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Polycondensation using hydrosilylation: a tool for preparing tailor-made polysiloxanes with anchoring groups

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Abstract

The synthesis of copolymers composed of dimethylsiloxane segments (DMS) of different lengths, regularly separated by one bisphenol A unit (BPA) is described. This was achieved by performing hydrosilylation of 2,2′-diallyl BPA with hydride terminated polydimethylsiloxanes in the presence of Pt(0) catalyst. The influence of several factors, including the control of the [Si–H]/[double bond] ratio and the protection of the –OH groups, on the molecular weight distribution of the polymers is described. Side reactions, such as the isomerization of the double bond and the O-silylation were studied by ^{1}H and ^{29}Si n.m.r. As expected, there is a strong influence of the DMS segment length and of the presence of H-bonding interactions on the thermal properties of the resulting polymers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polysiloxane; Bisphenol A; Polycondensation

1. Introduction

Polydimethylsiloxanes (PDMS) bearing pendant phenol groups are of interest for the modification of the properties of formaldehyde–phenol resins [1–5]. They are also widely used as photoresists for microlithography [6]. Phenol terminated PDMS were usually obtained by hydrosilylation of 2-allyl-6-methylphenol, 2-allyl-4,6-dimethylphenol or eugenol with hydride terminated PDMS [1–3]. Rushkin et al. prepared polymers bearing pending phenol groups by reacting polymethylhydrosiloxane (PMHS) and polymethylsilmethylene with protected 2-allylphenol, i.e. 1-(trimethylsilyloxy)-2-allylbenzene, in order to avoid the side reaction of O-silylation [7]. Recently polycondensation of 2,2′-diallyl bisphenol A (BPA) with tetramethyldisiloxane or hexamethyltrisiloxane was found to give oligomers without noticeable phenol group silylation [8]. A similar reaction was performed between 2,2′-diallyl bisphenol F and hydride terminated polydimethylsiloxanes which leads to polymers used as chemical sensors [9]. The aim of this work was to study in detail the polycondensation of hydride terminated siloxanes and carbosilanes with 2,2′-diallyl BPA [10], using our previous experience in the field of controlled polycondensation using the hydrosilylation reaction [11]. Polycondensation was performed with and without the protection of the phenol groups, as shown below (Fig. 1).

The properties of the resulting polymers were examined.

2. Experimental

2.1. Reagents

Tetramethyldisiloxane (**Ia**, $n = 1$, Hüls America Inc.), hexamethyltrisiloxane (**Ib**, $n = 2$, Hüls America Inc.), tetramethyldisilylethylene (**IIa**, $n = 1$, Hüls America Inc.) and trimethylchlorosilane (Me_3SiCl, Aldrich) were distilled before use. The average molecular weights of hydride terminated polydimethylsiloxanes (**Ic**, $n = 8$; **Id**, $n = 17$ and **Ie**, $n = 52$, Hüls America Inc.) were determined by several methods (see Table 1). They were used without further purification. 2,2′-diallyl BPA (**III**, Aldrich, 90%) was separated from its impurities, i.e. mono or diallyloxy BPA (**V**), using the procedure described in Fig. 2: a mixture of 6.605 g (21.4 mmol) of **III** and 21.4 ml of aqueous NaOH (3 N) were heated at 65°C for ^{1}H. The allyloxy containing BPA compounds were extracted with toluene (20 ml). The neutralisation of the aqueous phase with dilute HCl induced the precipitation of a brown product, which was dissolved in toluene, washed several times with water, and dried over

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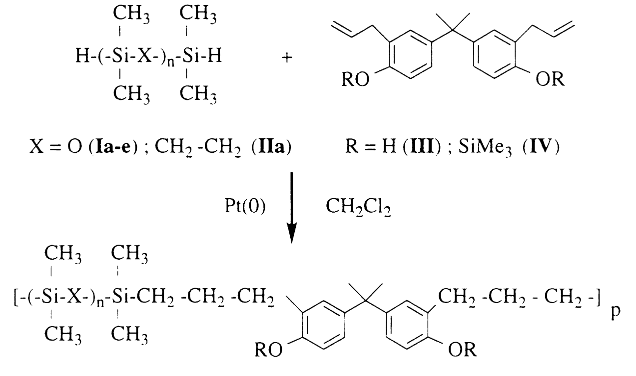

Fig. 1. Synthesis of poly(DMS-*alt*-BPA) by polycondensation. $X = O$: $n = 1, 2, 8, 17, 52$; $X = CH_2–CH_2$: $n = 1$.

