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Facile route to synthesis of functionalised poly(methylalkoxy)siloxane under mild and aerobic conditions in the presence of platinum catalysts

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ABSTRACT

A facile and high yield method of synthesis of novel and functional poly(methylalkoxy) siloxanes is reported. The Si–H groups of poly(methylhydrogen) siloxanes (PMHS) were treated with various simple (primary, secondary, tertiary) alcohols (1a–10a) in the presence of platinum based catalysts (Speier's and Karstedt's catalysts). Also oxyethylene, aldehyde, epoxide, halogen and allyl grafted polysiloxane were smoothly and quantitatively prepared by the alcoholysis between linear siloxanes polymer and functional alcohols (11a–20a) with use of Karstedt's catalysts. It is found that alcoholysis reaction in the presence of the Karstedt's catalyst proceed faster than Speier's catalyst .In addition, the rate of alcoholysis reaction is dependent on amount of the catalyst and reaction temperature. The polymers prepared were characterized by IR, NMR spectroscopy and GPC analysis.

1. Introduction

Polymethylsiloxanes are characterized by a number of interesting properties, e.g. excellent heat resistance, low toxicity, biocompatibility, high oxygen permeability, poor wettability, extremely low surface tension, low melting point and glass transition temperature, resistance to radiation, outstanding electrical isolating properties and others [1,2]. On the other hand, low cost, easy availability, and the presence of catalytically transformable Si–H bonds in poly(methylhydrogen) siloxanes (PMHS) make it a very attractive and interesting antecedent for macromolecular grafting studies [3]. Moreover, organic functionalization of the polymer chain can lead to fine-tuning of physical and chemical properties of the resulting siloxanes. For example, appropriate substitution on the polysiloxane backbone can lead to diverse materials such as liquid crystals [4–6], cross-linking agents [7], conductive [8] and electroluminescent polymers [9], non-linear optical materials [10], and bactericides [11].

The chemistry of linear polysiloxane with specific functions is a rapidly growing area due to the wide variety of the applications of this system and the easy preparation methods by catalytic reactions, such as hydrosilylation, dehydrocoupling, etc. The dehydrocoupling between Si–H bonds of poly(methylhydrogen)siloxane and E–H bonds (E = C, N, O, S, etc.) by the elimination of hydrogen molecules is a well-known catalytic procedure [12,13]. By the use of this procedure, the polymer could contain regular and characteristic properties on each backbone unit for example, the dehydrocoupling reaction between hydrosilane and function alcohol can easily result in the functional group attached to the silane with high conversion. The dehydrocoupling between alcohol and hydrosilane is a typical well-known method for the preparation of Si–O bonds. This reaction usually requires a catalyst; the most commonly used are the transition metal complexes [Co (I), Rh (I), Pd (0), and Pt (0)] [14]. Although functionalization of PMHS via hydrosilylation in the presence of platinum catalyst is widely studied [15], only a few studies about the alcoholysis reaction by use of platinum catalyst (especially Karstedt's catalyst) have recently been reported [16–18].

As a part of our continuing research on the organosilicon chemistry [19–24], we have particularly been interested in developing the alcoholysis reaction between PMHS and various simple and functional alcohols. The objective of this research is the preparation of novel and functional poly(methylalkoxysiloxane) in mild conditions and high yield approach in the presence of Speier's and Karstedt's catalyst. Also comparisons of these catalysts are investigated.

2. Results and discussion

Macromolecular grafting is a synthetic approach that involves the functionalization of a preformed polymer backbone containing reactive groups with an appropriate reagent. Since polymer properties are often heavily influenced by the identity of their pendant groups, a variety of different materials with a wide range of properties can be synthesized from only one antecedent. In this study,

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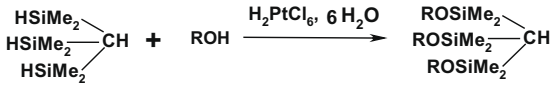
functionalization of polysiloxanes by grafting functional alcohols was achieved via alcoholysis of the respective alcohols with Si–H group of PMHS in the presence of two platinum catalysts.

2.1. Alcolysis reaction of PMHS with simple alcohols

A special feature of PMHS is their ability to undergo alcoholysis leading to poly(methylalkoxysiloxane) and gaseous hydrogen beneath transition metal catalyst process. In this paper two platinum catalysts were chosen. The former Platinum catalyst at Pt^{VI} oxidation state, H_2PtCl_6, $6H_2O$, is Speier's catalyst and the latter Platinum catalyst at Pt^0 oxidation state is Karstedt's catalyst [Pt(0)–divinyltetramethyldisiloxane complex]. Regarding to our recent paper in which we have reported the preparation of tris(alkoxydimethylsilyl)methanes via the alcoholysis reaction of tris(dimethylsilyl)methane and various alcohols in the presence of $H_2PtCl_6{\cdot}6H_2O$ as catalyst under mild and aerobic conditions [25] (Scheme 1). We were interested in extending the applied methodology in the grafting of PMHS with various alcohols. For this purpose, dehydrocoupling of some alcohols were examined in the presence of Speier's catalyst and the results are listed in Table 1.

The method is found to be applicable to primary and secondary alcohols and leads to selective formation of corresponding poly(alkoxysiloxanes) in good yields under aerobic conditions (see Table 1). Reaction of PMHS with primary alcohols is faster than secondary alcohols (Table 1, entry 3–6), but the slow rate of reaction in the case of the methanol and ethanol can be attributed to the low miscibility of these alcohols with PMHS. The conversion of PMHS was studied using a quantitative IR method on the basis of absorption measurements at the Si–H stretching band frequency (max. 2167 cm^{-1}) with reference to the standard curve. In the case of *ter*-butylalcohol (10a) the spectroscopic results show that alcoholysis reactions were not observed with Speier's catalyst, and it is found that reaction of PMHS with **11a** furnished coupling product dibenzyl ether. It can be generally stated that under the optimum conditions (given catalyst, temperature and appropriate time) reaction of PMHS with various alcohols can proceed quantitatively.



Scheme 1. Alcoholysis reaction of $(HMe_2Si)_3CH$.

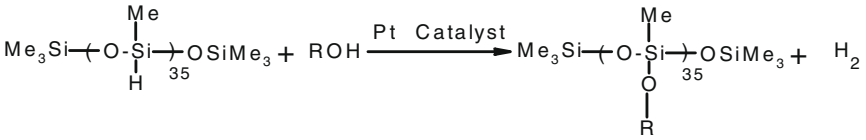
In view of more reactivity of Karstedt's catalyst the same reactions were carried out in the presence of this catalyst. In a typical alcoholysis experiment, optimum amount of Karstedt's catalyst ($[Pt^0]/[Si–H] = 15 \times 10^{-5}$) was added to a mixture of PMHS (2 g, 0.88 mmol) and alcohols (20 ml). The colorless reaction mixture gradually turned to a homogeneous black colored solution, indicating the generation of colloidal Pt^0 particles. Evolution of gas (presumably hydrogen) was also observed during the reaction. The reaction progress was monitored by FT-IR spectroscopy. The obtained results are summarized in Table 1. When we compare these results with those from the Speier's catalyst, we can see that in all cases reaction times significantly decreases in the presence of the Karstedt's catalyst. Also all reactions were carried out quantitatively in room temperature in contrast with Speier's catalyst. It must be pointed out that alcoholysis reactions in the presence of the Karstedt's catalyst were carried out under aerobic conditions unlike already similar works [17,18].

