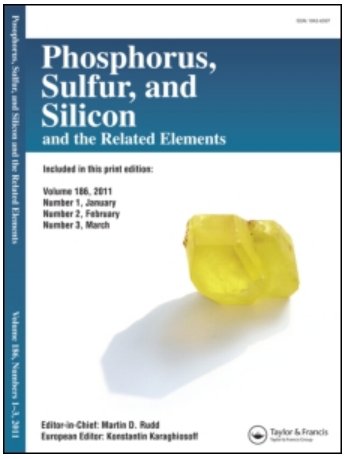

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Synthesis and Characterization of New Aromatic Silicone Diols

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Synthesis and Characterization of New Aromatic Silicone Diols

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Novel α,w-hydroxyoligosiloxane telechelics were synthesized by condensation of a functionalized monochlorosiloxanes with the well-defined α,w-disilanols followed by hydrosilylation reaction. The control of functionality, length, and purity of the resulting oligomers were ascertained by means of ^{1}H NMR, ^{29}Si RMN, IR, and GPC.

Keywords Oligosiloxane; synthesis; telechelics

INTRODUCTION

Telechelic polymers are compounds that carry reactive end groups. The main interest in these compounds is their use as building blocks for the production of segmented copolymers and polymer networks. By appropriate combination, telechelics lead to a large number of new materials with properties that could be varied over a wide range.[1,2] Scientists have been investigating methods to manipulate oligomer architectures to obtain new material properties for various applications. They have a number of parameters at their disposal to design and control the physical properties and behavior of macromolecules. In the domain of silicones, much chemistry is now available to make various linear siloxane and organo functional siloxane oligomers.

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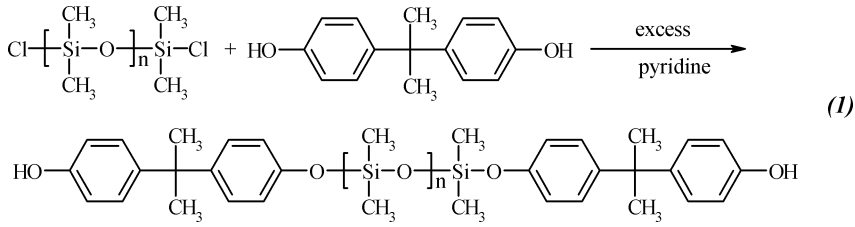


(I)

SCHEME 1

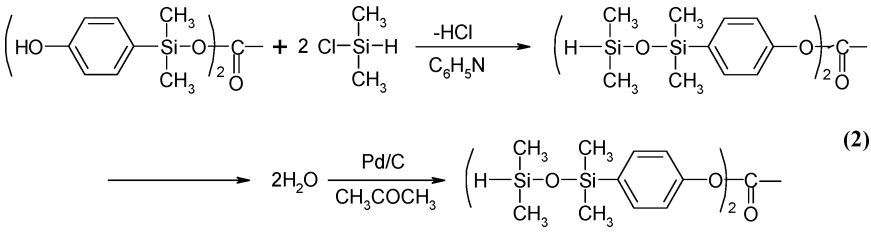
When incorporated into a polymeric system, the siloxanes bring a number of additional benefits to the polymeric system, including reduced water absorption, high gas permeability, good thermal and oxidative stabilities, low surface energies, adhesive properties and improved flame resistance.[3–8] However, they suffer from weak mechanical properties,and siloxane copolymers with organic side-groups seem to be attractive in several aspects and for numerous applications.[9,10]

Telechelic oligosiloxanes are obtained via ring opening polymerization of polycyclodialkylsiloxane, or via hydosilylation with α, w- bis hydrosilane oligosiloxane or via condensation between α, w- bis hydroxy oligosiloxane and an appropriate chlorosilane.[11]

The chemical modification of oligosiloxane end-groups has been the subject of many studies; Vaughn[12] has prepared α, w- diphenol (dimethylsiloxane) by reacting α, w- dichloro oligosiloxanes with an excess of bisphenol (Scheme 1).