Table 1
Molecular weights of the hydride terminated polydimethylsiloxanes

Ref.	From ^{1}H n.m.r.		From s.e.c.		From i.r. determination	
	M_n	n	M_n (M_w/M_n)	n	M_n	n
Ic	650	8	800 (1.2)	10	650	8
Id	1400	18	1300 (1.4)	17	1320	17
Ie	4200	56	3400 (3.5)	45	3950	52

Na_2SO_4, leading to pure **III** as checked by ^{1}H and ^{13}C n.m.r. (yield: 90%).

N,*O*-bis(trimethylsilyl)acetamide (BSA, Aldrich) and platinum (0) catalyst PCO72 (platinum-divinyltetramethyldisiloxane complex, 3–3.5% platinum concentration in xylene, Hüls America Inc.) [12] were used as received. Silylation of **III** was carried out in acetonitrile with BSA/Me_3SiCl ($[Me_3SiCl]/[BSA] = 0.05$) at 80°C for 4h, giving **IV** with a 80% yield after purification on silica gel using *n*-pentane/Et_2O (95/5) as the eluent [13]. 4,4′-diallyloxy-BPA (**V**) was obtained by reacting BPA with a 3-fold excess of allyl bromide under phase transfer catalysis conditions in toluene at 40°C, using NaOH (3 N) and tetrabutylammonium hydrogen sulfate (TBAH, 10 mol%) as the transfer agent. Potassium fluoride (KF, Fluka), *t*-butylbromide (*t*-BuBr, Aldrich) and tetrabutylammonium fluoride (TBAF, Merck) were used as received.

2.2. Polycondensation

Typical polycondensation reactions (Fig. 1) were performed in CH_2Cl_2 under nitrogen, with a 1:1 molar ratio of Si–H to allyl groups ($V_c = V_{reagents}/V_{total} \approx 0.4$). The platinum catalyst was added at 0°C ($[Pt]/[Si–H] = 5 \times 10^{-4}$) and the mixture was then heated at 40°C. Reactions were followed by monitoring the decrease of the Si–H i.r. band, at 2120–2130 cm^{-1} for the siloxane precursors (depending on the length of the precursor) and at 2110 cm^{-1} for **IIa**. Polymers were usually recovered by evaporation of CH_2Cl_2 and dried under vacuum. Experimental conditions are summarized in Table 2, in which the molecular weights of the crude polymers determined by s.e.c. are listed. Poly(**Ic** + **III**) (i.e. resulting from the polycondensation of monomers **Ic** and **III**) and poly(**Id** + **III**) were purified by selective precipitations by water from THF solutions, leading to several fractions, which were analyzed by s.e.c. and ^{1}H n.m.r.

2.3. Deprotection of the Ph–OH groups

2.3.1. With t-BuBr/KF [22]

t-BuBr (0.28 ml) and 0.24 g of KF were added to a solution of poly(**IIa** + **IV**) (0.6 g) in DMF (8 ml) and the mixture was stirred for two days at room temperature. The polymer was recovered after evaporation of the solvent and analyzed by i.r.

2.3.2. With TBAF [23]

A 1.05 ml solution of TBAF in THF (1.1 M) was added to a solution of poly(**IIa** + **IV**) (0.67 g) in THF (17 ml) under stirring at room temperature. After 5 h, the polymer, which precipitated was recovered by dissolution in CH_2Cl_2, and analyzed by i.r. Poly(**Ie** + **IV**) was deprotected using the same procedure, except that the reaction time was 24 h.

2.3.3. With HCl/EtOH [14]

Deprotection of poly(**IIa** + **IV**) was carried out by adding 50 ml of HCl 1% in EtOH to a solution of 1 g of poly(**IIa** + **IV**) in toluene (5 ml). After 5 h at 30°C, the mixture was washed with water until neutral pH, the polymer was extracted with CH_2Cl_2, dried over Na_2SO_4 and analyzed

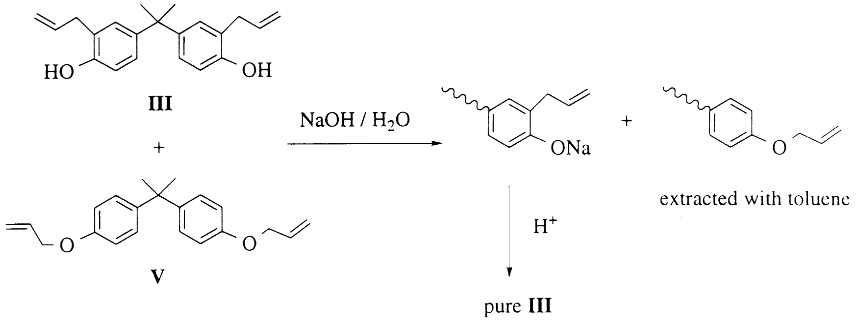

Fig. 2. Purification of **III** by selective extraction.

by i.r. and ^{1}H n.m.r. Deprotection of poly(**Ia** + **IV**) and poly(**Ie** + **IV**) were performed using the same procedure, at 25°C for 2 and 3 h, respectively.

