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Synthesis of siloxanes containing acid-sensitive side groups

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New siloxanes with acid-sensitive substituents have been synthesized by means of hydrosilylation, starting from methylhydrosiloxanes. Details of the preparation and characterization are reported. *p*-t-Butoxycarbonyloxystyrene, *p*-t-butoxystyrene and t-butyl methacrylate turned out to be excellent reagents in these experiments. ^{1}H, ^{13}C and ^{29}Si nuclear magnetic resonance techniques were used for characterization. The ratio between α and β addition appears to be strongly dependent on the substituents at the vinyl group of the organic moieties.

(Keywords: poly(siloxanes); hydrosilylation; n.m.r. characterization)

INTRODUCTION

Rapid developments in the field of microlithography technology have resulted in the design of new resists that satisfy the future requirements of microelectronic devices[1]. Multi-level processes prompted many scientists to develop polymers based on siloxanes or silanes[2-5]. These polymers have the advantage of high reactive ion etching (r.i.e.) resistance in oxygen plasmas and consequently high-resolution possibilities[6,7]. In addition, research has been carried out on the synthesis of resists based on chemical amplification. The advantage of these systems is the high sensitivity for deep u.v. and e-beam radiation as a result of acid-catalysed reactions[8,9].

This paper describes the synthesis of silicon-based polymers with acid-sensitive substituents suitable for chemical amplification. Hydrosilylation was used to attach the substituents to methylhydrosiloxanes[10,11]. In this way the advantages of silicon holding polymers (high r.i.e. O_2 resistance) and chemical amplification (high sensitivity) are combined.

EXPERIMENTAL

Materials and procedures

All reactions were carried out in an atmosphere of dry nitrogen using standard Schlenck techniques. Toluene (Janssen) was dried and distilled from sodium. Polymethylhydrosiloxanes (PMHS) with 35 and 80 repeat units (Hüls-Petrarch) were dried at 50°C and 1 mmHg and stored under nitrogen. Pentamethylhydrodisiloxane (PMDS), tetramethyldihydrodisiloxane (TMDS), Karstedt catalyst (platinum tris(divinyltetramethyldisiloxane) in *o*-xylene) (Hüls-Petrarch), Al_2O_3 (Merck, 70–230 mesh ASTM, II/III), activated charcoal (Merck) and methanol (Janssen) were used as received. Diethyl ether was distilled and dried on sodium. *p*-t-Butoxycarbonyloxystyrene (*p*-TBCS)[12], *p*-t-butoxystyrene (*p*-TBS)[13], *p*-acetoxystyrene (*p*-AS)[12] and *p*-t-butoxy-α-methylstyrene (*p*-TBαMS)[13] were synthesized according to literature procedures and were stored under nitrogen at −20°C. t-Butyl methacrylate (TBMA) (Tokyo Kasei Kogyo) was distilled from CaH_2 (b.p. 37°C at 20 mmHg); t-butyl acrylate (TBA) (Janssen) was distilled from $CaCl_2$ (b.p. 55°C at 65 mmHg).

Measurements

^{1}H and ^{13}C n.m.r. spectra were recorded on a Varian VXR 300 spectrometer operating at 299.9 MHz and 75.43 MHz, respectively. $CDCl_3$ was used as internal standard. ^{29}Si n.m.r. spectra were recorded on the Varian spectrometer (59.59 MHz) with tetramethylsilane (TMS) (0.0 ppm) as external standard. Fourier-transform mode was applied using the ^{2}H resonance of the solvent as field-frequency lock. Chemical shifts (in ppm) are positive in the low-field direction. The heteronuclear 2D experiments (HETCOR) and the DEPT sequence were carried out using the standard sequences supplied by Varian. The molecular weights of the addition products were determined by g.p.c. on a Waters ALC/GPC 150-C apparatus equipped with Styragel columns using $CHCl_3$ as eluant, relative to polystyrene standards. Glass transition temperatures were recorded at a heating rate of 10°C min^{-1} using a Perkin-Elmer DSC7 unit. Thermogravimetric analysis was carried out at a heating rate of 10°C min^{-1} using a Perkin-Elmer 7 unit. Elemental

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analyses carried out at the Microanalytical Department of the University of Groningen gave satisfactory results. I.r. spectra were recorded on a Mattson 4020 Galaxy *FT*i.r. spectrometer.

SYNTHESIS

Reaction of PMDS

PMDS with p-*TBCS*. First, 0.50 g (2.27 mmol) of *p*-TBCS and 0.67 g (4.53 mmol) of PMDS were dissolved in 3 ml of toluene. After the addition of three drops of 0.2 wt% Karstedt catalyst in *o*-xylene, the solution was stirred for 48 h at room temperature. After removal of the solvent and excess of PMDS under reduced pressure, an orange-yellow liquid was obtained. The liquid was purified by flash chromatography (Al_2O_3; eluant, diethyl ether) to yield 0.79 g (2.15 mmol, 95%) of a colourless liquid. ^{1}H n.m.r., β-addition isomer: δ 0.08 (s, 6H, $Si(CH_3)_2$), 0.09 (s, 9H, $Si(CH_3)_3$), 0.88 (m, 2H, $SiCH_2$), 1.56 (s, 9H, $C(CH_3)_3$), 2.64 (m, 2H, $PhCH_2$), 7.05–7.13 (m, 4H, ArH); α-addition isomer: δ − 0.05 (s, 6H, $Si(CH_3)_2$), 0.02 (s, 9H, $Si(CH_3)_3$), 1.34 (d, 3H, CH_3), 1.56 (s, 9H, $C(CH_3)_3$), 2.15 (m, 1H, CH), 7.04–7.07 (m, 4H, ArH). ^{13}C n.m.r., β-addition isomer: δ 0.2 ($Si(CH_3)_2$), 1.9 ($Si(CH_3)_3$), 20.3 ($SiCH_2$), 27.6 ($C(\underline{C}H_3)_3$), 28.7 ($Ph\underline{C}H_2$), 83.2 ($\underline{C}(CH_3)_3$), 120.9–148.6 (6C, ArC), 152.0 (C = O; α-addition isomer: δ − 1.6 ($Si(CH_3)_2$), 1.8 ($Si(CH_3)_3$), 14.4 (CH_3), 27.6 ($C(\underline{C}H_3)_3$), 30.7 (CH), 83.2 ($\underline{C}(CH_3)_3$), 120.5–148.6 (6C, ArC), 152.0 (C = O). ^{29}Si n.m.r., β-addition isomer δ 7.63 ($Si(CH_3)_3$), 6.98 ($Si(CH_3)_2$); α-addition isomer: δ 8.04 ($Si(CH_3)_3$), 5.37 ($Si(CH_3)_2$).

