Polymer Vol. 37 No. 15, pp. 3353–3360, 1996

0032-3861/96/$15.00+0.00

Contribution to a better knowledge of the crosslinking reaction of polydimethylsiloxane (PDMS) by end-linking: the formation of star-branched PDMS by the hydrosilylation reaction

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(Received 17 October 1994; revised 24 October 1995)

Monofunctional polydimethylsiloxanes with a dimethylsilyl or a dimethylsilylvinyl end-group were reacted with respectively 1,3,5,7-tetramethyltetravinylcyclotetrasiloxane and 1,3,5,7-tetramethylcycloterasiloxane. The hydrosilylation reaction, carried out in bulk and in the toluene solution, were followed by *FT*i.r. spectrometry and the star-branched samples formed analysed by SEC-LS. In the second case, for PDMS silylvinylic function at the chain-end, the reaction is noticeably faster and the final conversions reached are higher than in the first case. The principal parameter which limits the maximum conversion is the concentration of functional groups in the medium. Copyright © 1996 Elsevier Science Ltd.

(Keywords: crosslinking reaction; star-branched polydimethylsiloxane (PDMS); hydrosilylation reaction)

INTRODUCTION

Many investigations in the field of rubber-elasticity have used as an approach the ideal model-network of cross-linked polydimethylsiloxane (PDMS) networks prepared by endlinking of α,ω-difunctional precursors. A very efficient reaction applied to these syntheses has been the hydrosilylation reaction, i.e. the addition of a silyl function $\equiv$SiH to an unsaturated C=C bond. Thus PDMS with α,ω-dimethylsilylvinyl or α,ω-dimethylsilyl groups were reacted with crosslinkers carrying the corresponding antagonist functions[1,2]. However side reactions[3] or a limited extent of reaction may be responsible for defects in the network such as pendent chains or chain-extension, and thus affect the expected characteristics of the network.

In an insoluble crosslinked system it is not possible to determine directly the extent of the reaction. The sole, but indirect, method is based on the determination of the fraction of unreacted extractible precursor polymer. Its value allows an estimation of the extent of the reaction and of the number of pendent chains in the network[4,5]. In most cases the products extracted from these PDMS networks contain, in addition to the unreacted polymer, cyclic species. They are already present in the precursor but do not participate in the crosslinking reaction and often constitute the main fraction of extractables. It follows that an estimation of the actual amount of unreacted precursor requires a rather difficult quantitative analysis of the latter.

In the present article we will report a different approach to get a better understanding of the network formation by hydrosilylation, using a simplified model system, i.e. the reaction between well defined monofunctional PDMS with a narrow molecular weight distribution and tetrafunctional compounds. In this case the reaction leads to soluble star-shaped polymers. The kinetics of the reaction can be followed by Fourier transform infra-red spectrometry (*FT*i.r.) and the formation of the branched species by size exclusion chromatography using a device equipped with a refractometric and a light scattering detection (SEC-LS). Earlier experiments indicated that the concentration of reactive groups in the medium is a parameter limiting the yield of the reaction[6]. We have studied this concentration effect in the case of the above system in toluene solution, at different concentrations and in the bulk, using precursors with different average molecular weights.

EXPERIMENTAL

Precursor polymers

The monofunctional PDMS samples were prepared by anionic ring-opening polymerization of hexamethylcyclotrisiloxane and end-capped by reaction of the siloxanionic end-groups with chlorodimethylsilane or chlorodimethylvinylsilane. Their synthesis and characterization have been described elsewhere[7].

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Tetrafunctional reagents

The tetrafunctional products (Petrarch), 1,3,5,7-tetramethylcyclotetrasiloxane (bp 32°C, 19 mbar) and 1,3,5,7-tetramethyltetravinylcyclotetrasiloxane (bp 106°C, 18 mbar), were distilled twice under argon, the second compound over sodium, and stored under argon. Their purity was checked by vapour phase chromatography (v.p.c.): 99.2 and 99.6%, respectively.

Toluene

Toluene was distilled over sodium and kept under argon.

Hydrosilylation reactions

The reactions were carried out at the 1/1 stoichiometry at 70°C in the absence of oxygen and moisture which could produce an inhibition effect. To follow simultaneously the reaction kinetics by *FT*i.r. spectrometry and the formation of the star-branched polymers by SEC, coupled with an LS detection, we have carried out parallel experiments in the i.r. cell and in sealed glass tubes. The hydrosilylation catalyst was chloroplatinic acid $H_2PtCl_6 \cdot 6H_2O$ (Aldrich) in isopropanol solution (1.9×10^{-2} mol l^{-1}) used in the ratio of 2.5×10^{-4} mol per mol functional polymer.