2.4. Methods of analysis

Average molecular weights were determined by s.e.c. in toluene or in THF on a Waters apparatus, equipped for refractive index detection using a polystyrene calibration curve. ^{1}H, ^{13}C and ^{29}Si n.m.r. spectra were recorded at 200, 50.3 and 39.8 MHz, respectively, in $CDCl_3$ at 25°C with an AM 200 SY Bruker apparatus. Differential scanning calorimetry (d.s.c.) was performed on a Perkin–Elmer DSC-4 or on a Setaram DSC-92 apparatus with a 20°C/min heating rate. Thermogravimetric analyses were carried out under nitrogen with a 10°C/min heating rate on a TGA V5.0A DuPont 9900 apparatus.

3. Results and discussion

3.1. Synthesis of poly(DMS-alt-BPA)s

Polycondensation reactions of diallyl BPA (**III**) with hydride terminated polysiloxanes having 1–52 siloxy units were performed in CH_2Cl_2 in the presence of a Pt(O) catalyst, leading to copolymers made up of dimethylsiloxane segments (DMS) of different lengths, regularly separated by one bisphenol A unit (BPA), to which the general name poly(DMS-*alt*-BPA) was given. As already pointed out [8], polycondensation of **Ia** with **III** was strongly exothermic. After 0.5 h at 0°C, the reactions were heated at 40°C until a complete disappearance of the Si–H i.r. band was observed. The results are collected in Table 2. Polymers, which contain OH groups, are soluble in methanol and insoluble in *n*-hexane (except for $n = 52$). Their average molecular weights were determined by s.e.c. in THF. Polymers having relatively high molecular weights were obtained: M_n varies from 7200 to 27 400, depending on *n*. As expected, a slight decrease of *p*, as defined in Fig. 1 (from 16 to 6), is observed when the siloxane segment length increases. A typical chromatogram (poly(**Id** + **III**), run 5) is shown in Fig. 3(a). The limits used for the determination of the average molecular weights are indicated along with the total elution volume characteristic of the columns. At elution volumes higher than 18 ml appeared peaks corresponding to low molecular weight products, the amount of which can be strongly decreased by selective precipitation of polymers in a THF/water mixture, as shown in Fig. 3(b). The structure of these low molecular weight oligomers (cyclic/linear), which represent 10% of the samples, as determined from the peak areas, is under investigation. Polydispersity indexes around 3 were observed, which are much lower than those reported by Mathias et al. in the case of the polycondensation of commercial **III** with **Ia** ($M_n = 2200$, $I_p = 12$) [8], and by Grate et al. for the polycondensation of 2,2′-diallyl bisphenol F with **Ib** using the “one monomer deficient method” ($M_n =$ 10 300, $I_p = 11.4$) [9].

Table 2
Synthesis of poly(DMS-*alt*-BPA)s by polycondensation (for abbreviations, see the experimental part) ([=]/[Si–H] = 1; catalyst, PCO72; [Pt]/[Si–H] = 5×10^{-4}; solvent, CH_2Cl_2; $V_c = V_{reagents}/V_{total} \approx 0.4$; θ, 40°C; yield >95%)

Run	Monomers	n	t (h)	$(\overline{M_n})_{(s.e.c.)}$[a]	I_p	p	T_g[b]
1	**Ia** + **III**[c]	1	48	3100 (T)	1.6	7	21
2	**Ia** + **III**[d]	1	10	7200 (T)	3.0	16	32
3	**Ib** + **III**[d]	2	10	8500 (T)	3.0	16	16
4	**Ic** + **III**[d]	8	12	9300 (T)	3.4	10	−27
5	**Id** + **III**[d]	17	12	10 000 (T)	3.1	6	−90
6	**Ie** + **III**[d]	52	12	27 400 (T)	2.6	6	−114
7	**Ia** + **IV**	1	24	5900 (t)	2.1	10	−15
8	**Ib** + **IV**	2	20	9800 (t)	3.2	15	−25
9	**Ic** + **IV**	8	20	27 300 (t)	4.0	23	−65
10	**Id** + **IV**	17	22	46 200 (t)	2.7	9	−95
11	**Ie** + **IV**	52	26	63 400 (t)	2.1	14	−115
12	**IIa** + **III**[c]	1	48	3900 (T)	2.5	9	35
13	**IIa** + **III**[d]	1	10	7600 (T)	2.4	17	28
14	**IIa** + **IV**	1	48	13 400 (t)	3.2	22	−14
15	**Ia** + **V**	1	24	4000 (t)	1.8	9	−20
16	**IIa** + **V**	1	45	8000 (t)	2.5	17	2

[a] In toluene (t) or in THF (T) using a polystyrene calibration curve.
[b] By d.s.c. at 20°C/min, second heating.
[c] Commercial sample III.
[d] Purified III.

