The reactions with Nap result in the highest conversion degrees of the Si–H groups as related to the reactions with Naa and Nach in the corresponding systems. Polymer functionalization degrees with Nap moieties, established on the basis of ^{29}Si NMR spectroscopy, are also higher. Therefore our investigations suggest that the structure of this molecule is more advantageous for hydrosilylation than the structure of Naa and Nach. To explain this finding a separate study should be conducted. Moreover, NMR analysis clearly showed that hydrosilylation reactions of Naa, Nach and Nap with PHMS lead both, to the β and α addition products, however the β addition prevails.

Functionalization of PHMS with (4VP)

Our previously reported results concerning functionalization of M_2^{H} by 4VP showed that the reaction does not take place in the studied conditions (60 °C, toluene, 24 h) [36]. We decided, however, to verify whether the hydrosilylation of 4VP with a polymeric compound, PHMS occurs as there are reports showing that 4VP can be hydrosilylated by a macromolecular compound, PHMS-DMS copolymer, in the presence of Karstedt's catalyst [34, 35]. We changed reaction conditions with respect to those applied in the functionalization of PHMS by *N*-allyl compounds: the temperature of the process was raised to 110 °C (similar to that used in Ref. [34, 35]), reactions were conducted with and without the solvent (toluene), at four different Si–H:CH₂=CH- groups molar ratios equal to 1:1.5; 1:1; 1:0.5 or 1:0.25 (Experimental Section). All these changes were aimed at getting conclusive results.

During treatment of PHMS with 4VP, similarly to the reactions of the polymer with *N*-allyl amines, FTIR spectra of the reaction mixtures were measured. It was found that regardless of the molar ratio of Si–H:CH₂=CH- groups, and regardless of whether the process is carried out with or without the solvent, the intensity of the band at 2169 cm^{−1}, ascribed to the Si–H stretching vibrations [37], decreases over time (Fig. 8). These changes, however, are not as

Table 3 Conversion degrees of Si–H groups in the reactions of PHMS with 4VP evaluated by FTIR spectra analysis

Sample	Conversion degree of the Si–H groups [%] ^a	
	Solvent conditions	Solvent-free conditions
PHMS_4VP_1.5	34.6	34.7
PHMS_4VP_1	27.9	32.6
PHMS_4VP_0.5	25.9	16.2
PHMS_4VP_0.25	23.3	12.1

^a Estimated by comparing the ratios of integral intensities of Si–H (at 2169 cm^{−1}) and Si–CH₃ (at 1262 cm^{−1}) bands in the FTIR spectra of PHMS and final reaction mixtures

significant as in the case of modification of PHMS with *N*-allyl compounds (Fig. 2). This suggests that after the reactions in the PHMS_4VP systems, significant amounts of unreacted Si–H groups remain in the polymer.

The final conversion degrees of Si–H groups calculated based on FTIR spectra for all the investigated systems (Table 3) depend on the molar ratio of the reactants used. Quite expectedly for polymer functionalization, they decrease with the reduction in the amount of 4VP applied in the reaction. However, the influence of the solvent on the Si–H groups conversion degrees is not systematic. It does not affect transformations of these groups in the PHMS_4VP_1.5 system as their conversion degrees are the same for the reactions performed with and without the solvent (~34.6%). In contrast, for PHMS_4VP_1 the Si–H groups are converted to higher extent for the reaction conducted in the non-solvent conditions. In the remaining systems, higher degrees of conversion of Si–H groups are observed in the case of syntheses carried out in the solvent than without it. For PHMS_4VP_0.25 the difference is the most significant. This suggests that in the reaction media with lower amounts of 4VP (PHMS_4VP_0.25 and PHMS_4VP_0.5) the presence of toluene is beneficial for the transformations of Si–H groups. In the reactions performed with higher amounts of 4VP (PHMS_4VP_1 and PHMS_4VP_1.5), the role of pyridine on the reaction course seems to be crucial.

