Erika Pusztai[a,]*, József Nagy and Ödön Wagner

Synthesis and characterization of some bis(hydroxyalkyl)- and bis(hydroxyester)-functionalized disiloxanes

Abstract: Novel hydroxyester disiloxanes (1,3-bis(6-hydroxyhexanoylmethyl)-1,1,3,3-tetramethyl disiloxane and 3-bis(2-hydroxypropanoylmethyl)tetramethyl disiloxane) were synthesized, and preparation of other known monomers, namely 1,3-bis(hydroxypropyl)-1,1,3,3-tetramethyl disiloxane, 1,3-bis(hydroxyethoxypropyl)-1,1,3,3-tetramethyl disiloxane and 1,3-bis(hydroxymethyl)-1,1,3,3-tetramethyl disiloxane was developed to obtain better yields and reduce production time and expense. All compounds were characterized by infrared spectroscopy, using ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR and were reacted with diisocyanates, resulting in poly(siloxane-urethane) copolymers with unique properties.

Keywords: biocompatibility; bis(hydroxyalkyl) functionalized disiloxane; bis(hydroxyester) functionalized disiloxane; flame retardance; phase miscibility; poly(siloxane-urethane) copolymers.

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Introduction

Poly(siloxane-urethane) copolymers have received increasing attention in recent decades. They may satisfy the demand for waterborne polyurethanes to produce environmentally friendly waterproof polymers with excellent weather resistance (Kozakiewicz, 1996; Prabu and Alagar, 2004; Rath et al., 2009), moisture curable coatings for medical uses that are biocompatible and antithrombogenic (Briganti et al., 2006; Spiller et al., 2007; Losi et al., 2010; Soldani et al., 2010), general flexible elastomers with approved heat-resistance (Krol et al., 2010) and high tensile strength (Chuang et al., 2004), flame retardants or synergists in various polymers (Benrashid and Nelson, 1995; Lin et al., 2001; Nishihara et al., 2003; Chen and Jiao, 2009; Hamdani et al., 2009; Singh and Jain, 2009; Chrusciel and Lesniak, 2011) and other special applications (Ekin et al., 2007).

Blending the unique properties of polysiloxanes and polyurethanes in copolymers has challenged several research groups. Theoretically, the wide service temperature (from -120°C to 120°C), hydrolytic and oxidative stability, low surface energy, good biocompatibility and good hemocompatibility of polysiloxanes can be aided by the excellent mechanical properties of polyurethanes. Investigations have revealed that simple blending of these materials is totally unsatisfactory; the major reason for deterioration of physical properties is the incompatibility of non-polar siloxane segments with polar urethane hard segments and the weak interfacial adhesion between them. There have been several attempts to achieve better phase miscibility (Ebdon et al., 1986; Stanciu et al., 1999a,b; Ioan et al., 2002) to improve mechanical properties. Different preparation techniques were compared (Majumdar and Webster, 2007); the polysiloxane backbone was modified with polar side chains or end groups, or a second comacrodiol (typically a polyether polyol) was added to the polysiloxanes (Adhikari et al., 1999, 2000; Gunatillake et al., 2000). But only a very few efforts have approached the phase miscibility problem by altering the chain extender in the hard segment (Adhikari et al., 2002, 2003; Chuang et al., 2004).

That soft and hard segments in polyether and polyester polyurethanes can be observed is well known (Krol, 2007). Hard segments consist of diisocyanate units and chain extender molecules, typically in the case of 4,4′-diphenylmethane diisocyanate (MDI) and butane-1,4-diol (BDO), the MDI_2-BDO units. Better phase miscibility might be obtained by tailoring not only the soft segment molecules with polar groups but also producing disiloxane chain extenders so that the hard segments

contain – $(CH_3)_2$Si-O- units. Different chain extenders benefit different macrodiols and diisocyanates. Varying the end groups on the disiloxane chain permits them to be used in a wide range of poly(siloxane-urethane) copolymers.

Hydroxyester functionalized disiloxanes are the object of only one patent, published in 1956 (Merker, 1956), and no other references are available. Accordingly, no basic physical and spectroscopic data have been yet reported. Their application in polyurethanes has never been mentioned, although, due to their polar carbonyl group, they possess very desirable properties.