Fourier transform infra-red spectrometry

The progress of the hydrosilylation reaction at 70°C, which consumes the silyl functions, was followed by a continuous recording of the i.r. spectra using a Nicolet 60 SX spectrometer. The characteristic strong i.r. absorption of the $\equiv$SiH groups at 2127 cm^{-1} does not interfere with any other band of the spectrum. Thus the progressive decrease of this band allows one to follow accurately their disappearance. The i.r. measuring cell was thermoregulated and a thermocouple placed in the cell allowed a precise temperature control inside the sample (±0.5°C). The optimal resolution was obtained with a path between the cell windows of 0.05 mm. The minimum times between two successive scannings were 20 s and 1 min 46 s with respectively 32 and 200 accumulations. The experimental conditions were chosen according to the rate of the reaction. A syringe was used to introduce the reaction mixture, under argon, into the cell.

Size exclusion chromatography

To characterize the precursor polymers and the branched species formed in the reaction we have used a classical SEC device: a Schimadzu LC-6A pump, a 6-way injector Rheodine with a 0.5 ml loop and three columns with microstyragel fillings (mixed porosity) allowing an efficient separation in the molar mass range between 2000 and 200 000 g mol^{-1}. The system was equipped with a differential refractometric detection WATERS 403 and a light scattering detector, a modified FICA 42000 photogoniometer[8]. PDMS standards with a narrow molecular weight distribution were used for calibration, and toluene used as elution solvent ($dn/dc = -0.0904$ at 633 nm) 0.5 ml samples of the polymer solutions were injected ($c = 0.7$ g l^{-1}).

Determination of the rate of the hydrosilylation reaction

The conversion of the reaction is given by the relation $\tau = [SiH]_{t_0} - [SiH]_t/[SiH]_{t_0}$, where $[SiH]_{t_0}$ and $[SiH]_t$ are the concentrations at the initial time t_0 and at time t of the reaction. Since the concentration is related to the optical density D_0 by the Beer-Lambert expression $D_0 = \epsilon \times c \times l$, this relation becomes $\tau = D_{0_{t_0}} - D_{0_t}/D_{0_{t_0}}$; ϵ is the extinction coefficient and l the path. Since ϵ is temperature-dependent, the optical density $D_{0_{t_0}}$ at the start of the reaction has to be measured when the i.r. cell is at the desired temperature (70°C), after 2 min; this instant was considered as starting time. The optical densities at 2127 cm^{-1} were calculated on the basis of a reference band situated at 1944 cm^{-1} which remains unchanged during the reaction.

The i.r. device allows also the measure of the areas corresponding to the absorption peaks at 2127 cm^{-1}. The conversion τ is then given by the relation $\tau = A_0 - A_t/A_0$ where A_0 and A_t are the areas at the initial time t_0 and the time t of the reaction.

The results obtained by both methods were consistent.

RESULTS AND DISCUSSION

Reaction of α-dimethylsilyl PDMS with 1,3,5,7-tetramethyltetravinylcyclotetrasiloxane

Experiments in the bulk: influence of the precursor chain-length. It could be expected that the hydrosilylation reaction depends on the concentration of reactive groups, as already mentioned in the literature[1-6]. Below a concentration of approx. 8×10^{-3} functional groups/l the reaction no longer takes place. When the reaction between the precursor PDMS and the plurifunctional compound is carried out in the bulk, the initial concentration depends on the molecular weight of the polymer: it decreases with increasing molecular weight.

a) *FT*i.r. investigation of the reaction kinetics

As in the earlier studies[6], we again observed the existence of a limiting concentration of reactive sites. Since the reaction stops when the concentration of the sites falls below this limit, the reaction yield is also limited. Assuming the value of this concentration already indicated above, we have calculated the maximum conversions $\tau_{(lim)}$ and compared them with the experimentally observed conversions $\tau_{(exp)}$. In *Table 1* are displayed the molar masses $\overline{M}_n$ of the precursors, the corresponding initial concentrations of silyl groups $C_{(SiH)}$ and the calculated and experimental conversions. These values are quite close, at least in the case of the lower molecular weight samples. *Figure 1* shows a typical example illustrating the decrease of the SiH absorption band at 2127 cm^{-1} with time for a PDMS precursor with

Table 1 Reaction of α-dimethylsilyl PDMS with the tetrasilylvinylic compound

$\overline{M}_n$ (g mol^{-1})	$C_{(Si-H)}$ (mol l^{-1})	$\tau_{(lim)}$ (%)	t (h)	$\tau_{(exp)}$ (%)
4200	0.23	96.5	10	96.6
6200	0.15	94.8	10	92.3
10 200	0.09	91.6	9	91.7
15 300	0.06	87.4	18	91.5
16 600	0.06	86.1	20	90.1
18 100	0.05	85.1	44	80.7
41 800	0.02	65.6	105	23.9

$C_{(SiH)}$, concentration of dimethylsilyl functions in the medium
$\tau_{(lim)}$, calculated maximum conversion
$\tau_{(exp)}$, experimental maximum conversion

Table 2 Molecular characteristics of the α-dimethylsilyl PDMS and the corresponding branched reaction products (reaction in the bulk, 70°C)

