Crosslinking of polyether networks by hydrosilylation and related side reactions

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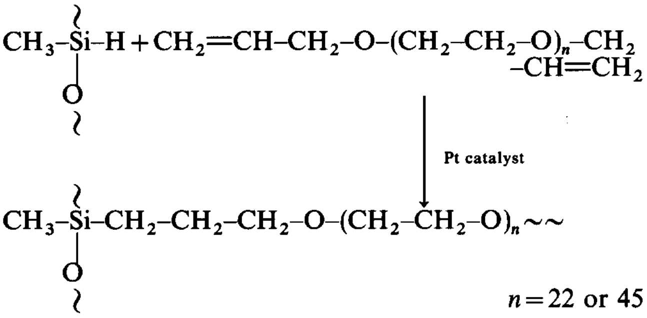
The synthesis of a well defined poly(ethylene oxide) network is described. This was achieved by performing hydrosilylation of α,ω-diallyl PEO with 2,4,6,8-tetramethyltetrahydrocyclosiloxane (D_4H). The influence of several factors, including the nature of the catalyst, temperature, (SiH)/(double bond) ratio and traces of water, on the hydrosilylation reaction is described. Side reactions were studied by ^1H and ^{29}Si n.m.r.

(Keywords: poly(ethylene oxide); hydrosilylation; 2,4,6,8-tetramethylcyclotetrasiloxane; crosslinking; ^{29}Si n.m.r.)

INTRODUCTION

The synthesis of block and graft copolymers containing poly(dimethylsiloxane) (PDMS) and poly(ethylene oxide) (PEO) segments has been described previously[1,2]. Such copolymers complexed with alkali metal salts have been receiving attention as solid electrolytes[3–7]. The main reason for this is that, in general, polysiloxanes have very low glass transition temperatures and this feature is known to enhance ionic conductivity. The PEO networks prepared for this purpose contained Si–O–C linkages between the polysiloxane and the polyether segments which are sensitive to hydrolysis.

The aim of the present work was to prepare well defined PEO networks with low T_g values and with the following features for the crosslinks: the smallest possible size and a significantly lower degree of interaction towards the PEO segments. This was achieved by performing hydrosilylation of α,ω-diallyl PEO with 2,4,6,8-tetramethylcyclotetrasiloxane (D_4H) because the silyl hydride addition to allyl group, in the presence of platinum catalysts, is known to give a Si–C linkage[8] which has a higher hydrolytic stability than the Si–O–C linkage.



$$CH_3{-}\overset{|}{\underset{|\atop O}{Si}}{-}H + CH_2{=}CH{-}CH_2{-}O{-}(CH_2{-}CH_2{-}O)_n{-}CH_2{-}CH{=}CH_2 \xrightarrow{\text{Pt catalyst}} CH_3{-}\overset{|}{\underset{|\atop O}{Si}}{-}CH_2{-}CH_2{-}CH_2{-}O{-}(CH_2{-}CH_2{-}O)_n{\sim\sim}$$

$n = 22$ or 45

In the present paper, the results concerning the preparation of such networks, as well as the side reactions which were observed, are described. The electrical conductivity studies for lithium salts in these networks have been made[9] and will be reported in a forthcoming paper[10].

EXPERIMENTAL

Reagents

Commercial D_4H (Petrarch Systems), b.p. 134–135°C, had a purity of 97.5% (g.l.c.) and contained other cyclics. It was purified through vacuum distillation. 1,1,1,3,3-Pentamethyldisiloxane (Petrarch Systems) was used without further purification. Poly(ethylene glycol) oligomers (average molecular weights 1000 and 2000) were obtained from Janssen. Allyl bromide (Janssen) was distilled just before use. Toluene was dried by several distillations on sodium films under vacuum. Hexachloroplatinic acid: $H_2PtCl_6 . 6H_2O$ (Prolabo) was used in 1-octanol solution (2×10^{-2} mol l^{-1}). This red solution was prepared just before use. This catalyst was also employed as a black powder after drying under high vacuum. Commercial divinyltetramethyldisiloxane platinum complex (Pt/Si complex) in xylene solution (10^{-2} mol l^{-1}) (Petrarch Systems) was used as received.

