Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 44 (2003) 6449–6455

polymer

www.elsevier.com/locate/polymer

Telechelic polydimethylsiloxanes with terminal acetylenic groups prepared by phase-transfer catalysis

Sylvie Boileau[1], Laurent Bouteiller*, Anna Kowalewska[2]

Laboratoire de Recherche sur les Polymères, CNRS, U.M.R. C7581, 2-8, rue Henri Dunant, 94320 Thiais, France

Received 3 January 2003; received in revised form 29 July 2003; accepted 17 August 2003

Abstract

Telechelic, hydroxyalkyl terminated polydimethylsiloxanes were obtained under mild conditions via hydrosilylation of allyl alcohol or ethylene glycol monoallyl ether by oligomeric αω-hydride terminated polydimethylsiloxanes, with the use of a platinum catalyst. They were subsequently modified in a phase transfer catalyzed reaction by propargyl bromide, to give telechelic polysiloxanes terminated by acetylenic groups. The synthetic pathway is described and the characterization of the obtained products is presented.

Keywords: Polymer synthesis; Hydrosilylation; Phase-transfer catalyzed modification

1. Introduction

Acetylene terminated monomers have been studied as thermosetting resins, printing inks photocurable coatings, etc [1,2]. These precursors are often synthesized utilizing propargyl bromide and organic diols [3–6], as the preparation of the propargyl ether function, based on classical phase-transfer catalyzed (PTC) reactions is very easy [7,8]. However, no reports have been found on propargyloxy terminated telechelic siloxane oligomers, in spite of the fact that polydimethylsiloxanes (PDMS), due to their properties such as high thermal stability, low surface energy, low glass transition temperature (below −120 °C) and high gas permeability and biocompatibility are very interesting materials. Telechelic organofunctional polysiloxanes are typically prepared by equilibration of octamethylcyclotetrasiloxane (D_4) and disiloxanes bearing the functional groups, in the presence of acid or base [9]. Another preparation of functional oligosiloxanes is the hydrosilylation of alkenyl compounds in the presence of a platinum catalyst [10]. Because the hydroxy functions are prone to side reactions [11], they are often protected as trimethylsilyl ethers. Deprotection is performed either by hydrolysis in the presence of an acid [12] (but side reactions can occur as a consequence of the cleavage of siloxane bonds) or by methanolysis, under milder conditions [10]. In this article, we propose a two step synthetic pathway to well-defined acetylene terminated oligodimethylsiloxanes [13]. In the first step, αω-hydroxyalkyl terminated PDMS is obtained by hydrosilylation of unprotected alkenols. In the second step, it is modified under PTC conditions in order to obtain telechelic acetylene terminated siloxane oligomers, that could be further chain extended via oxidative coupling [14]. The reactivity of three polysiloxanes differing by the alkenyl spacer between the siloxane part and the hydroxyl group was studied. They were modified by propargyl bromide with sodium hydroxide, in the presence of tetrabutylammonium bromide as the catalyst. The results show that there is a large influence of the nature of hydroxyalkyl terminating groups.

---

* Corresponding author. Address: CNRS, Laboratoire de Chimie des Polymères, Université Paris 6, 4 place Jussieu, Paris, cedex 05, France. Tel.: +33-1-44-27-73-78; fax: +33-1-44-27-70-89.

E-mail addresses: bouteil@ccr.jussieu.fr (L. Bouteiller), boileau@glvt-cnrs.fr (S. Boileau).

[1] Fax: +33-1-49-78-11-91.

[2] Present address: Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland.

0032-3861/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2003.08.023

2. Experimental

2.1. Materials

The following chemical reagents were used (without purification):

αω-Hydride-terminated polydimethylsiloxane ((**1**) $M_n = 500 - 600$—ABCR), αω-hydroxyhexyl-terminated polydimethylsiloxane ($M_n = 2300$—Goldschmidt), allyl alcohol (Eastman Organic Chemicals), ethylene glycol monoallyl ether (98%—Tokyo Kasei Organic Chemicals), platinum divinyltetramethyldisiloxane complex in xylene (PTDD—2.25 wt% of Pt—ABCR), propargyl bromide (PB, 80 wt% solution in toluene—Aldrich), dipropargyl ether (Aldrich), sodium hydroxide (pellets, analytical grade—SDS), tetrabutylammonium bromide (TBAB, 99%—Aldrich), dichloromethane (98%—Prolabo), diethyl ether (analytical grade—SDS), isopropanol (iPA—pure—Analytical Carlo Erba), toluene (pure—SDS), magnesium sulfate (pure—Prolabo).

2.2. Characterization of polymers

^{1}NMR, ^{13}C NMR and ^{29}Si NMR spectra were recorded in $CDCl_3$ with an AC 200 Bruker spectrometer. The following symbols stand for: doublet—d., multiplet—m., singlet—s., triplet—t.