Precursor polymers				Star-branched samples				
$\overline{M}_n$ (i.r.)	$\overline{M}_n$ (SEC)	$\overline{M}_w$ (SEC)	$\overline{M}_w/\overline{M}_n$ (SEC)	$\overline{M}_n^*$ (SEC-LS)	$\overline{M}_w^*$ (SEC-LS)	$\overline{M}_w/\overline{M}_n$ (SEC-LS)	t (h)	$R_{(exp)}$
4200	4300	4600	1.07	16 400	17 100	1.04	18	3.7
6200	6000	6400	1.06	20 100	22 900	1.14	20	3.6
10 200	10 000	10 700	1.07	33 300	38 200	1.14	23	3.6
15 300	14 800	15 700	1.06	54 000	59 000	1.10	31	3.8
18 100	16 800	17 900	1.06	37 100	56 800	1.50	65	3.2
24 100	21 200	22 800	1.07	53 500	76 600	1.43	82	3.4
41 800	36 500	40 200	1.10	38 000	46 600	—	122	—

$R_{(exp)} = \overline{M}_w^*/\overline{M}_w$; $\overline{M}_w$ and $\overline{M}_w^*$, weight-average molar masses of the precursors and of the branched samples

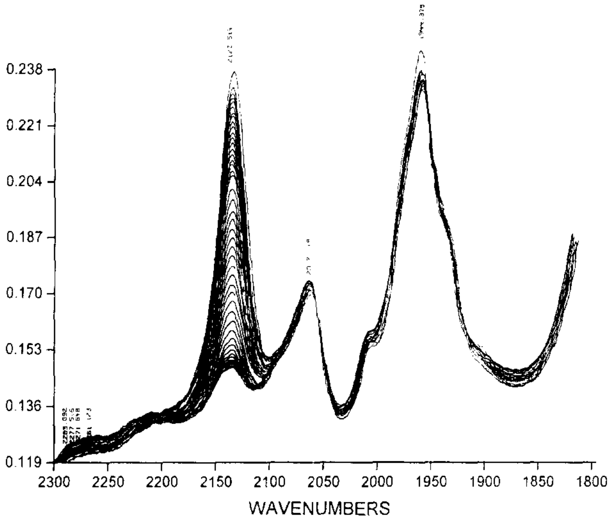


Figure 1 Decrease of the silyl absorption band at 2127 cm^{-1} with time PDMS precursor: $\overline{M}_n$ = 10 200 g mol^{-1}

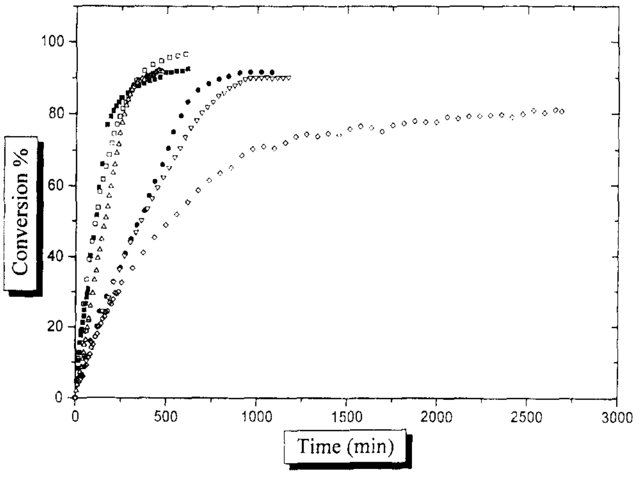


Figure 2 Reaction in the bulk: conversion rate versus time. $\overline{M}_n$ of the precursor PDMS (g mol^{-1}): □, 4200; ■, 6200; △, 10 2000; ●, 15 300; ▽, 16 600; ◇, 18 100

molar mass 10 200 g mol^{-1}. As already specified, we chose the stable absorption band at 1944 cm^{-1} as an internal reference to calculate the optical densities. In *Figure 2* are plotted the conversions determined by *FT* i.r. *versus* time for six PDMS precursors in the molar mass range between 4200 and 18 000 g mol^{-1}, reacted with the tetrafunctional compound. As expected, the reaction rate depends on the length of the precursor chain, i.e. the initial concentration of functional groups: the higher the molecular weight, the lower the rate of monomer conversion. In all cases the reaction slows down. The observed behaviour is not simple and does not correspond to a first or second order reaction. One reason could be that the four functions of the plurifunctional compound are not equireactive. Another parameter to be considered could be the steric hindrance. The curves on *Figure 2* also indicate the existence of a conversion limit depending on the molecular weight, i.e. the concentration of functional end-groups in the polymer, which confirms the earlier observed limitation of the final yield of the reaction.

b) Characterization of the polymer species formed by SEC-LS

Using the same precursor polymers as in the *FT* i.r. investigation we have carried out a series of experiments in glass tubes under comparable experimental conditions. The reaction times corresponding to the maximum conversion were fixed according to the kinetic results obtained from the *FT* i.r. study. In *Table 2* are gathered the molecular characteristics of the PDMS precursors, of the resulting branched species and the ratio $R_{(exp)} = \overline{M}_w^*/\overline{M}_w$, where $\overline{M}_w$ and $\overline{M}_w^*$ are the weight-average molecular weights of the precursor and of the branched polymers. The values of $R_{(exp)}$ are systematically lower than 4, even when the yields of the reaction are very high. This means that the resulting star-branched polymer contains always species with less than four branches. In all cases the fraction of unreacted precursor is very small. Two examples of SEC-LS diagrams are shown in *Figures 3a* and *3b* ($\overline{M}_w$ = 4600 and 15 700 g mol^{-1}). For higher molar mass precursors ($\overline{M}_w$ > 18 000 g mol^{-1}) the reaction becomes rather slow, and even when the maximum conversion is reached, the samples contain, in addition to the remaining precursor, simply coupled and three-branched species which appear as shoulders on the SEC-LS diagrams. With the highest molar mass polymer ($\overline{M}_w$ = 40 000 g mol^{-1}) practically no reaction occurred.