PMDS with p-*TBS*. According to the same procedure as used for PMDS with *p*-TBCS, a clear colourless liquid was obtained; yield 99%. ^{1}H n.m.r., β-addition isomer: δ 0.06 (s, 6H, $Si(CH_3)_2$), 0.09 ($Si(CH_3)_3$), 0.89 (m, 2H, $SiCH_2$) , 1.35 (s, 9H, $C(CH_3)_3$), 2.65 (m, 2H, $PhCH_2$), 6.90–7.09 (m, 4H, ArH); α-addition isomer; δ − 0.02 (s, 6H, $Si(CH_3)_2$), 0.00 ($Si(CH_3)_3$), 1.35 (d, 3H, CH_3), 1.34 (s, 9H, $C(CH_3)_3$), 2.12 (m, 1H, CH), 6.88–6.96 (m, 4H, ArH). ^{13}C n.m.r., β-addition isomer: δ 0.3 ($Si(CH_3)_2$), 1.9 ($Si(CH_3)_3$), 20.2 ($SiCH_2$), 28.8 ($C(\underline{C}H_3)_3$), 28.6 ($PhCH_2$), 77.9 ($\underline{C}(CH_3)_3$), 124.0–152.9 (6C, ArC); α-addition isomer: δ − 1.7 ($Si(CH_3)_2$), 1.8 ($Si(CH_3)_3$), 14.4 (CH_3), 28.8 ($C(\underline{C}H_3)_3$), 30.4 (CH), 77.9 ($\underline{C}(CH_3)_3$), 123.8–152.9 (6C, ArC). ^{29}Si n.m.r., β-addition isomer: δ 7.49 ($Si(CH_3)_3$), 7.16 ($Si(CH_3)_2$); α-addition isomer: δ 7.73 ($Si(CH_3)_3$), 5.34 ($Si(CH_3)_2$).

PMDS with p-*AS*. According to the same procedure as used for PMDS with *p*-TBCS, a clear colourless liquid was obtained; yield 49%. ^{1}H n.m.r., β-addition isomer: δ 0.10 (s, 6H, $Si(CH_3)_2$), 0.11 (s, 9H, $Si(CH_3)_3$), 0.90 (m, 2H, $SiCH_2$), 2.30 (s, 3H, CH_3), 2.66 (m, 2H, $PhCH_2$), 7.00–7.22 (m, 4H, ArH); α-addition isomer: δ 0.01 (s, 6H, $Si(CH_3)_2$), 0.04 (s, 9H, $Si(CH_3)_3$), 1.36 (d, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.17(m, 1H, CH), 6.97–7.08 (m, 4H, ArH). ^{13}C n.m.r., β-addition isomer: δ 0.3 ($Si(CH_3)_2$), 2.0 ($Si(CH_3)_3$), 20.3 ($SiCH_2$), 21.1 ($CO\underline{C}H_3$), 28.8 ($PhCH_2$), 121.2–148.5 (6C, ArC), 169.7 (C = O); α-addition isomer: δ −1.6 ($Si(CH_3)_2$), 1.8 ($Si(CH_3)_3$), 14.4 (CH_3), 21.1 ($CO\underline{C}H_3$), 30.7 (CH), 120.8–147.6 (6C, ArC), 169.7 (C = O). ^{29}Si n.m.r., β-addition isomer: δ 7.66 ($Si(CH_3)_3$), 6.99 ($Si(CH_3)_2$); α-addition isomer: δ 8.08 ($Si(CH_3)_3$), 5.34 ($Si(CH_3)_2$).

PMDS with TBMA. Following the same procedure as for the reaction of PMDS with *p*-TBCS but with a reaction temperature of 40°C and a reaction period of 72 h, a clear colourless liquid was obtained; yield 96%. ^{1}H n.m.r., β-addition isomer: δ 0.08 (s, 6H, $Si(CH_3)_2$), 0.09 (s, 9H, $Si(CH_3)_3$), 0.82 (m, 2H, $SiCH_2$), 1.15 (d, 3H, CH_3), 2.44 (m, 1H, CH), 1.44 (s, 9H, $C(CH_3)_3$). ^{13}C n.m.r., β-addition isomer: δ 1.3 ($Si(CH_3)_2$), 1.9 ($Si(CH_3)_3$), 20.0 (CH_3), 22.8 ($SiCH_2$), 35.9 (CH), 28.0 ($C(\underline{C}H_3)_3$), 79.5 ($\underline{C}(CH_3)_3$), 177.2 (C = O). ^{29}Si n.m.r., β-addition isomer: δ 7.68 ($Si(CH_3)_3$), 6.69 ($Si(CH_3)_2$).

PMDS with p-*TBαMS*. Following the same procedure as for the reaction of PMDS with TBMA, a white turbid oil was obtained. Apart from starting material, the reaction mixture contained about 5% of the addition product (^{1}H and ^{13}C n.m.r evidence). ^{29}Si n.m.r. gave two peaks (δ 7.7 ($Si(CH_3)_3$) and δ 6.5 ($Si(CH_3)_2$)) for the β-addition product.

PMDS with TBA. Hydrosilylation at room temperature for 24 h resulted in insoluble gel-like products.

Reactions of TMDS

Reactions of TMDS with the unsaturated organic groups were all carried out in the same way. A fourfold excess of the organic compound was added to TMDS and dissolved in toluene. After addition of three drops of 0.2 wt% Karstedt catalyst in *o*-xylene, the solution was stirred at room temperature until i.r. spectra showed no Si–H absorption to be present. Removal of the solvent under reduced pressure and purification by flash chromatography (Al_2O_3; eluant, diethyl ether) gave clear viscous oils.