Some polycondensations were carried out, starting from tetramethyldisilethylene **IIa**. No significant differences in the time necessary for a complete disappearance of the Si–H bond during the polycondensation of **III** with **Ia** or **IIa** were observed, and similar molecular weights were obtained (runs 2 and 13 in Table 2).

3.2. Influence of the stoichiometry of the starting monomers

A key point of the control of polycondensation is the stoichiometry of the starting monomers. It was important to examine two factors.

First, the average molecular weights of the hydride terminated polydimethylsiloxanes (**Ic**, **Id** and **Ie**) were determined by several methods, as indicated in Table 1: s.e.c. in toluene using a polystyrene calibration curve and ^{1}H n.m.r. integration of $Si–CH_3$ versus Si–H of the precursors seemed to give satisfactory results, except for the longest polysiloxane precursor **Ie**, where the discrepancies were assumed to come from a less accurate integration of the end group signal by ^{1}H n.m.r. Preliminary polycondensation reactions were carried out, taking into account the average molecular weights determined by ^{1}H n.m.r., but these values were probably overestimated, as shown by the presence of remaining Si–H in all cases on the i.r. spectra, even after long reaction times. The exact values of Si–H mol-equivalent for **Ic**–**e** were thus determined by adding **III** via a microsyringe during the course of these preliminary

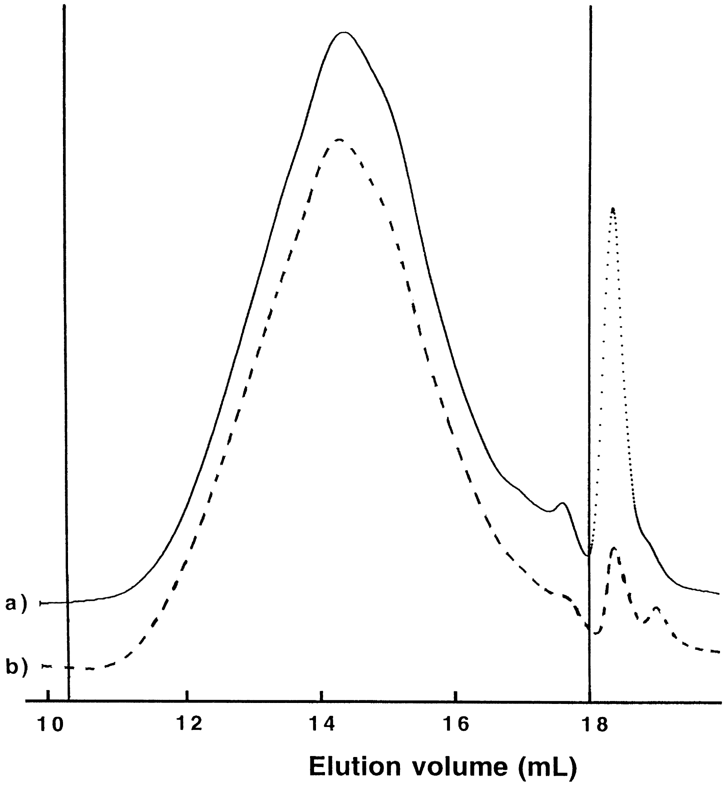

Fig. 3. S.e.c. chromatograms of poly(**Id** + **III**) (run 5, in THF): (a) crude polymer (full line); (b) after fractionation (first fraction, dotted line).

experiments, until a complete disappearance of the Si–H bond was observed by i.r. At this point, the exact stoichiometry ([Si–H]/[double bond] = 1) was assumed to have been reached and the deduced values of M_n are reported in Table 1. Another set of polycondensation reactions, reported herein, were conducted, using these last M_n values for the [Si–H]/[double bond] ratio calculation.

Then, the influence of the 5% impurities of commercial **III** was checked. The main impurities characterized by ^{1}H n.m.r. are mono and diallyloxy BPA (**V**). These compounds can be easily removed since they are less soluble in aqueous NaOH than the sodium salt of **III** (see Fig. 2). The disappearance of the Si–H function followed by i.r. was faster during the polycondensations conducted between the purified monomer **III** and **Ia** or **IIa** than with the commercial monomer (runs 2 and 13 compared to runs 1 and 12). Higher molecular weights were observed, probably because of better control of the stoichiometry. The ^{1}H and ^{13}C n.m.r. spectra of the polymers obtained by reaction of **Ia** with commercial or purified **III** are consistent with the regular structure proposed in Fig. 1 (see below for the spectroscopic analyses of the polymers), but their ^{29}Si spectra are different, as shown by the presence (run 1) or the absence (run 2) of a signal at 8.0 ppm which corresponds to the addition of Si–H onto the allyloxy groups. This assignment was made with the help of the 'model' polycondensation of **Ia** with **V** (run 15, Fig. 4).