Considering the solid form of all final reaction products (Experimental Section), and taking into account that for the solid samples of PHMS functionalized with *N*-allyl compounds ^{29}Si MAS-NMR spectroscopy proved crosslinking of the polymer by condensation of silanol groups, it could be supposed that in the PHMS_4VP systems Si–OH groups were formed as well. Most probably, they resulted from hydrolysis of Si–H groups present in the polymer caused by water existing in 4VP and/or the solvent (despite their drying before the reactions). Based on quantitative FTIR

Table 4 Results of elemental analysis of the final, purified samples of PHMS functionalized by 4VP

PHMS_4VP solvent system	Contents of ele- ments [wt.%]					PHMS_4VP solvent-free system	Contents of ele- ments [wt.%]				
	N		C	H	SiO ^c		N		C	H	SiO ^c
	calc. ^a	found ^b					calc. ^a	found ^b			
1.5	8.35 (9.54)	3.63 (43.5)	34.62	5.58	56.18	1.5	8.35 (9.54)	9.03 (108.1)	68.36	6.64	15.97
1	8.35	1.67 (20.0)	25.84	6.13	66.36	1	8.35	1.28 (15.3)	20.97	5.49	72.26
0.5	6.08	1.26 (20.7)	28.15	6.17	64.42	0.5	6.08	3.11 (51.2)	33.99	6.05	56.85
0.25	3.94	0.79 (20.1)	23.39	6.55	69.28	0.25	3.94	1.07 (27.2)	20.21	4.07	74.66

^a Without brackets-the maximum possible nitrogen content [%] resulting from the stoichiometry of the reaction are given; in brackets-resulting from the amount of the 4VP in the reaction;

^b In brackets fractions of N incorporated into the polymer, calculated as $(N_{\text{found}}/N_{\text{calc.}}) \cdot 100\%$ are given;

^c %SiO $100\% - \Sigma \%C, \%H, \%N$. In order to draw final conclusions on the reactions proceeding in the PHMS_4VP systems, the obtained, purified PHMS_4VP samples were subjected to FTIR and ²⁹Si MAS-NMR investigations

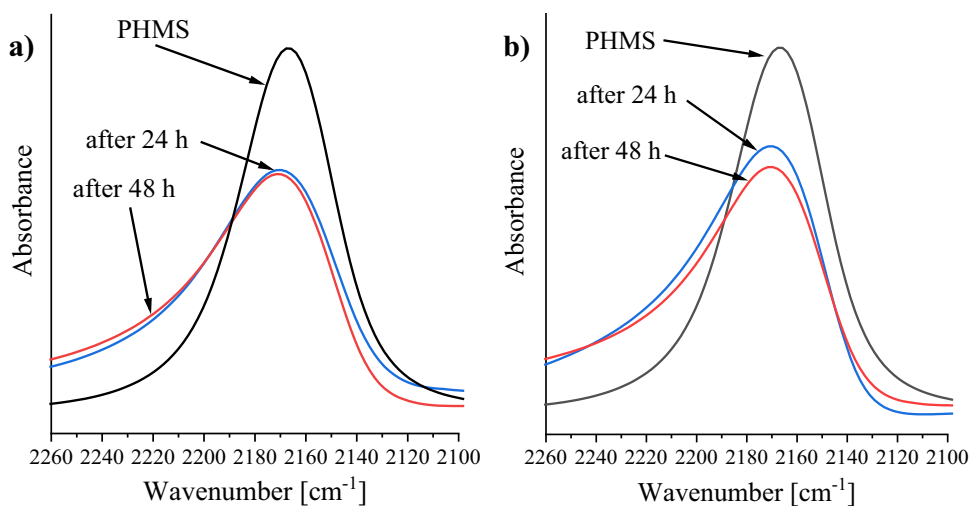
spectra analysis (Table 3) it can be assumed that the conversion of Si–H groups during the processes carried out in toluene in the PHMS_4VP_0.25 and PHMS_4VP_0.5 systems, with lower amounts of 4VP with respect to the polymer, water contained in the solvent was the predominant cause of hydrolysis. This is suggested by higher conversion degrees of Si–H groups in both systems when the reactions were performed in toluene. For the processes conducted with larger amounts of 4VP, in turn, hydrolysis seems to be related mainly to water contained in 4VP since Si–H groups transformed to a higher degree in the solvent-free medium (PHMS_4VP_1 system) or the presence of toluene did not affect their conversion degree (PHMS_4VP_1.5 system).