TMDS with p-*TBCS*. The addition product contained 5 wt% *p*-TBCS, which could not be removed by distillation or flash chromatography. The ^{1}H and ^{13}C data are like those obtained for PMDS with *p*-TBCS except for the $Si(CH_3)_2$ signals. ^{1}*H* n.m.r., β–β addition isomer: δ 0.08 (s, 12H, $2Si(CH_3)_2$); α–β addition isomer: δ 0.01 (s, 6H, $Si(CH_3)_{2\alpha}$), 0.02 (s, 6H, $Si(CH_3)_{2\beta}$); α–α addition isomer: δ − 0.06 (s, 12H, $2Si(CH_3)_2$). ^{29}Si n.m.r., β–β addition isomer: δ 7.26 ($Si(CH_3)_2$); α–β addition isomer: δ 7.75 $(Si(CH_3)_2)_\beta$, 5.71 $(Si(CH_3)_2)_\alpha$; α–α addition isomer: δ 6.31 ($Si(CH_3)_2$). (Here and elsewhere, subscripts α and β correspond to α and β addition, respectively.)

TMDS with p-*TBS*. The addition product could be purified by distillation (b.p. 240°C/0.08 mmHg); yield 60%. The ^{1}H and ^{13}C data are like those obtained for PMDS with *p*-TBS except for the $Si(CH_3)_2$ signals. ^{1}H n.m.r. β–β addition isomer: δ 0.12 (s, 12H, $2Si(CH_3)_2$); α–β addition isomer: δ 0.02 (s, 6H, $Si(CH_3)_{2\alpha}$), 0.05 (s, 6H, $Si(CH_3)_{2\beta}$); α–α addition isomer: δ − 0.06 (s, 12H, $2Si(CH_3)_2$). ^{29}Si n.m.r., β–β addition isomer: δ 7.45 ($Si(CH_3)_2$); α–β addition isomer: δ 7.75 $(Si(CH_3)_2)_\beta$, 5.71 $(Si(CH_3)_2)_\alpha$; α–α addition isomer: δ 6.18 ($Si(CH_3)_2$).

TMDS with p-*AS*, The ^{1}H and ^{13}C data correspond with those obtained for PMDS with *p*-AS but differ slightly for the $Si(CH_3)$ signals. Concerning the $Si(CH_3)$ protons, the addition product showed exactly the same chemical shifts as obtained for TMDS with *p*-TBCS in relation to the β–β, α–β, and α–α addition isomers.

TMDS with TBMA. The addition product, yield 62%, showed only β addition with exactly the same ^1H, ^{13}C and ^{29}Si n.m.r. values as found for the addition product of PMDS with TBMA.

TMDS with p-*TBαMS.* No addition product was obtained even after 4 days of stirring at 40°C.

Reactions of $PMHS_{35}$ and $PMHS_{80}$

$PMHS_{35}$ with p-*TBCS.* First, 3.6 g (16.8 mmol) of *p*-TBCS and 0.51 g (0.23 mmol) of $PMHS_{35}$ were dissolved in 10 ml of toluene. After addition of three drops of 0.2 wt% Karstedt catalyst in *o*-xylene, the solution was stirred for 24 h at 30°C. The light-yellow solution was precipitated in 150 ml of methanol followed by decantation of the methanol. The yellow solid polymer was dissolved in 10 ml of toluene and stirred for 3 h with activated charcoal. After filtration and precipitation the white solid polymer obtained was dried in high vacuum at room temperature; yield 0.95 g (53%). In the same way *p*-TBCS was added to $PMHS_{80}$ resulting in a white solid polymer; yield 55%.

Following the same procedures, hydrosilylation reactions were carried out with *p*-TBS and TBMA. In all cases viscous oils were obtained with yields varying from 30 to 50%.

PMHS with p-*TBCS.* ^1H n.m.r.: δ 0.04 (m, $SiCH_3$, $Si(CH_3)_3)_{\beta,\alpha}$, 0.83 (m, 2H, $SiCH_2)_\beta$, 1.54 (s, 9H, $C(CH_3)_3$), 2.60 (m, 2H, $PhCH_2)_\beta$, 7.02 (br, $ArH)_{\beta,\alpha}$, 1.30 (m, 3H, $CH_3)_\alpha$, 2.16 (m, 1H, $CH)_\alpha$. ^{13}C n.m.r.: $\delta - 0.4$ ($SiCH_3$), 20.3 $(SiCH_2)_\beta$, 28.4 $(PhCH_2)_\beta$, 27.7 $(C(\underline{C}H_3)_3)_{\beta,\alpha}$, 83.0 $(\underline{C}(CH_3)_3)_\beta$, 141.7–149.0 (6C, $ArC)_{\beta,\alpha}$, 151.9 $(C=O)_{\beta,\alpha}$, 14.5 $(CH_3)_\alpha$, 30.7 $(CH)_\alpha$, 82.9 $(\underline{C}(CH_3)_3)_\alpha$. ^{29}Si n.m.r.: δ 7.3 ($Si(CH_3)_3$), −22.8 (br, $SiCH_3)_\beta$, −26.8 (br, $SiCH_3)_\alpha$.

PMHS with p-*TBS.* ^1H n.m.r.: δ 0.02 (m, $SiCH_3$, $Si(CH_3)_3)_{\beta,\alpha}$, 0.88 (m, 2H, $SiCH_2)_\beta$, 1.30 (s, 9H, $C(CH_3)_3)_\beta$, 2.62 (m, 2H, $PhCH_2)_\beta$, 6.85–6.99 (br, $ArH)_{\beta.\alpha}$, 1.26 (s, 9H, $C(CH_3)_3)_\alpha$, 1.28 (m, 3H, $CH_3)_\alpha$, 2.10 (m, 1H, $CH)_\alpha$. ^{13}C n.m.r.: $\delta - 0.3$ $(SiCH_3)_{\beta,\alpha}$, 19.4 $(SiCH_2)_\beta$, 28.3 $(PhCH_2)_\beta$, 28.8 $(C(\underline{C}H_3)_3)_{\beta,\alpha}$, 77.8 $(\underline{C}(CH_3)_3)_\beta$, 139.2–153.1 (6C, $ArC)_{\beta,\alpha}$, 15.0 $(CH_3)_\alpha$, 29.8 $(CH)_\alpha$, 77.7 $(\underline{C}(CH_3)_3\ )_\alpha$. ^{29}Si n.m.r.: δ 7.2 ($Si(CH_3)_3$), −23.0 (br, $SiCH_3)_\beta$, −26.7 (br, $SiCH_3)_\alpha$.