3.3. Spectroscopic determination of the side reactions

Fig. 5 shows the ^{1}H n.m.r. spectrum of poly(**Ib** + **III**) (run 3). This spectrum is consistent with the regular structure described in Fig. 1. Only β addition units are observed and no signals corresponding to Si–H or allyl end groups are detected. However, some side reactions occurred as shown by a careful examination of the spectrum.

Isomerization of allyl benzene, leading to methylstyrene, is a well-known reaction, which occurs in the presence of transition metal catalysts. Here, the characteristic signals of the isomerization of the double bond of **III** can be seen at 1.8 ppm (H_c, d), 6.1 ppm (H_b, m) and 6.5 ppm (H_a, d) (see Fig. 5 for attributions). These values as well as the coupling

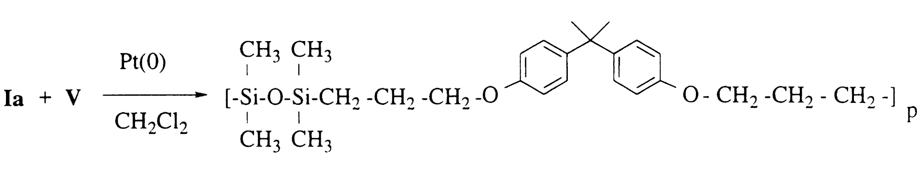

Fig. 4. Scheme of the model reaction **Ia** + **V**.

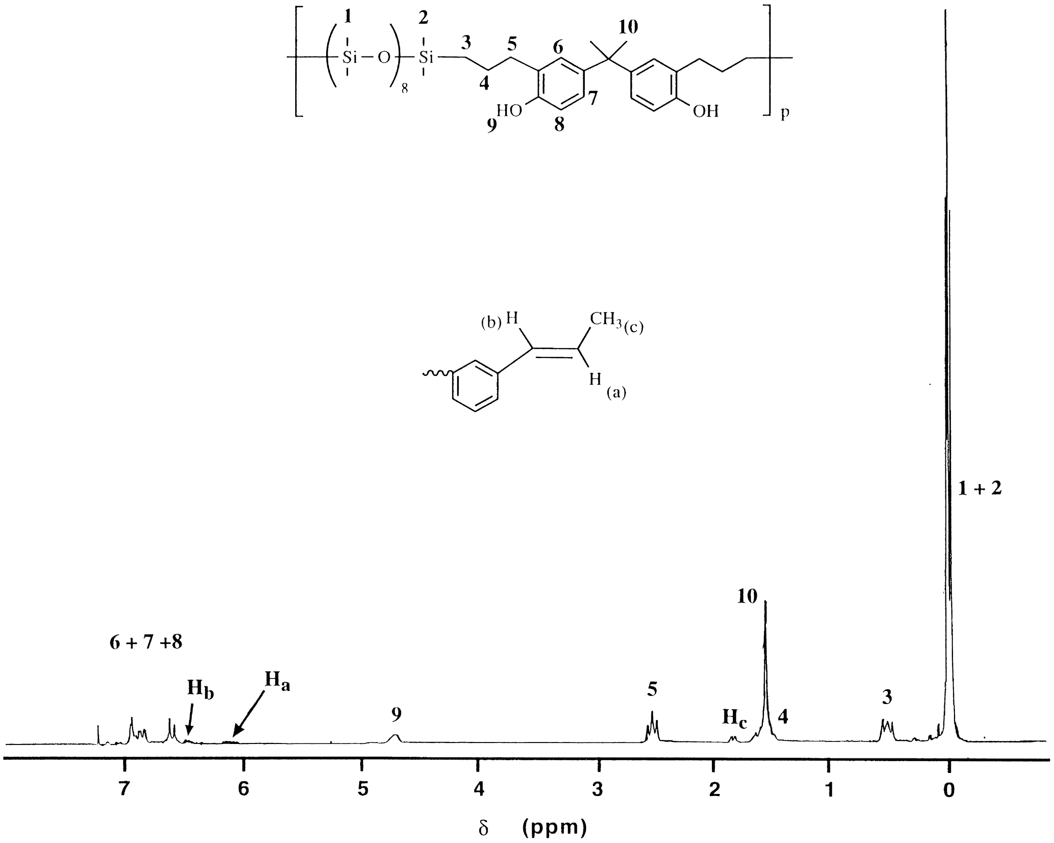

Fig. 5. ^{1}H n.m.r. spectrum of poly(**Ic** + **III**) (run 4) ($CDCl_3$).