Synthesis of α,ω-diallyl PEO

Allyl-terminated PEO were prepared by reaction of hydroxyl end-groups with a large excess of allyl bromide in bulk, in the presence of NaOH pellets ([NaOH]/[OH] = 2), at 70°C for 24 h. After filtration and evaporation of the unreacted allyl bromide, the functionalized polymers were dried under high vacuum at 60°C. The allyl group content was determined by ^1H n.m.r. and was found to be better than 1.9 per macromolecule. In this paper, PEO samples are designated by PEO *M* where *M* indicates the average molecular weight of the starting PEO.

Hydrosilylation reactions

Hydrosilylation reactions were carried out either in a

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flask or in a flat mould, consisting of two parallel glass plates assembled by a flat silicone joint, to prepare membranes of controlled thickness (0.9 mm). In the first case, experiments were carried out at 80°C with a value of V_c equal to 0.45 [V_c = volume of reagents (PEO + D_4H)/total volume (reagents + solvent)]. In the second case, they were performed at 60°C with $V_c = 0.70$. A molar ratio [Pt catalyst]/[SiH] of 10^{-4} was used in all cases.

Typically, diallyl PEO 1000 (2.21 g; 4.52 allyl meq) and toluene (3.0 ml) were heated at 80°C under nitrogen in a 20 ml flask. D_4H (0.40 ml; 1.65 mmol) and the platinum catalyst were added to the mixture. The reaction was stopped when the system became highly viscous. The crude material was dried under high vacuum. The soluble products were extracted using toluene as the solvent in a Soxhlet apparatus and they were analysed by ^1H n.m.r.

In a typical reaction carried out in a flat mould, the two glass plates were silylated with trimethylchlorosilane before each experiment in order to ensure proper conditions for mould removal. Preparation of the mixture to be crosslinked, as well as the filling of the mould, were performed in a glove box under nitrogen. Diallyl PEO 1000 (5.30 g; 10.80 allyl meq) and toluene (2.5 ml) were stirred in a flask while slightly heated at 40°C to ensure a homogeneous medium. D_4H (0.75 ml; 3.10 mmol) and the Pt/Si complex were added to the mixture which was then poured into the mould between the glass plates. After 0.5 h the mould was heated at 60°C in an oven for 3 h, i.e. until sufficient crosslinking developed to allow easy removal from the mould. The membrane was dried under high vacuum at 60°C. The amount of soluble products was determined after extraction with toluene in a Soxhlet apparatus.

Methods of analysis

^1H (200 MHz) and ^{29}Si (39.8 MHz) n.m.r. spectra were recorded on an AM 200 Brüker apparatus in $CDCl_3$ at 25°C, with $CHCl_3$ at 7.26 ppm and TMS at 0 ppm, respectively, as internal standards. The dynamic mechanical properties were determined with a Metravib viscoelastometer.

RESULTS AND DISCUSSION

Preliminary study of network formation

The results of the reaction of D_4H with diallyl PEO 1000 in a flask, in the presence of different catalysts, are reported in *Table 1*. They show that the Pt/Si complex is more efficient than hexachloroplatinic acid either under its 'black' or 'red' form because it leads to a highly viscous medium after a shorter time. Although the 'black' catalyst has been successfully used for hydrosilylation of perfluoroalkyl allyl ethers[11,12], our results can be explained by a coordinating effect of PEO. A decrease of the rate of hydrosilylation has been observed in the presence of ethylene glycol diethylether[13]. Thus it can be suggested that platinum in H_2PtCl_6 is complexed by the ethereal type oxygen atoms which do not have any detrimental effect on the Pt/Si complex. Consequently, the Pt/Si complex catalyst was further used for the experiments made in the flat mould.

Table 1 Reaction of D_4H with α,ω-diallyl PEO 1000 in a flask in the presence of different catalysts [Pt catalyst]/[SiH] = 10^{-4}; $V_c = 0.45$; $t = 80$°C

Run	Catalyst	(SiH)/(C=C)	Reaction time (h)	Weight of extracted products (%)
1	'Black' H_2PtCl_6	1.00	18	100
2	'Black' H_2PtCl_6	1.45	18	18
3	'Black' H_2PtCl_6	1.80	18	24
4	'Red' H_2PtCl_6	1.00	18	100
5	'Red' H_2PtCl_6	1.45	18	14
6	Pt/Si complex	1.45	8	9

In the case of a quantitative reaction, the best results, i.e. the lowest yield of extracted products, should be observed for a molar ratio f = [SiH]/[C=C] equal to 1. However it was found experimentally that network formation occurred only for f values higher than 1. This unexpected behaviour was assumed to be due to reactions other than hydrosilylation which consumed SiH functions. This will be discussed later. An increase of f from 1.10 to 1.50 did not induce a tremendous increase of the amount of soluble products (between 10 and 18% depending on the experimental conditions) whereas this amount increased significantly for f higher than 1.50.