Moreover, quantitative FTIR spectra analysis shows that conversion degrees of Si–H groups in the PHMS_4VP

systems are markedly lower than those found for systems with *N*-allyl compounds. This indicates that, if functionalization of PHMS with 4VP occurs, then to a low extent.

According to elemental analysis, all the obtained samples contained nitrogen (Table 4). Importantly, its content decreased after extraction of the samples with toluene in a Soxhlet apparatus (results not shown), which indicates the presence of unreacted 4VP in the crude reaction products, removed during the purification process (Experimental Section). In the final, purified samples obtained in toluene, nitrogen content decreased as the amount of 4VP used in the reaction was reduced (Table 4). This is what was expected for polymer functionalization and agrees with FTIR results which showed lowering in the conversion degrees of Si–H groups as the amount of 4VP in the systems decreased

Fig. 8 FTIR spectra showing the decrease of the Si–H stretching vibrational band during preparation of **a** PHMS_4VP_1.5 sample and **b** PHMS_4VP_0.25 sample, in toluene



(Table 3). In the case of the samples obtained in solvent-free conditions, however, the results are not consistent. Excessive amount of nitrogen as compared to the maximum possible for the fully functionalized polymer (108.1%) is observed for the PHMS_4VP_1.5 sample obtained in the solvent-free conditions (Table 4). This indicates the presence of unreacted 4VP in this sample which could not be excluded in the other ones, either. Removal of 4VP molecules located in the cross-linked polymer network might have been difficult. Hence, the presence of nitrogen in the studied systems does not prove that the moieties originating from 4VP were introduced into the polymer molecule, i.e. that hydrosilylation of 4VP by PHMS took place.

It is worth noting that the products of hydrosilylation of *N*-allyl compounds with PHMS contained higher amounts of nitrogen (4.53–5.87 wt.% and 4.95–7.50 wt.% for the molar ratios of Si-H:CH₂=CH-CH₂- equal to 1:0.5 and 1:1.5, respectively, Table 2) than found for PHMS treated with 4VP (1.26 wt.% and 3.63 wt.% for the reaction in toluene with molar ratios of Si-H:CH₂=CH- equal to 1:0.5 and 1:1.5, respectively, Table 4). Simultaneously, content of nitrogen in the 4VP molecule (~13 wt.%) is higher than those in *N*-allyl amines applied in the experiments (Nach: ~11 wt.%, Naa: ~10 wt.%, Nap: ~11 wt.%). Thus, lower contents of nitrogen in the materials obtained with 4VP confirm that incorporation of its moieties into the systems was lower than those of *N*-allyl compounds.

All FTIR spectra (Fig. 9) are dominated by the bands due to PHMS corresponding to: asymmetric stretching vibrations of Si-O-Si groups (1130–1000 cm⁻¹), as well as, of C-H bond in Si-CH₃ groups vibrations: symmetric bending (1262 cm⁻¹) and symmetric (2917 cm⁻¹) and asymmetric (2967 cm⁻¹) stretching [37, 38, 42]. Moreover, in all the spectra the band at 2169 cm⁻¹, ascribed to Si-H stretching vibrations, is clearly visible. The presence of this band