constant $J(H_a - H_b) = 16.4$ Hz are consistent with the formation of the *trans* compound [15]. These signals were observed in all cases and also on the ^{1}H n.m.r. spectra of poly(**Ic** + **III**) and poly(**Id** + **III**) purified by selective precipitations. This indicates that the isomerization of the allyl double bond led to vinyl end groups which seemed to be relatively inert towards hydrosilylation, thus stopping the polycondensation process, although hydrosilylation of trans

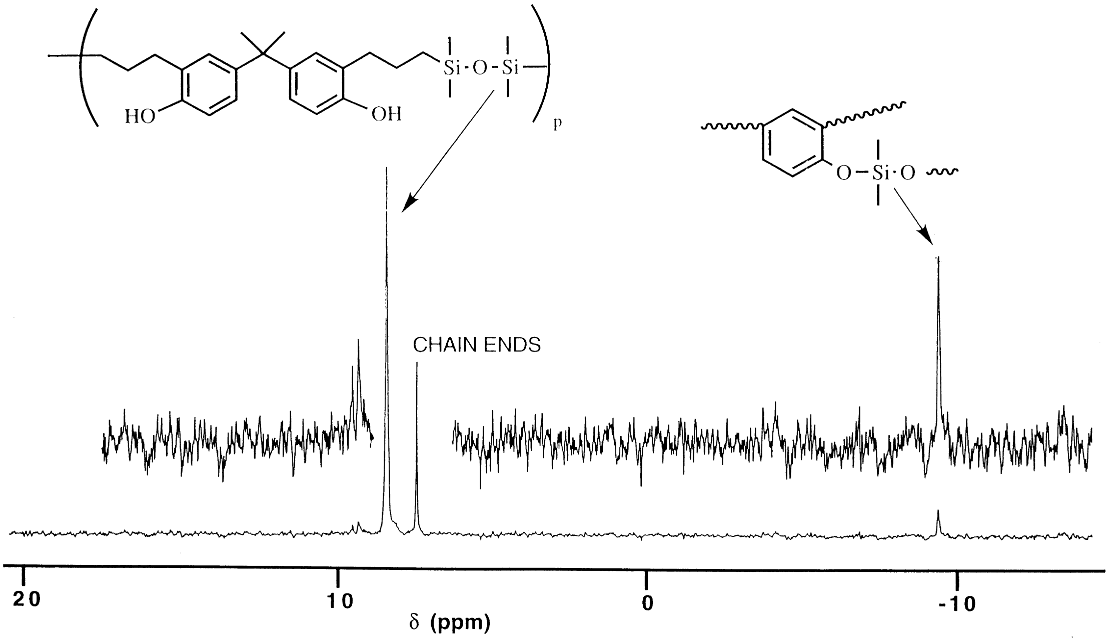

Fig. 6. ^{29}Si n.m.r. spectrum of poly(**Ia** + **III**) (run 2) ($CDCl_3$).

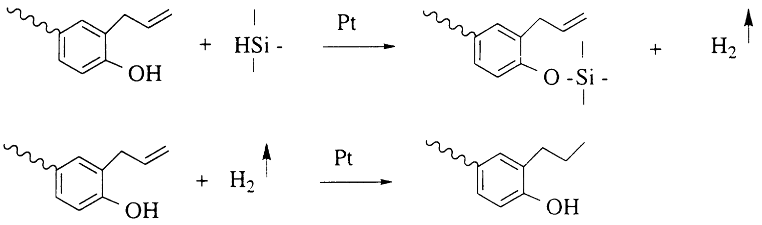

Fig. 7. O-silylation and hydrogenation of the allyl double bond as possible side reactions.

propenylbenzene has been already mentioned in the presence of H_2PtCl_6 catalyst [16].

It has been previously reported that metallic salts used for the hydrosilylation of unsaturated phenols behave also as catalysts for the silylation of the oxygen atom [17], although this reaction is less common than the O-silylation of aliphatic alcohols [18]. This type of side reaction was examined by ^{29}Si n.m.r. on the polymer obtained in run 2 (Fig. 6).