The preparation of membranes in a flat mould between two glass plates revealed unexpected peculiarities. The first was that the system became highly viscous much more quickly, within 0.5 h at room temperature in contrast to more than 8 h in a flask. We have no explanation for this difference. The second peculiarity was that when PEO was allowed to crystallize before hydrosilylation took place, the formation of many tiny bubbles in the bulk of the membrane, which migrated slowly up to the surface, was observed. Consequently the reaction temperature had to be adjusted so as to prevent crystallization and this depends on the molecular weight of the PEO sample.

Another parameter, V_c, had to be adjusted. If it was too high (0.75), the system became too viscous to flow homogeneously and to allow the bubbles to escape from the membrane. If it was too low (0.50), a satisfactory crosslinking occurred but the excess toluene evaporated at the curing temperature (60°C) which induced cracking of the membrane. The optimal value chosen for V_c was 0.70.

It is noteworthy that, in spite of optimization of factors such as temperature and V_c, the formation of bubbles was not completely suppressed. They appeared mostly at the silicone joint. The chemical inertness of this joint was controlled by several blank experiments. It will be seen later on that this phenomenon was due to the destruction of SiH bonds in the presence of catalyst and very small amounts of water, which led to the formation of hydrogen. According to this finding, membranes must be prepared with carefully dried reagents under an anhydrous atmosphere, for instance in a glove box.

The percentage of extracted products was the key parameter which allowed control of the network formation. Some results of experiments of membranes preparation under various conditions are reported in *Table 2*. This percentage was found to vary very slightly with f. The best results were obtained with $f = 1.45$ for both PEO 1000 and PEO 2000 samples.

Membranes are transparent for PEO 1000 whereas they are opaque for PEO 2000. This relates to the crystallinity of the latter. They are unexpectedly friable despite the fact that their dynamic mechanical properties are similar to those of PEO networks containing urethane

Table 2 Characterization of networks prepared in a flat mould with different molar ratios $f=[\mathrm{SiH}]/[\mathrm{C{=}C}]$; $[\mathrm{Pt/Si\ complex}]/[\mathrm{SiH}]=5\times10^{-5}$; $V_c=0.70$; $t=60°\mathrm{C}$; 3 h

Run	Polyether	f	Weight of extracted products (%)
7	PEO 1000	1.05	3
8	PEO 1000	1.15	4.5
9	PEO 1000	1.45	2
10	PEO 2000	1.10	9
11	PEO 2000	1.45	2.5

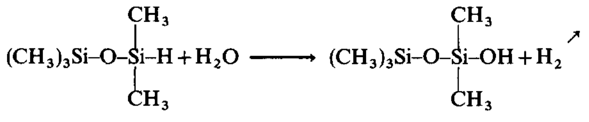
linkages prepared from polyethylene glycols crosslinked by a triisocyanate[14]. At room temperature, the Young's modulus of PEO networks is around $4\times10^6\,\mathrm{N\,m^{-2}}$. These networks seem to be homogeneous on a macroscopic scale, however the friability could be tentatively assigned to the well known incompatibility between PEO and siloxane derivatives, which results in segregation of microphases, leading to heterogeneity on a molecular scale.

Spectroscopic studies of the reaction products

An unexpected behaviour observed during the preparation of membranes in a flat mould was the formation of bubbles. A specific study of the reactivity of the starting materials and of a model molecule such as pentamethyldisiloxane was carried out in order to get a better insight into this problem. Moreover, some information was obtained by analysis of the products extracted from the networks using n.m.r. spectroscopy.

First of all, the stability of the starting materials was checked by ^{1}H n.m.r. No modification of the spectrum of PEO was observed after heating at 60°C for 24 h in the presence of platinum catalysts. When toluene solutions of D_4H were heated under the same conditions, with and without PEO, in the absence of catalyst, no variation of the SiH concentration was noticed. However, when D_4H was heated in the presence of a platinum catalyst, gas bubbles were detected. The amount of evolved gas was larger in the case of H_2PtCl_6 than in the case of Pt/Si complex after a given time. Moreover, it increased on increasing the catalyst concentration or on adding small amounts of water to the system. Analysis by gas chromatography showed that this gas was hydrogen. Traces of methane were also detected at high reagent concentrations. The amount of evolved H_2 seemed too important to be assigned only to the first step of the recently published mechanism of platinum-catalysed hydrosilylation[15].