c) Statistical evaluation of the polymer composition in linear and star-branched molecules as a function of the conversion

In the course of the hydrosilylation reaction the precursor chains are progressively attached to the

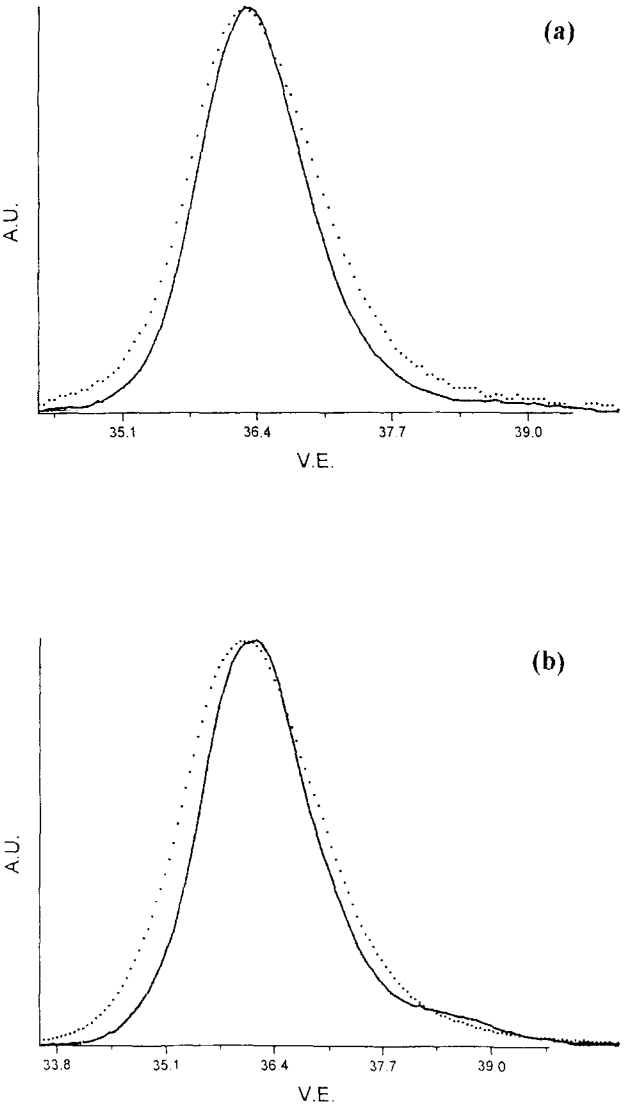


Figure 3 SEC curves of the branched samples: (a) $\overline{M}_w = 4600\,\mathrm{g\,mol^{-1}}$; (b) $\overline{M}_w = 15\,700\,\mathrm{g\,mol^{-1}}$. — — . Molar mass determined by elution volume; .... molar mass determined by light scattering

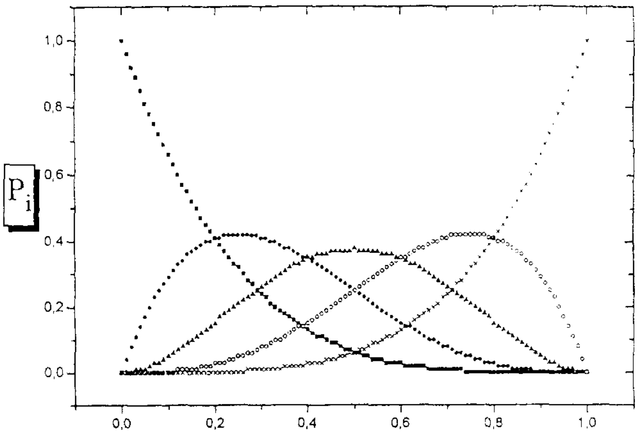


Figure 4 Calculated distribution of the polymer species P_i *versus* conversion p. ■, Unreacted precursor; ●, one branch; s, two branches; ○, three branches; × four branches

tetrafunctional reagent and consequently the composition in polymer species of the medium changes when the reaction goes on. This composition can be evaluated at any stage of the reaction by a statistical calculation. In this approach we admitted the statistical character of the reaction and the equireactivity of the functions of the plurifunctional compound.

If p is the probability that any of the four functions has reacted, $(1 - p)$ will be the probability that a function has not reacted. In fact p can be identified with the conversion of the reaction τ defined by the consumption of the silane or silylvinylic functions. In the general case of the reaction between a n-functional compound and a monofunctional polymer chain the probability that i functions have reacted is:

$$P_1 = \frac{n!}{i!(n-i)!} \times p^i \times (1-p)^{(n-i)}$$

where $n!/i!(n-i)!$ is the combination of i among the n branches.

