

## POLYETHYLENEGLYCOL-BRIDGED POLYSILOXANE GELS: REACTIVITY AND STRUCTURAL EFFECTS OF GLYCOL CHAIN LENGTH

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**ABSTRACT:** Polyethylene glycol-bridged polysiloxane-derived gels were synthesized by hydrosilylation reaction between polymethylhydrosiloxane and polyethylene glycols of different chain lengths. The obtained polymers have been characterized by elemental analysis, by FTIR,  $^{29}\text{Si}$  CP-MAS NMR and  $^{13}\text{C}$  CP-MAS NMR.  $^{29}\text{Si}$  and  $^{13}\text{C}$  solid-state analysis allowed to show the presence of unreacted hydroxyl ether groups, the occurrence of side reactions and to calculate the degree of cross-linking in the polymers.

**Key words:** polymethylhydrosiloxane, polyethylene glycol, hybrid gel

**RESUME:** Des gels à base de polysiloxane et de polyéthylène glycols ont été synthétisés par réaction d'hydrosilylation entre le polyméthylhydrosiloxane et des polyéthylène glycols avec différentes longueurs de chaînes. Les polymères obtenus ont été caractérisés par analyse chimique élémentaire, par FTIR, RMN CP-MAS  $^{29}\text{Si}$  et RMN CP-MAS  $^{13}\text{C}$ . La spectroscopie RMN  $^{29}\text{Si}$  et  $^{13}\text{C}$  en phase solide a permis de montrer la présence de groupements hydroxyl n'ayant pas réagi, de calculer le taux de greffage des polyéthylène glycols et d'identifier les réactions secondaires ayant lieu dans le milieu réactionnel.

**Mots clés:** polyméthylhydrosiloxane, polyéthylène glycol, gel

### 1. Introduction

Polysiloxane hybrid materials prepared by sol-gel route such as ORganically MODified SILicates (ORMOSILs) have received increasing interest owing to their wide field of use [1]. These gels can be obtained from different silicon precursors as silicon alkoxides, chlorosilanes, alkoxy silanes or siloxanes [2,3].

This wide variety of precursors permit to tailor polysiloxane gels with particular properties allowing various applications (optical, biosensing, chromatography, photomeric, sensing, ceramics ...) [4-11]. Specially, many works have focused on the preparation and use of hybrid organic-inorganic gels prepared from polysiloxanes (polydimethylsiloxane, polydiethylhydrosiloxane, polymethylhydrosiloxane) as silicon precursors and/or polyethylene oxides as chemical modifier [12-14].

However, only few authors have reported detailed study on the structure of these polymers.

This paper deals with the preparation and characterization of modified polysiloxane-based polymers by using, as cross-linking agent, compounds containing ether groups. Three molecules of polyethylene glycol, with different chain length, are introduced into the three-dimensional polysiloxane structure through the sol-gel process. The structure of the materials and precisely the nature of the formed species is studied by solid state NMR spectroscopy: solid-state  $^{29}\text{Si}$  NMR spectroscopy provided useful information on the nature of local environment of the polysiloxane framework silicon atoms and  $^{13}\text{C}$  NMR gives information about organic part of the materials.

## 2- Experimental

### 2.1. Starting materials

Chemical structures of starting materials are shown in chart I. Polymethylhydrosiloxane (PMHS), diethylene glycol (DEG), tetraethylene glycol (TEG), polyethylene glycol 400 (EG400, MW400) are purchased from Fluka.  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  is purchased from Aldrich. Tetrahydrofuran (THF, Rectapur) is analytical grade and was distilled over sodium before use.

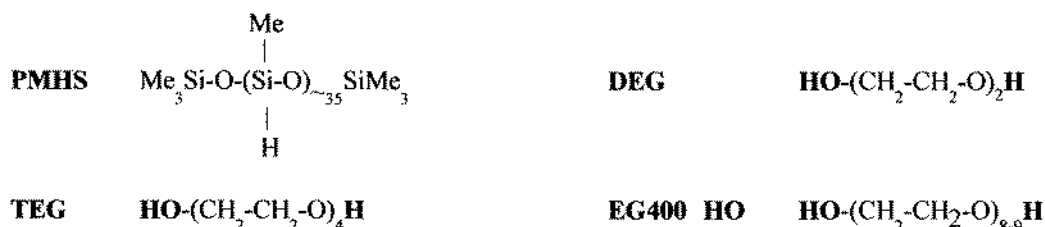
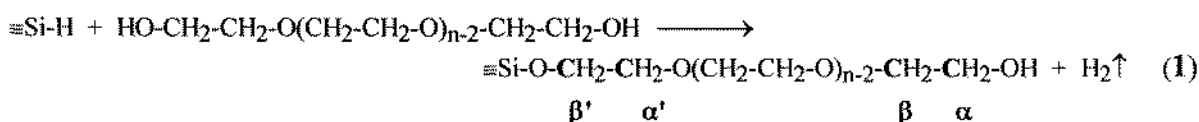