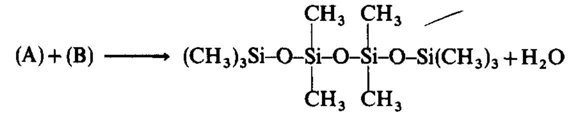
The reaction products were examined by ^{29}Si n.m.r. on a model compound such as pentamethyldisiloxane. When this silane (20 mmol) was heated at 60°C with Pt/Si complex (3×10^{-3} mmol) in toluene (6 ml) saturated with water, the corresponding silanol was formed:



$$(CH_3)_3Si\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}H+H_2O \longrightarrow (CH_3)_3Si\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}OH+H_2\nearrow \quad (1)$$

(A) (B)

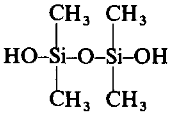
as shown in *Figure 1a*. Complete disappearance of the SiH groups was then observed after a couple of hours, which corresponds to the condensation of silanol (B) with silane (A) leading to the formation of decamethyltetrasiloxane (C) (*Figure 1b*):



$$(A)+(B) \longrightarrow (CH_3)_3Si\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}Si(CH_3)_3+H_2O \quad (2)$$

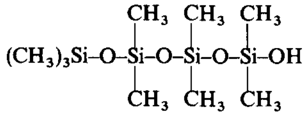
(C)

Besides the silicon signals of (C) located at 7.3 and −20.7 ppm and those of remaining (B) located at 7.7 and −11.9 ppm, some other signals are observed which can be attributed to the following structures:



$$HO\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}OH$$

(D)



$$(CH_3)_3Si\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}OH$$

(E)

The presence of methane detected in the evolved gas comes from the scission of a Si–CH_3 bond in (B) and (C) which leads to the formation of the corresponding silanols (D) and (E). The observed chemical shifts (*Figure 1b*) for these structures are in good agreement with those given in the literature[16,17]. Such a scission reaction has been already described when silanes were reacted with water or alcohols in the presence of palladium, platinum or sulphuric acid[18,19]. Thus on heating tetramethylsilane in ethanol/water solution with H_2PtCl_6 at 120°C for 10 h, a quantitative yield of hexamethyldisiloxane formed by condensation of trimethylsilanol was obtained[19]. This scission reaction was also assumed to occur for hydrosilylations catalysed by H_2PtCl_6 but the resulting structures were not established[20].

In the same manner, ^{29}Si n.m.r. spectroscopy was used to analyse the reaction products of a reaction carried out at $f=1.0$ with 'black' H_2PtCl_6 as the catalyst. No

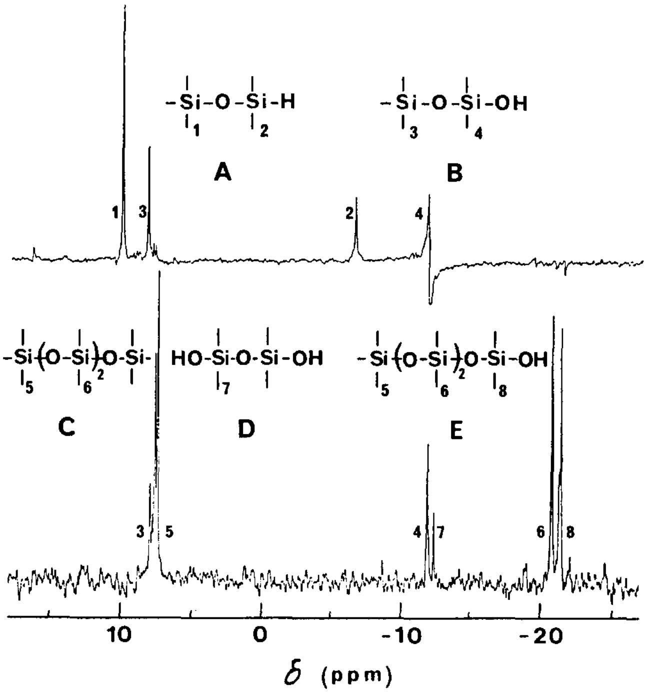


Figure 1 ^{29}Si n.m.r. spectrum at 39.8 MHz in C_6D_6/toluene of (a) pentamethyldisiloxane (A) heated with Pt/Si complex and traces of water, and produced pentamethyldisilanol (B), (b) decamethyldisiloxane (C) and other products of reaction between (A) and (B)