PMHS with TBMA. ^1H n.m.r.: δ 0.12 (m, $SiCH_3$, $Si(CH_3)_3$), 0.82 (m, 2H, $SiCH_2$), 1.14 (m, 3H, CH_3), 1.44 (s, 9H, $C(CH_3)_3$), 2.43 (m, 1H, CH). ^{13}C n.m.r.: δ 0.07 ($SiCH_3$), 19.6 (CH_3), 21.8 ($SiCH_2$), 35.3 (CH), 28.0 ($C(\underline{C}H_3)$), 79.4 ($\underline{C}(CH_3)_3$), 176.4 ($C=O$). ^{29}Si n.m.r.: δ 7.9 (br, $Si(CH_3)_3$), −23.4 (br, $SiCH_3$).

RESULTS AND DISCUSSION

Relatively few studies have been published about hydrosilylation reactions of acid-sensitive groups with polymethylhydrosiloxanes. Examples are pendent epoxysiloxanes or pendent methacryloylsiloxanes[14]. *p*-TBCS, *p*-TBS, *p*-TBαMS, TBMA, TBA and *p*-AS were selected as acid-sensitive groups. The 'small-molecule model' system has been used as a substitute for polymer systems. The objective is to use small molecules for explorative studies and to apply the information thus obtained to the polymer systems. In our case reactions were carried out first on small disiloxanes, pentamethylhydrodisiloxane (PMDS) and tetramethyldihydrodisiloxane (TMDS) (*Figure 1*).

As will be shown later, some of the organic reagents appear not to be suitable for hydrosilylation with polymethylhydrosiloxanes (PMHS).

On account of results obtained earlier from hydrosilylation reactions, platinum tris (divinyltetramethyldisiloxane) was used as a catalyst[15]. All reactions were monitored by ^1H and ^{29}Si n.m.r. and i.r. and were terminated when no Si–H groups could be detected.

^{29}Si n.m.r. is an important technique for identification of α and β isomers. *Figures 2a* and *2b* show the ^{29}Si n.m.r. spectra of the addition products of *p*-TBCS and TBMA with PMDS. The four signals in *Figure 2a* point to four different silicon atoms arising from α- and β-addition products. On the contrary, *Figure 2b* shows only two signals, which suggests only the β-addition isomer to be formed during reaction of TBMA with PMDS.

Figure 3 shows a 2D (HETCOR) spectrum of the addition isomers from *p*-TBS with PMDS. This spectrum offers the possibility to relate the different carbon and hydrogen atoms to each other, thus clarifying the different isomers formed during the hydrosilylation reaction. As an example, the methyl group formed after the α addition is not visible in the ^1H n.m.r. but the correlation spectrum shows this group to be present behind the resonance signal of the t-butyl groups. In the same way the ethyl group at 2.65 ppm in the ^1H n.m.r. can be correlated to the resonance of the t-butyl groups at 28.7 ppm in the ^{13}C n.m.r. spectrum. Secondly, the four cross-points around 0 ppm clearly show the existence of α and β addition.

Reactions with PMDS

Hydrosilylation of PMDS with *p*-TBCS gives a mixture of α- and β-addition isomers in a ratio of about 1 : 3 (*Figure 1*). The same applies for the combination of PMDS with *p*-TBS and *p*-AS.

On the contrary TBMA shows only β addition (*Figure 1*). Possibly, steric hindrance exerted by the α-methyl group prevents α addition. This explanation is supported by the results of the reaction of *p*-TBαMS with PMDS, where after a reaction period of three days approximately 5% β addition occurred. Both the bulky phenyl and the α-methyl group are here responsible for the low reactivity of the double bond towards hydrosilylation. TBA showed a number of side reactions during hydrosilylation with PMDS. The explanation of these side reactions can be found in the electron-withdrawing effect of the COOR group directly attached to the double bond, resulting in an electron-deficient double bond and therefore a lower reactivity to hydrosilylation. Earlier studies show the importance of side reactions in the case of hardly reactive monomers[14]. In these cases carbonyl groups can undergo addition reactions with –SiH forming Si–O–C bonds, which can react further in the presence of a very small amount of water to insoluble products. The electron-donating α-methyl group in TBMA compensates this effect, leading to complete hydrosilylation without unwanted side reactions.

Reactions with TMDS

Hydrosilylation of TMDS with *p*-TBCS, *p*-TBS and *p*-AS gives addition products consisting of the three possible isomers (viz. β–β, α–β and α–α), with a strong preference for β addition, as was found also in reactions with PMDS (*Table 1*).

TBMA showed, as expected, only β–β addition. In the case of *p*-AS and TBMA, small impurities were detected, possibly as a result of side reactions from TMDS with the Pt catalyst. This is in line with the observations of Gustavson[16] who found that TMDS has a tendency to give polysiloxane-like products with loss of Si–H bonds in the presence of Pt catalysts and low-reactivity double bonds. It is noteworthy that under the same reaction conditions PMHS showed no reaction with the Karstedt catalyst. *p*-TBαMS gave after three days no appreciable amounts of addition product, which was compatible with the results obtained from reactions with PMDS.