Such a process needs careful control of humidity because the α,w-dichloro oligosiloxanes are very sensitive to water.[13] Fortunately, there has been some very valuable work on the reaction of chlorosiloxane end-groups with bisphenol A. Indeed, Williams et al.[14,15] have carefully controlled the structure of the oligomers and the corresponding copolymer blocks.

In some cases, the polycondensation followed the chemical modification. Thus, Rosenberg et al.[16] has modified oligo(arylene siloxanylene)s by reaction with chlorodi-methylsilane (Scheme 2).



(2)

SCHEME 2

Then by reacting the end-group with phosgene to obtain a polycarbonate with oligo (arylenesiloxane) blocks and controlled end-groups.

Different works have been published up to now about α,w-functional oligosiloxanes.[17–19] With a view to obtain new materials for new applications, the design of oligomers with new architectures to give specific properties is required. In this article, we describe the synthesis of poly dimethylsiloxanes telechelic with hydroxy aromatic end-groups by condensation of functional monochlorosilanes with α,w-disilanols and hydrosilylation reaction of the resulting products with 4-acetoxystyrene. The hydroxyl contents in the resulted diol after hydrolysis of the acetate groups were determined by titration. Its structure was characterized by IR and NMR spectra. It is well known that the introduction of aromatic groups in the main chain increases the glass transition temperature (Tg) of the aromatic diol. For this reason, we describe in this paper the synthesis of aromatic hydroxy oligosiloxanes. The obtained structure can be chemically modified or associated with other compounds to obtain new materials with better mechanical properties. Their characterization, properties, and potential applications are also discussed.

EXPERIMENTAL

Spectroscopy

^{1}H NMR Spectra were obtained using a Bruker WP 200 apparatus with TMS as reference and $CDCl_3$ as solvent. ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker WP 80 apparatus (80 MHz). The chemical shifts are reported in ppm. IR spectra were recorded on a Perkin Elmer 1310 Spectrophotometer. The band positions are given in cm^{-1} with an accuracy of $\pm$ 2 cm^{-1}.

Materials

All solvents were commercially available and were of analytical-grade, toluene, hexane and diethyl ether were dried over $CaCl_2$ prior to use. Chlorodimethylsilane, hexachloroplatinic acid, and 4-acetoxy-styrene are purchased from Chemical Co Aldrich. The α,w-hydroxyoligo(dimethylsiloxane) (48V50) was purchased from Rhone–Poulenc. They were all used without further purification.

Condensation of chlorodimethylsilane with α,w-disiloxanols:Compound (1)

In a 50 ml two-necked flask fitted, with a condenser; (5.84 g, 10 mmol) of α, w- disiloxanediol; (1.90 g, 20 mmol) of a chlorodimethylsilane,

10 ml of toluene and 0.3 ml of pyridine were introduced. The mixture was stirred and refluxed for 18 h. After cooling, the white precipitate formed was filtered out. The organic layer was washed with water dried with Na_2SO_4 and concentrated. A yellow viscous product was obtained.

Hydrosilylation of the 4-Acetoxy- styrene: Compound (2)

In a 100 ml three necked flask, fitted with a condenser and a dropping funnel; (3.24 g, 20 mmol) of the 4-acetoxy- styrene, 10 ml of hexane and 20 μl of a solution of H_2PtCl_6 in 2-propaonol[20] were introduced. A solution of (7.00 g, 10 mmol) of α,w-bis silane poly dimethylsilane in 10 ml of hexane was added drop wise. Then, the mixture was stirred for 18 h at 70°C. After cooling, hexane was removed, and the product was distilled under vacuum.

Hydrolysis of the Acetate Groups: Compound (3)

Synthesis of compound **(3)**: The diacetate compound **(2)** (0.90 g, 0.88mmol) was placed in a flask with 100 ml of methanol and some THF (milliliters) to obtain homogenous medium. Potassium cyanide (KCN; 1 wt% of the acetate function) was added under stirring, and the mixture was left at room temperature for 48 h. The solvent mixture (MeOH/THF) was evaporated, and the residue was washed with water and then extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and concentrated to give 84% of a viscous liquid.

Hydroxy Titration

To determine the OH group's number, an exact amount (0.50 g, 0.53 mmol) of sample **(3)** has been refluxed for 130 min in 10 ml of an acetylating mixture (pyridine/acetic anhydride) and subsequently, the excess of acetic anhydride was titrated using a 0.1 N of KOH solution.