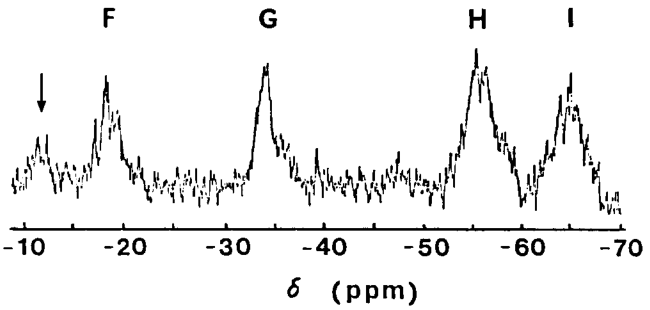


Figure 2 ^{29}Si n.m.r. spectrum at 39.8 MHz in $CDCl_3$ of the reaction products of D_4H with diallyl PEO 1000 in a flask in the presence of 'black' H_2PtCl_6 with $f = 1.0$ (run 1, *Table 1*). For assignment see text

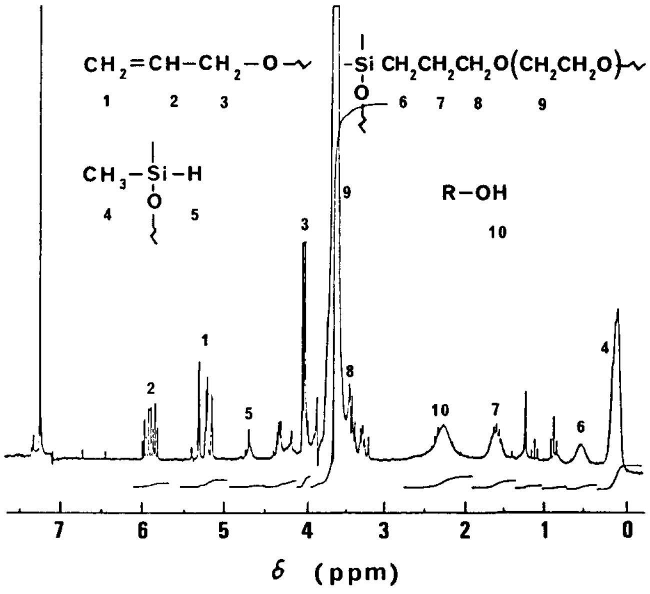


Figure 3 ^{1}H n.m.r. spectrum at 200 MHz in $CDCl_3$ of the same reaction products as indicated in *Figure 2*

network formation was observed and 100% of extracted products were obtained (run 1, *Table 1*). On the spectrum shown in *Figure 2*, signals can be attributed to the following structures: the expected product of hydrosilylation (−19 ppm; F); non-reacted SiH bonds (−34 ppm; G); silanol bonds due to the reaction between SiH and H_2O (−56 ppm; H); and siloxane bonds resulting from the condensation of a silane with a silanol, or between two silanols (−65 ppm; I). A small signal is also observed at −12 ppm, which could not be assigned to middle-chain silicon atoms but to silanol end groups formed by ring opening of the cyclosiloxane units.

The ^{1}H n.m.r. spectrum of the same mixture shown in *Figure 3* indicates that the reaction was not complete because non-reacted SiH bonds (4.7 ppm) and allyl functions (4.0, 5.2 and 5.85 ppm) are detected. The signals of the reaction product of hydrosilylation are located at 0.6, 1.6 and 3.4 ppm. It is noteworthy that the side products identified by ^{29}Si n.m.r. could not be differentiated by ^{1}H n.m.r. In fact, labile hydrogens of the silanol functions located in the middle or at the end of the chains as well as water due to the hygroscopic character of PEO are included in the same broad signal at 2.2 ppm. Unfortunately, ^{29}Si n.m.r. requires high concentrations of silicon atoms, which prevent the use of this technique for an extensive study of the composition of the extracted products. In future work we plan to consider that the functionality of the crosslinks is four even if an undetermined percentage of the crosslinks can be trifunctional (if one SiH of the tetrafunctional D_4H is transformed into a silanol) or can be of higher functionality if condensation between silane and silanol groups occurs.