2.2. Optimizing of reaction conditions

Optimum reaction conditions were examined employing butyl alcohol (5a) with PMHS in the presence of platinum catalysts (Speier's and Karstedt's catalysts) and the best results were achieved for the conditions collected in Table 2. Evident from Table 2 increasing the amount of the Speier's catalyst to a certain extent can affect reaction time. For instance in the reaction of PMHS with **5a**, by increasing the amount of Pt catalyst from $[Pt^0]/[Si–H] = 8.6 \times 10^{-5}$ to $[Pt^0]/[Si–H] = 34 \times 10^{-5}$, we were able to reduce reaction time from 24 to 16 h. However the alcoholysis reactions have not been take place at 20 °C in the presence of the Speier's catalyst (during 72 h).

As shown in Table 2 the amount of Karstedt's catalyst has a significant affect on the reaction rate. Similar to Speier's catalyst, increasing of the amount of the catalyst to a certain extent leads to a faster reaction, resulting in alcoholysis in a shorter time. For example, it takes only 60 min to reach 100% grafting in the reaction of PMHS and **5a** when the amount of Pt catalyst is $[Pt^0]/[Si–H] = 15 \times 10^{-5}$. The effect of the temperature on the reaction rate is obvious in Table 2. The increase of the temperature from 20 to 80 °C in all cases led to a faster reaction in the presence of Karsted's

Table 1
Alcoholysis of PMHS in the presence of optimum amounts of Speier and Karstedt catalysts.



Entry	Alcohol ROH	Products	Time (h)		Yield %	
			Method[a]	Method[b]	Method[a]	Method[b]
1	CH_3OH **1a**	**1b**	24	2	78	80
2	CH_3CH_2OH **2a**	**2b**	24	2	80	80
3	$CH_3CH_2CH_2OH$ **3a**	**3b**	16	1	90	90
4	$(CH_3)_2CHOH$ **4a**	**4b**	24	2	90	90
5	$CH_3(CH_2)_2CH_2OH$ **5a**	**5b**	16	1	98	99
6	$(CH3)_2CHCH_2OH$ **6a**	**6b**	16	2	98	92
7	$CH_3CH_2CHOHCH_3$ **7a**	**7b**	16	2	95	90
8	$CH_3(CH_2)_3CH_2OH$ **8a**	**8b**	16	1	95	99
9	$CH_3(CH_2)_4CH_2OH$ **9a**	**9b**	16	1	95	99
10	$(CH_3)_3COH$ **10a**	**10b**	–	5	–	90
11	$PhCH_2OH$ **11a**	**11b**	–	10	–	90

[a] Method A: Speier catalyst ($[Pt^0]/[Si–H]$ 34×10^{-5}, 80 °C.
[b] Method B: Karstedt catalyst ($[Pt^0]/[Si–H]$ 15×10^{-5} 20 °C.

Table 2
Optimizing of alcoholysis reaction of PMHS with **5a** in the presence of Pt catalysts.[a]

Entry	Alcohols	Reaction conditions			
		Catalyst	$[Pt^0]/[Si–H]$	Temp (°C)	Time (h)
1	**5a**	Speier's	8.6×10^{-5}	20	-
		Speier's	8.6×10^{-5}	80	20
2	**5a**	Speier's	34.4×10^{-5}	20	-
		Speier's	34.4×10^{-5}	80	16
3	**5a**	Speier's	68.8×10^{-5}	20	-
		Speier's	68.8×10^{-5}	80	16
1	**5a**	Karstedt's	1.8×10^{-5}	20	-
		Karstedt's	1.8×10^{-5}	80	10
2	**5a**	Karstedt's	3.76×10^{-5}	20	8
		Karstedt's	3.76×10^{-5}	80	2
3	**5a**	Karstedt's	7.53×10^{-5}	20	2
		Karstedt's	7.53×10^{-5}	80	1
4	**5a**	Karstedt's	15×10^{-5}	20	1
		Karstedt's	15×10^{-5}	80	0.5
5	**5a**	Karstedt's	30×10^{-5}	20	1
		Karstedt's	30×10^{-5}	80	0.5

[a] In all cases concentration of the PMHS and **5a** are kept constant.

catalyst. Note that in the case of **11a** and **17a**, raising of the reaction temperature to 80 °C caused side reaction that result in coupling product (dibenzyl ether) and cross-inked polymer, respectively.

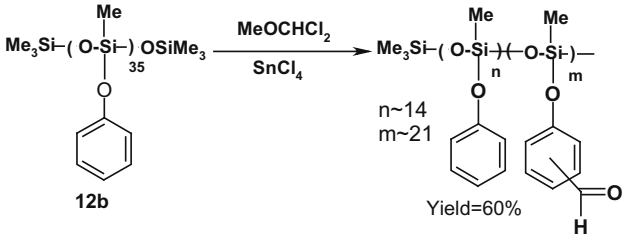
2.3. Alcoholysis reaction of PMHS with functional alcohols

Encouraged by above mentioned results, platinum catalytic reactions were extended to reactions of functional alcohols with use of Karsted's catalyst. Since grafting of PMHS with functional alcohols can offer a way to further modification of the polymer backbone with functionalities, which are otherwise difficult to substitute directly to the polysiloxane chain.

2.3.1. Alcoholysis reaction of PMHS with aromatic alcohol

Similarly, alcoholysis reaction with phenol (**12a**) furnished the corresponding product (**12b**) in high yield according to the applied method (A, B see Table 1 – entry 12). In the following we were interested in carrying out alcoholysis reaction with 4-hydroxyl benzaldehyde in order to introduce of formyl group in side chain of Poly(methyl)siloxanes. With Speier's catalyst, alcoholysis reaction was unsuccessful, but in the presence of Karstedt's catalyst reaction took place during 5 h in 60% yield at 80 °C and since 4-hydroxyl benzaldehyde is solid, direct reaction with PMHS carried out in toluene as solvent. As shown in Table 1 (entry 13) the yield of this reaction was low. This is due to the difficulties in the separation of this alcohol (needs chromatography, see Section 4). Thus indirect approach was examined for its simple separation and workup. Poly(methylphenoxyloxy)siloxane was dissolved in CH_2Cl_2, then was treated with methyl dichloromethyl ether in the presence of anhydrous $SnCl_4$ (mole ratio 1:1:2, 20–25 °C, 3 h) (Scheme 2) [26]. After hydrolysis and successively washing with water, dioxane and conc. HCl, the product exhibiting strong infrared absorption at 1690 and 2720 cm^{-1} was obtained. The percentage of introduction of formyl groups on the side chain calculated 60%. It determined from the ^1H NMR spectrum (Fig. 1a). The mole fraction of the formylated aromatic ring was calculated from the ratio of the peaks at 9.89 ppm assigned to aldehyde groups to the total area between 6.59 and 7.51 ppm, attributed to the nine aromatic protons of the both aromatic rings.