CHART I: Chemical structures of PMHS, DEG, TEG and EG400

### 2.2. Preparation

Polymers were prepared by hydrosilylation reaction (reaction 1) between PMHS and DEG, TEG or EG400. 1.00 g of PMHS ( $1.55 \cdot 10^{-2}$  mol of Si-H) is dissolved in tetrahydrofuran (THF), then the polyethylene glycol (PEG) is added to the obtained solution in a stoichiometric ratio  $r = \frac{\text{PEG mole number}}{\text{Si-H mole number}} = 0,5$ . The reaction is catalysed by 0.1 ml of a  $10^{-2}\text{M}$  hexachloro-platinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) solution in THF. For all samples the total volume of the reaction medium was 10 ml. The reaction is conducted at  $60^\circ\text{C}$ . We noticed that gelification time decreases with the length of polyethylene glycol chain (table I).



with  $n=2$  for DEG,  $n=4$  for TEG and  $n=8-9$  for EG400.

PS-DEG, PS-TEG and PS-EG400 designate polyethylene glycol-bridged polysiloxanes prepared by the polymerization of PMHS with DEG, TEG and EG400 respectively.

Table I: gelation time of the prepared gels.

Gels	PS-DEG	PS-TEG	PS-PG400
Gelation times	4 h	3 h 15mn	1 h 20mn

### 2.3. Characterization

The obtained samples were characterized by Fourier Transformed Infra-Red (FTIR), chemical analysis,  $^{13}\text{C}$  and  $^{29}\text{Si}$  solid state nuclear magnetic resonance with cross polarization at magic angle spinning (CP-MAS NMR). FTIR spectra were recorded on a Perkin-Elmer 1000 spectrometer using the KBr pellet technique. The number of scans was 5.

PMHS  $^{29}\text{Si}$  NMR spectrum was recorded on a Bruker AM 250 spectrometer.  $^{13}\text{C}$  and  $^{29}\text{Si}$  CP-MAS NMR spectra were recorded on a Bruker ASX 500 spectrometer working at 99.35 MHz. For the  $^{13}\text{C}$  CP-MAS NMR experiments, pulse width, relaxation delay and contact time were 5.0  $\mu\text{s}$ , 4 s and 2 ms, respectively. For the  $^{29}\text{Si}$  CP-MAS NMR experiments, these parameters were 5.2  $\mu\text{s}$ , 4 s and 5 ms, respectively.  $^{13}\text{C}$  CP-MAS NMR spectra were simulated with Origin 4.1 software

(Microsoft). Powders were chemically analyzed by Service Central d'Analyse of the CNRS (Vernaison, FRANCE). A Nanoscope III multimode AFM (Digital Instrument) was used in the tapping mode to produce AFM images.

### 3. Results and discussion

#### 3.1. FTIR characterization

PS-DEG, PS-TEG and PS-EG400 gels have similar FTIR spectra. Figure 1 shows PS-TEG FTIR spectrum. Characteristic IR bands observed on PMHS, PEG (polyethylene glycol) and PS-PEG spectra are listed in table II [15-19]. The band due to stretching Si-H vibration ( $2160\text{ cm}^{-1}$ ) gives valuable information about the evolution of the hydrosilylation reaction (reaction 1). Disappearance of this band in PS-PEG spectra clearly indicates that Si-H groups have almost totally reacted. Likewise, the broad and intense band between  $835$  and  $900\text{ cm}^{-1}$  relative to  $\delta_{\text{Si-H}}$  and  $\rho_{\text{asym}(\text{CH}_3)}$  present in PMHS spectrum transforms into a weak band at  $850\text{ cm}^{-1}$  in PS-PEG spectra. The environment of silicon atom linked to the carbon influences the frequency of the symmetric deformation of C-H in Si-CH<sub>3</sub> moiety. The shift of  $\delta_{\text{sym}(\text{CH}_3)}$  band from  $1263$  to  $1273\text{ cm}^{-1}$  on going from PMHS to PS-PEG is due to silicon environment modification which is consistent with the disappearance of Si-H group vibrations.

