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Synthesis and characterization of monofunctional polydimethylsiloxanes with a narrow molecular weight distribution

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Polydimethylsiloxanes (PDMSs) with a narrow molecular weight distribution and fitted at one chain end with a hydrogenodimethylsilyl or a dimethylvinylsilyl function were prepared by the anionic ring-opening reaction of hexamethylcyclotrisiloxane in a 50 vol% benzene–tetrahydrofuran solution, followed by endcapping with chlorodimethylsilane or chlorodimethylvinylsilane. The experimental conditions were chosen on the basis of preliminary experiments in order to minimize the contribution of reshuffling reactions and it was checked that the possible formation of difunctional species was negligible. The functionalization was quantitative. The functional polymers were characterized by i.r. spectroscopy and by s.e.c. α-Hydrogenodimethylsilyl and α-dimethylvinylsilyl PDMS were prepared in the molecular mass range between 2500 and 40 000 g mol^{-1}.

(Keywords: polydimethylsiloxane; anionic polymerization; ring-opening polymerization)

INTRODUCTION

Crosslinked polydimethylsiloxanes (PDMSs) with well defined molecular characteristics, prepared by endlinking of α,ω-difunctional precursors, have been extensively used as models in many fundamental investigations concerning the elastic behaviour of networks in relation to their structural parameters, the conformation of network chains or the influence of structural defects such as pendent or entangled chains.

However, the question remains to what extent a network obtained by this method can be considered as a model system. It depends first on the chemical reaction involved in the crosslinking process, and this is difficult to control in the case of an insoluble system. Generally the extent of the reaction is estimated by a calculation based on the amount of extractable products in the network. Another way to proceed is to follow the reaction on a model system where monofunctional precursor chains are reacted with the plurifunctional compound under the same experimental conditions as those used for the corresponding network synthesis. In this case soluble star polymers are formed which can be carefully analysed in solution. This investigation requires the use of perfectly defined monofunctional PDMS precursors with a narrow molecular weight distribution. This paper deals with the synthesis of these precursor polymers by anionic ring-opening polymerization of hexamethylcyclotrisiloxane[1–5] and their characterization.

One of the first papers giving a detailed synthesis of linear PDMS with narrow molecular weight distributions was by Zilliox *et al.*[4]. They proceeded by anionic polymerization of hexamethylcyclotrisiloxane (D_3) in tetrahydrofuran (THF) using sec-butyllithium as initiator.

More recently, several publications have reported the synthesis of monofunctional PDMS macromonomers by anionic polymerization followed by an end-capping reaction[6–9].

In our investigation three requirements had to be fulfilled: narrow molecular weight distribution, practically quantitative functionalization yields and the absence of any difunctional species. The latter has to be taken into consideration, since in the course of anionic or cationic polymerizations, backbiting and reshuffling reactions may occur, especially at high monomer conversions. They lead, respectively, to cyclic compounds and to a broadening of the molecular weight distribution with the possible formation of difunctional macromolecules. In the scope of the present study we are particularly concerned with the latter species.

EXPERIMENTAL

Solvents and reagents

THF was distilled over sodium wire and treated with sodium benzophenone. The dry solvent obtained by distillation from this solution was stored under argon.

Benzene and toluene were distilled twice over sodium wire and kept under argon.

Hexamethylcyclotrisiloxane (D_3) (98%, Aldrich) was used in benzene solution at 20 wt%. It was first distilled in the presence of CaH_2 (b.p. 70–75°C, 12–14 kPa) and collected in a burette under argon. To prepare the solution, the required volume of benzene was transferred under argon to the D_3. The concentration of the monomer solution was checked by an accurate simple ponderal determination.

sec-Butyllithium in a 0.8 N benzene solution was the

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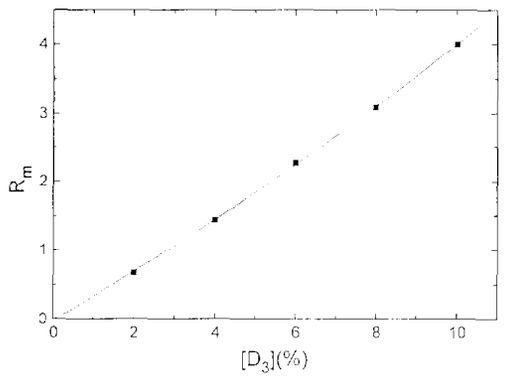


Figure 1 Calibration curve of R_m ([D_3]/[reference]) *versus* monomer concentration

polymerization initiator. The exact concentration was checked by titration before use.