Comparing direct and indirect method show that in direct method the yield of the reaction is low, but aldehyde grafting onto of PMHS side chain took place completely. As can see in Fig. 1c, disappearance of Si–H bond vibration at 2170 cm^{-1} in FT-IR spectroscopy and the concomitant complete disappearance of the protons related to Si–H bond at 4.3 ppm in ^1H NMR and at −34 ppm in ^{29}Si NMR clearly indicated that in direct method all of the Si–H group of PMHS were reacted with 4-hydroxybenzaldehyde.



Scheme 2. Formylation of 12b to obtain poly(siloxane) containing formyl pendant.

2.3.2. Grafting of PMHS with both oligo ethylene oxide and epoxide pendants

Graft copolymers containing oligo ethylene oxide side chains are an interesting group of copolymers due to their solution and surface properties as well as their ability to form phase-separated morphologies [27]. In order to prepare grafting polysiloxane containing oxy ethylene pendant, reaction of PMHS with **14a**, **15a** and **16a** were examined in the presence of Karstedt's catalysts (Scheme 3).

In the case of **16a**, dialysis tube was used to remove of unreacted polyethylene glycol monomethyl ethers ($Mw = 750$) from the reaction mixture. As shown in Table 4 witch comparing solubility of the obtained polymers with PMHS in various solvents, addition of hydrophilic group on the side chain of hydrophobic poly (methyl)siloxane backbone in **16b** affect dramatically in solubility of obtained polymer .

Synthesis of a polymer that possesses both the polysiloxane and epoxide moieties is of grate interest, since the epoxide groups can undergo ring opening reaction on treatment with various reagents, leading to cross-linked polymers. In the present work a polysiloxane grafted epoxide group was obtained in high yield from the reaction of glycidol (**17a**) with PMHS at 20 °C in the presence of Karstedt's catalyst. (Table 3 – entry 6).

2.3.3. Alcolysis reaction of PMHS with haloalcohols

Polysiloxane containing halo functionalities on the side chain are highly valued materials because halo group can be utilized for further modification of the macromolecules formed. However, the routs to these materials such as hydrosilylation of allyl halides often suffer from complex methodologies, side reaction involving rearrangement, or minimal characterization of the products [28,29]. As depicted in Scheme 4, mild and selective reactions with 2-chloro and 2-bromo ethanol were observed without any side reactions and led to the corresponding alkoxysiloxanes in excellent yields according to the mentioned method (B) (Table 3, entry 7, 8)

2.3.4. Alcoholysis reaction of PMHS with allyl alcohol (*20a*)

Dehydrocopling reaction of allyl alcohol with tetramethyldisiloxane [30] and polydimethylsiloxane with terminal Si–H group [31] have been already reported in literature. It is reported that in the reaction of allyl alcohol and Si–H group with the use of Pt catalyst, O-silylation (alcoholysis) competes with C-silylation (hydrosilylation) (As shown in Scheme 5).

It has been previously observed that ratio of the O-silylation to C-silylation in reaction of allyl alcohol with hydrosilane strongly depended on the many factors such as catalyst type, catalyst concentration, solvent type and allyl alcohol amount [17]. Based on above mentioned works, reaction of allyl alcohol and PMHS in var-

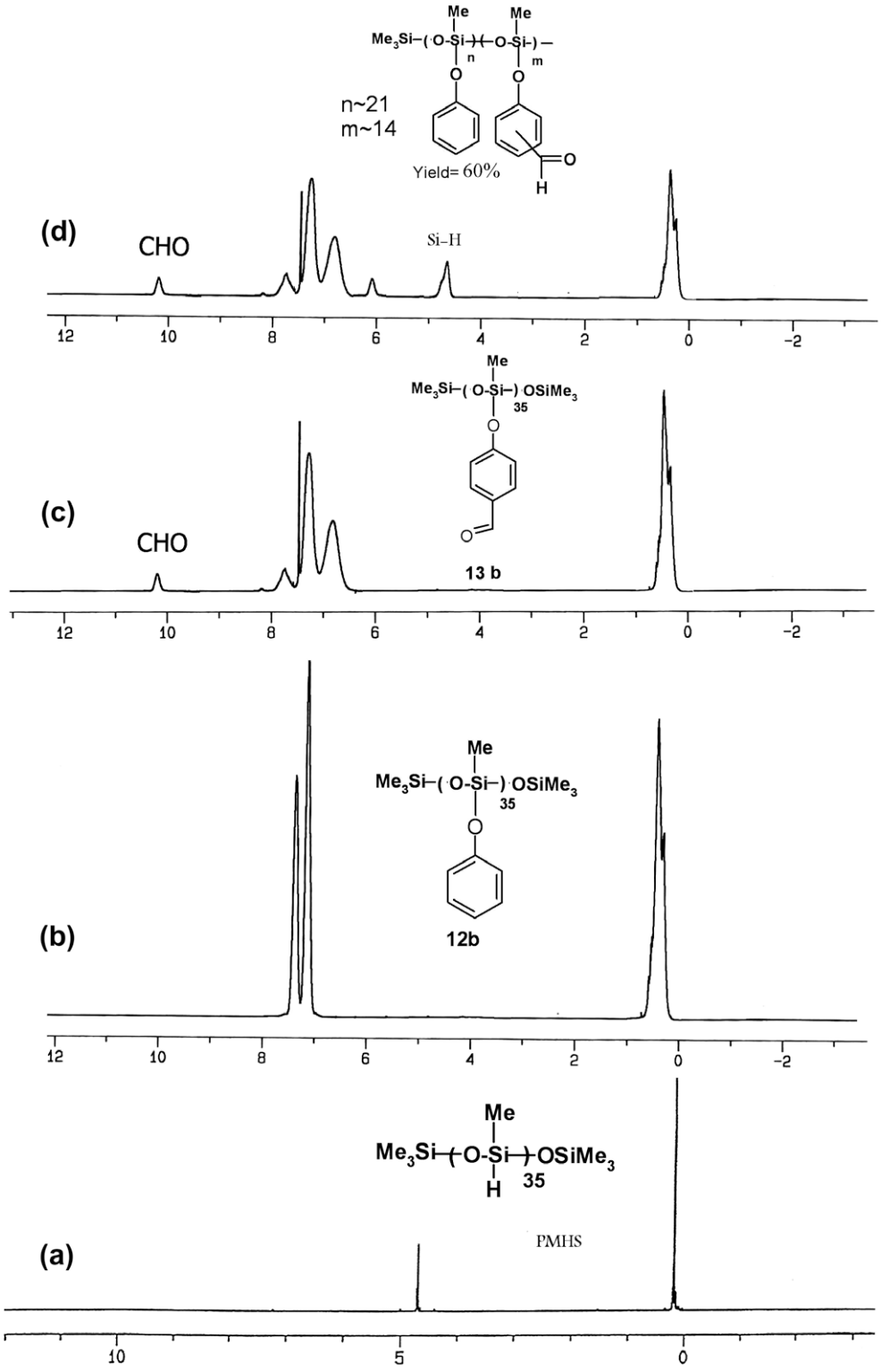
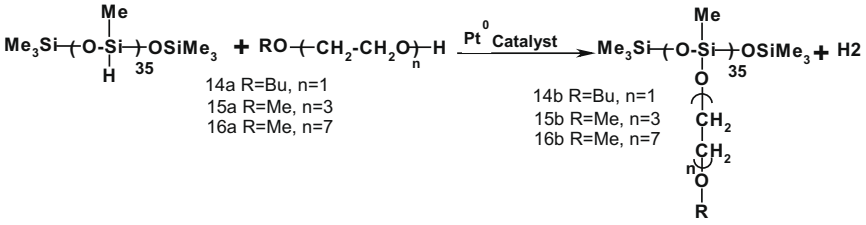