The PS-PEG (gels obtained with the polyethylene glycols spectra) show a broad  $\nu_{\text{O-H}}$  band at  $3470\text{ cm}^{-1}$  revealing the presence of unreacted OH-PEG end groups. The large  $\nu_{\text{C-H}}$  band includes C-H stretching modes of polysiloxane methyl groups and PEG methylene groups. Symmetrical and asymmetrical CH<sub>2</sub> deformation modes of PEG appear in the spectra of PS-PEG at  $1350$  and  $1458\text{ cm}^{-1}$  respectively. The strong band in the  $1000$ - $1150\text{ cm}^{-1}$  region involves Si-O-Si and C-O stretching modes. Both bands at  $1035$  and  $1130\text{ cm}^{-1}$  correspond to the Si-O-Si asymmetric stretching vibration [20,21]. FTIR spectra of modified polysiloxanes show additional bands associated with C-O stretching appearing between those relative to Si-O-Si ( $1035$ - $1130\text{ cm}^{-1}$ ).

**Table II:** FTIR characteristic bands of PMHS, PEG and PS-PEG

	PMHS	PEG	PS-DEG	PS-TEG
$\nu_{\text{OH}}$	-	3300-3500 vst 3600-3660 vw	w	3468
$\nu_{\text{C-H}}$	2962 m	2993-2861 st	2927	2975 2927
$\nu_{\text{Si-H}}$	2160 vst	-	-	-
$\delta_{\text{asCH}_2}$	-	1455 m	vw	1459 w
$\delta_{\text{SCH}_2}$	-	1351 m	vw	1353 w
$\delta_{\text{asCH}_3}$	1405 w	-	-	1411 vw
$\delta_{\text{SCH}_3}$	1263 m	-	1273 m	1273
$\nu_{\text{Si-O-Si}}$	1180-1035 vst	-	1032 1140	1030 1125
$\nu_{\text{C-O}}$	-	1077-1105 st 1120-1135 st	1074	1071 1100
$\delta_{\text{Si-H}}$ and $\rho_{\text{as}(\text{CH}_3)}$	925-835 vst	-	847	848 w
$\nu_{\text{Si-C}}$	770 st; 710 sh	-	778	778
$\gamma_{\text{Si-H}}$	628	-	-	-
$\delta_{\text{Si-O-Si}}$	400 st	-	438	438 st

vst: very strong, st: strong, m: middle, vw: very weak, w: weak.

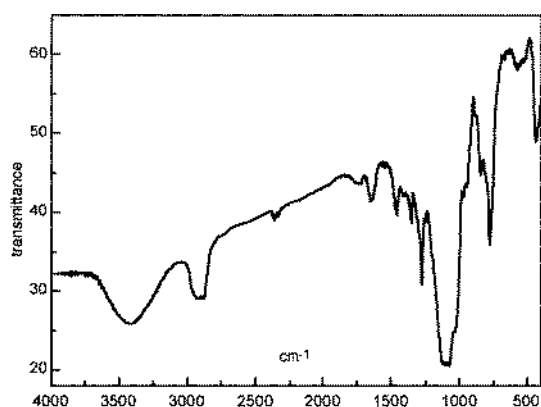


Figure 1: FTIR spectrum of PS-TEG

### 3.2. $^{29}\text{Si}$ CP-MAS NMR study

$^{29}\text{Si}$  NMR spectrum of PMHS (figure 2) shows two main resonances. The weak peak at 10 ppm is due to terminal silicon atoms  $(\text{CH}_3)_3\text{Si}-\text{O}_{1/2}$  (designated  $\text{C}_M$ ). The silicon in  $\text{CH}_3(\text{Si}-\text{O})_2\text{Si}-\text{H}$  structure (designated  $\text{D}_2^{\text{H}}$ ) gives a signal around -35 ppm which appears as a doublet due to spin-spin coupling between Si and H ( $J_{\text{Si}-\text{H}}^1 = 240 \text{ Hz}$ ) [22].

$^{29}\text{Si}$  NMR spectra of the three samples are presented in figure 3. The chemical shift values are listed in table III. All spectra show three main peaks appearing around -36, -58 and -67 ppm, corresponding to  $\text{D}_2^{\text{H}}$ ,  $\text{T}_2$  and  $\text{T}_3$  units, respectively. PS-TEG spectrum shows a supplementary weak signal corresponding to  $\text{T}_1$  unit. The various silicon units are shown on chart II.