In the present case $n = 4$ and $0 \leqslant i \leqslant 4$m, thus the probabilities are:

$$\text{no functions reacted } P_0 = (1-p)^4$$

$$\text{1 function reacted } P_1 = 4p(1-p)^3$$

$$\text{2 functions reacted } P_2 = 6p^2(1-p)^3$$

$$\text{3 functions reacted } P_3 = 4p^3(1-p)$$

$$\text{4 functions reacted } P_4 = p^4$$

Figure 4 shows the probability curves P_i *versus* the conversion p of the reaction. These curves allow estimation of the fraction of each polymer species in the medium at any stage of the reaction. It can be noted that at the beginning of the reaction the total fraction of branched molecules remains very low, hardly detectable by SEC-LS, even at 20% conversion. Above 60% conversion only the fraction of four-branched species increases noticeably. Taking into account the results obtained from the kinetic study by *FT* i.r., it is possible to calculate the average molecular weight reached at the maximum conversion $\overline{M}_{w(th)}$ and to compare the theoretically expected ratios $R(\mathrm{th}) = \overline{M}^*_{w(th)}/\overline{M}_{w(br)}$ with the experimental ratios $R_{(exp)} = \overline{M}^*_{w(exp)}/\overline{M}_{w(br)}$. The agreement between experimental and calculated values is rather consistent.

Reaction in toluene solution.

a) *FT* i.r. experiments

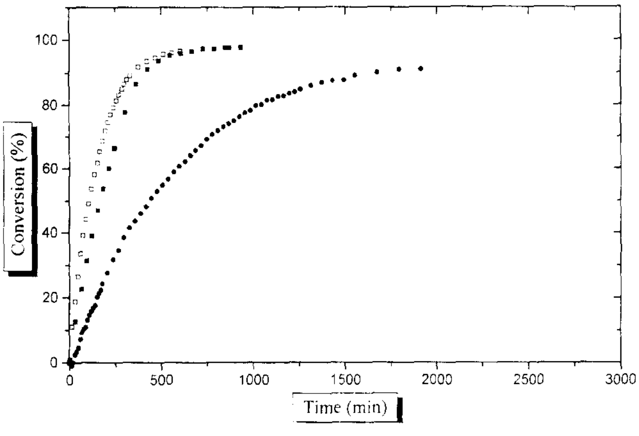
One could expect that for a comparable concentration of functional groups the reaction between the functional chain-ends and the tetrafunctional compound in this non-polar solvent should not be very different from the bulk reaction.

PDMS precursors with average molar masses 4200 and 11 000 g mol^{-1} were reacted at 40 and 70 wt% concentration but only the lower molecular weight sample yielded highly reproducible results. Traces of impurities may be absorbed in the i.r.-cell and diffuse into the solution when heated at 70°C; their influence might be more important at lower concentrations. In *Figure 5* we have plotted the conversion *versus* time for

Table 3 Molecular characteristics of the α-dimethylsilyl PDMS and the corresponding branched reaction products (reaction in tolueme solution, 70°C)

Precursor polymers				Star-branched samples							
$\overline{M}_n$ (i.r.)	$\overline{M}_w$ (SEC)	$C_{(pol)}$	$C_{(Si-H)}$	$t_{(h)}$	$\overline{M}_n^*$	$\overline{M}_{w(exp)}^*$	I	$\tau_{(lim)}$	$\overline{M}_{w(th)}^*$	$R_{(th)}$	$R_{(exp)}$
4200	4600	100%	0.23	18	16 400	17 100	1.04	0.97	17 700	3.7	3.7
		70%	0.16	22	14 500	16 800	1.16	0.95	17 100	3.8	3.7
		40%	0.09	43	10 900	15 200	1.39	0.91	16 400	3.7	3.4
10 200	10 700	100%	0.10	23	33 300	38 200	1.14	0.92	39 500	3.7	3.6
	11 500	70%	0.07	52	33 000	42 700	1.29	0.88	40 500	3.5	3.7
	11 500	40%	0.04	60	13 800	17 300	1.25	0.79	36 300	3.2	1.5

$C_{(pol)}$, polymer concentration (weight %)
$C_{(SiH)}$, concentration of dimethylsilyl functions (mol l^{-1})
t, reaction time (h)
$\tau_{(lim)}$, calculated maximum conversion
$R_{(th)}$ and $R_{(exp)}$, calculated and experimental ratios $\overline{M}_w^*/\overline{M}_w$