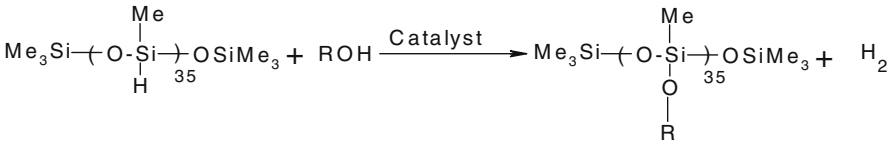
Fig. 1. ^{1}H NMR spectra of (a) PMHS, (b) **12b**, (c) **13b** and (d) product obtained of indirect formylation of **12b**.

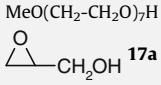
ious conditions was examined. The obtained results are summarized in Table 5. It is found that if the reaction of allyl alcohol (**20a**) and PMHS carried out without the solvent, both C and O-silylation occur and allyl alcohol serves as bifunctional cross-linker to give gel polymer (Table 5, entry 1, 2). For this reason we had to carry out related reactions in a solvent such as toluene. In the process of optimizing the reaction conditions in toluene, we interested in studying the effect of the concentration of Karstedt's catalyst on regioselectivity of the alcoholysis reaction of **20a** with PMHS. When the concentration of the catalyst is $[Pt^0]/[Si–H] = 1.8 \times 10^{-5}$, the reaction required heating at reflux (110 °C) for 24 to go to completion to give a viscous liquid (Table 5, entry 3). For $[Pt^0]/[Si–H] = 7.53 \times 10^{-5}$ the reaction goes to completion in 2 h to give a very oily compound (Table 5, entry 4). Increasing

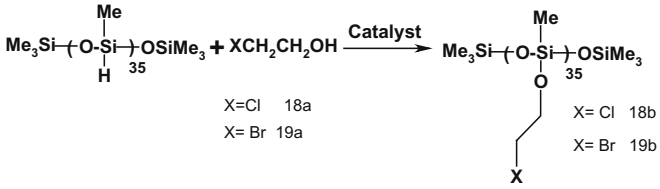


Scheme 3. Synthesis of polysiloxane containing oligo ethylene oxide in side chain.

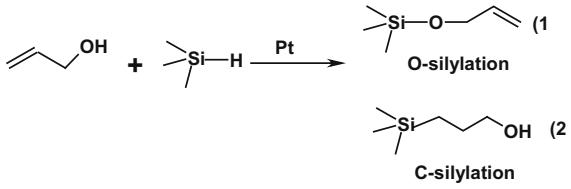
Table 3
Alcoholysis of PMHS with various alcohols in the presence of the optimum amount of Karstedt catalyst ($[Pt^0]/[Si–H] = 15 \times 10^{-5}$).



Entry	Alcohol ROH	Products	Temp (°C)	Solvent	Time (h)	Yield (%)
1	PhOH **12a**	**12b**	80	–	1	98
2	4-CHOPhOH **13a**	**13b**	80	Toluene	10	50
3	$BuOCH_2CH_2OH$ **14a**	**14b**	80	–	0.5	98
4	$MeO(CH_2\text{-}CH_2O)_3H$ **15a**	**15b**	80	–	0.5	98
5	$MeO(CH_2\text{-}CH_2O)_7H$ **16a**	**16b**	80	–	0.5	60
6	 **17a**	**17b**	RT	Toluene	2	90
7	$ClCH_2CH_2OH$ **18a**	**18b**	80	–	0.5	99
8	$BrCH_2CH_2OH$ **19a**	**19b**	80	–	0.5	99



Scheme 4. Dehydrocoupling reaction of PMHS with haloalcohols.



Scheme 5. dehydrocoupling reaction of allyl alcohol and Si–H group with use of Pt catalyst.

Table 4
The solubility of PMHS and Polymer **14b**, **15b** and **16b** in different solvents.

Solvents	PMHS	**14b**	**15b**	**16b**
Chloroform	+	+	+	+
Dichloromethane	+	+	+	+
n-Hexane	+	–	–	–
Toluene	+	+	–-	–
THF	+	+	+	+
Methanol	–	–	–	+
Water	–	–-	–	+

+, Soluble; –, insoluble.

of the catalyst concentration from $[Pt^0]/[Si–H] = 7.53 \times 10^{-5}$ to $[Pt^0]/[Si–H] = 15 \times 10^{-5}$ led to the cross-linking of the obtained product (Table 5, entry 5). Products from the above reactions were analyzed using NMR. At lower concentration of catalyst, for example, $[Pt^0]/[Si–H] = 7.53 \times 10^{-5}$, only O-silylation was observed (see Fig. 2a). A higher Pt^0 concentration, for example, $[Pt^0]/[Si–H] = 1.8 \times 10^{-5}$ about 40% O-silylation was observed (see Fig. 2b) and only 60% the product of β-addition to the double bond of allyl alcohol(C-silylation) was detected. It was found that given the higher Pt^0 concentration increase significantly reaction rate and favor dramatically C-Silylation ratio to O-silylation.