It can be concluded from the results mainly obtained from the 'small-molecule model' approach that *p*-TBCS, *p*-TBS, TBMA and *p*-AS may be suitable for hydrosilylation reactions with polymethylhydrosiloxanes

Table 1 Distribution of α and β isomers in addition products of *p*-TBCS, *p*-TBS, *p*-AS and TBMA with TMDS

	Isomer content (%)		
	β–β	α–β	α–α
p-TBCS	57	35	8
p-AS	52	39	9
p-TBS	50	40	10
TBMA	100	0	0

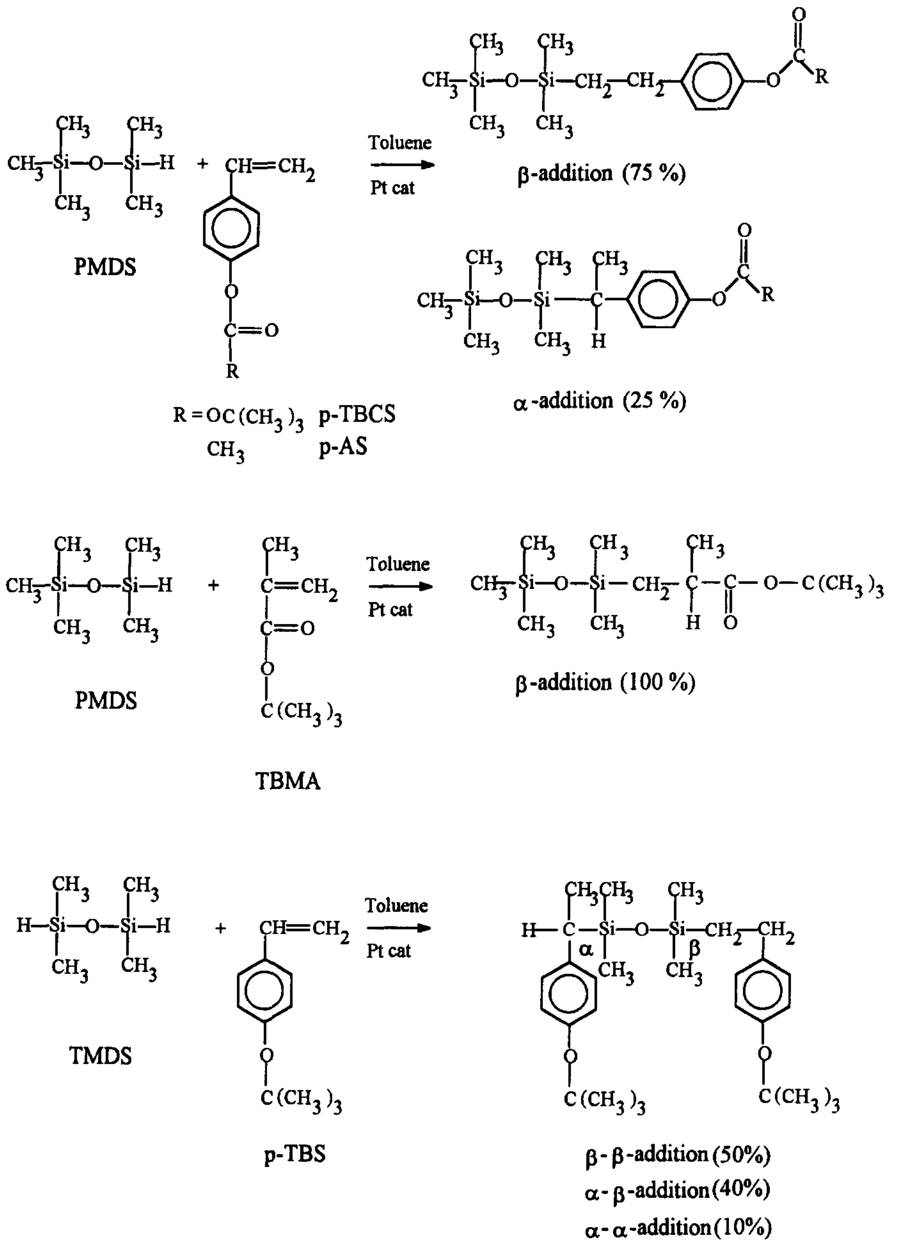

Figure 1 Addition products of *p*-TBCS and TBMA with PMDS

(PMHS). The side reactions found in the case of TBMA and *p*-AS are supposed not to occur in reactions with PMHS.

Reactions with PMHS$_{35}$ and PMHS$_{80}$

p-TBCS was added in a twofold excess to PMHS$_{35}$ and again α and β addition took place. The twofold excess of *p*-TBCS was necessary to accomplish complete substitution of every Si–H group. This is clearly shown by the ^{29}Si n.m.r. spectrum (*Figure 4*) in which two broad peaks are indicative of α and β addition at the polymer backbone. The peak at −35 ppm of the Si–H groups had completely disappeared.

The temperature at which the reaction is carried out is extremely important. When carried out above 40°C the reaction gives rise to the formation of insoluble products. This can be explained by a competitive addition of Si–H groups to the carbonyl group. Excess of vinyl compounds do not give rise to formation of side products because blank hydrosilylation experiments in the absence of PMHS showed no reaction or polymerization of the vinyl compounds.

The formation of side reactions during hydrosilylation of allylcarbonates with PMHS has been reported by Yu *et al.*[17]. They found at hydrosilylation temperatures of 60°C cleavage of the carbonate functionalities. The side products were characterized by ^{29}Si n.m.r. and peaks at −60 ppm showed the formation of MeSiO$_3$ units. In our case when hydrosilylation reactions were carried out at temperatures above 40°C completely insoluble products were obtained. N.m.r. characterization was impossible but *FT*i.r. spectroscopy showed a decrease of the amount of carbonyloxy moieties indicating side reactions at the carbonate bonds. However, below 40°C hydrosilation