SEC measurements were recorded in toluene with a refractive index detection, using a polystyrene calibration curve. The columns used were two 5 μm PLGel Mixed-D. All polymer samples were kept in toluene for 24 h at room temperature before SEC measurements were performed.

IR spectra were recorded with a Perkin-Elmer 1760 FTIR spectrometer.

2.3. Synthesis of αω-(hydroxy propyl) polydimethylsiloxane (2)

A αω-hydride-terminated polydimethylsiloxane (**1**) (58.3 g, 0.183 mol of Si–H) was placed under nitrogen in a two necked flask equipped with a condenser and diluted with isopropanol (44 ml) and allyl alcohol (18 ml, 0.265 mol). Platinum divinyltetramethyldisiloxane complex in xylene (440 μl, $[Pt^0]/[Si{-}H] = 2.4 \times 10^{-4}$) was diluted in isopropanol (7 ml) and added dropwise to the magnetically stirred mixture. After 15 min at room temperature, IR analysis revealed that only a very small amount (less than 10%) of SiH bonds remained. The reaction mixture was then stirred for an additional 17 min at 65 °C in order to reach full conversion. Solvent and excess allyl alcohol were evaporated from the reaction mixture which was not further purified. 67.2 g of a brown oligomer were obtained (97% yield).

^{1}H NMR: 0.0 ppm s. $Si(C\mathit{H}_3)_2$, 0.5 ppm m. $Si{-}C\mathit{H}_2$, 1.3 ppm m. $CH_2{-}C\mathit{H}_2{-}CH_2$ and $O\mathit{H}$, 3.5 ppm t. $O{-}C\mathit{H}_2$

^{13}C NMR: 0.00 and 0.94 ppm $SiMe_2$, 13.84 ppm $Si{-}\mathit{C}H_2$, 26.45 ppm $CH_2{-}\mathit{C}H_2{-}CH_2$, 65.40 ppm $O{-}\mathit{C}H_2$

^{29}Si NMR: 7.9 ppm $O\mathit{Si}Me_2(CH_2)_3OH$, − 21.4 ppm $O\mathit{Si}Me_2OSiMe_2\text{-}(CH_2)_3OH$, − 22.0 ppm and − 22.1 ppm $O\mathit{Si}Me_2O$.

2.4. Synthesis of αω-(2-hydroxy-ethyl)oxypropyl polydimethylsiloxane (3)

A αω-hydride-terminated polydimethylsiloxane (**1**) (51.4 g, 0.161 mol of Si–H) was placed under nitrogen in a two necked flask equipped with a condenser and diluted with toluene (40 ml) and ethylene glycol monoallyl ether (22.5 g, 0.22 mol). To the magnetically stirred mixture, platinum divinyltetramethyldisiloxane complex in xylene (380 μl, ($[Pt^0]/[Si{-}H] = 2.4 \times 10^{-4}$) was added. After about 2 min of an induction time, a very exothermic reaction took place and the solution turned yellow. The stirring was continued for the next 1 h at room temperature. The IR and ^{1}H NMR spectra recorded after that time revealed the total disappearance of Si–H bonds. Toluene was evaporated from the reaction mixture and the residue was then diluted with Et_2O (150 ml) and washed with water (4 × 100 ml) before drying over $MgSO_4$. After filtration, the volatile parts of the solution were evaporated, and the residue was dried under vacuum for 18 h to give 66 g (97% yield) of purified product that is a pale brown liquid.

^{1}H NMR (Fig. 1): 0.0 ppm s. $SiMe_2$ (a), 0.5 ppm m. CH_2 (b), 1.5 ppm m. CH_2 (c), 2.0 ppm broad peak OH (g), 3.3 ppm t. CH_2 (d), 3.4 ppm m. CH_2 (e), 3.7 ppm m. CH_2 (f)

^{13}C NMR: − 0.93 ppm $SiMe_2$ (a′), 0.00 ppm $SiMe_2$ (a), 13.09 ppm CH_2 (b), 22.33 ppm CH_2 (c), 60.57 ppm CH_2 (d), 70.92 ppm CH_2 (e), 73.01 ppm CH_2 (f)

^{29}Si NMR: 7.8 ppm $O\mathit{Si}Me_2(CH_2)_3O(CH_2)_2OH$, − 21.3 ppm $O\mathit{Si}Me_2OSiMe_2\text{-}(CH_2)_3O(CH_2)_2OH$, − 21.9 ppm, − 22.0 ppm and − 22.1 ppm $O\mathit{Si}Me_2O$.