Hydroxyalkyl functionalized siloxanes are known in the literature. They are usually synthesized in a hydrosilylation reaction with H_2PtCl_6 $6H_2O$ (Speier's catalyst) or Pt-divinyl-tetramethyl-disiloxane complex (Karstedt catalyst) (Greber and Jager, 1962; Braun et al., 1989, 2007). The hydrosilylation reaction is fundamental in silicone chemistry; investigation of both the catalysts and the resultant products has been the objective of several patents and scientific publications (Speier et al., 1956, 1957; Ryan et al., 1960; Kossmehl et al., 1986; Chu and Frye, 1993; Lappert and Scott, 1995; Sabourault et al., 2002; Jankowiak et al., 2005; Zhu et al., 2005).

In this work, we provide a new bis(hydroxyester) functionalized disiloxane [1,3-bis(6-hydroxyhexanoylmethyl)-1,1,3,3-tetramethyl disiloxane (**1**)], as well as a simple preparation method for 3-bis(2-hydroxypropanoylmethyl) tetramethyl disiloxane (**2**), and characterization of both compounds. These diols can be used as chain extenders in poly(siloxane-urethane) copolymers, improving the phase miscibility between hard and soft segments due to their polar ester groups.

Furthermore, we provide detailed characterization and synthesis methods for preparing more efficiently three other monomers that were partially described in earlier studies: 1,3-bis(3-hydroxypropyl)-1,1,3,3-tetramethyl disiloxane (**3**), 1,3-bis(6-hydroxyethoxypropyl)-1,1,3,3-tetramethyl disiloxane (**4**) and 1,3-bis(hydroxymethyl)-1,1,3,3-tetramethyl disiloxane (**5**) (Speier et al., 1949; Greber and Jager, 1962; Adhikari et al., 2003; Braun et al., 2007; Frampton et al., 2010). All compounds were analyzed by FT-IR, ^{1}H-NMR, ^{13}C-NMR and ^{29}Si NMR.

Results and discussion

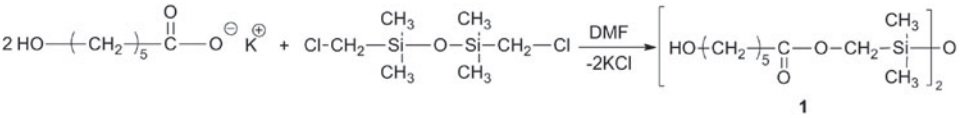
Synthesis and characterization of hydroxyester disiloxanes

Compound **1** was prepared as depicted in Scheme 1. **2** was prepared as depicted in Scheme 2. After the procedure described in the Experimental section, only technical grade products of >90% purity were obtained. For further analysis, they were purified on a semi-preparative HPLC column. The novel compound **1** is expected to provide the most flexible polymers, as well as high tensile strength. Compound **2** is expected to provide a slower reaction with diisocyanates due to its secondary hydroxyl group, and thus pot time may be lengthened using compound **2**.

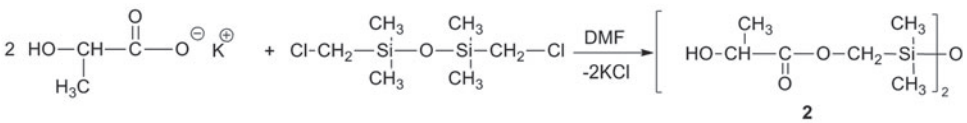
The hydrolytic stability of the monomers was investigated by boiling **1** and **2** separately in water. After 1 day boiling, they were totally decomposed, but after being stored for 1 year in air at ambient temperature, they did not show any change. Polymers prepared from these monomers are hydrolytically stable. No reduction in tensile strength or change in hardness was measureable after 1 day boiling in 0.1 M KOH solution.

Synthesis and characterization of hydroxyalkyl disiloxanes by hydrosilylation reaction

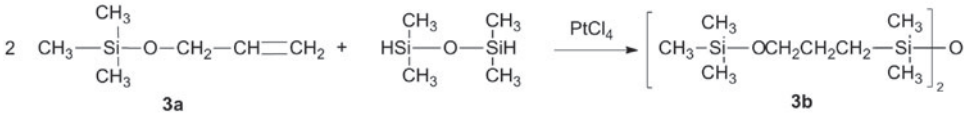
Compounds **3** and **4** were synthesized by the hydrosilylation reaction depicted in Schemes 3–6. Among all



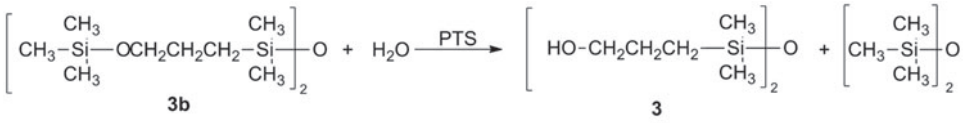
Scheme 1 Synthesis of 1,3-bis(5-hydroxyhexanoylmethyl)tetramethyl disiloxane (**1**).