It has been observed by Boleau and coworkers [30], that some C-silylation products are formed in the case of reaction of **20a** by hydride terminated polydimethylsiloxanes at low concentration of Pt^0 catalyst. But we were able to eliminate completely side reactions with **20a**. Our observation could be explained by the fact that we used a pt catalyst concentration four times lower than that used by Boleau and coworkers. It has indeed been shown by these authors that an increase of the catalyst concentration leads to a dramatic decrease of O-silylation products.

2.4. Study of thiolysis reaction of PMHS

To further understanding the dehydrocoupling reaction of PMHS in the presence of Pt catalysts, we sought to carry out thiolysis reaction. The reaction of PMHS with thiophenol and benzyl thiol was examined. No thiolysis reaction was observed, even in the presence of Karstedt's catalyst (in various concentrations of catalyst and temperature). The mechanism of Si–H alcoholysis reaction has already been studied [32].

Most of the mechanistic studies suggest transition metal activation of Si–H bonds, either through oxidative addition (1) or formation of an σ complex (2), which favors attack of the alcohol on Si (Scheme 6).

Table 5
The result of the alcoholysis of allyl alcohol (**20a**) with PMHS in the presence of Karstedt's catalyst.

Entry	$[Pt^0]/[Si–H]$	Solvent	Temp (°C)	Time (h)	O-silylation (%)	Product
1	1.8×10^{-5}	–	20	8	–	Gel polymer
2	3.76×10^{-5}	–	20	6	–	Gel polymer
3	1.8×10^{-5}	Toluene	110	24	100[a]	**20b**
4	7.53×10^{-5}	Toluene	110	2	40[a]	**21b**
5	15×10^{-5}	Toluene	110	2	–	Gel polymer

[a] O- and C-silylation ratio were calculated by ^{1}H NMR spectroscopy.

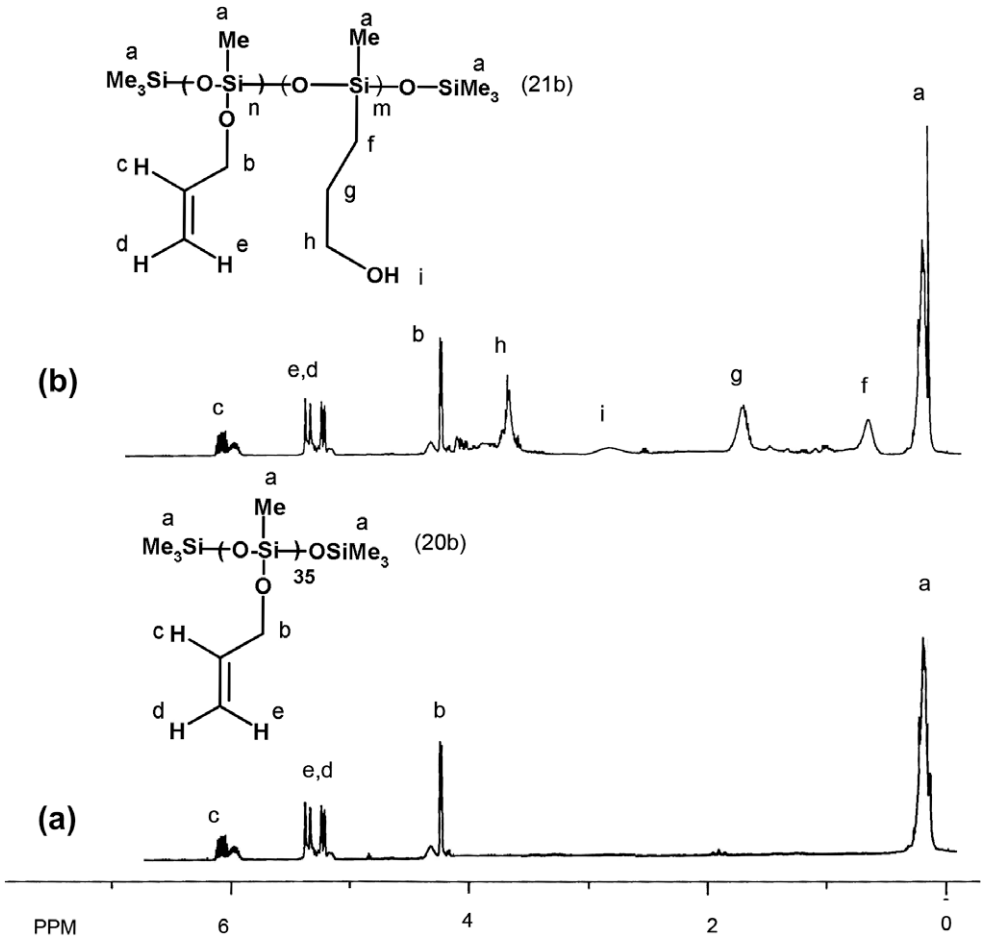
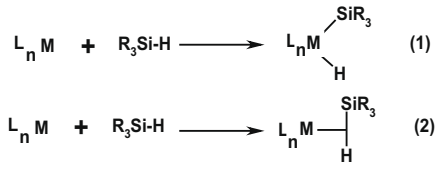


Fig. 2. ^{1}H NMR spectra of the obtained products (A) 20b and (B) 21b.



Scheme 6. The mechanistic pathway for alcoholysis reaction.

On the basis of above mentioned mechanism, probably strong coordination ligands, such as thiols can be bind strongly to the Pt catalysts and make them unreactive for activation of Si–H bonds. This presumption is supported by the fact that alcoholysis reaction of PMHS and alcohols (such as methanol, ethanol and phenol) were unsuccessful in the presence of thiophenol.

3. Conclusions

In this study, functionalization of polysiloxane by grafting functional alcohols was achieved via alcoholysis of the respective alcohols with Si–H group of PMHS in the presence of platinum catalysts. A fair number of alcohols with diverse structure (primary, secondary, sterically and functional) were selectively and efficiently grafted onto the polysiloxane backbone under moderate conditions. The salient features of the present methodology are as follows: firstly, the reaction conditions are mild and lead to selective dehydrocoupling of Si–H bonds, without the side reaction and degradation of the backbone under aerobic conditions. Secondly, the progress of the reaction can be monitored easily by FT-IR spectroscopy. Thirdly, the methodology provides flexibility for a introducing various functional groups on the side chain of PMHS, which are otherwise difficult to substitute directly to the polysiloxane

chain. The obtained results indicated that Karstedt's catalyst is a better catalyst than Speier's catalyst for alcoholysis reaction of PMHS. Finally, it is reported here the first example of regioselective alcoholysis of allyl alcohol at hydroxyl group, which provides one access to poly(siloxanes) pendant allyl groups .