2.5. Synthesis of αω-[2-(propyn-1)oxyethyl]oxypropyl polydimethylsiloxane (6)

A αω-(2-hydroxyethyl)oxypropyl polydimethylsiloxane (**3**) (58 g, containing 0.129 mol of hydroxy groups), propargyl bromide (80% solution in toluene, 48.1 g, 0.4 mol) and solid NaOH (11 g, 0.28 mol) were placed under nitrogen in a two necked flask. Then TBAB (2.1 g, 6.5 mmol) was added to the magnetically stirred mixture. The ^{1}H NMR spectrum recorded after 24 h of stirring at room temperature proved that the reaction was complete. The oligomeric product was then diluted with toluene (100 ml) and washed with water (until neutral pH) and dried over $MgSO_4$. After filtration, the solvent was evaporated and the reaction product was dried under vacuum for 16 h. 54.7 g of the functionalized product (yellow liquid, $Mn_{SEC} = 900$, Ip = 1.3) were obtained (91% yield).

^{1}H NMR (Fig. 2): 0.0 ppm s. $SiMe_2$ (a), 0.45 ppm m. CH_2 (b), 1.55 ppm m CH_2 (c), 2.35 ppm t. ≡CH (d),

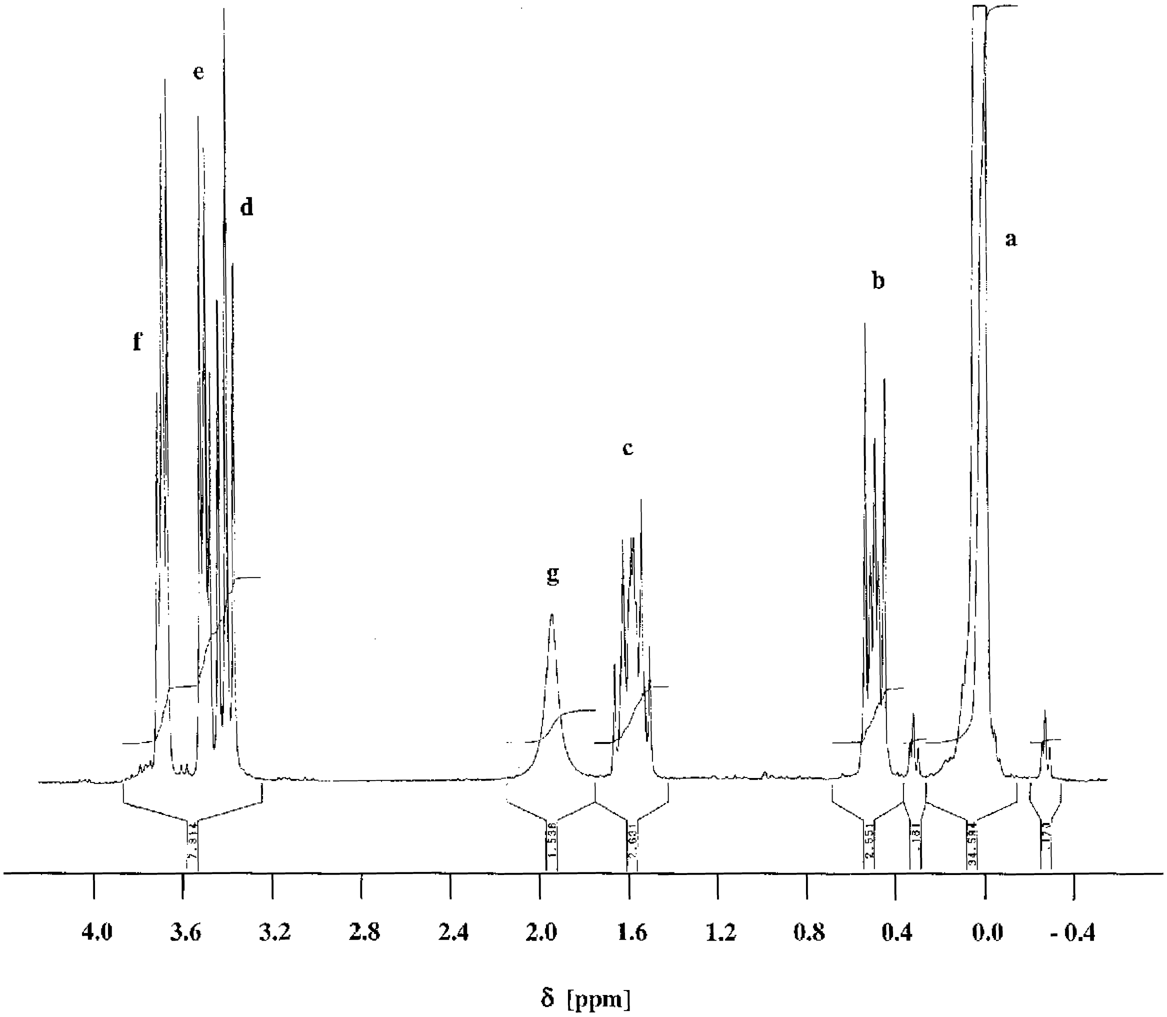

Fig. 1. ^{1}H NMR spectrum of (**3**).