Chlorodimethylsilane and chlorodimethylvinylsilane (Aldrich, >98%) were used in THF solution at a concentration of $\sim 0.7\ mol\ l^{-1}$. The chlorosilanes were first placed on a molecular sieve (4 Å) to eliminate HCl, filtered and distilled under argon into a glass device in which they were diluted and stored under inert atmosphere.

1,11-Dihydrogenododecamethylhexasiloxane was prepared by the acid-catalysed reaction of octamethylcyclotetrasiloxane with 1,3-dihydrogenotetramethyldisiloxane, distilled and kept under argon (b.p. 70°C, 1×10^2 Pa).

1,4-Bis(dimethylvinylsilyl)benzene (99.8%) was obtained according to a method described by Prud'homme[9].

1,3,5,7-Tetramethylcyclotetrasiloxane (b.p. 134°C) and 1,3,5,7-tetramethyltetravinylcyclotetrasiloxane (b.p. 110°C, 1.4 kPa) (Petrarch) were distilled and kept under argon.

The hydrosilylation catalyst was $H_2PtCl_6.6H_2O$ (Prolabo) in isopropanol solution (concentration 1.9×10^{-2} $mol\ l^{-1}$) used at a ratio of 2.5×10^{-4} mol per mole of functional PDMS.

Polymer synthesis

This was carried out in solution in a 50 vol% benzene–THF mixture in a hermetic glass reactor under a slight argon pressure. The whole device was flamed and traces of absorbed moisture or air eliminated by repeated cycles of vacuum and argon pressure.

Gas chromatography

This technique allows the decrease in D_3 concentration during the polymerization reaction to be followed, in the presence of an internal reference compound, and enables the experimental conditions for the polymer synthesis to be determined.

The gas chromatograph used was a Varian 3400 equipped with a 4 m long column (type OV 17). We preferred the flame ionization detection method to the often recommended but less sensitive catarometric detection. It yielded well reproducible results. We used 1,3-diethylbenzene as the internal reference compound since its chromatographic peak is well separated from that corresponding to D_3. The g.c. column was calibrated with solutions of D_3 in the 50 vol% benzene–THF mixture containing a standard fraction of the reference. *Figure 1* shows the calibration curve.

Alcoholysis of D_3

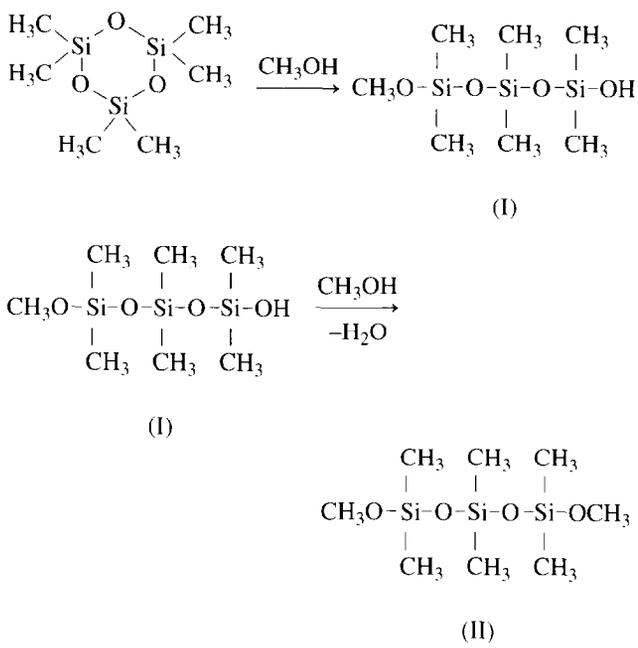
Usually, to follow the polymerization reaction, samples of the reaction bath are cut off and precipitated in a non-solvent of the polymer. G.c. analysis of the solvent/non-solvent mixture containing the monomer and the reference compound allows the accurate determination of the remaining monomer concentration. The generally used precipitant of PDMS is methanol. In the present case however much care has to be taken since blank experiments showed that D_3 undergoes quite a rapid transformation in this solvent. The g.c. peak corresponding to D_3 vanishes progressively and a second peak appears.