The two main signals at 8.4 and 7.4 ppm are attributed to the midchain and end chain silicon atoms respectively. The O-silylation side reaction gave a small signal at −9.6 ppm. This reaction was not very important, otherwise crosslinking should have been observed during the course of the reaction, which was not the case. Moreover, the O-silylation reaction is accompanied by hydrogen evolution, which should induce the hydrogenation of the allyl double bond, as already seen in the presence of platinum catalyst (Fig. 7) [19]. Here, no signals corresponding to such a hydrogenation, especially the CH_3 group at 0.9 ppm, were observed on the ^{1}H n.m.r. spectra. It is thus assumed that the hydrosilylation reaction of diallyl BPA as performed here was fast enough to avoid such side reactions.

3.4. Polycondensation with protected –OH functions

Another set of experiments was carried out by reacting **IV**, obtained by protecting the OH groups of **III** with BSA/Me_3SiCl, with the hydride terminated polysiloxanes (runs 7–11 in Table 2). Polycondensations with **IV** were much less exothermic than those with **III**. As expected, polymers bearing trimethylsilyloxy groups are soluble in aromatic and aliphatic hydrocarbons, such as *n*-hexane, and they are insoluble in methanol in contrast with the free OH-group containing poly(DMS-*alt*-BPA). They were analyzed by s.e.c. in toluene. Except for $n = 1$, their molecular weights are higher than those obtained when the polycondensations were carried out without protecting the OH groups. When the carbosilane precursor **IIa** was reacted with **IV**, a polymer with a quite high molecular weight was obtained (run 14). In all cases, the amount of low molecular weight compounds is lower in the case of the polycondensations performed with protected OH groups than for the polycondensations carried out with free-OH containing monomers, as seen on the s.e.c. chromatograms.

3.5. Deprotection of the OH groups

Although the use of an excess of ice-cold water was reported to regenerate the hydroxyl group in $Me_3Si–O–Ph–(CH_2)_3SiMeCl_2$ [20], more drastic conditions are generally reported in the literature [21–23]. However, a complete deprotection of poly(**IIa** + **IV**) was not reached by using *t*-BuBr/KF [22] or TBAF [23] as desilylating agents. Deprotection of the OH groups of poly(**IIa** + **IV**) was thus performed in an acidic medium (HCl/EtOH) (Fig. 8) and was complete after 8 h at 30°C, as checked by i.r. by looking at the disappearance of the band characteristic of the PhOSi groups at 920 cm^{-1}. No significant degradation of the chain occurred, as shown by the similar *p* values observed before and after the deprotection reaction ($p = 22$ and 21, respectively). This is in good agreement with the previous observation that polycarbosilanes are stable even when reacted with strong acids or bases [7,11].

The ^{1}H n.m.r. spectrum of the deprotected polymer is

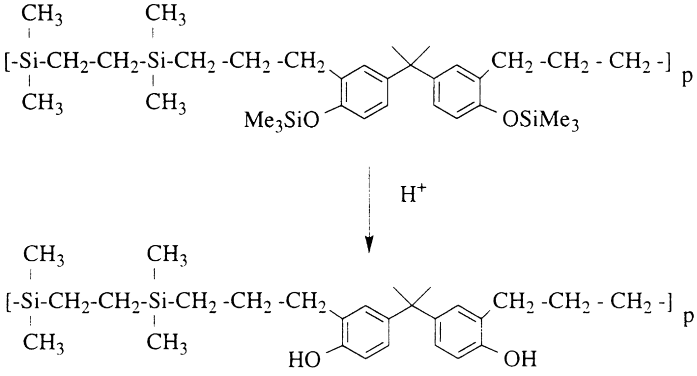

Fig. 8. Desilylation of poly(**IIa** + **IV**).