3.35 ppm t. CH_2 (h), 3.5 ppm m.CH_2 (e), 3.6 ppm m. CH_2 (f), 4.15 ppm d. CH_2 (g)

^{13}C NMR: -0.59 ppm $SiMe_2$ (a′), 0.94 ppm $SiMe_2$ (a), 14.04 ppm CH_2 (b), 23.28 ppm CH_2 (c), 58.24 ppm CH (h), 68.98 ppm CH_2 (d), 69.75 ppm CH_2 (e), 74.08 ppm CH_2 (f), 79.56 ppm CH_2 (g).

3. Results and discussion

Telechelic polydimethylsiloxane oligomers of the general formula $HC{\equiv}C{-}CH_2OCH_2{-}X{-}(CH_2)_2{-}(SiMe_2O)_nSiMe_2{-}(CH_2)_2{-}X{-}CH_2OCH_2{-}C{\equiv}CH$ (X = –none–, $-(CH_2)_3-$, $-CH_2OCH_2-$) were synthesized according to the proposed reaction pathway (Fig. 3).

3.1. Hydrosilylation of alkenyl alcohols

αω-Hydroxypropyl (**2**) and (2-hydroxyethyl)-oxypropyl (**3**) terminated polydimethylsiloxanes were synthesized by hydrosilylation of allyl alcohol and monoallyl ether of ethylene glycol, respectively, by αω-hydride terminated polydimethylsiloxane (**1**) ($M_{SEC} = 700$, Ip = 1.1) with a complex of platinum and divinyltetramethyldisiloxane as the catalyst (Fig. 3). The hydroxy groups of alkenols were not protected during the hydrosilylation step, unlike previous procedures of the synthesis of hydroxyalkyl terminated oligosiloxanes [10].

3.1.1. Hydrosilylation of $HOCH_2CH{=}CH_2$ (**2**)

In the process of optimizing the reaction conditions, it was found (Table 1, line 1), that a low concentration of the platinum catalyst ($[Pt^0]/[Si{-}H] < 10^{-4}$) leads to a large amount of condensation products between SiH groups and the hydroxy groups of allyl alcohol and isopropanol (which was used as the solvent). The molecular weight of the oligomeric product was estimated by the end groups analysis by ^{1}H NMR (M_{NMR}). The measured value (Table 1, line 1) was found to be larger than the expected one, which can be due to simultaneous hydrosilylation to the double bond and condensation with hydroxyl group of the same molecule of allyl alcohol. Increasing the amount of

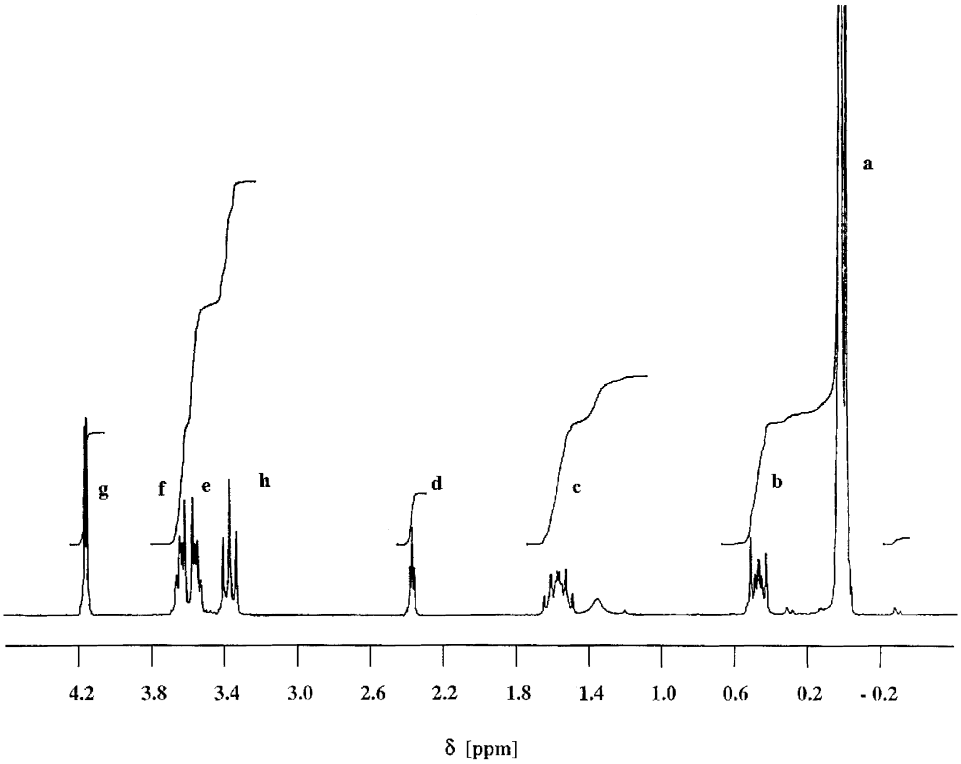

Fig. 2. ^{1}H NMR spectrum of (**6**).