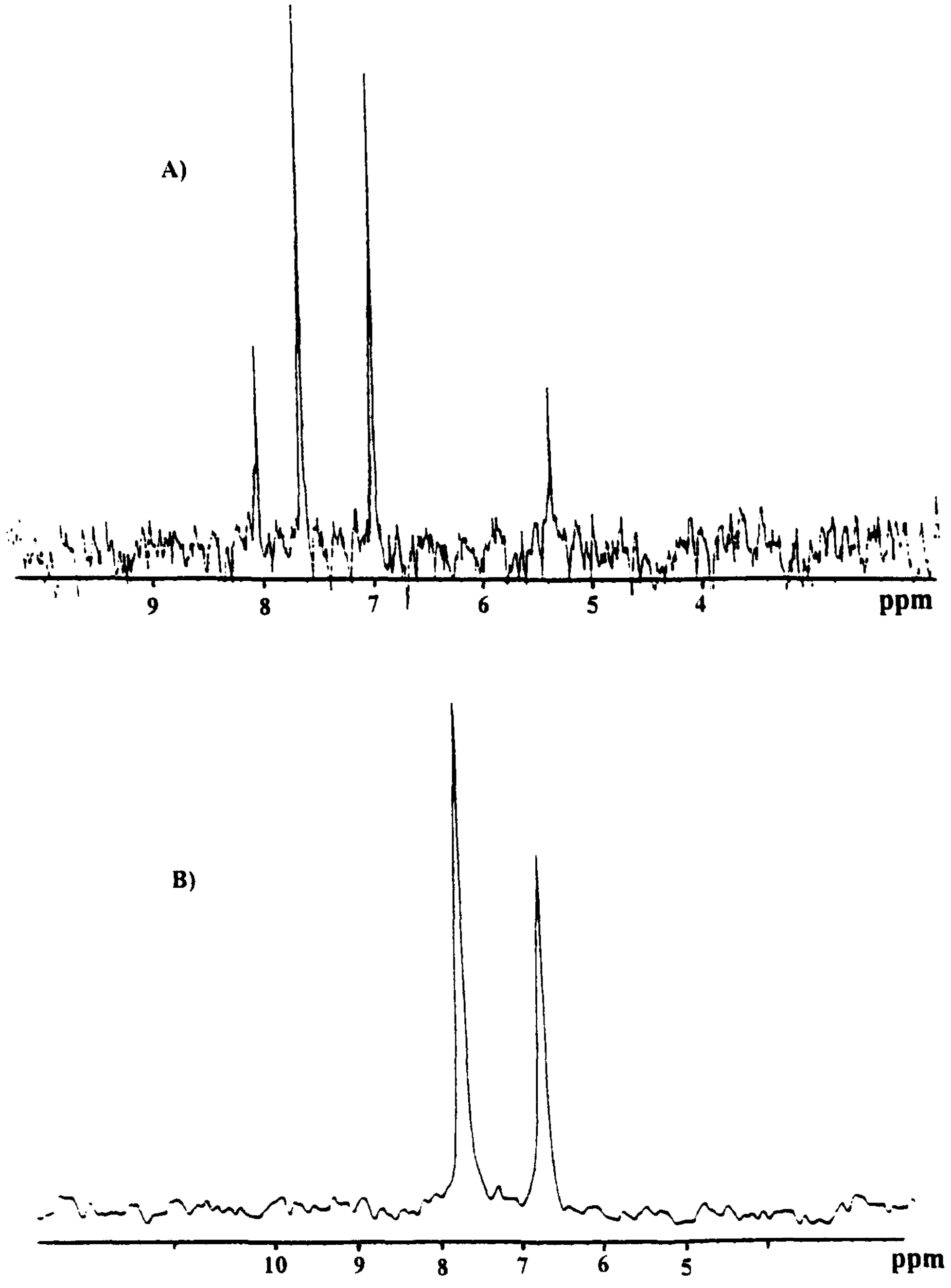

Figure 2 ^{29}Si n.m.r. spectra of some addition products: (A) *p*-TBCS with PMDS; (B) TBMA with PMDS

took place without any side reactions. This was confirmed by ^{29}Si n.m.r., which showed no extra peaks at −60 ppm while ^{1}H n.m.r. revealed a good agreement between the amount of $SiCH_3$ and the amount of substituents. In addition, g.p.c. experiments showed a good agreement between calculated and measured molecular weight of the addition product of *p*-TBCS with PMHS$_{35}$ ($\bar{M}_{n,calc}$ 12 700 g mol^{-1}, $\bar{M}_{n,found}$ 14 300 g mol^{-1}, $D = 2.0$). Hydrosilylation of *p*-TBS also occurred via α and β addition. In this case no side reactions were observed, even above 40°C. This can be explained by the absence of carbonate functionalities. Again, n.m.r. and g.p.c. measurements confirmed the desired amount of addition product ($\bar{M}_{n,calc}$ 11 600 g mol^{-1}, $\bar{M}_{n,found}$ 13 350 g mol^{-1}, $D = 1.8$). As expected TBMA with PMHS$_{35}$ gives a polymer with only β addition. Although Lin and Nakos[18] mentioned cleavage of ester functionalities during hydrosilylation of methacrylates with PMHS, in our case with reaction temperatures below 40°C no side reactions were observed ($\bar{M}_{n,calc}$ 10 400 g mol^{-1}, $\bar{M}_{n,found}$ 10 200 g mol^{-1}, $D = 1.7$). Above 40°C an appreciable amount of side products was formed as in the case of *p*-TBCS with PMHS.

The addition reactions proceed almost quantitatively. Extensive purification of the crude reaction products to remove residual platinum lowered the yield to about 30–50%.

Hydrosilylation of *p*-AS with PMHS$_{35}$, resulted in insoluble gels. Changes in temperature, total reaction