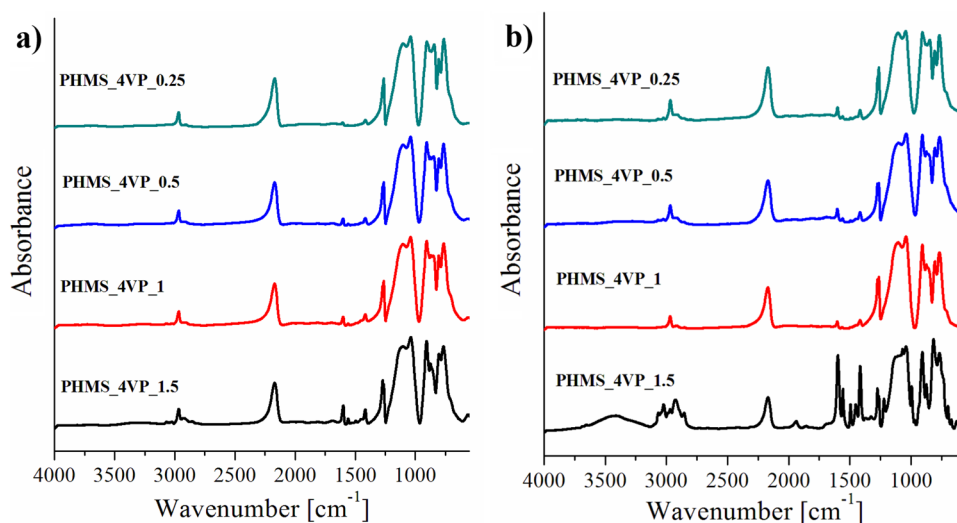
and its significant intensity show that the vast majority of Si-H groups in the polymer remained unreacted, which was revealed by the quantitative analysis of FTIR spectra already discussed.

The bands indicating the presence of 4VP units exhibit generally low intensity in the FTIR spectra of the materials and occur at (Fig. 9): 2917 cm⁻¹ (symmetric C-H stretching vibrations), 1599 cm⁻¹ (C=C stretching vibrations in the aromatic ring), 1416 cm⁻¹ (deformation vibrations of =C-H). The exception is the spectrum of PHMS_4VP_1.5-the reaction carried out without solvent (Fig. 9b), which contains intense bands originating from 4VP at 3401, 3024, 1599 cm⁻¹ and a characteristic combination of bands and overtones in the range of 2000–1600 cm⁻¹ [46]. In this spectrum, the band of low intensity at 1633 cm⁻¹ due to stretching vibrations of C=C bonds in unreacted vinyl groups, is also visible [37]. This confirms the results of elemental analysis which revealed the presence of unreacted 4VP in the PHMS_4VP_1.5 sample.

It should be noted that the bands at 2900–2850 cm⁻¹ and 1140 cm⁻¹ (C-H bonds vibrations: asymmetric stretching and deformation, respectively [37, 38, 42]) attributed to -CH₂- groups in ethylene bridges (-CH₂CH₂-) at silicon atoms resulting from hydrosilylation (Fig. 9), do not appear in the spectra of the final systems. Thus, analysis of FTIR spectra of PHMS_4VP samples leads to the conclusion that functionalization of PHMS in none of the studied systems takes place.

The conclusions drawn from FTIR are fully corroborated by ²⁹Si MAS-NMR spectra (Fig. 10). We measured the spectra of selected samples: PHMS_4VP_1.5 and PHMS_4VP_0.25, obtained in toluene and solvent-free conditions. The analysis of the data clearly shows that the hydrosilylation of 4VP by PHMS does not occur. The absence of the signals in the range of -20 to -22 ppm

Fig. 9 FTIR spectra of the final, purified products of the reactions in the PHMS_4VP systems carried out in **a** solvent (toluene), **b** solvent-free conditions