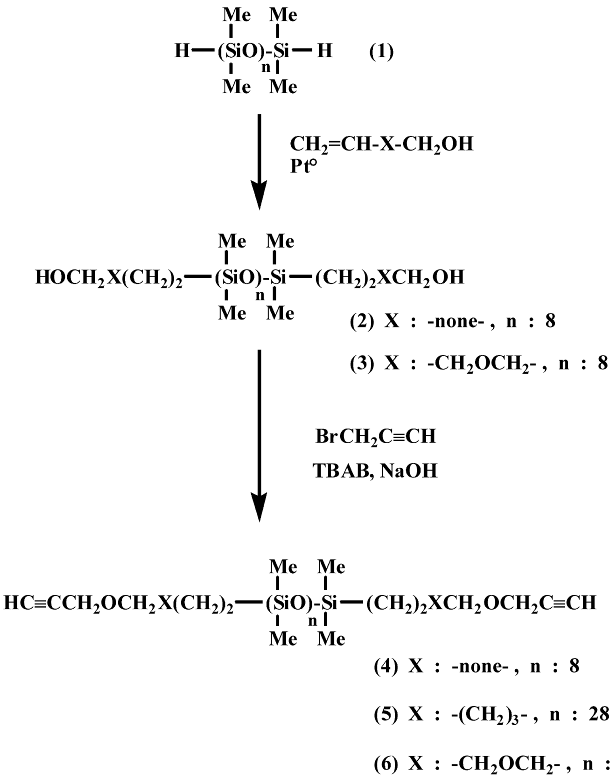

Fig. 3. Synthesis of telechelic acetylene terminated polydimethylsiloxanes.

platinum catalyst to $[Pt^0]/[Si{-}H] = 2.4 \times 10^{-4}$, we were able to eliminate completely side reactions with alcohols (Table 1, line 2). Only the product of β-addition to the double bond of allyl alcohol was detected. It has been observed by Zhang and Laine [15], that some O-silylation products are formed in the case of hydrosilylation of allyl alcohol by hydride terminated polydimethylsiloxanes. Our observations could be explained by the fact that we used a Pt catalyst concentration four times higher than that used by Zhang and Laine. It has indeed been shown by these authors that an increase of the catalyst concentration leads to a dramatic decrease of O-silylation products in the case of octakis(dimethylsiloxy)octasilsesquioxane.

3.1.2. *Hydrosilylation of $HO(CH_2)_2OCH_2CH{=}CH_2$ (3)*

In the case of the synthesis of αω-(2-hydroxyethyl)oxypropyl polydimethylsiloxane, similar conditions (solvent and catalyst concentrations) as for allyl alcohol were applied during the first experiments (Table 1, line 3). However, in spite of the fact that $[Pt^0]/[Si{-}H] = 2.4 \times 10^{-4}$, the reaction product analysis indicated the occurrence of some condensation with isopropanol. Much better results were obtained using toluene (Table 1, line 4) that is a standard solvent for hydrosilylation. No condensation with the hydroxy group of $HO(CH_2)_2OCH_2CH{=}CH_2$ was detected. The addition of the SiH group to the double bond occurred according to Farmer's rule, giving only the products of β-addition.

Table 1
The results of the hydrosilylation of alkenyl alcohols of the general formula $HO{-}CH_2{-}X{-}CH{=}CH_2$ by αω-hydride terminated polydimethylsiloxane

Polymer	X	Solvent	$[\mathrm{Pt}^0]/[\mathrm{SiH}]$[a]	Time[b] (h)	Temp.(°C)	Addition[c] (%)	Condensation[d]		M_{NMR}[e]	M_{NMR}[f] expected
							AA (%)	iPA (%)		
2	None	iPA	6.5×10^{-5}	76	90	69	6	25	920	770
2	None	iPA	2.4×10^{-4}	17	65	100	0	0	770	770
3	CH_2OCH_2	iPA	2.4×10^{-4}	6	*RT*	99	0	1	780	860
3	CH_2OCH_2	Toluene	2.4×10^{-4}	1	*RT*	100	0	0	710	860

[a] The molar ratio of the concentration of platinum to SiH groups.
[b] Time between catalyst addition and recording of the IR spectrum.
[c] The percentage of addition to the double bond of an alkenol.
[d] The amount of condensation between Si–H and hydroxyl group of an alkenyl alcohol (AA) or isopropanol (iPA).
[e] The molecular weight of the hydrosilylation product estimated by the chain end analysis by ^1H NMR.
[f] M_{NMR} calculated on the basis of M_{NMR} of the starting αω-hydride terminated PDMS.