The evolved hydrogen led to the hydrogenation of allyl end groups of PEO with the formation of the corresponding saturated product R–O–CH_2–CH_2–CH_3 as can be seen on the ^{1}H n.m.r. spectrum shown in *Figure 4*. The signals located at 0.9, 1.57 and 3.40 ppm were identified by selective irradiations. The reaction was observed in all cases (either in a flask or in a flat mould and whatever the catalyst) and represents 5 to 10% of the disappearance of the allyl functions and even more if the starting materials were not well dried.

Some papers[21,22] point out the transition metal (Pd, Pt, etc.) catalysed isomerization of allyloxy groups into isopropenyl ether moieties. In the case of hydrosilylation catalysed by the Pt/Si complex, the ^{1}H n.m.r. spectrum contains some small signals which can be attributed to the *cis* and *trans* structures of PEO isopropenyl ether (*Figure 5*). The chemical shifts (*cis* protons at 4.4 and

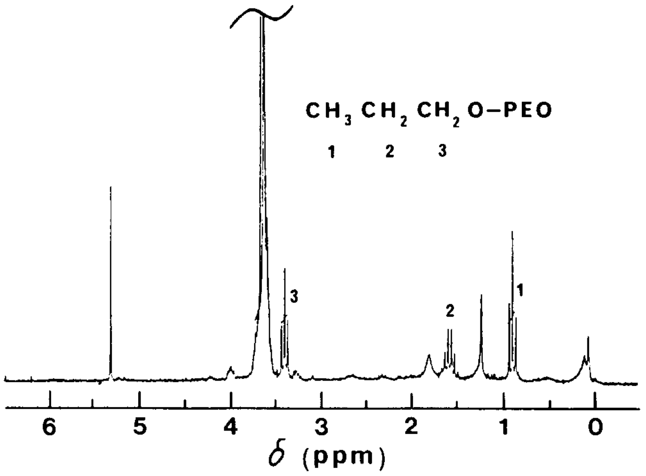


Figure 4 ^{1}H n.m.r. spectrum at 200 MHz in $CDCl_3$ of the extracted products of run 2, *Table 1*. Identification of the hydrogenated allyl PEO

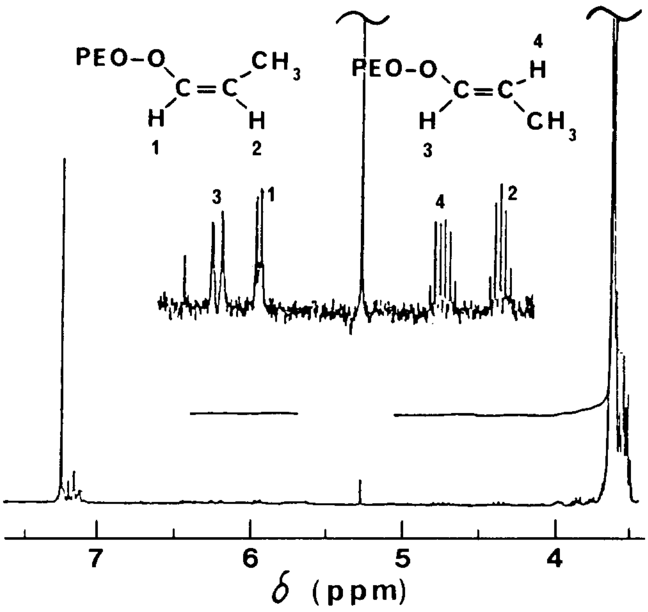


Figure 5 ^{1}H n.m.r. spectrum at 200 MHz in $CDCl_3$ of the extracted products of run 6, *Table 1*. Identification of the isopropenyl protons

5.95 ppm and *trans* protons at 4.8 and 6.25 ppm) are in good agreement with literature values[23]. Those isopropenyl functions were assumed to be inert towards hydrosilylation[23].

From the results of ^{1}H n.m.r. of the extracted products obtained after the hydrosilylation reaction in a flat mould, the following conclusions can be drawn. None or a few residual SiH groups and allyl functions are detected. The extracted products seems to be due to the loss of the functionality of two of α,ω-diallyl PEO either by hydrogenation or by isomerization of the allyl groups, which prevents complete crosslinking.

CONCLUSIONS

Hydrosilylation reactions are often described in the literature, but are difficult to bring completely under control. The presence of water leads to several side reactions. However, networks with low percentage weights of extracted products and good mechanical properties were obtained and, as will be described in a forthcoming paper, were filled with ionizable salts in order to determine the transport properties in well defined PEO networks with low T_g values.

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