The reaction of D_3 in alcohol as shown in *Scheme 1* is well known. It yields 5-methoxyhexamethyltrisiloxanol (I). A condensation reaction between this silanol and methanol may occur to produce 1,5-dimethoxyhexamethyltrisiloxane (II).

The alcoholysis reaction was described in several patents[10,11] but under much more severe conditions (4 h under reflux). On the other hand, a study of the condensation reaction was reported in the literature in acid or base but not in a neutral medium[12]. We observed a very rapid alcoholysis reaction even at room temperature: the conversion of D_3 to silanol (I) occurred within 4 h. The latter was identified by ^1H n.m.r. and mass spectrometry (m.s.). When the methanolic solution is kept at room temperature the condensation product (II) is formed as shown by g.c. It was isolated and identified by ^1H n.m.r. and m.s. After 1 month, ~50% of I was spontaneously converted to II. The ^1H n.m.r. and m.s. characteristics of both products are given below.

For 5-methoxyhexamethyltrisiloxanol (I): ^1H n.m.r. (CCl_4) δ: 0.00 (s, Si–CH_3, 18H), 3.06 (s, –OH, 1H), 3.38 (s, –O–CH_3, 3H). M.s. (70 eV): $m/e = 207(100)$, 223(25), 193(16), 191(8), 133(4), 177(3), 89(3), 75(3), molecular peak absent; M–CH_3 = 239 (1.6).

For 1,5-dimethoxyhexamethyltrisiloxane (II): ^1H n.m.r. (CCl_4) δ: 0.00 (s, $SiCH_3$, 18H), 3.34 (s, –O–CH_3, 6H). M.s. (70 eV): $m/e = 253(100)$, 223(41), 207(18), 193(11),



Scheme 1

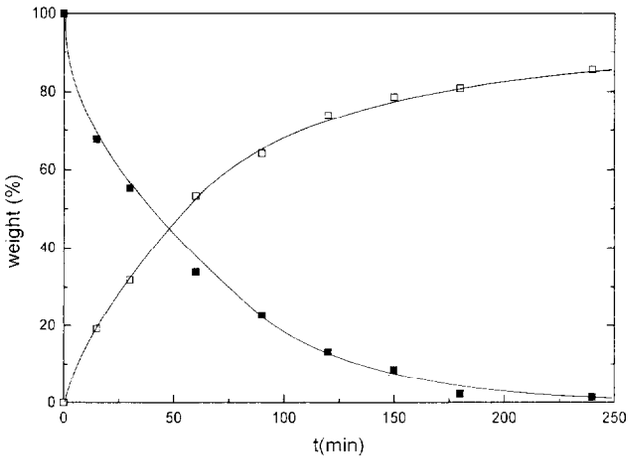


Figure 2 Polymer formation (□) and monomer conversion (■) *versus* time

104(7), 89(7), 119(6), 73(5), molecular peak absent; $M-CH_3=253$ (100).

Polymer characterization

The number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) of the functionalized PDMS samples were determined by s.e.c. A classical chromatographic device was used with a Shimadzu LC-6A pump, a six-path injector Rheodyne and three microstyragel columns allowing efficient separation in the molecular weight range between 2000 and 200 000 (mixed porosity of the column filling). The apparatus was equipped with a refractometric detector and coupled with a light scattering device.

The low molecular weight standards used to calibrate the s.e.c. columns were prepared by anionic polymerization. The standards used in the higher molecular weight range were fractionated samples obtained by cationic polymerization.

The number of functional end groups in the PDMS samples had to be accurately established. In the case of the silane-terminated polymers it was determined by i.r. spectroscopy[13,14]. The Si-H end groups present a characteristic, very strong and well separated absorption band at 2126 cm^{-1} which allows their determination with good accuracy, at least in the molecular weight range below $\bar{M}_n=20\,000$. The transmission spectra were obtained by averaging 32 scans with a 2 cm^{-1} resolution using a Nicolet SX Fourier transform spectrometer.