During the hydrosilylation, traces of a side reaction giving $HO(CH_2)_2OCH{=}CHCH_3$ (*cis* and *trans* isomers) were observed. This kind of isomerization of allyloxy compounds into isopropenyl ether derivatives was reported in the literature [16] as caused by the presence of Pt^0 as well as other transition group metals. Because these isopropenyl alcohols are inert towards hydrosilylation [17], and only traces are generated (compared to the large excess of $HO(CH_2)_2OCH_2CH{=}CH_2$ used), their influence on SiH conversion is negligible. They are removed easily during the purification process.

3.2. Phase transfer catalyzed modification of hydroxyalkyl polydimethylsiloxanes

Phase transfer catalysis was chosen as an easy and effective way to functionalize αω-hydroxyalkyl terminated polysiloxanes (Fig. 3). Propargyl bromide was used because of its expected high reactivity under conditions of a PTC reaction. It was used as an 80% solution in toluene, and tetrabutylammonium bromide (TBAB) and solid NaOH were used as the PT catalyst/base system [18]. Reactions were carried out at room temperature and monitored by ^1H NMR. The results are shown in Table 2. It was found that the activity of TBAB in the reaction was limited to 3 days, presumably because of Hofman degradation [19]. Prolonged stirring did not improve the reaction result and some catalyst had to be added regularly. Moreover, due to their low reactivity, αω-hydroxyalkyl terminated polysiloxanes had to be treated for a long time with high concentrations of the catalyst and NaOH, compared to the reaction conditions used in the case of model molecules.

3.2.1. Reactivity of hydroxyalkyl groups

A significant difference in the behavior of hydroxyl group terminated oligomers, during PTC modifications, was observed. Reactivity of hydroxyalkyl moieties decreases in the following order of alkyl linkages between polysiloxane backbone and hydroxy group: $-(CH_2)_2O(CH_2)_3- > -(CH_2)_6- \sim -(CH_2)_3-$ (Table 2). The best results were obtained for the polysiloxane terminated with (2-hydroxyethyl)oxypropyl groups, presumably because of the presence of the oxyethylene unit in the alkyl chain that gives additional catalytic effect. Indeed, ethylene oxide moieties are well known for their catalytic properties in liquid–solid PTC reactions [20].

Table 2
Conditions of PTC modification of $HO{-}CH_2{-}X{-}(CH_2)_2{-}PDMS{-}(CH_2)_2{-}X{-}CH_2{-}OH$ by propargyl bromide

Oligomer	X	Time (h)	Temp. (°C)	[NaOH]/[OH][a]	[PB]/[OH][b]	[TBAB]/[OH][c]	Conv.[d] (%)	[DPE]/[OH][e]	M_{SEC}[f]	I_p[g]	M_{NMR}[h]	M_{NMR}[i] exp
4	None	170	*RT*	6.3	5.2	0.17	91	1.335	800	1.7	800	800
5	$(CH_2)_3$	480	*RT*	3.1	3.1	0.12	83	0.840	1900	2.5	2700	2400
6	CH_2OCH_2	24	*RT*	2.1	3.1	0.05	~100	0.308	900	1.3	1000	900

[a] Ratio of the concentration of base to the concentration of hydroxy chain ends of polydimethylsiloxane.
[b] Ratio of the concentration of propargyl bromide to the concentration of hydroxy chain ends of polydimethylsiloxane.
[c] Ratio of the concentration of the PTC catalyst to the concentration of hydroxy chain ends of polydimethylsiloxane.
[d] Conversion of the hydroxyl groups estimated by ^1H NMR.
[e] Ratio of the concentration of dipropargyl ether (DPE—the side reaction product) to hydroxy chain ends of polydimethylsiloxane.
[f] Number average molecular weight of the reaction product estimated by SEC in toluene.
[g] Polydispersity index.
[h] Molecular weight estimated by chain ends analysis in ^1H NMR.
[i] M_{NMR} calculated on the basis of M_{NMR} of the starting αω-hydroxy terminated PDMS.