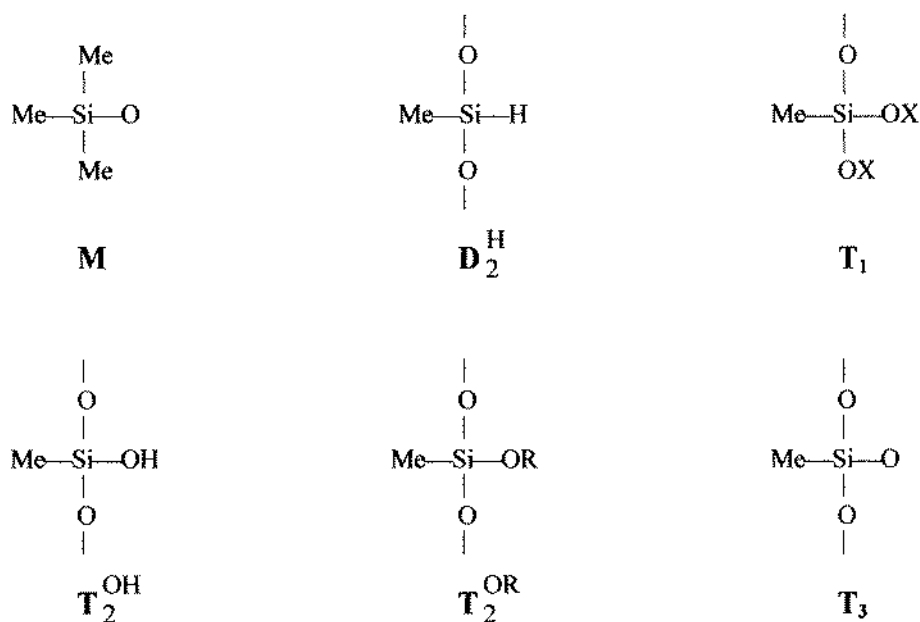


CHART II : Nomenclature of functional silicon units

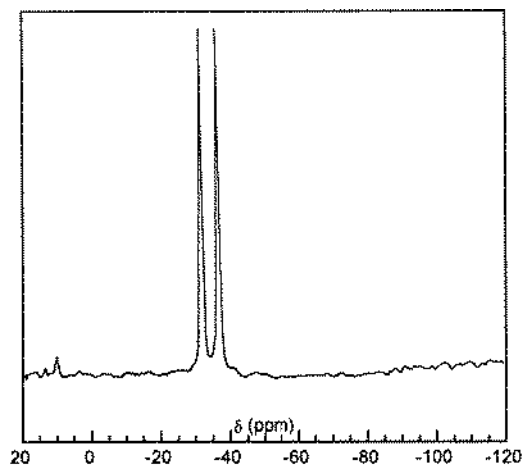


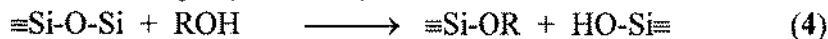
Figure 2:  $^{29}\text{Si}$  NMR spectrum of PMHS

Silicon chemical shifts undergo a high field shift on going from M to  $T_3$  silicon units [23,24]. This effect is known to be due to the change of electronic environment of the silicon atom. The main peak around -58 ppm is assigned to  $T_2$  units. This is consistent with the reaction of Si-H groups and formation of Si-OX groups ( $X = R$  or H). The  $T_2$  peak consists of two components,  $T_2^{\text{OR}}$  and  $T_2^{\text{OH}}$  displaying signals at -58 and -57 ppm respectively. The distinction between these two moieties is possible owing to the very high sensitivity of silicon to its electronic environment. G. Engelhardt and D. Michel [25] have largely studied this effect and established relation between  $^{29}\text{Si}$  chemical shifts and electronic structure of the system investigated. Increasing silicon net charge due to increasing effective electronegativity of oxygen bonded to it, causes proportional high-field shifts of the silicon signal. The type of its next-nearest neighbour atom determines the effective electronegativity of a particular oxygen atom.

The silanol groups of the  $T_2^{\text{OH}}$  units ( $\equiv\text{Si-OH}$ ) are formed from side reaction occurring in the presence of moisture traces (reaction 2), probably carried by THF solvent or by the catalyst. The formation of Si-O-Si linkages by condensation of silanol groups (reaction 3) leads to the apparition of a signal at -66 ppm ( $T_3$  units) observed in all PS-PEG  $^{29}\text{Si}$  NMR spectra.



The small amount of  $T_1$  units detected in PS-TEG, indicates that some cleavage of siloxane chain had taken place in this sample (reaction 4).