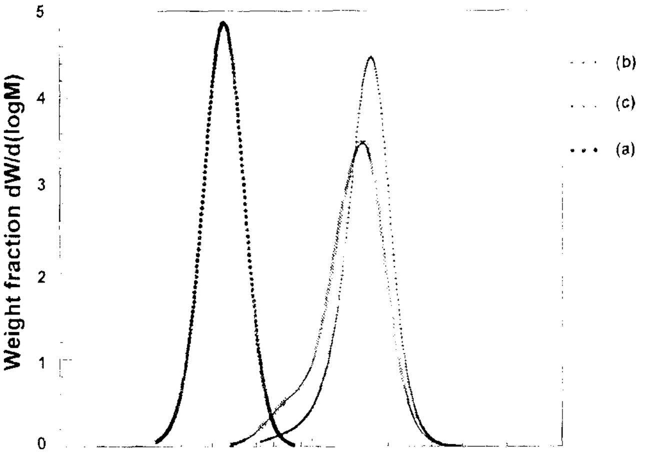


Figure 6 Reaction in toluene solution: SEC curves of the precursor and of the coupled products. PDMS precursor (a): $\overline{M}_w = 4600\,\mathrm{g\,mol^{-1}}$. Concentration (wt%): (b) 70; (c) 40

the first precursor (in the bulk and in the 40 and 70 wt% solutions). At 70% concentration the behaviour is practically the same as in the bulk. At 40% concentration the reaction is slower but, as will be shown below, the final conversion can be higher than could be expected from these curves. Probably in this case the presence of the already mentioned impurities could play a role.

b) SEC-LS investigation

The hydrosilylation reactions were carried out in sealed glass tubes, stopped after different reaction times and the mixtures of the polymer species formed characterized by SEC coupled with the LS detection.

In *Table 3* are the characteristics of the precursors and of the products obtained, the calculated conversion limits $\tau_{(lim)}$ and the calculated and experimental values of $R_{(th)}$ and $R_{(exp)}$ (the ratios of the average molecular weights of the branched products on the molecular weight of the precursor PDMS).

In the case of the first precursor ($\overline{M}_w = 4600\,\mathrm{g\,mol^{-1}}$) reacted at a 70% concentration ($C_{(SiH)} = 0.16\,\mathrm{mol\,l^{-1}}$) the average molecular weight of the branched products formed is close to the predicted value assuming the previously indicated conversion limit. The total fraction of branched species should be close to 99% (82% of four-branched molecules). This is illustrated in *Figure 6*, which shows the SEC curves of the coupled products and of the precursor PDMS. The shape of the curve corresponding to the branched sample produced at 70% concentration is very similar to that of the precursor. But when the reaction is carried out at 40% concentration ($C_{(SiH)} = 0.09\,\mathrm{mol\,l^{-1}}$) a shoulder appears on the SEC curve of the branched product which corresponds to the coupled polymer with twice the molecular weight of the precursor. This is not surprising, since the calculation predicts the presence of 4% linear, mainly coupled species with twice the initial molecular weight. Approximately 70% of the branched polymer is composed of four-branched species.

In the case of the second PDMS precursor ($10\,700\,\mathrm{g\,mol^{-1}}$) the functional group concentration in the bulk is the same order as that for the previous sample in toluene solution at 40% concentration ($C_{(SiH)} = 0.10\,\mathrm{mol\,l^{-1}}$). At 70% concentration ($C_{(SiH)} = 0.07\,\mathrm{mol\,l^{-1}}$) the reaction still yields a product with an average molecular weight close to the calculated value. The sample contains approximately 93% of branched polymer but the fraction of four-branched molecules is already quite reduced (about 60%). This results in a broadening of the SEC curve but separated peaks corresponding to three and four-branched species respectively were not observed, as could be expected. At 40% concentration ($C_{(SiH)} = 0.04\,\mathrm{mol\,l^{-1}}$) the reaction becomes very incomplete. Only coupled species with

Table 4 Characteristics of the α-dimethylsilylvinyl PDMS and the corresponding branched samples (reaction in the bulk, 70°C)

Precursor polymers				Star-branched samples			
$\bar{M}_n$ (C=C)	$\bar{M}_n$ (SEC)	$\bar{M}_w$ (SEC)	$M_w/\bar{M}_n$	M_n^*	$\bar{M}_w^*$	t (h)	$R_{(exp)}$
3100	3200	3400	1.06	12 800	13 200	15	3.9
4800	4600	4900	1.06	16 600	19 400	15	3.9
8600	8300	8700	1.06	25 000	33 500	20	3.9
9600	8800	9400	1.07	23 900	36 500	25	3.9
13 300	13 500	14 300	1.05	38 500	55 600	30	3.9
17 100	16 800	18 000	1.06	46 900	65 500	42	3.6
24 000	22 900	24 400	1.055	68 100	87 500	68	3.5

$\bar{M}_n$ (C=C), number-average molar mass given by vinyl bond titration

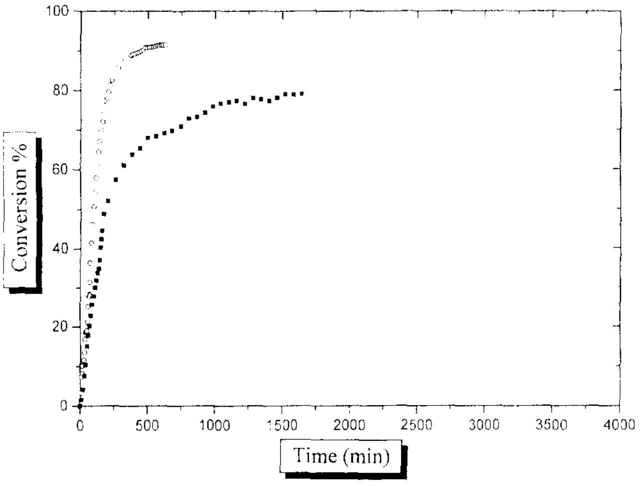


Figure 7 Conversion rates *versus* time. PDMS precursors with silylvinyl end-groups: ■, $\bar{M}_n$ = 17 100; ○, 8600 (g mol^{-1})

twice the initial molecular weight appear on the SEC diagram.