4. Experimental

4.1. Materials

Alcohols such as methanol, ethanol, *n*-propanol, *i*-propanol, *n*-butanol, *s*-butanol, *i*-butanol, *n*-pentanol, *s*-pentanol, *n*-hexanol, *ter*-butanol, benzyl alcohol, allyl alcohol, phenol, 4-hydroxy benzaldehyde, ethylene glycol buthyl monoether, triethylene glycol methyl monoether and glycidol (Merck), were used as received. Polyethylene glycol monomethyl ethers, PEGM, with $M_n = 750$ were purchased from Aldrich Chemical Company. The hexachloroplatinic acid, Speier's catalyst, was used (0.05 m solution in ethanol) and platinum–divinyltetramethyldisiloxane complex, Karstedt's catalyst, with 2 wt% platinum in xylene (Aldrich) were used as received. Toluene was distilled from sodium immediately before use. Dialysis tube (Flat width 32 mm) which useful for separating compounds with a molecular weight of <1200 from compounds with a molecular weight >2000 was supplied from Aldrich company.

4.2. Measurements

Infrared spectra from KBr pellets were recorded with a 4600 Unicam FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were run on a Bruker 400 MHz spectrometer at room temperature with $CDCl_3$ as a solvent. ^{29}Si NMR spectra were obtained on a Varian Inova 400 MHZ NMR .The molecular weights (M_w and M_n) were determined using a waters 501 gel permeation chromatograph fitted with 10^2 and 10^3 mm Waters styragel columns. $CHCl_3$ was used as an elution solvent at a flow rate of 1 ml/min and polystyrene standards were employed for calibration.

4.3. Method A: general procedure for the alcoholysis of PMHS with Speier's catalyst ($H_2PtCl_6{\cdot}6H_2O$)

Optimum amount of 0.05 solution of $H_2PtCl_6{\cdot}6H_2O$ in EtOH ([Pt/[Si–H] = 34.4×10^{-5} were added to a solution of poly(methyl hydrogen)siloxane (2 g, 0.88 mmol) in ROH (20 ml). The mixture was heated at 80 °C for 24 h. The colorless reaction mixture gradually turned to a homogeneous black colored solution, indicating the generation of colloidal Pt particles. The solution was filtered for separation of Pt particles. Then the alcohol evaporated from the filtrate, and the residue again filtered to give oily related product.

4.4. Method B: general procedure for the PMHS with Karstedt's catalyst

A 50 ml round-bottom two-neck flask with magnetic stirring was charged with poly(methylhydrogen)siloxane (2 g, 0.88 mmol) and ROH (20 ml), then optimum amount of Pt as Karstedt's catalyst ([Pt/[Si–H] = 15×10^{-5}) was added. To follow the reaction progress, several samples were taken at different times and were analyzed infrared (FT-IR) spectroscopy. The intensity of the Si–H (2170 cm^{-1}) was monitored The Mixture was stirring at 20 °C until complete disappearance of Si–H bond in FT-IR spectroscopy. After completing of reaction, the mixture was allowed to cool to room temperature. Then the alcohol was evaporated to give oily related product.

4.5. Poly(methylmethoxy)siloxane (**1b**)

Alcoholysis reaction was carried out according to general procedures (Method A, B) FT-IR (KBr, cm^{-1}), 2962 (C–H), 1265, 842 (Si–CH_3), 1080 (Si–O), 1008 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.06 (br s, terminal SiMe), 0.11 (br s, SiMe), 3.60 (CH_3O); ^{13}C NMR ($CDCl_3$) δ, ppm: −5.9.0, −5.1 (Si–Me), 59.4 (CH_2O); ^{29}Si NMR (400 MHz, $CDCl_3$, ppm): δ −53.2 (br s, SiMe), 9.7 (terminal SiMe).

4.6. Poly(methylethoxy)siloxane (**2b**)

Alcoholysis reaction was carried out according to general procedures (Method A, B). FT-IR (KBr, cm^{-1}), 2960 (C–H), 1260, 852 (Si–CH_3), 1082 (Si–O), 1010 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.07 (br s, terminal SiMe), 0.12 (br s,SiMe), 1.12 (CH_3), 3.42 (CH_2O); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.0, −5.3 (Si–Me), 25.6 (CH_3), 60.2 (CH_2O).

4.7. Poly(methylpropyloxy)siloxane (**3b**)

Alcoholysis reaction was carried out according to general procedures (Method A, B). FT-IR (KBr, cm^{-1}), 2964 (C–H), 1255, 852 (Si–CH_3), 1081 (Si–O), 1009 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.07 (br s, terminal SiMe), 0.13 (br s, SiMe), 0.88 (CH_3), 1.54 (CH_3CH_2), 3.45 (CH_2O); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.1, −5.0 (Si–Me), 14.5 (CH_3), 24.8 (CH_3CH_2), 62.4 (CH_2O); GPC $M_n = 3900$, $M_w = 7410$, $M_n/M_w = 1.9$.

4.8. Poly(methyl-1-methylethoxy)siloxane (**4b**)

Alcoholysis reaction was carried out according to general procedures (Method A, B). FT-IR (KBr, cm^{-1}), 2959 (C–H), 1252, 830 (Si–CH_3), 1080 (Si–O), 1011 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.07 (br s, terminal SiMe), 0.13 (br s, SiMe), 1.11 ((CH_3)$_2$CH), 3.95 ((CH_3C)$_2$CHO); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.3, −5.3 (Si–Me), 24.8 (CH_3)$_2$CH), 62.4 (CHO).

4.9. Poly(methylbuthyloxy)siloxane (**5b**)

Alcoholysis reaction was carried out according to general procedures (Method A, B). FT-IR (KBr, cm^{-1}), 2962 (C–H), 1262, 859 (Si–CH_3), 1085 (Si–O), 987 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.07 (br s, terminal SiMe), 0.13 (br s,SiMe), 0.88 (CH_3), 1.27 ($CH_2CH_2CH_2$), 1.53 (CH_2CH_2O), 3.69 (CH_2O); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.0, −5.1(Si–e), 15.5 (CH_3), 30.1 (CH_3CH_2), 33.1 (CH_2CH_2O), 60.4 (CH_2O); ^{29}Si NMR (400 MHz, $CDCl_3$, ppm): δ −52.2 (br s, SiMe), 10.1 (terminal SiMe); GPC $M_n = 4600$, $M_w = 7360$, $M_n/M_w = 1.6$.

4.10. Poly(methyl-2-methylpropyloxy)siloxane (**6b**)

Alcoholysis reaction was carried out according to general procedures (Method A, B). FT-IR (KBr, cm^{-1}), 2960 (C–H), 1266, 854 (Si–CH_3), 1085 (Si–O), 1003 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.06 (br s, terminal SiMe), 0.12 (br s, SiMe), 0.90 (CH_3), 1.67 (CH), 3.5 (CH_2O); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.2, −5.0 (Si–Me), 18.5 (CH_3), 29.1 (CH), 68.4 (CH_2O).