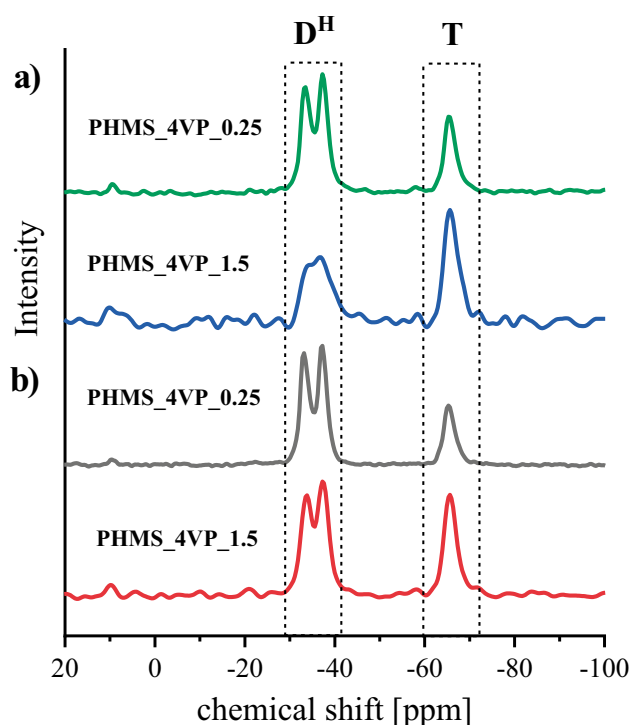


Fig. 10. ^{29}Si MAS-NMR spectra of PHMS treated with 4VP in: **a** solvent-free conditions, **b** solvent (toluene)

proves that no $-\text{Si}-\text{CH}_2\text{CH}_2-$ or $-\text{Si}-\text{CH}(\text{CH}_3)-$ moieties were formed during the reactions, which precludes successful hydrosilylation.

In all the spectra, however, the lines at -33.9 to -37.1 ppm, ascribed to the D^{H} units $[\text{SiO}_2(\text{CH}_3)\text{H}]$ and at ~ -65.0 ppm, related to the presence of the T units $[(\text{SiO}_3\text{C})]$ in the polymer structure, are clearly visible [45]. Thus, ^{29}Si MAS-NMR spectroscopy unambiguously confirms the presence of unreacted $\text{Si}-\text{H}$ groups and polymer cross-linking resulting from partial hydrolysis of $\text{Si}-\text{H}$ groups of PHMS followed by condensation of silanol groups formed.

According to the quantitative analysis of ^{29}Si MAS-NMR spectra relative contributions of the signals of D^{H} units constitute from 51 to 76% and those of T units – from 24 to 49% (Table 5). This shows that high amounts of $\text{Si}-\text{H}$ groups were left in the polymer after the reactions. The relative contributions of the signals of T units in the spectra of the samples obtained at the same molar ratios of $\text{Si}-\text{H}:\text{CH}_2=\text{CH}$ -groups, were higher for those obtained in the solvent while among the samples prepared in the same conditions (with or without solvent), more T units were formed in the systems with excess of 4VP (Table 5). These results show that hydrolysis of $\text{Si}-\text{H}$ groups occurring in the studied systems involved residual water from the chemicals used, both toluene and 4VP.

Table 5 Chemical shifts, assignments and relative contributions of signals in the ^{29}Si MAS-NMR spectra of PHMS_4VP_0.25 and PHMS_4VP_1.5 samples

Sample	Unit	δ [ppm]	Relative contribution [%]
PHMS_4VP_0.25 without toluene	D^{H}	-32.9	37
		-36.9	39
PHMS_4VP_1.5 without toluene	D^{H}	-65.1	24
		-33.3	31
PHMS_4VP_0.25 in toluene	D^{H}	-37.1	35
		-65.3	34
PHMS_4VP_0.25 in toluene	D^{H}	-33.1	33
		-37.1	38
PHMS_4VP_1.5 in toluene	D^{H}	-65.3	29
		-33.1	9
PHMS_4VP_1.5 in toluene	D^{H}	-36.5	42
		-65.5	49

The PHMS_4VP samples contained more T units than PHMS functionalized with *N*-allyl compounds (relative contribution of T units: 9–11%, Table 1). This can be explained by the lack of functionalization of the polymer with 4VP – hence, more $\text{Si}-\text{H}$ groups are prone to hydrolysis, as well as by higher reaction temperature (110°C for 4VP and 60°C for *N*-allyl compounds), which makes hydrolysis of $\text{Si}-\text{H}$ groups and subsequent condensation of $\text{Si}-\text{OH}$ groups faster. It should be also noted that the way of purification of the final PHMS_4VP samples may have also influenced the cross-linking reactions. Side processes could have occurred during extraction of the PHMS_4VP systems after synthesis, using toluene in a Soxhlet apparatus conducted for 24 h (Experimental Section) as well.