According to our results the reaction, in the bulk as well as in solution, between α-dimethylsilyl PDMS and the tetrasilyvinylic compound depends only on the initial concentration of functional chain-ends and consequently on the molecular weight. The extrapolation of these results to the case of network synthesis by end-linking, using the corresponding α,ω-difunctional PDMS suggests the following. If we consider an α,ω-difunctional precursor with an average molar mass of 10 000 g mol^{-1}, the number of functional groups per unit weight of polymer is the same as for a monofunctional precursor with a 5000 g mol^{-1} molar mass. If we assume that in both cases the possible influence of steric hindrance or viscosity is the same, we can admit that the crosslinking reaction yields a network in which the number of elastically effective crosslinks is close to the theoretical number, even at a 70% polymer concentration. This means that each plurifunctional molecule generates an effective crosslink. Chain-extension by simple coupling should be negligible. However three-functional crosslinks could exist, which implies the presence of pendent chains linked by only one chain-end to a crosslink (it has to be specified that here we call functionality the number of chains attached to a crosslink, pendent as well as elastic chains). When a network is prepared, again at 70% concentration, but with a precursor with twice the molar mass (20 000 g mol^{-1}), chain-extension by simple coupling should still remain negligible but the fraction of three-functional branch-points becomes more important. This also implies the existence of elastically ineffective three-functional branch-points, which are not crosslinks. They are linked to only two neighbouring crosslinks and to a pendent chain, a type of coupling equivalent to a chain extension.

Reaction of α-dimethylsilylvinyl PDMS with 1,3,5,7-tetramethylcyclotetrasiloxane

In spite of the fact that in comparison with the previous system this case represents a symmetrical situation, it is not exactly identical. The environment of the functional groups is not the same and the behaviour of the reaction could be different. As previously, we have studied the reaction first in the bulk and then in solution in toluene.

Reaction in the bulk: influence of the precursor chain-length. Since the i.r. absorption of the silylvinylic function at 1412 cm^{-1} is very weak, we have based our analysis on the silyl absorption band at 2175 cm^{-1} of the tetrafunctional cyclosiloxane which is slightly shifted with respect to that of a silyl group at PDMS chain-end (2127 cm^{-1}). We have used two precursors with number average molar masses 8600 and 17 100 g mol^{-1} and the stoichiometric amount of silyl groups (concentration: $C_{(SiH)}$ = 0.14 and 0.60 mol l^{-1} respectively).

Figure 7 shows for both samples the conversion curves *versus* time; their initial slopes seem to indicate that for the same molar mass of precursor (or concentration of functional groups) the reaction is faster than in the previous, symmetrical, system. The conversions reached after 10 and 27 h were 91 and 78% respectively for the lower and the higher molecular weight PDMS.

We have studied by SEC-LS the reaction products corresponding to a series of PDMS precursors in the molar mass range between 3000 and 24 000 g mol^{-1} reacted with the tetrafunctional compound. In *Table 4* are displayed the molecular characteristics of the precursors and of the polymer species formed, the ratio $R_{(exp)} = \bar{M}^*_{w(exp)}/\bar{M}_{w(br)}$, and the reaction times.

These results indicate that the conversions observed at the end of the above *FT* i.r. measurements did not correspond to the final conversions. The actual final conversions are even higher than those calculated

Table 5 Characteristics of the α-dimethylsilylvinyl PDMS and the corresponding branched samples (reaction in toluene solution, 70°C)

Precursor polymer					Star branched samples								
$\tau_{(exp)}$ (%)	$\bar{M}_n$ (C=C)	$\bar{M}_n$ (SEC)	$\bar{M}_w$ (SEC)	$\bar{M}_w/\bar{M}_n$	$C_{(SiH)}$ ($mol\,l^{-1}$)	$\tau_{(lim)}$ (%)	$\bar{M}_w^*$ (th)	$R_{(th)}$	$\bar{M}_n^*$ (SEC-LS)	$\bar{M}_{w(exp)}^*$ (SEC-LS)	t (h)	$R_{(exp)}$
98	8600	8300	8700	1.05	0.05	82.5	28 600	3.3	21 000	34 100	25	3.9
97	9600	8800	9400	1.07	0.04	80.5	30 300	3.2	31 300	36 700	25	3.9
97	13 300	13 500	14 300	1.05	0.03	74.2	42 400	3.0	51 600	55 300	32	3.9
87	17 100	16 800	18 000	1.06	0.02	65.9	47 700	2.7	51 100	62 500	37	3.5