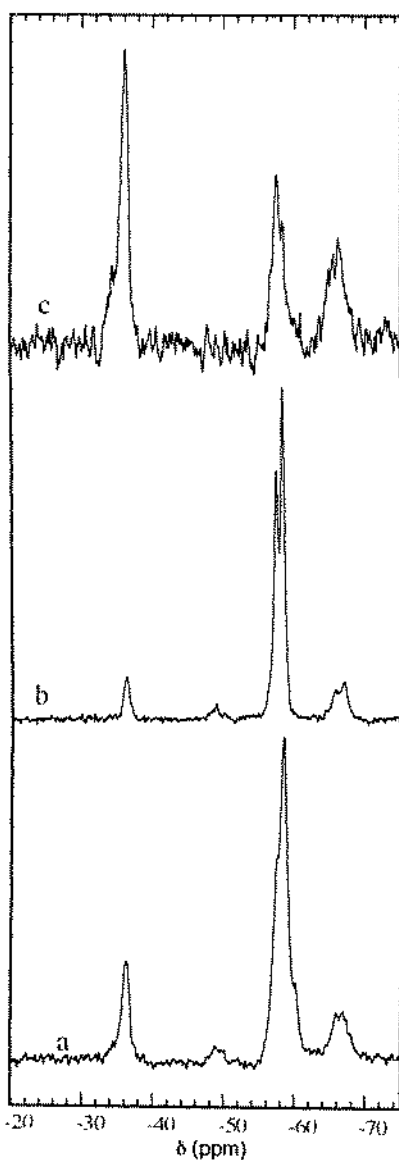
In contrast to FTIR results,  $^{29}\text{Si}$  NMR spectra of all samples show the presence of residual Si-H groups in the materials as evidenced by the peaks at c.a. -36.2 ppm (figure 3-a, b and c). This can be explained to the sensitivity difference between both techniques. The CP-MAS method used for recording  $^{29}\text{Si}$  NMR spectra artificially enhances the peak areas of protonated silicon atoms (i.e.  $D_2^{\text{H}}$  units).

The relative high intensity of Si-H signal in PS-EG400 spectrum indicates a high percentage of residual silane groups in this gel and, consequently a low reaction yield. This is in relation with the low gelation time observed for this sample: in this case sol to gel transition occurs before the silylation reaction goes to completion.

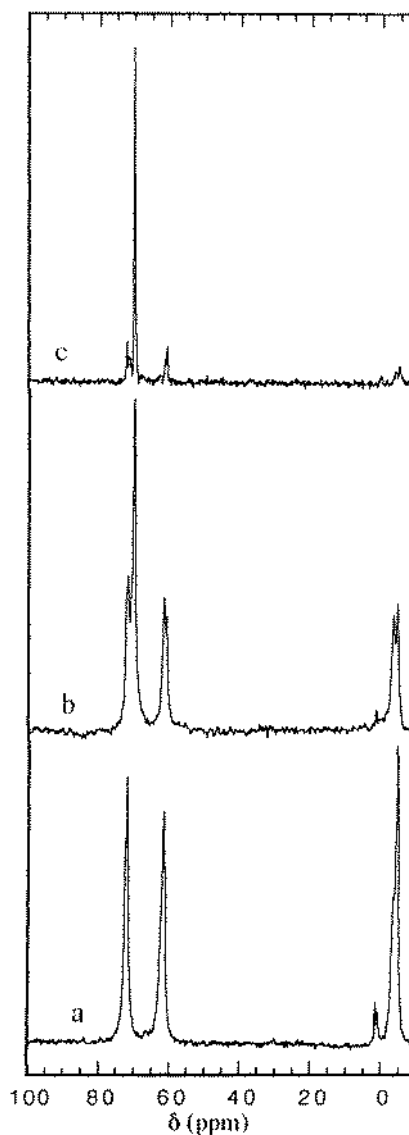
**Table III:**  $^{29}\text{Si}$  chemical shifts (ppm) of the polysiloxane-polyethylene glycol gels

Samples	Chemical Shift	Assignment
PS-DEG	-36.27	$\text{D}_2^{\text{H}}$
	-57.51 ; -58.34	$\text{T}_2^{\text{OH}}$ ; $\text{T}_2^{\text{OR}}$
	-66.85	$\text{T}_3$
PS-TEG	-36.19	$\text{D}_2^{\text{H}}$
	-48.83	$\text{T}_1$
	-57.35 ; -58.26	$\text{T}_2^{\text{OH}}$ ; $\text{T}_2^{\text{OR}}$
	-66.94	$\text{T}_3$
PS-EG400	-36.12	$\text{D}_2^{\text{H}}$
	-57.45 ; -58.26	$\text{T}_2^{\text{OH}}$ ; $\text{T}_2^{\text{OR}}$
	-66.27	$\text{T}_3$

\* All  $^{29}\text{Si}$  chemical shifts are reported relative to TMS.