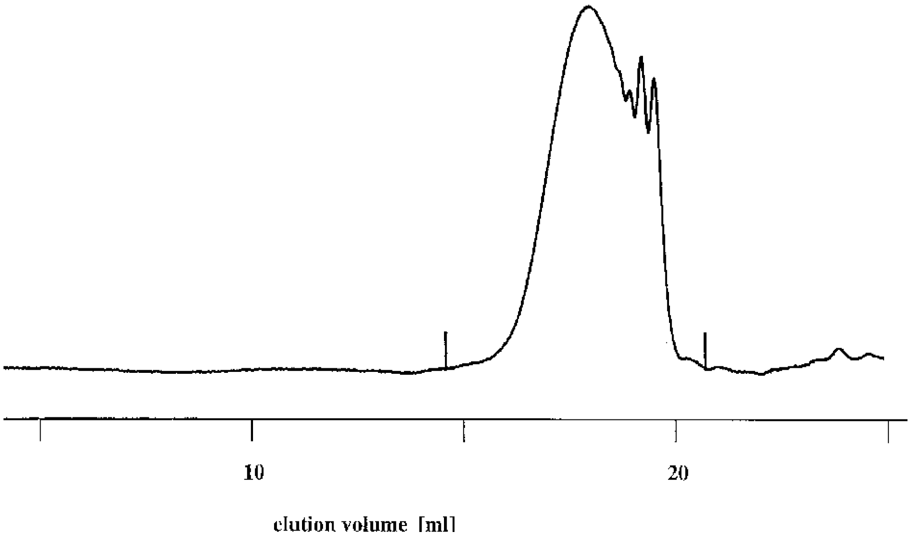

Fig. 4. Size exclusion chromatogram of oligomer (**4**).

3.2.2. Low molecular weight oligomer formation

SEC diagrams of the PTC modification products, apart from the main peak, show also low molecular weight peaks (Figs. 4 and 5). Their intensity differs for different alkyl spacers between hydroxy group and polysiloxane backbone. Especially the product obtained in the modification of αω-hydroxypropyl terminated PDMS contained a significant amount of short oligomers as side reaction products, and the polydispersity index Ip increased from 1.1 to 1.7. This probably results in side reactions leading to backbiting and scission of the polysiloxane backbone instead of expected reaction with propargyl bromide.

The reaction with αω-hydroxyhexyl polydimethylsiloxane is also relatively slow (80% of functionalization were obtained after 13 days at room temperature). SEC chromatogram revealed the presence of oligomers in a much lower amount than in the case of $HO(CH_2)_3$–PDMS–$(CH_2)_3OH$, but still significant. The sensitivity for alkaline conditions seems to be quite pronounced, because a repeated experiment with a larger amount of sodium hydroxide resulted in about twice higher oligomeric fractions.

In the case of (2-hydroxyethyl)oxypropyl terminated polydimethylsiloxane, the increase of reactivity due to the presence of a heteroatom in the terminating alkyl chain seems to reduce the side reaction tendency. The fraction of oligomeric product is negligible and the polydispersity index is close to 1.3. However, it was observed that the amount of oligomers increased slightly when the reaction time was longer than 24 h.

The difference in the amount of oligomeric fraction might be related to the difference in the structure of the hydrocarbon bridge. Indeed, this feature seems to be crucial for the reactivity and stability of hydroxyalkyl terminated polydimethylsiloxanes. It was published in the literature [21], that αω-hydroxyhexyl and αω-(2-hydroxypentyl) terminated polydimethylsiloxanes are stable upon heating,

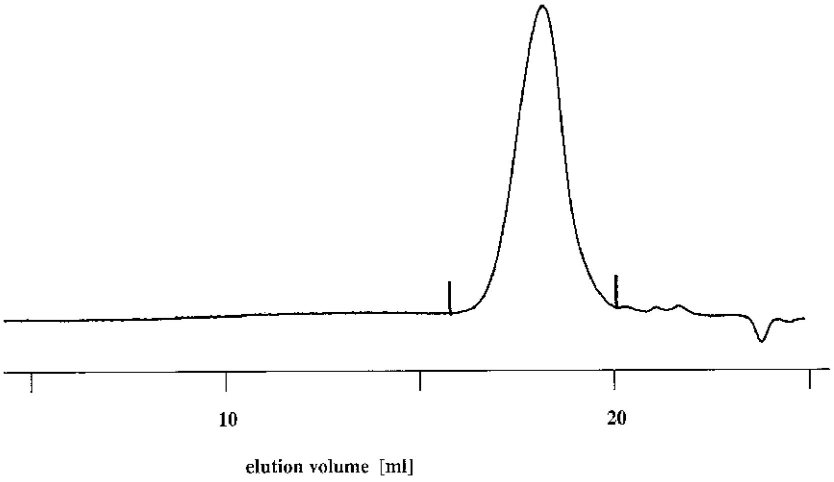

Fig. 5. Size exclusion chromatogram of oligomer (**6**).

on the contrary to the ones terminated by αω-hydroxybutyl and αω-hydroxypropyl groups which undergo degradation above 130 °C. It was implied that this thermal instability is due to the back biting of the terminal silicon in the αω-hydroxypropyl PDMS by the alkoxyde end-group, leading to the formation of stable 5 and 6 membered heterocyclic compounds. However, whether such a mechanism occurs in the present experiments remains to be proved.