$C_{(SiH)}$, concentration of saline functions of the tetrafunctional compound ($mol\,l^{-1}$)

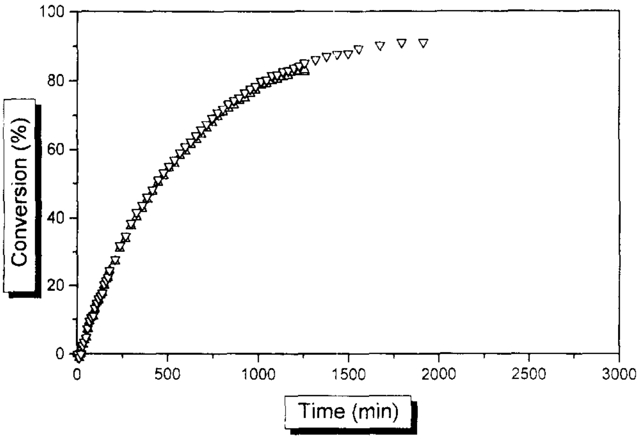


Figure 8 Comparison between silyl and silylvinyl functional precursors: reaction in solution (40 wt%); conversion *versus* time. (▽) α-silylvinyl precursor; $\bar{M}_n = 8600\,g\,mol^{-1}$. (△) α-silyl precursor; $\bar{M}_n = 4200\,g\,mol^{-1}$

assuming the limiting concentration of $8 \times 10^{-3}\,mol\,l^{-1}$ below which, in the 'symmetrical' system, the reaction no longer continues. This implies that in the present case this concentration limit is lower.

Reaction in solution. We have limited our experiments in toluene to the 40 wt% polymer concentration using four precursors with average molar masses $\bar{M}_n = 8600$, 9600, 13 300 and 17 100 $g\,mol^{-1}$ (*Table 5*). Only the lowest molecular weight sample was used in the *FT* i.r. experiments, for the reason already mentioned before ($C_{(SiH)} = 0.05\,mol\,l^{-1}$).

At the end of the reaction the average molecular weights of the samples obtained in the second system correspond to conversions of 97–98%, and in the case of the highest molecular weight precursor still close to 87%. Under the same conditions almost no reaction occurred in this molar mass range in the case of a precursor with the silyl group at chain-end.

To illustrate the significant difference in reactivity between dimethylsilylvinyl and dimethylsilyl terminated PDMS, *Figure 8* shows the conversion *versus* time curves at 40% concentration for two samples: a silylvinylic- and a silyl-functional sample with molar masses 8600 and 4200 $g\,mol^{-1}$, respectively. In spite of the fact that in the second case the concentration of functional chain-ends is twice as great, the curves are practically superposable.

CONCLUSION

The present investigation contributes to a better insight into the behaviour of the hydrosilylation reaction between a functional group at a PDMS chain-end and a tetrafunctional compound, a frequently used reaction in network synthesis by endlinking. It was confirmed that the reaction does no longer take place below a given concentration, which depends upon the system. A consequence of this effect is a limitation of the extent of the reaction. A quite important difference was observed between the behaviour of a PDMS precursor fitted at chain-end with a dimethylsilyl function and one with a dimethylsilylvinyl end-group, when reacted with the corresponding tetrafunctional compounds. In the second case the reaction is noticeably faster and the final conversions reached are higher. This means that the concentration of functional groups which limits the reaction is lower than for precursors with dimethylsilyl end-groups. These differences could be related to steric effects, which could have an influence on the formation of the platinic complex with the silylvinylic functions and on the reactivity of the silyl functions. The dimethylsilylvinyl group at the chain-ends might be complexed more easily than the more hindered vinyl functions of the tetrafunctional compound. However, this is still hypothetical and more experimental support is required to establish these points.

The principal parameter which limits the maximum yield reached at the end of the reaction is thus the initial concentration of functional groups in the medium, which depends on the molecular weight of the precursor and, of course, on the concentration. It has to be emphasized that, even when the extent of the reaction is very high, the average number of branches of the star-shaped samples obtained remains below four. The final products always contain a fraction of three-branched species even in the absence of any detectable linear polymer.

Extrapolation of our results to the case of network synthesis by endlinking suggests the following observations: It has to be specified that in most investigations in the field of network behaviour the crosslinked samples used were prepared with low molar mass precursors (<20 000 $g\,mol^{-1}$), either in the bulk or in solution at relatively high polymer concentration. These conditions are rather favourable especially because the number of functional groups is twice that for monofunctional polymers used here with the same molar mass. However, even when the amount of extractible precursor PDMS is extremely low, we have to admit that a fraction of the tetrafunctional crosslinker is linked to only three elastically effective chains (three-functional crosslinks), which implies the presence of pendent chains. But in this case the total number of effective crosslinks should still be close to that of the tetrafunctional molecules involved.

ACKNOWLEDGEMENTS

The authors express their gratitude to Dr Cl. Strazielle for advice and helpful discussions, to M. J. Druz for his contribution to *FT* i.r. measurements and to M. F. Isel for his very valuable technical assistance.

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