Thus, all the presented data show clearly that the reaction of PHMS with 4VP, as in the case of M_2^{H} -despite modification of the conditions-does not occur. This confirms that Karstedt's catalyst is deactivated by pyridine moieties, which can be explained by their strong coordinative ability towards platinum. As previously reported, pyridine shows stronger affinity to platinum than amines since in its bonding with this metal not only the lone electron pair on nitrogen atom, but also π electrons of the ring are involved [47]. Hence, a strong competition between coordination of $>\text{C}=\text{C}<$ bonds and pyridine moieties to Pt centers in the catalyst in these systems can be postulated.

As revealed in the studies, the only way by which $\text{Si}-\text{H}$ groups are transformed in the PHMS_4VP systems in the presence of Karstedt's catalyst is their hydrolysis followed

by condensation of the Si–OH groups formed. It is well known that platinum is a catalyst of hydrolysis of Si–H groups; hence this process in the presence of Pt is facilitated.

The experiments conducted with *N*-allyl compounds, discussed in the previous section, prove that hydrolysis of Si–H groups can be a side reaction that accompanies hydrosilylation, i.e. hydrolysis of Si–H groups does not preclude hydrosilylation. This supports the conclusion that deactivation of Pt centers in the catalyst, and not water present in the reaction medium, is the reason for the lack of 4VP hydrosilylation by PHMS.

It should be pointed out that our work demonstrates clearly that the most reliable technique to establish that hydrosilylation in the PHMS_4VP system does not take place is ^{29}Si NMR spectroscopy. Reported in Ref. [34, 35] materials prepared by treatment of PHMS-DMS copolymer with 4VP were not analyzed by this method. It seems therefore that their characterization was insufficient to conclude unambiguously that 4VP was hydrosilylated by PHMS-DMS copolymer.

Finally, it is worth mentioning that the presented results show that M_2^{H} is a good compound to perform model investigations on reactivity of 4VP in hydrosilylation by high-molecular-weight hydrosiloxanes in the presence of Karstedt's catalyst as was postulated in our previous work [36].

Conclusions

The studies conducted in the work on functionalization of polyhydromethylsiloxane (PHMS) by unsaturated nitrogen-containing organic compounds: *N*-allylaniline (Naa), *N*-allylcyclohexylamine (Nach), *N*-allylpiperidine (Nap) and 4-vinylpyridine (4VP) via hydrosilylation in the presence of Karstedt's catalyst show that:

1. Functionalization of PHMS by hydrosilylation in the presence of Karstedt's catalyst takes place only with the *N*-allyl compounds, the reaction with 4VP does not proceed. This indicates that during the reactions of PHMS with *N*-allyl amines Pt catalyst is not deactivated while upon polymer treatment with 4VP catalyst's deactivation occurs. These findings are consistent with those obtained for hydrosilylation of all the studied *N*-containing compounds by a low-molecular-weight hydrosiloxane (M_2^{H}).
2. Functionalization of PHMS with *N*-allyl amines in all the systems is not complete. For the samples with the higher amount of unreacted Si–H groups left, crosslinking of the polymer, due to hydrolysis of Si–H and subsequent condensation of silanol groups, is observed. These processes are the only ones that occur in PHMS_4VP systems.

3. Hydrosilylation of Naa, Nach and Nap with PHMS leads both, to the β and α addition products, the former being the dominant one in all the cases. Hence, for the polymer the process is not as selective as for M_2^{H} which in the reactions with Naa and Nap gives exclusively the β product. Thus, elongation of the hydrosiloxane chain reduces regioselectivity of the hydrosilylation reaction.

In conclusion, the studies show unequivocally that it is possible to prepare polysiloxanes containing amine side groups using a readily available and inexpensive polymer, PHMS and a simple reaction, hydrosilylation conducted under mild conditions with a highly efficient in this process Karstedt's catalyst. Thus functionalized polymers, due to high reactivity of amine moieties, may serve as starting compounds for further modifications leading to new materials of attractive properties, suitable for various applications.

Data availability The raw and the processed data required to reproduce these findings are available from the corresponding author upon reasonable requests.

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