**Figure 3:**  $^{29}\text{Si}$  CP-MAS NMR spectra of a- PS-DEG, b- PS-TEG and c- PS-EG400



**Figure 4:**  $^{13}\text{C}$  CP-MAS NMR spectra of a- PS-DEG, b- PS-TEG and c- PS-EG400

### 3.3. $^{13}\text{C}$ CP-MAS NMR study

Further information about the structure of the ether chain linked to polysiloxane, are obtained from  $^{13}\text{C}$  CP-MAS NMR spectra (figure 4). The polyether carbons display signals in 58-75 ppm region. The  $\alpha$  carbons give a composite signal (60-62 ppm), and a distinguishable doublet is observed. The down field component is assigned to  $\text{C}'_{\alpha}$  (grafted  $\text{CH}_2$  groups) and the high field one to the  $\text{C}_{\alpha}$  (non-grafted  $\text{CH}_2$  groups) with a  $\Delta\delta = \delta_{\text{C}'_{\alpha}} - \delta_{\text{C}_{\alpha}} = 0.74$  ppm for PS-DEG and PS-TEG and  $\Delta\delta = 0.54$  ppm for PS-EG400.

Similarly to the  $\alpha$  carbons, the  $\beta$  ones display composite signals (71.5-72.5 ppm). But in this case the high field component corresponds to carbons of grafted polyethylene glycol chains, i.e. the grafting reaction causes a high field shift of the  $\text{C}_{\beta}$  carbons signal. The chemical shifts of the other ether carbon atoms in PS-TEG and PS-EG400 samples ( $\text{C}_R$ ) are not affected by change of the environment at terminal oxygen atom of ether chain.

This assignment is done by analogy with a structurally similar compound obtained by Spindler and Shriver [26] from the reaction between polyethylene glycol (MW = 300) and PMHS. Spindler and Shriver have observed a similar down field shift of 0.6 ppm for the signal corresponding to the  $\text{C}_{\alpha}$  carbon after reaction.

The presence of composite signals for  $\alpha$  and  $\beta$  carbons shows the presence of unreacted OH ether groups. The proportions of  $\frac{\text{reacted OH ether groups}}{\text{total OH ether groups}}$  are calculated from either the ratios  $\frac{\text{C}'_{\alpha}}{\text{C}_{\alpha} + \text{C}'_{\alpha}}$  or

$\frac{\text{C}'_{\beta}}{\text{C}_{\beta} + \text{C}'_{\beta}}$ . These ratios are obtained from simulated spectra and give 93% for PS-DEG, 88% for

PS-TEG and 50% for PS-EG400. This indicates that the grafting reaction has gone for a higher extent in PS-DEG and PS-TEG systems.