In the case of silylvinyl polymer end groups this method cannot be applied since the corresponding i.r. band is too weak and interferes with other bands. Therefore we determined the number of functional end groups by a chemical titration of the vinyl double bonds according to the mercury acetate method of Johnson and Fletcher[15].

POLYMER SYNTHESIS

The best method to prepare functional PDMS with a narrow molecular weight distribution is the anionic ring-opening polymerization of hexamethylcyclotrisiloxane. However the experimental conditions have to be carefully chosen in order to avoid possible side effects such as reshuffling reactions (chain scission and recombination) which can lead to a broadening of the molecular weight distribution[4,5]. The contribution of side effects can be important at the end of the reaction. Moreover, according to several authors, a concentration dependent association between oxanions may have an influence on the rate constant of the polymerization reaction[4,6,16–18]. This implies that, for a given monomer concentration, the polymerization rate depends upon the desired molecular weight, since the required concentration of growing chains (oxanionic chain ends) decreases when the latter increases.

In the present case, we were interested in the low molecular weight range ($\bar{M}_n<40\,000$). To establish the optimal experimental conditions for the synthesis of polymer samples with the required molecular characteristics, we carried out a series of preliminary experiments in the 50 vol% benzene–THF mixture at 20 wt% monomer concentration. Theoretical amounts of sec-BuLi initiator required to obtain molecular weights of $\bar{M}_n\sim10\,000$ and 20 000 were used. The polymerization reactions were followed by means of two techniques; g.c. and a ponderal method. In the first method the remaining fraction of D_3 was determined and in the second, the weight fraction of polymer was determined. Both methods allow monomer conversion with time to be followed.

Samples (10 ml) of the reaction medium containing the growing polymer, the remaining D_3 and the internal reference compound were introduced into calibrated vessels under argon and the siloxanionic sites rapidly deactivated by addition of chlorotrimethylsilane. These samples were immediately analysed by g.c. After evaporation under vacuum of the solvents, excess chlorosilane and the unreacted monomer, only the polymer remained; its weight was accurately determined.

Figure 2 shows the variation of weight per cent polymer formed and of the remaining D_3 in solution *versus* time for a siloxanion concentration of 10^{-2} mol l^{-1}. *Figure 3* is a plot of the weight per cent of polymer *versus* time for two expected final molar masses (10 000 and 20 000 mol l^{-1}). In both cases the initial monomer concentration is the same but the concentration of siloxanions is halved in the second case. Thus the concentration dependent association effect mentioned in the literature appears. However, in the present experiments

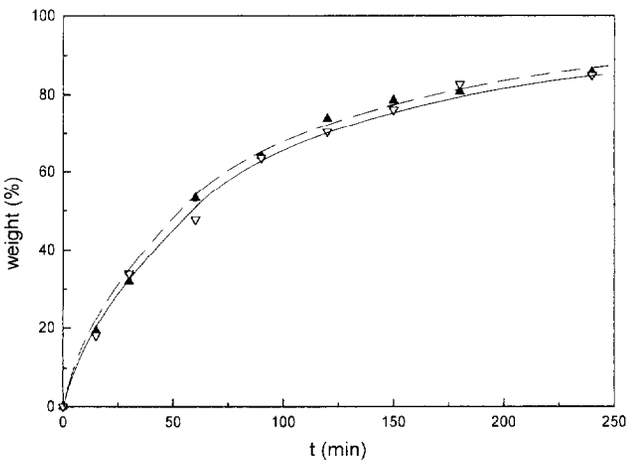
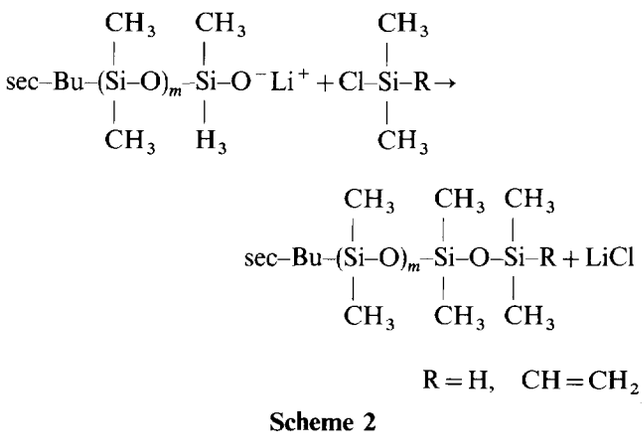


Figure 3 Polymer formation (wt%) *versus* time. Expected final molecular masses: (▲) 10 000 g mol^{-1}; (▽) 20 000 g mol^{-1}

it is less important than expected. To avoid any contribution of the already mentioned side reactions, we fixed, on the basis of the above experimental results, a polymerization time of 3 h (at 30°C) where conversions of 85–90% are reached.