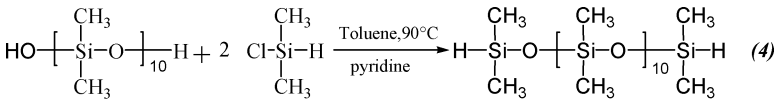
RESULTS AND DISCUSSION

The polymerization of silanes is usually performed according to Scheme 3.[21]

Many catalysts such as $C_6H_5CH_2N(CH_3)_3^+$ OH^-, or n-butyl lithium are often used for ring opening.[22] Various other catalysts have been used, e.g., salts of tin, alkali metals, or alkaline- earth complexes of

$$Cl{-}Si(CH_3)(R){-}Cl \xrightarrow{H_2O} \left[\overline{Si(CH_3)(R)O}\right]_n \xrightarrow{Cat} \left[Si(CH_3)(R)O\right]_n \quad (3)$$

SCHEME 3



(4)

1

SCHEME 4

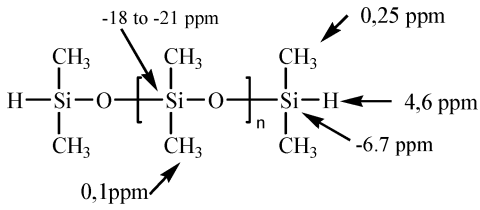
tertiary amines or cryptands.[23] However, introduction of long groups into the silane leads to important changes of the silane's reactivity and favors the formation of stables cycles over the linear polymers, also.

Synthesis and Characterization of α,w-Bis silane Polydimethylsiloxane

The α,w- silane polydimethylsiloxanes are synthesized by the reaction of α,w-bis silanol polydimethylsiloxanes (PDMS SiOH), with chlorodimethylsilane. This condensation reaction is carried out in toluene at 90°C in the presence of a catalytic amount of pyridine. This well-known reaction is very fast and proceeds quantitatively as indicated in Scheme 4.

The HO-[$Si(CH_3)_2O$-]$_n$H was a commercial product. However, its structure was precisely determined by ^{1}H NMR [–$Si(CH_3)_2O$) = 0.1 ppm]. The obtained product was also characterized in IR by the occurrence of a strong absorption band at 2127 cm^{-1} characteristic of the –SiH vibration ν(-SiH) for α,w- bis silane polydimethylsiloxanes. The IR spectrum also does not show any band at 3690 cm^{-1}(vibration of –$Si(CH_3)_2OH$), and the vibration band attributed to SiCl ν(Si-Cl) around 475 cm^{-1} could not be detected; but it exhibits –$Si(CH_3)_2O$- bands at 1260 cm^{-1} and 800 cm^{-1} and –$Si(CH_3)_2O$-$Si(CH_3)_2$- bands at 1220, 1090, and 1020 cm^{-1}. The α,w-bis silane polydimethylsiloxanes are also easily characterized by ^{1}H NMR. The signal of the silane proton is located at 4.6 ppm, and the methyl protons of the terminal silane group are observed at 0.25 ppm as a doublet, whereas the methyl protons of the siloxane chain are located at 0.1 ppm.

The ^{29}Si NMR spectrum exhibits different signals between $\delta = -18$ and -21 ppm characteristic of diverse structures: -O-$Si(CH_3)_2$-O-. We note also the disappearance of the peaks at $\delta = +30.3$ and $\delta = -11$ ppm, which, respectively, correspond to the silicon with a chlorine atom -Si-Cl and to the silicon of the –$OSi(CH_3)_2OH$ groups. Furthermore, our analyses using ^{1}H and ^{29}Si NMR and IR techniques indicate clearly the absence of any other side-product. Moreover, we noticed that the resulted



(5)