4.11. Poly(methyl-1-methyl-1-propyloxy)siloxane (**7b**)

Alcoholysis reaction was carried out according to general procedures (Method A, B). FT-IR (KBr, cm^{-1}), 2965 (C–H), 1265,845 (Si–CH_3), 1081 (Si–O), 1002 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.04 (br s, terminal SiMe), 0.10 (br s, $SiMe_3$), 0.88 (CH_3), 1.07 (3H, CH_3CHO), 1.42 (2H, CH_2), 3.69 (CH_2O); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.0, −5.3 (Si–Me), 15.5 (CH_3CH_2), 21.9 (CH_3CHO), 31.1(CH_2), 68.4 (CH_2O).

*4.12. Poly(methylpentyloxy)siloxane (**8b**)*

Alcoholysis reaction was carried out according to general procedures (Method A, B). FT-IR (KBr, cm^{-1}), 2965 (C–H), 1260, 840 (Si–CH_3), 1081 (Si–O), 1010 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.07 (br s, terminal SiMe), 0.12 (br s, SiMe), 0.88 (CH_3), 1.27 (4H, $CH_2(CH_2)_2$), 1.48 (CH_2CH_2O), 3.60 (CH_2O); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.0, −5.3 (Si–Me), 13.5 (CH_3), 21.5 (CH_3CH_2), 27.2 (CH_2CH_2), 31.4 (CH_2CH_2O), 60.4 (CH_2O); ^{29}Si NMR (400 MHz, $CDCl_3$, ppm): δ −53.2 (br s, SiMe), 10.1 (terminal SiMe); GPC M_n = 5200, M_w = 9800, M_n/M_w = 1.9.

*4.13. Poly(methylhexyloxy)siloxanes (**9b**)*

Alcoholysis reaction was carried out according to general procedures (Method A, B). FT-IR (KBr, cm^{-1}), 2929 (C–H), 1266, 862 (Si–CH_3), 1084 (Si–O), 1030, 962 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.07 (br s, terminal SiMe), 0.13 (br s, $SiMe_3$), 0.88 (CH_3), 1.27 (6H, $CH_2CH_2CH_2$), 1.53 (CH_2CH_2O), 3.69 (CH_2O); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.6, −5.5 (Si–Me), 15.5 (CH_3), 30.1 (CH_3CH_2), 33.1 (CH_2CH_2O), 60.4 (CH_2O); ^{29}Si NMR (400 MHz, $CDCl_3$, ppm): δ −53.2 (br s, SiMe), 10.8 (terminal SiMe); GPC M_n = 5600, M_w = 9520, M_n/M_w = 1.7.

*4.14. Poly(methyl-1,1-dimethylethoxy)siloxane (**10b**)*

Alcoholysis reaction was carried out according to general procedures (Method A, B). FT-IR (KBr, cm^{-1}), 2958 (C–H), 1253, 830 (Si–CH_3), 1083 (Si–O), 1005 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.11 (br s terminal SiMe), 1.30 (9H, CH_3); ^{13}C NMR ($CDCl_3$,) δ, ppm: −6.1, −5.0 (Si–Me), 21 (3C, Me), 62.2 (CH_2O); GPC M_n = 5500, M_w = 9900, M_n/M_w = 1.8.

*4.15. Poly(methylbenzyloxy)siloxane (**11b**)*

Alcoholysis reaction was carried out according to general procedures (Method B). FT-IR (KBr, cm^{-1}), 2962 (C–H), 1255, 832 (Si–CH_3), 1080 (Si–O), 1008 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.25 (br s, terminal SiMe), 0.29 (br s 3H,SiMe), 4.91 (CH_2Ph), 7.36–7.39(Ph); ^{13}C NMR (CDCl3) δ, ppm: −6.0, −5.2 (Si–Me), 70.9 (OCH_2Ph) 126.3, 126.5, 127.3, 137.1 (Ph)); ^{29}Si NMR (400 MHz, $CDCl_3$, ppm): δ −57.5 (br s, SiMe), 9.3 (terminal SiMe).

Alcoholysis reaction according to method A, gave dibenzyl ether as product. b.p 120 °C/2 mm Hg., ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 4.66 (s,4H, CH_2O), 7.45–7.47 (10H, Ph).

*4.16. Poly(methylphenoxy)siloxane (**12b**)*

Alcoholysis reaction was carried out according to general procedure in the presence of Karstedt's catalyst (Method B). FT-IR (KBr, cm^{-1}), 3066(=CH), 2973, 1595, 1494 (C=C), (C–H), 1286, 897 (Si–CH_3), 1127 (Si–O), 935 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.22 (br s, terminal SiMe), 0.26 (br s 3H,SiMe), 6.99–8.24 (Ph); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.3, −5.3 (Si–Me), 115.3, 128.8, 131.3, 163.42 (ph); ^{29}Si NMR (400 MHz, $CDCl_3$, ppm): δ −58.4 (br s, SiMe), 12.8 (terminal SiMe); GPC M_n = 5800, M_w = 11020, M_n/M_w = 1.9.

*4.17. Poly(methyl-4-formylphenoxy)siloxane (**13b**)*

Alcoholysis reaction was carried out according to general procedure in the presence of Karstedt's catalyst (Method B). FT-IR (KBr, cm^{-1}), 3066 (=CH), 2980 (C–H), 2842, 2730 (CHO), 1693 (CO), 1601, 1449 (Ph) 1262, 855 (Si–CH_3), 1101 (Si–O), 1018 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.20 (br s, terminal SiMe), 0.21 (br s 3H,SiMe), 6.91–7.42 (Ph), 9.20 (CHO); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.0, −5.1(Si–Me), 115.2, 124.3,, 133.3, 162.42, (Ph), 191.6(CHO); GPC M_n = 6400, M_w = 16000, M_n/M_w = 2.5.

*4.18. Grafting of ethylene glycole monobuthylether onto PMHS (**14b**)*

Alcoholysis reaction was carried out according to general procedure in the presence of Karstedt's catalyst (Method B). FT-IR (KBr, cm^{-1}), 2959 (C–H), 1267, 842 (Si–CH_3), 1082 (Si–O), 1030, 1002 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.07 (br s, terminal SiMe), 0.11 (br s, SiMe), 0.82 (CH_3), 1.26 (CH_3CH_2), 1.44 ($CH_3CH_2CH_2$), 3.33 (CH_2O), 3.76 (OCH_2–CH_2O); ^{13}C NMR (CDCl3) δ, ppm: −6.9, −5.67 (Si–Me), 12.6 (CH_3), 18.4 (CH_3CH_2), 30.5, ($CH_3CH_2CH_2$), 60.6 ($SiCH_2O$), 62.8(CH_2O); ^{29}Si NMR (400 MHz, $CDCl_3$, ppm): δ −58.1 (br s, SiMe), 10.0 (terminal SiMe); GPC M_n = 6100, M_w = 12200, M_n/M_w = 2.0.