PDMS samples fitted at one chain end with either a hydrogenodimethylsilyl or a dimethylvinylsilyl function were prepared in the molecular mass range between 2500 and 40 000 g mol^{-1}. Since the formation of polymers with a narrow molecular weight distribution requires a very fast initiation rate compared to the polymerization rate, the initiation reaction of D_3 (i.e. the ring opening by sec-BuLi with formation of siloxanions) was completely separated from the propagation reaction. A 20 wt% solution of the monomer in benzene was first placed in a glass reactor under argon. To this solution were first added some drops of 1,1-diphenylethylene and then sec-BuLi: after neutralization of all traces of protonic impurities, the characteristic red colour of the stable 1,1-diphenyl-3-methylpentyl anion appeared. It was checked that after at least 1 h the colour remained unchanged. Then, the required amount of sec-BuLi solution was added and reacted with the monomer for 2 h, followed by the addition of THF to obtain the 50 vol% benzene–THF mixture (10 wt% D_3). Polymerization only starts at this point in the polar medium (considered as the starting time in the preliminary experiments). After 3 h the end-capping of the growing chains was achieved by addition of a 10% excess of chlorodimethylsilane and chlorodimethylvinylsilane, respectively, in THF (*Scheme 2*). The functional PDMSs were precipitated in methanol, after addition of ~1% pyridine to the polymer solution to complex the HCl formed during the precipitation by the excess chlorosilane. The PDMSs were recovered by decantation, washed three times with methanol and dried under vacuum.



Scheme 2

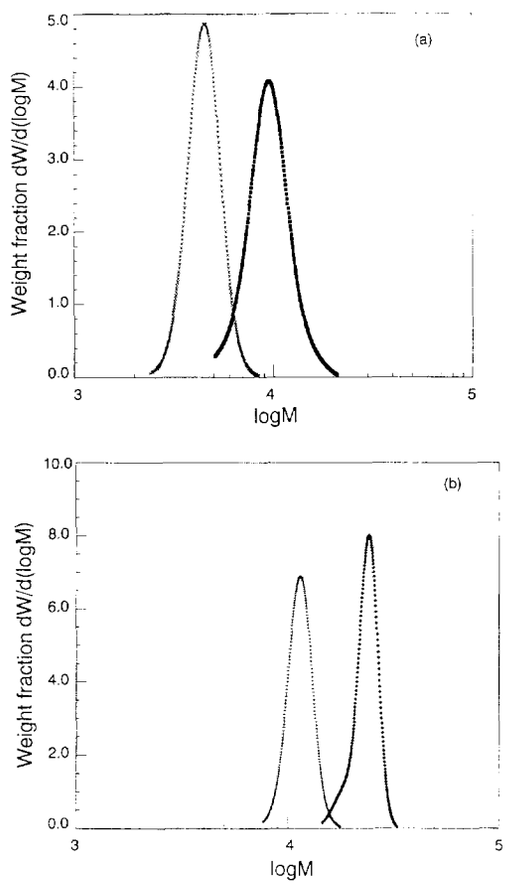


Figure 4 S.e.c. diagrams of PDMS precursors (α-SiH) and the corresponding coupled polymers. (a) Precursor $\bar{M}_w = 4600$ g mol^{-1} (×); polymer $\bar{M}_w = 8900$ g mol^{-1} (■). (b) Precursor $\bar{M}_w = 10\,700$ g mol^{-1} (+); polymer $\bar{M}_w = 20\,400$ g mol^{-1} (◆)

Table 1 Molecular characteristics of the PDMS samples determined by s.e.c. and by titration of the functional groups