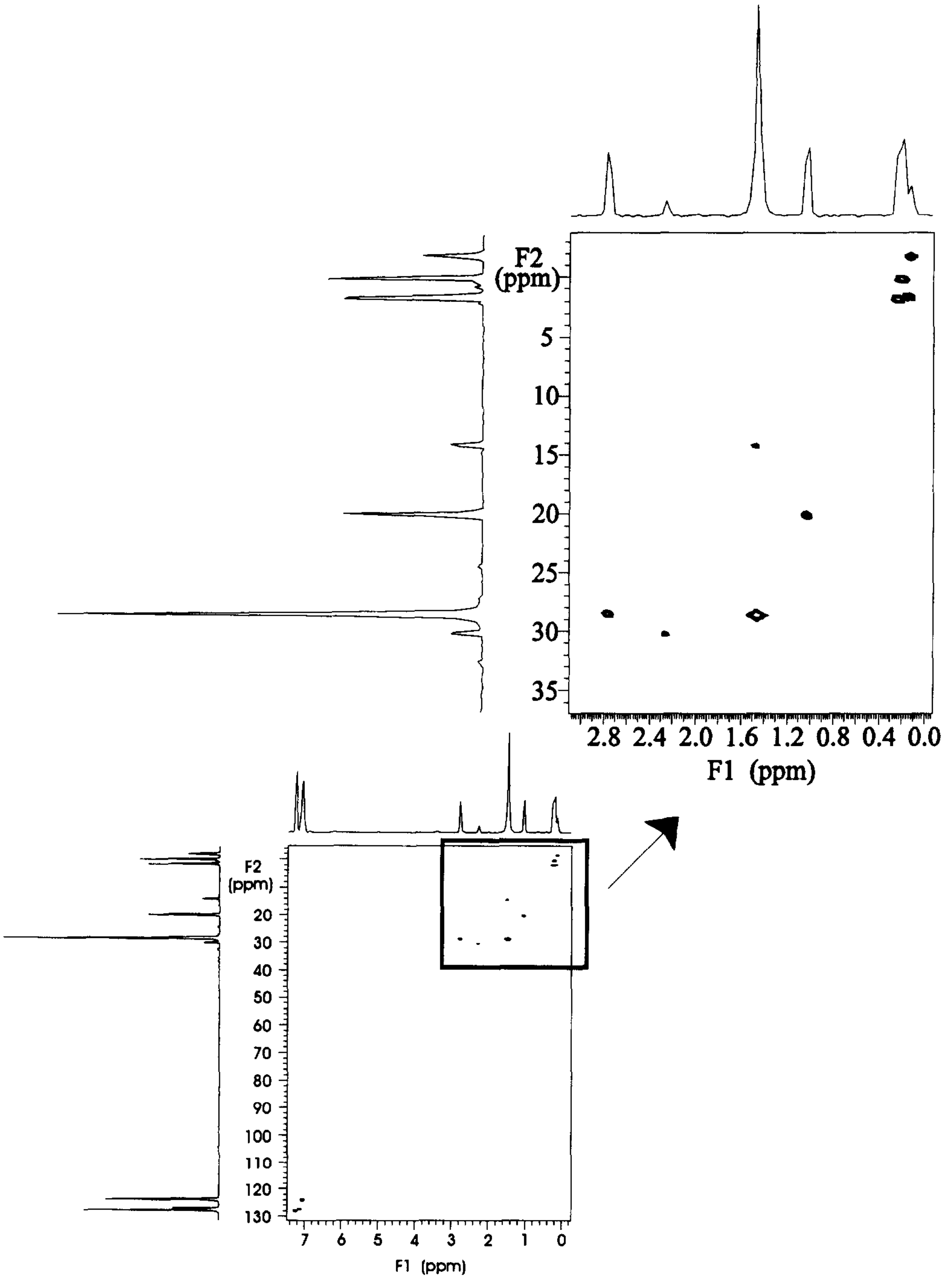

Figure 3 2D HETCOR (^{13}C, ^{1}H) spectrum of the reaction product of *p*-TBS with PMDS

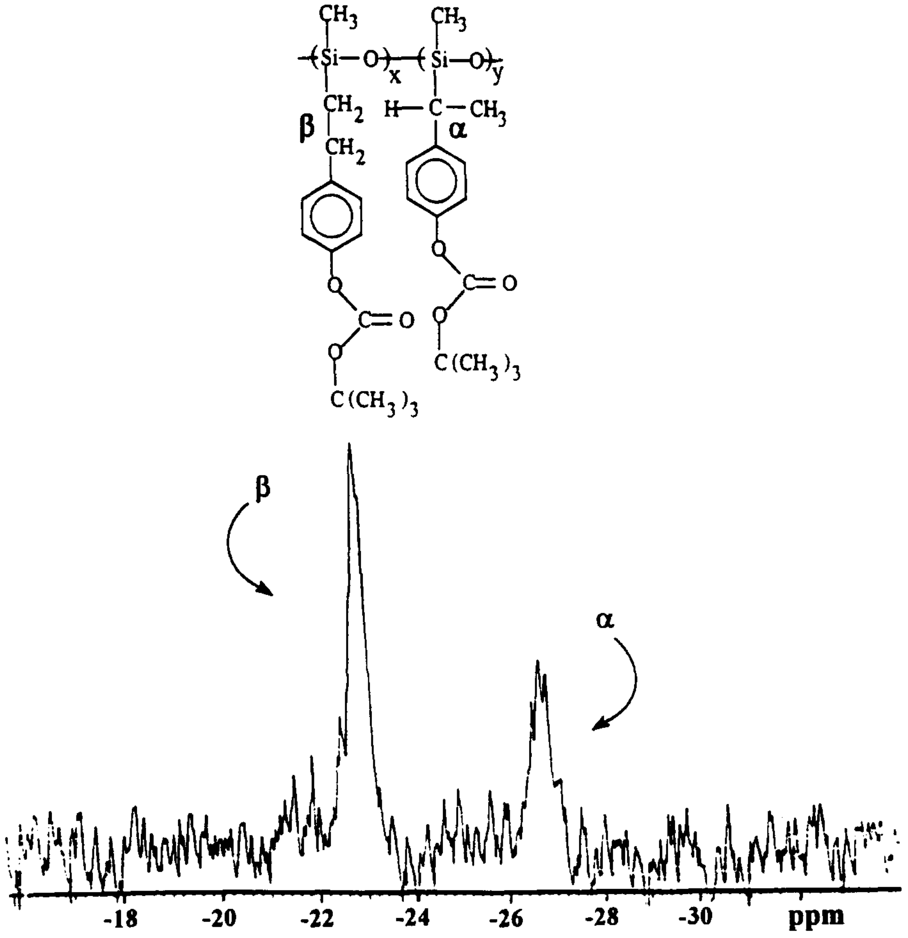

Figure 4 ^{29}Si n.m.r. spectrum of the reaction product of *p*-TBS with PMHS$_{35}$