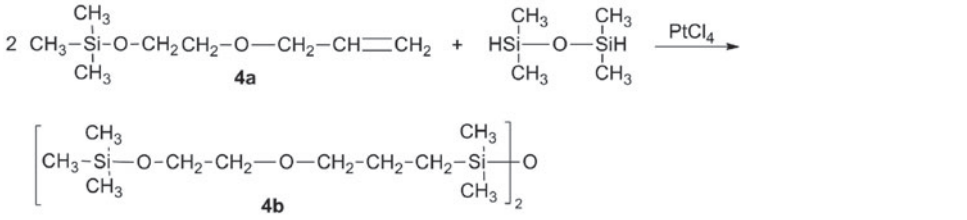
Scheme 2 Synthesis of 1,3-bis(2-hydroxypropanoylmethyl)tetramethyl disiloxane (**2**).



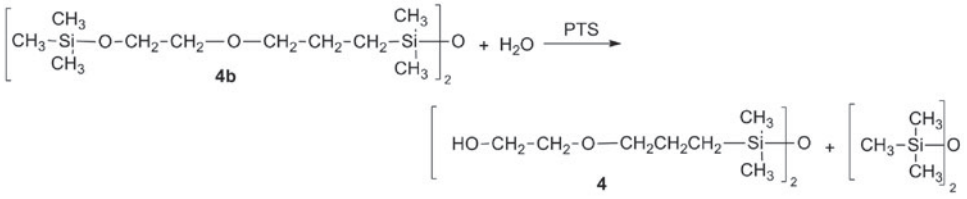
Scheme 3 Synthesis of 1,3-bis(3-trimethylsiloxypropyl)tetramethyl disiloxane (**3b**).



Scheme 4 Synthesis of 1,3-bis(3-hydroxypropyl)tetramethyl disiloxane (**3**) by hydrolysis of 1,3-bis(3-trimethylsiloxypropyl)tetramethyl disiloxane (**3b**).



Scheme 5 Synthesis of 1,3-bis(6-trimethylsiloxyethoxypropyl)tetramethyl disiloxane (**4b**).



Scheme 6 Synthesis of 1,3-bis(6-hydroxyethoxypropyl)tetramethyl disiloxane (**4**) by hydrolysis of 1,3-bis(6-trimethylsiloxyethoxypropyl) tetramethyl disiloxane (**4b**).

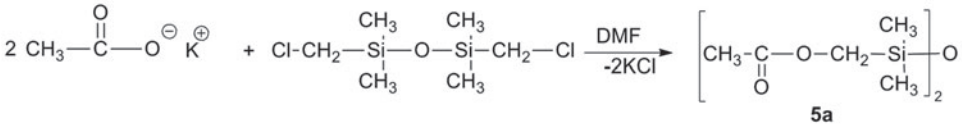
disiloxanes of this study, **3** is most entirely described because it is one of the simplest examples of hydrosilylation reactions (Greber and Jager, 1962; Adhikari et al., 2003; Braun et al., 2007; Frampton et al., 2010).

Several research groups have investigated the mechanism of these reactions and developed new catalysts. Although it is known that the basis of the catalysis is the oxidation reduction process of Pt(0) and Pt(IV) (Chu and Frye, 1993), and though it was found to be a very active catalyst in the presence of ionic liquids (Hofmann et al., 2008; Maciejewski et al., 2012), $PtCl_4$ salt catalyst is not frequently used in hydrosilylation. $PtCl_4$ is commercially available, and, with regard to efficient Pt-content, it is more cost-efficient than, for example, H_2PtCl_6. Additionally, $PtCl_4$ is acquirable as a dry salt, which is quite important due to the fact that even small traces of water can greatly decrease the effect of a catalyst (Feng and Cui, 2000). In our experiments, we found $PtCl_4$ to be a very efficient catalyst in hydrosylilation reactions according to our earlier expectations based on the mechanism of catalysis of Pt(IV) (Chu and Frye, 1993).