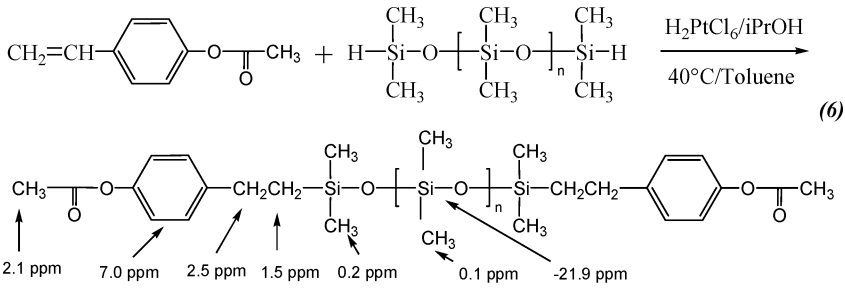
1

SCHEME 5

PDMS (700 g/mol) presents a glass transition temperature, which is similar to that mentioned earlier by other authors (Scheme 5).[24]

In the present work, we have focused our research on preparing a novel oligosiloxanes liquid with an aromatic hydroxy end-group. The intermediate oligodiacetate siloxane [compound (**2**)] was synthesized with a good yield *ca.* 80%, via hydrosilylation reaction of the functional acetate compound (4 -acetoxy- styrene) in hexane with α, w-bis silane polydimethylsiloxane. This reaction was carried out in the presence of a catalyst (H_2PtCl_6/iPrOH). After hydrosilylation, the resulted oligodiacetate siloxane was also characterized by IR and NMR spectroscopies. The IR analysis of the diacetate compound (**2**), showed that the hydrosilylation reaction proceeds quantitatively at 90 °C for 24 h, since the ν(-SiH) band around 2127 cm^{-1}has totally disappeared. We note also the appearance of the vibration band corresponding to the carbonyl of the acetate group at 1730 cm^{-1}. ^{29}Si NMR spectrum showed that the signal at –6.7 ppm typical of the silane function has completely disappeared. However, the spectrum exhibits a signal at $\delta = -21.9$ ppm, which we have attributed to the –OSi $(CH_3)_2$O- chain (Scheme 6).

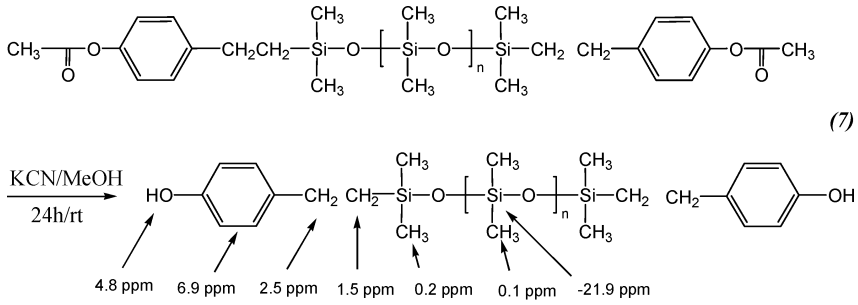
The examination of the ^{1}H NMR spectrum relative to compound (**2**), reveals that both signal at 4.6 ppm corresponding to -Si-H proton



(6)

2

SCHEME 6



3

SCHEME 7

and signal corresponding to the olefinic chemical precursor (CH_2 =CH-) around $\delta = 5.5$–6.75 ppm have disappeared. Furthermore, the methylene signals resulting from the hydrosilylation reaction appeared at $\delta =$ 1.5 ppm (–$SiCH_2$-). The singlet of the methyl of the acetate group (CH_3-COO) and the aromatic protons appeared respectively at $\delta = 2.1$ ppm and around 7 ppm.

The heights of integration fit very well with the ones expected from the given chemical formula. In conclusion, our results from the NMR and IR analyses support the fact that hydrosilylation is a quantitative reaction in the present conditions. Moreover, our observations show that the double bonds have quantitatively reacted with α,w-bis silane polydimethylsiloxane and the addition is actually selective since it occurs according to an anti-Markovnikov process.

Hydrolyze of the Acetate Group

The acetate group was transformed into alcohol by a hydrolyze process in a KCN/CH_3OH (1% of KCN) mixture at room temperature for 24 h, as it had been previously done.[25,26] In these conditions, we have obtained the product **(3)** with the following structure (Scheme 7).

The elimination of KCN was realized by addition of ether to this mixture, and the compound**(3)** was obtained quantitatively after the evaporation of the different solvents.