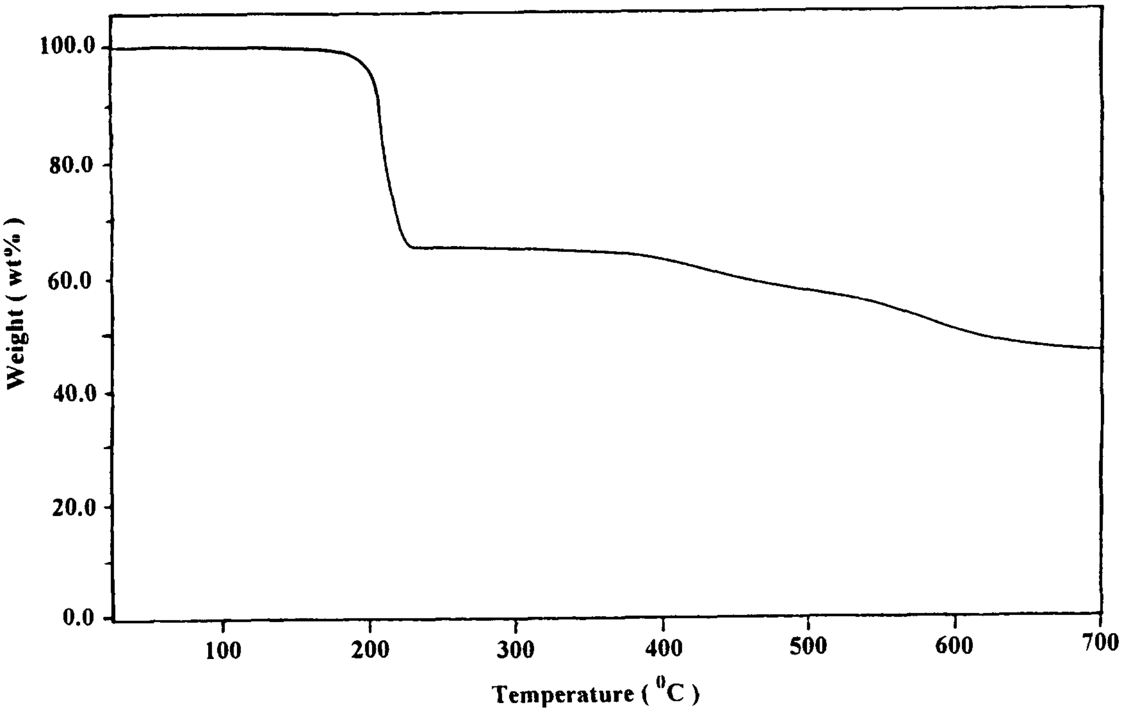

Figure 5 Thermogravimetric analysis of the addition product of *p*-TBCS with PMHS$_{80}$

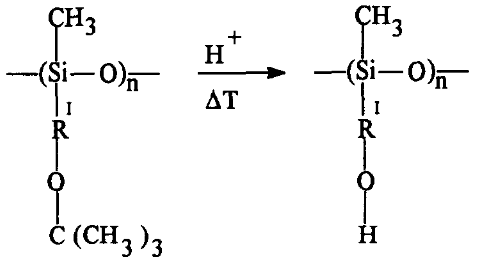

Figure 6 Reaction of polysiloxanes with acid-sensitive substituents during chemical amplification

Table 2 T_g values (°C) of addition products of *p*-TBCS, *p*-TBS and TBMA with $PMHS_{35}$ and $PMHS_{80}$

	$PMHS_{35}$	$PMHS_{80}$
p-TBCS	37	32
p-TBS	4	1
TBMA	−50	−51

time or solvent do not prevent cross-linking. Therefore *p*-AS is not suitable for hydrosilylation reactions with polymethylhydrosiloxanes. Comparing the results obtained from *p*-AS with PMDS, TMDS and PMHS one can conclude that side reactions (addition of SiH to the carbonyl group) become more manifest with increasing amount of SiH groups.

Addition of the compounds mentioned to $PMHS_{80}$ gave similar results.

D.s.c. and t.g.a. analysis

Table 2 reports T_g values for the *p*-TBCS, *p*-TBS and TBMA addition products with $PMHS_{35}$ and $PMHS_{80}$ obtained from d.s.c. measurements. The T_g of PMHS is −140°C[19] while the addition products show an enormous increase of the T_g caused by incorporation of bulky substituents, which decreases the flexibility of the main chain. For this reason the addition product of *p*-TBCS with $PMHS_{35}$ shows the highest T_g (37°C) and the product of $PMHS_{35}$ with TBMA the lowest T_g (−50°C). In addition, anisotropy introduced by carbonyl groups increases the T_g value. For that reason the addition product of *p*-TBS with $PMHS_{35}$ shows a lower T_g value ($T_g = 4°C$) compared to the T_g of *p*-TBCS with $PMHS_{35}$.

Comparable T_g values are obtained when incorporating these organic groups into longer polymethylhydrosiloxanes ($PMHS_{80}$).

The thermogravimetric analysis (t.g.a.) of the addition product of *p*-TBCS with $PMHS_{80}$ shows a sharp loss of 35% of the initial mass of the polymer near 190°C (*Figure 5*). This was also found by Fréchet *et al.*[12], indicating a loss of carbon dioxide and 2-methylpropene. Deprotection takes place in quantitative yield by thermolysis without destroying the siloxane backbone. After heating to 700°C, 46% of the initial mass remains as a black powder.

Possible applications

The coupling of acid-sensitive substituents like *p*-TBCS, *p*-TBS and TBMA to polysiloxanes gives the opportunity to use these polymers as negative and positive resists in microlithography based on chemical amplification (*Figure 6*). However, the addition products of *p*-TBS and TBMA have very low T_g values, which makes them less suitable for resist applications. It is noteworthy that the addition product of *p*-TBCS with PMHS possesses, in spite of a T_g of 37°C, good resist properties in deep u.v. as well in e-beam microlithography. In addition to a high sensitivity it possesses a sufficient r.i.e. resistance to O_2 plasma[20].

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