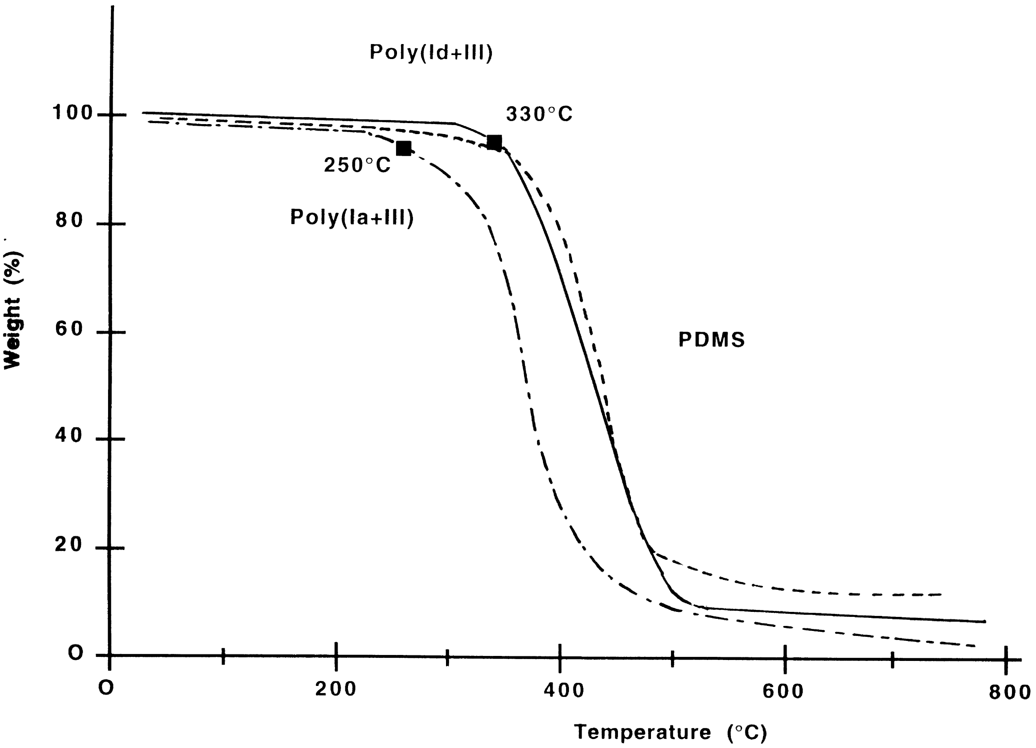

Fig. 9. T.g.a. thermograms of poly(**Ia** + **III**) (run 2, —.—); poly(**Id** + **III**) (run 5, full line) and pure PDMS (dotted line)

very similar to that of the polymer obtained by direct synthesis, i.e. by polycondensation of **IIa** with non protected diallyl BPA (**III**) (run 13). Deprotection of poly(**Ia** + **IV**) cannot be performed under these acidic conditions (HCl/EtOH), due to a severe degradation of the siloxane segments during the course of the reaction. Degradation of the chains was also observed when TBAF was used as the deprotecting agent. Basic conditions must also be avoided since the use of catalytic amounts of K_2CO_3 for the deprotection of polysiloxanes having phenoxy side groups led to the degradation of the siloxane main chain [7].

3.6. Physico-chemical characterization

The glass transition temperatures (T_g) of the polymers were determined by d.s.c. and are reported in Table 2. A decrease in T_g is observed on increasing the siloxane segment length as expected (runs 2–6 and 7–11). There is a strong influence of H bonding interactions of the OH groups upon T_g as shown by the high T_g values observed for poly(**Ia** + **III**) (run 2) and poly(**IIa** + **III**) (run 13) compared to the lower values for poly(**Ia** + **IV**) (run 7) and poly(**IIa** + **IV**) (run 14) in which the OH groups are protected by trimethylsilyl groups.

Table 3
Thermal stability of poly(DMS-*alt*-BPA)s

Run	Polymer	*n*	*R*	T_{max} (°C)[a]
2	**Ia** + **III**	1	H	355
3	**Ib** + **III**	2	H	400
4	**Ic** + **III**	8	H	405
5	**Id** + **III**	17	H	410
—	PDMS	∞	—	440
7	**Ia** + **IV**	1	$SiMe_3$	440
12	**IIa** + **III**	1	H	435

[a] Temperature of decomposition at the maximum of the derivative thermodynamic curve.

The thermal stability of the polymers containing phenol groups was examined by thermogravimetric analysis (t.g.a.) under nitrogen at a heating rate of 10°C/min and some thermograms are reported on Fig. 9. Temperatures at the maximum of decomposition (T_{max}) of some polymers as well as that of pure PDMS are reported in Table 3. It is clearly shown that an increase of the siloxane segment length leads to an increase of the polymer thermal stability, T_{max} values ranging from 355°C for poly(**Ia** + **III**) to 440°C for pure PDMS. An increase of the stability was also reached by protecting the OH functions with trimethylsilyl groups, or by replacing the siloxane chains by a carbosilane segment.

4. Conclusion

Polycondensation using hydrosilylation was successfully applied to the synthesis of well-defined polysiloxanes and carbosilanes with phenol units regularly distributed along the chains. The main side reaction, which limits the molecular weights of the resulting polymers, is the isomerization of the allyl double bond. By protecting the OH functions with trimethylsilyl groups, less exothermic polycondensations were observed and polymers having higher molecular weights were obtained. Deprotection of the OH functions without degradation of the chains was achieved only in the case of the carbosilane containing polymers. Poly(DMS-*alt*-BPA) having glass transition temperatures ranging from −115 to 32°C were obtained. Such an increase of T_g is due to the presence of BPA units and to the strong influence of hydrogen bonding interactions on the mobility of the chains. Poly(DMS-*alt*-BPA) showed a quite good thermal stability. This type of polycondensation using hydrosilylation has been applied to other diallyl precursors and the results will be published in a forthcoming paper.

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