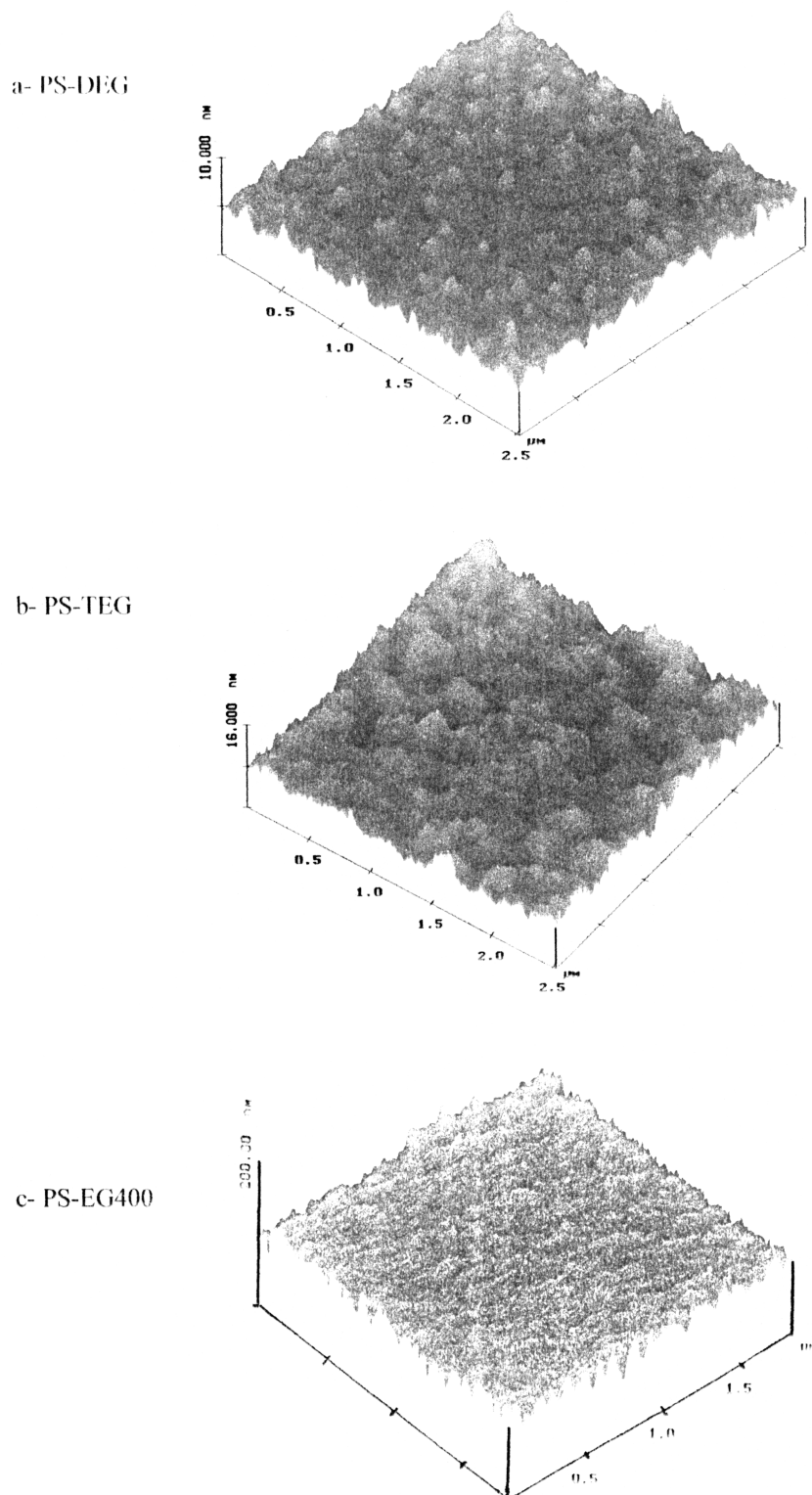
This result is in agreement with  $^{29}\text{Si}$  NMR data, which show that residual Si-H groups are more abundant in PS-EG400 polymer, and that formation of Si-OH ( $\text{T}_2^{\text{OH}}$ ) and Si-O-Si ( $\text{T}_3$ ) linkages are more important in this sample. In addition, the integration of peaks made from  $^{13}\text{C}$  NMR spectra are in good correlation with chemical structure. Ratio of  $\alpha:\beta$  is close to one in all cases (1.06 for PS-DEG, 0.98 for PS-TEG and 1.02 for PS-EG400). Also, the ratio  $\text{C}_R:\text{C}_{\beta}$  is exactly equal to the theoretical value of 2.00 and 4.00 in PS-TEG, and PS-EG400, respectively.

The chemical shifts of methyl groups belonging to the siloxane backbone are sensitive to the silicon atom environment and the correspondent signals appear between -5 to 5 ppm. A weak peak relative to  $(\text{CH}_3)_3\text{-Si-O}_{1/2}$  ( $\text{C}_M$ ) is observed at 1.93 and 1.73 ppm in PS-DEG and PS-TEG spectra, respectively. In PS-EG400  $^{13}\text{C}$  spectrum, resonance relative to  $\text{C}_M$  is not observed. In fact, PEG400 chains are very long (compared to DEG and TEG). Then  $\text{C}_M$  percentage is too low (c.a. 1%) to give a detectable signal.

PS-EG400  $^{13}\text{C}$  spectrum shows a peak at 0,44 ppm corresponding to carbons of residual  $\text{D}_2^{\text{H}}$  moieties. This signal is absent in PS-DEG and PS-TEG spectra, which is in agreement with the high yield of the silylation reaction (calculated from  $\frac{\text{C}'_{\alpha}}{\text{C}_{\alpha} + \text{C}'_{\alpha}}$  or  $\frac{\text{C}'_{\beta}}{\text{C}_{\beta} + \text{C}'_{\beta}}$ ) in these two samples.