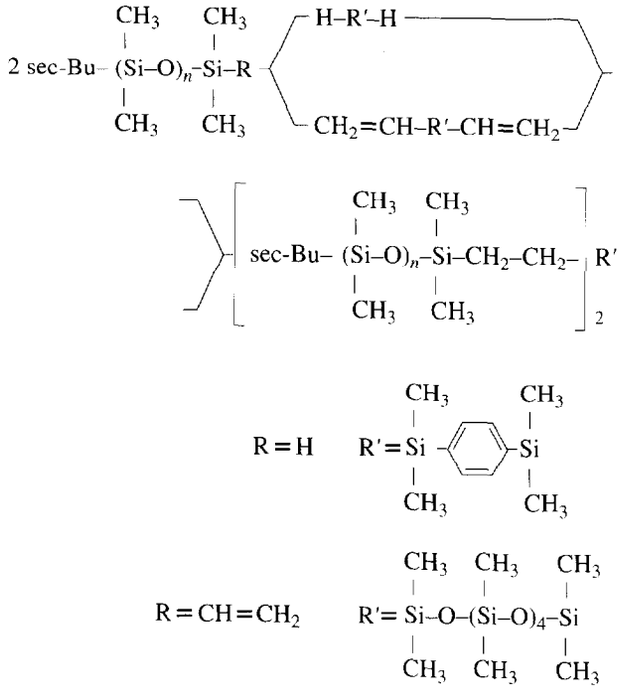
PDMS: α-dimethylsilyl					PDMS: α-dimethylvinylsilyl				
Code	$\bar{M}_n$ (i.r.)[a]	$\bar{M}_n$ (s.e.c.)	$\bar{M}_w$ (s.e.c.)	$\bar{M}_w$ (s.e.c.)/$\bar{M}_n$ (s.e.c.)	Code	$\bar{M}_n$ (a)[b]	$\bar{M}_n$ (s.e.c.)	$\bar{M}_w$ (s.e.c.)	$\bar{M}_w$ (s.e.c.)/$\bar{M}_n$ (s.e.c.)
SB20	4200	4300	4600	1.07	SBV0	3100	3200	3400	1.06
SB21	5000	5200	5500	1.06	SBV1	4800	4600	4900	1.06
SB22	6200	6000	6400	1.06	SBV2	9600	8800	9400	1.07
SB23	10 200	10 000	10 700	1.07	SBV3	8600	8300	8700	1.05
SB24	15 300	14 800	15 700	1.06	SBV4	13 300	13 500	14 300	1.05
SB25	16 600	15 200	15 300	1.07	SBV5	17 100	16 800	18 000	1.06
SB26	18 100	16 400	17 900	1.06	SBV6	24 000	22 900	24 400	1.05
SB27	24 100	21 200	22 800	1.07					
SB28	29 200	30 300	31 800	1.05					
SB29	41 800	37 500	39 400	1.05					

[a] Number-average molecular weight obtained from spectrometric titration of the SiH functions
[b] Number-average molecular weight obtained from the chemical titration of the Si–CH=CH$_2$ functions

Table 2 Molecular characteristics (s.e.c.) of the PDMS samples before and after the coupling reaction with a difunctional reagent

Precursor α-SiH			Coupled polymer				Precursor α-SiCH=CH$_2$			Coupled polymer			
$\bar{M}_n^P$	$\bar{M}_w^P$	$\bar{M}_w^P/\bar{M}_n^P$	$\bar{M}_n^C$	$\bar{M}_w^C$	$\bar{M}_w^C/\bar{M}_n^C$	$\bar{M}_w^C/\bar{M}_w^P$	$\bar{M}_n^P$	$\bar{M}_w^P$	$\bar{M}_w^P/\bar{M}_n^P$	$\bar{M}_n^C$	$\bar{M}_w^C$	$\bar{M}_w^C/\bar{M}_n^C$	$\bar{M}_w^C/\bar{M}_w^P$
4300	4600	1.07	8100	8900	1.08	1.93	3200	3400	1.06	6000	6500	1.08	1.91
10000	10700	1.07	19000	20400	1.07	1.91	8300	8700	1.05	16100	16900	1.05	1.94

Superscripts: P, precursor; C, coupled polymer



Scheme 3

Table 1 gives the molecular characteristics of the functional polymers. For all the samples the molecular weight distribution is quite narrow. The $\bar{M}_n$ values calculated from the concentration of functional groups (obtained by i.r. spectroscopy or by chemical titration) are consistent with those obtained by s.e.c.