From the ^{1}H NMR spectrum, one may note specially the disappearance of the singlet at $\delta = 2.1$ ppm which correspond to the acetyl group. These results were also confirmed by IR spectroscopy, which demonstrates the loss of the carbonyl band at 1730 cm^{-1} and the presence of the hydroxyl band at 3500 cm^{-1}. The ^{29}Si NMR spectrum relative to this compound does not show any variations compared to the diacetate

TABLE I ^{1}H and ^{29}Si NMR Data for the Compounds 1, 2, and 3

Compounds	δppm ^{1}H NMR	δppm ^{29}Si NMR
1	(-OSi($\underline{CH_3}$)$_2$O)$_n$ 0.10	(-O$\underline{Si}$(CH$_3$)$_2$O)$_n$ -18 to -21
	-OSi($\underline{CH_3}$)$_2$H 0.25	-O$\underline{Si}$(CH$_3$)$_2$H -6.70
	-OSi($\underline{CH_3}$)$_2\underline{H}$ 4.60	
2	(-OSi($\underline{CH_3}$)$_2$O)$_n$ 0.10	(-O$\underline{Si}$(CH$_3$)$_2$O)$_n$ -21.90
	-OSi($\underline{CH_3}$)$_2$CH$_2$ 0.20	
	-OSi(CH$_3$)$_2\underline{CH_2}$ 1.50	
	-OSi(CH$_3$)$_2$CH$_2$ $\underline{CH_2}$ph- 2.50	
	$\underline{CH_3}$COO- 2.10	
	-OSi(CH$_3$)$_2$CH$_2$ CH$_2$ph- 7.00	
3	(-OSi($\underline{CH_3}$)$_2$O)$_n$ 0.10	(-O$\underline{Si}$(CH$_3$)$_2$O)$_n$ -21.90
	-OSi($\underline{CH_3}$)$_2$CH$_2$ 0.20	
	-OSi(CH$_3$)$_2\underline{CH_2}$ 1.50	
	-OSi(CH$_3$)$_2$CH$_2$ $\underline{CH_2}$ph- 2.50	
	-O-$\underline{H}$ 4.80	
	-OSi(CH$_3$)$_2$CH$_2$ CH$_2\underline{ph}$- 6.90	

compound **(2)**. All data NMR analysis of the compounds prepared are summarized in Table I. The hydroxyl number of the obtained polysiloxane diols was determined according to the equation:

$$\%\mathrm{OH} = \frac{(V_b - V_a) \,.\, N_{NaOH} \,.\, 17.100}{m_e \,.\, 1000}; \qquad (1)$$

where V_b = necessary volume of NaOH for the blank test (ml); V_a = necessary volume of NaOH for the sample test (ml); N_{NaOH} = normality of NaOH; and m_e = mass of the sample. The classic acetylation method in anhydride acetic-pyridine mixture was used and the acetic acid was titrated by the NaOH solution.

Using Equation (1), the experimental percentage $\%OH_{Exp}$ was found equal to 2.95%. The comparison with the theoretical one $\%OH_{Theo}$ = 3.02% is clearly satisfactory.

CONCLUSION

The synthesis of a novel telechelic α,w- hydroxyoligosiloxane by condensation of functional monochlosiloxanes with the well defined α,w- disilanols and hydrosilylation was achieved with a very good yield and in a simple way. This method allows the control of functionality, length, and purity of the resulting oligomers. The chemical ^{1}H NMR, ^{29}Si RMN, IR, and GPC characteristics are in good agreement with the proposed structures. We have demonstrated that our synthesis strategy is a successful

method for the introduction of aromatic end-groups into the side-chains of oligosiloxanes. Such products may take part in the synthesis of block copolymers, like, for example, thermoplastic elastomers including siloxane blocks and which may exhibit interesting thermal, mechanical, and anti-adhesive properties. The correlation between the polymers structure and their properties indicated that these compounds may have a high Tg and improved thermal stabilities compared to that of the starting silanol, this increase (improvement) is due to the presence of an aromatic group in the main chain. These new oligosiloxanes may be used as potential materials in the field of coatings and in the area of vapor permeation membranes.

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