The methyl resonance of T units appears at c.a. -3 and -4 ppm for PS-TEG attributed to  $(\text{T}_3 + \text{T}_2^{\text{OH}})$  for the first and  $\text{T}_2^{\text{OR}}$  for the second. This attribution is done on the basis of  $^{29}\text{Si}$  NMR results: the more intense peak corresponds to the prevalent group, i.e.  $\text{T}_2^{\text{OR}}$ . In PS-DEG and

PS-EG400, resonance due to T units is more complex. The two main peaks at -3.74 and -4.81 ppm are assigned to  $(T_3 + T_2^{\text{OH}})$  and  $T_2^{\text{OR}}$ , respectively.



**Figure 5:** AFM images of a- PS-DEG, b- PS-TEG and c- PS-EG400.



### 3.4. Elemental analysis

Elemental analysis was performed out for all synthesized polymeric gels; the obtained results are summarized in table IV. Theoretical formulae are calculated from an ideal structure where all polyether chains are assumed to be linked by both OH groups to silicon atoms of PMHS chains (reaction 1). The chemical analysis data show an excess of H:Si and O:Si ratios. The deviation from the ideal structure is expected from the NMR data that shows the presence of remaining R-OH ether moieties and the formation of silanol groups partially condensed into T<sub>3</sub> units. Unreacted ether OH groups lead to an excess of the hydrogen amount in the experimental formula compared to the theoretical one. Excess of oxygen is due to side reactions: hydrolysis and condensation of Si-H groups (reactions 2 and 3) which introduces additional oxygen. Moreover, we note that the excess of H:Si and O:Si ratios is higher in PS-EG400 sample, than in the two others. This can be explained by the side reaction which was shown to be more important for PS-EG400 sample.

**Table IV :** Elemental analysis (wt %) of PS-DEG, PS-TEG and PS-EG400 gels, experimental and theoretical formulae.

	Wt %				Experimental formulae	Theoretical formulae
	Si	C	H	O*		
PS-DEG	25.43	32.27	6.63	35.66	SiC <sub>2.96</sub> H <sub>7.30</sub> O <sub>2.45</sub>	SiC <sub>3.00</sub> H <sub>7.10</sub> O <sub>2.39</sub>
PS-TEG	17.75	30.05	7.73	39.47	SiC <sub>4.63</sub> H <sub>12.27</sub> O <sub>3.92</sub>	SiC <sub>4.89</sub> H <sub>10.89</sub> O <sub>3.34</sub>
PS-EG400	10.30	40.86	8.15	40.69	SiC <sub>9.27</sub> H <sub>22.18</sub> O <sub>6.96</sub>	SiC <sub>6.26</sub> H <sub>19.75</sub> O <sub>5.55</sub>

\*: deduced by difference.

### 3.5. Morphology of the gel based membranes

AFM images of PS-DEG, PS-TEG and PS-EG400 gel based membranes deposited on glass slices (Figure 4 -a, -b and -c, respectively) show morphological differences between samples. Despite the longer chain of EG400, PS-EG400 appears as a less porous structure and presents a smaller pore size compared to PS-DEG and PS-TEG. This is very likely due to the rapid gelation and the low grafting degree observed in the case of PS-EG400.

As NMR showed it, PS-EG 400 provides a more condensed structure. In this case, the system undergoes a rapid gelation giving a partially grafted polyether chains. The use of EG400 as cross-linking agent did not allow the formation of an expanded network. The polyether chains that are not involved in cross-linkages fill up the pores of the gel.

## 4. Conclusion

Fonctionnalized polysiloxane-based polymers were synthesized via reaction of polymethylhydrosiloxane and polyethylene glycols. <sup>13</sup>C CP-MAS NMR study of the obtained gels shown that grafting degree of the polyethylene glycol is high for the short chains (93% for PS-DEG and 88% for PS-TEG) and relatively low for the long one (50% for PS-EG400). Chemical analysis shows an excess of H:Si and O:Si ratios due to presence of unreacted polyethylene glycols and to side reaction that occurred between Si-H groups and moisture traces as evidenced by <sup>29</sup>Si CP-MAS NMR. The prepared hybrid gels can be potentially used as host matrices in preparing ion sensitive membranes. PS-DEG and PS-TEG systems, giving a good porosity and the best reticulation degree, are selected to prepare membranes deposited on EIS (Electrolyte Insulator Semiconductor) devices. Preliminary tests are in course to study their sensitivity towards some alkali ions (Li<sup>+</sup> and K<sup>+</sup>).

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