VERIFICATION OF POLYMER FUNCTIONALITY

The side reactions, like reshuffling reactions, not only produce a broadening of the molecular weight distribution but in the present case they could also lead to the formation of unreactive and α,ω-difunctional species. Hence, it was essential to make sure that the contribution of such an effect was negligible. The determination of the reactive sites does not answer this question even if their number is consistent with the $\bar{M}_n$. Therefore, we carried out a direct test by reacting α-hydrogenodimethylsilyl and α-dimethylvinylsilyl functional polymers with difunctional reagents, 1,4-bis(dimethylvinylsilyl)benzene and 1,6-dihydrogenododecamethylhexasiloxane, respectively (*Scheme 3*). If α,ω-difunctional polymer species were present in the sample, the hydrosilylation coupling reaction should yield not only polymer with twice the initial molecular weight but also higher molecular weight species, due to chain extension, with a broadening of the molecular weight distribution. These reactions were carried out in the bulk at 70°C in the presence of the hydrosilylation catalyst.

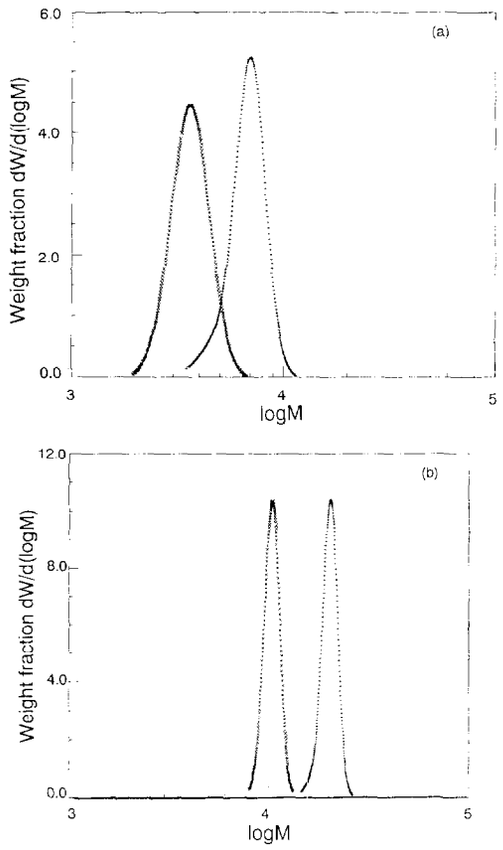


Figure 5 S.e.c. diagrams of PDMS precursors (α-Si-CH=CH$_2$) and the corresponding coupled polymers. (a) Precursor $\bar{M}_w = 3400$ g mol^{-1} (×); polymer $\bar{M}_w = 6500$ g mol^{-1} (+). (b) Precursor $\bar{M}_w = 8700$ g mol^{-1} (×); polymer $\bar{M}_w = 16900$ g mol^{-1} (+)

The molecular characteristics of the PDMS samples before and after the coupling reaction are given in *Table 2*. *Figures 4* and *5* show the s.e.c. traces of the α-SiH and α-Si-CH=CH$_2$ precursor PDMS and of the corresponding coupled polymers.

In all cases, only coupled polymers with approximately twice the initial molecular weight are formed. The molecular weight distribution of the coupled species is still narrow. No broadening of the s.e.c. traces is observed which would indicate the presence of higher molecular weight polymer formed by multiple coupling of α,ω-difunctional molecules. Moreover the absence of a second peak or shoulder which would correspond to the unreacted precursor PDMS not only means that the yield of the hydrosilylation reaction is very high, but also implies that the contribution of reshuffling reactions with a possible formation of unreactive PDMS species is negligible.

In conclusion, we can state that the PDMS samples, as prepared above, meet the two essential requirements — a narrow molecular weight distribution and a well defined monofunctionality. They can be considered as convenient precursor polymers for the formation of star-shaped PDMS by hydrosilylation coupling. This work will be published in a subsequent paper.

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