*4.19. Grafting of triethylene glycole monomethylether onto PMHS (**15b**)*

Alcoholysis reaction was carried out according to general procedure in the presence of Karstedt's catalyst (Method B). FT-IR (KBr, cm^{-1}), 2878 (C–H), 1268, 850 (Si–CH_3), 1194 (Si–O), 1111, 1034 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.03 (br s, terminal SiMe), 0.08 (br s SiMe3), 3.25 (br s, CH_3O), 3.44 (br m, 12H, OCH_2–CH_2O); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.9, −5.28 (Si–Me), 57.74 (CH_3O), 60.2 ($SiOCH_2$), 69.2 (OCH_2CH_2O); ^{29}Si NMR (400 MHz, $CDCl_3$, ppm): δ −56.1 (br s, SiMe), 10.5 (terminal SiMe); GPC M_n = 8200, M_w = 17220, M_n/M_w = 2.1.

*4.20. Grafting of polyethylene glycole monomethyl ether (Mw = 750) onto PMHS (**16b**)*

Alcoholysis reaction was carried out according to general procedure in the presence of Karstedt's catalyst (Method B). After disappearing of Si–H bond vibration in FT-IR spectrum, the reaction mixture (0.5 g) was packed into a dialysis tube. The tube was then put into a flask which contained distilled water. The solution was stirred for 48 h at room temperature .Then a new tube which contained the same solution was replaced and the reaction was continued for more 48 h. Then Solvent was removed in vacuum to leave the polymer as an oily liquid. The FT-IR (KBr, cm^{-1}), 2965 (C–H), 1255, 842 (Si–CH_3), 1075 (Si–O), 1000 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.1 (SiMe), 3.22(br s, CH_3O), 3.45–3.55(OCH_2); ^{13}C NMR (CDCl3) δ, ppm: −5.9, −5.0 (Si–Me), 57.5 (CH_3O), 68.6 ($SiOCH_2$), 68.7 (CH_2O).

*4.21. Grafting of glycidol onto PMHS (**17b**)*

Alcoholysis reaction was carried out according to general procedure in the presence of Karstedt's catalyst (Method B). FT-IR (KBr, cm^{-1}), 2962 (C–H), 1257, 853 (Si–CH_3), 1116 (Si–O), 1008 (C–O), 908 (cyclic C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.1 (br s, SiMe), 2.82 (cyclicCHO), 3.18 (cyclicCH_2), 3.50–3.99 (cyclicCH_2O, CH_2O), ^{13}C NMR ($CDCl_3$) δ, ppm: −5.9, −5.0 (Si–Me), 44.5 (cyclic CHO), 53.2(cyclic CH_2O), 62.2 (CH_2O).

*4.22. Poly(methyl-2-chloroethoxy)siloxane (**18b**)*

Alcoholysis reaction was carried out according to general procedure in the presence of Karstedt's catalyst (Method B). FT-IR (KBr, cm^{-1}), 2965 (C–H), 1271, 847 (Si–CH_3), 1083 (Si–O), 1045 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.18 (br s, SiMe), 3.57 (CH_2Cl), 3.95 (OCH_2); ^{13}C NMR ($CDCl_3$) δ, ppm: −5.9, −5.0 (Si–Me), 47.2 (CH_2Cl), 63.4 (OCH_2); GPC M_n = 5100, M_w = 8760, M_n/M_w = 1.7.

*4.23. Poly(methyl -2-bromoethoxy)siloxane (**19b**)*

Alcoholysis reaction was carried out according to general procedure in the presence of Karstedt's catalyst (Method B). FT-IR (KBr, cm^{-1}), 2962 (C–H), 6 1268, 840 (Si–CH_3), 1086 (Si–O), 1001 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.12 (br s, SiMe), 3.51 (CH_2Br), 3.94 (OCH_2); ^{13}C NMR ($CDCl_3$) δ, ppm: −5.9, −5.0 (Si–Me), 37.2 (CH_2Br), 62.4 (OCH_2); ^{29}Si NMR (400 MHz, $CDCl_3$, ppm): δ −57.4 (br s, SiMe), 10.8 (terminal SiMe).

*4.24. Poly(methyl-2-propenoxy)siloxane (**20b**)*

Alcoholysis reaction was carried out under conditions that summarized in Table 5. FT-IR (KBr, cm^{-1}), 3110 (=CH), 2932 (C–H), 1647, 1411(C=C), 1263, 850 (Si–CH_3), 1086 (Si–O), 1001 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.09 (br s, SiMe), 4.16 (CH_2O), 5.17, 5.26 (=CH_2), 5.93 (=CH); ^{13}C NMR ($CDCl_3$) δ, ppm: −5.7, −4.7 (Si–Me), 60.4 (Si–OCH_2), 112 (=CH_2), 135(=CH).

Spectroscopic result of copolymer **21b** is followed:

FT-IR (KBr, cm^{-1}), 3300 (OH), 3110 (=CH), 2930 (C–H), 1646, 1420 (C=C), 1253, 850 (Si–CH_3), 1086 (Si–O), 990 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.10(br s, SiMe), 0.15 (CH_2–Si), 1.61 (CH_2–CH_2), 3.01 (br s, OH), 3.64 (CH_2OH), 4.17 (CH_2OSi), 5.21–5.27 (=CH_2), 5.9 (=CH); ^{13}C NMR ($CDCl_3$) δ, ppm: −5.7, −4.3 (Si–Me), 12 (CH_2–Si), 19 (CH_2–CH_2), 56.3 (CH_2OH), 61.2 (Si–OCH_2), 113 (=CH_2), 136 (=CH).

4.25. Formylation of polymer 12b to indirect introduce formyl group on the side chain of poly(siloxanes)

Dissolved polymer **12b** (1 g) in 20 ml CH_2Cl_2 was treated with methyl dichloromethyl ether (Cl_2CHOMe) in the presence of anhydrous tin (IV) chloride ($SnCl_4$) (mole ratio1:1:2, 20–25 °C, 3 h). After hydrolysis and successively washing with water, 1,4-dioxane and HCl mixture, the organic layer was poured into cooled methanol to precipitate the formylated polymer. FT-IR (KBr, cm^{-1}), 3066 (=CH), 2980 (C–H), 2842, 2732 (CHO), 1696 (CO), 1601, 1449 (Ph) 1250, 835 (Si–CH_3), 1100 (Si–O), 1028 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.20 (br s, terminal SiMe), 0.23 (br s 3H,SiMe), 6.91–8.22 (Ph), 9.25 (CHO); ^{13}C NMR ($CDCl_3$) δ, ppm: −6.0, −5.1 (Si–Me), 115.3, 115.8 122.1, 126.3, 128.8, 132.1, 131.3, 161.42, 163.2 (Ph), 190.6(CHO); GPC M_n = 4700, M_w = 13160, M_n/M_w = 2.8.

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