3.2.3. Generation of dipropargyl ether

A close inspection of ^{1}H NMR spectra of the crude reaction mixture revealed that not only the substitution reaction of propargyl bromide with hydroxyalkyl groups and polysiloxane degradation take place, but also a side reaction that leads, presumably via propargyl alcohol, to dipropargyl ether occurs: $HC{\equiv}CCH_2OCH_2C{\equiv}CH$ (DPE) was identified by comparison with ^{1}H NMR spectrum of pure, genuine dipropargyl ether. The amount of the side product in the reaction mixture decreases on increasing the reactivity of hydroxyalkyl group (see the [DPE]/[OH] ratio in Table 2).

Although this side product was easily eliminated during the work-up and does not contaminate the oligomeric product, one should be aware that this side reaction consumes a large quantity of propargyl bromide, which should be taken into consideration when adjusting the reaction stoichiometry.

4. Conclusions

The synthesis of αω-hydroxyalkyl terminated polydimethylsiloxanes by the hydrosilylation of alkenyl alcohols with telechelic, hydride terminated PDMS has been worked out. It was found that the addition to the double bond gives the β-addition product only. The chosen reaction conditions allowed eliminating the condensation with hydroxyl functions. αω-Hydroxyalkyl terminated polysiloxanes can be functionalized under PTC conditions to give oligomers with acetylenic groups and with ether linkages at both ends of the oligomer chains. Sodium hydroxide and TBAB seem to be a good catalytic system. However, the presence of NaOH affects the siloxane chain to some extent, as indicated by SEC measurements. Depending on the nature of the spacer between the polysiloxane chain and the OH end-group, different amounts of short oligomers are formed.

Summarizing the different behavior of three polydimethylsiloxanes terminated by different hydroxyalkyl groups, it should be said that a longer alkyl chain makes the oligomer chain more resistant towards alkaline conditions.

Acknowledgements

Support from General Electric Company is gratefully acknowledged. We thank Dr M. D. Butts and Dr S. Rubinsztajn for valuable discussions and comments.

References

[1] Dirlikov SK. Chemtech 1993;10:32. and references therein.
[2] Dirlikov SK, Chen Z, Wang D. Polymer 1993;34:705.
[3] Makosza M. Tetrahedron Lett 1975;4669.
[4] Freeman HH, Dubois RA. Tetrahedron Lett 1975;3251.
[5] Lucote G, Delfort B. Polym Bull 1991;26:1.
[6] Nishikubo T, Hayashi Y, Iizawa T, Sasaki T, Matsumoto T, Fukudome T. J Appl Polym Sci 1992;44:107.
[7] Parker DG, Wheatley GW. Polym Int 1994;33:321.
[8] Mathias LJ, Tregre GJ. J Appl Polym Sci 1998;68:475.
[9] Yilgor I, McGrath JE. Adv Polym Sci 1988;86:1.
[10] Braun F, Willner L, Hess M, Kosfeld R. J Organomet Chem 1987;332:63.
[11] Kojima K, Gore CR, Marvel CS. J Polym Sci 1966;4:2325.
[12] Greber G, Jäger R. Makromol Chem 1962;57:150.
[13] Boileau S, Kowalewska A, Bouteiller L, Butts M, Rubinsztajn S. US patent 6,271,280; 2001.
[14] Boileau S, Bouteiller L, Kowalewska A. The coupled oligomers contain diacetylenic units which make UV curing possible. Polym Int. Accepted for publication.
[15] Zhang C, Laine RM. J Am Chem Soc 2000;122:6979.
[16] Boileau S, Cheradame H, Lestel L. Polymer 1990;31:1154. and references therein.
[17] Torrès G, Madec PJ, Maréchal E. Makromol Chem 1989;190:203.
[18] The use of a milder base, such as potassium carbonate yielded a poor conversion.
[19] Starks CM, Liotta CL, Halpern M. Phase transfer catalysis, 1st ed. New York: Chapman and Hall; 1994. Chapter 6, p. 288–92 and references therein.
[20] Starks CM, Liotta CL, Halpern M. Phase transfer catalysis, 1st ed. New York: Chapman and Hall; 1994. Chapter 4, p. 158–65 and references therein.
[21] Yilgor I, Yilgor E. Polym Bull 1998;40:525.