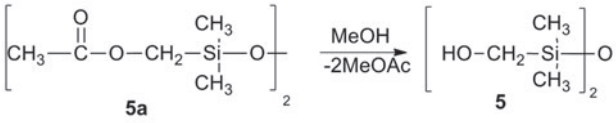
To reduce time and cost in the preparation of **3**, we developed the hydrolysis reaction. Because of several side reactions that occur with an excess of water, methanolysis is the usual procedure (Braun et al., 1987). We applied water in an approximately stoichiometric amount with p-toluene sulphuric acid as catalyst. With this method, the desired product was obtained in very good yield within 2 h and without much organic solvent waste.

Synthesis and characterization of 1,3-bis(hydroxymethyl)tetramethyl disiloxane

Compound **5** was synthesized by the reaction depicted in Schemes 7 and 8. Although compound **5** is one of the earliest examples of disiloxanes, no detailed NMR characterization has been available (Speier et al., 1949). This preparation method was improved by ameliorateing the process of methanolysis.



Scheme 7 Synthesis of 1,3-bis(acetoxymethyl)tetramethyl disiloxane (**5a**).



Scheme 8 Synthesis of 1,3-bis(hydroxymethyl)tetramethyl disiloxane (**5**).

Reaction with diisocyanate

All prepared disiloxanes were reacted with Lupranat MI (BASF) diisocyanate and Lupranol-1301 (BASF) trifunctional polyether polyol in a molar ratio of 2:4:1, respectively. Disiloxanes were prepared as described in the Experimental section. Preparation occurred by one-pot reaction in n-butyl acetate solution (30% polymer content) at 115°C for 2 h stirring. After drying at room temperature, residual solvent was revealed at 60°C, and the films were annealed at 120°C for 3 h.

All received films were clear, tough, cross-linked polymers with about 90 ShA hardness and 35–75 MPa ultimate tensile strength. Considering the fact that these polymers contain at least 25% disiloxane compound, these properties are unique. Detailed investigation of the use of these disiloxane compounds and the polymers made from them will be the objective of further studies.

Conclusion

Two hydroxyester disiloxanes were synthesised and characterized by NMR and IR spectroscopy. Three other hydroxyalkyl disiloxanes were prepared using newly developed synthesis methods and characterized similarly. All compounds were shown to be potential monomers in the preparation of new poly(siloxane-urethane) copolymers. By adding these disiloxanes, especially the novel hydroxyester functionalized disiloxanes, to polysiloxane-polyurethane blends as chain extenders, advanced phase miscibility is expected, which results in better mechanical properties.

Experimental

Materials and methods

Chloromethyldimethylchlorosilane was synthesized in our laboratory after Speier's method (Speier, 1951) from trimethylchlorosilane (Merck, Germany, >99%) and distilled two times before use on a laboratory column with 20 theoretical plates. 1,1,3,3-tetramethyl disiloxane, hexamethyl disilazane (Wacker, Germany) and dimethyl formamide (>99.8%) from Carlo Erba Reagenti (Italy) were distilled prior to use. Allyl alcohol, allyloxy ethanol, diethyl ether and petroleum ether were purchased from Sigma-Aldrich (USA) and used as received. Potassium hydroxide (>99%), potassium carbonate (>99%), calcium chloride (>99%) and sodium sulphate (>99%) are the products of Molar Chemicals (Hungary), and were used as received. Platinum (IV) chloride (>98%), lactic acid (70% aqueous solution) and ε-caprolactone (>98%) were purchased from Merck (Germany), and used without further treatment.

^{1}H and ^{13}C NMR experiments were performed on a Bruker DRX-300, and ^{29}Si NMR experiments were performed on a Bruker DRX-500 spectrometer. All compounds were dissolved in $CDCl_3$. Compound **1** and **2** were purified before analysis on a semi-preparative HPLC column with Perkin Elmer Series 200 equipment; methanol-water eluent was used. IR spectra were recorded with a Bruker ALPHA FT-IR spectrometer analyzing neat film on KBr pellets.

Chemical synthesis

Hydrolysis of chloromethyl dimethylchlorosilane

2.24 mol (320.5 g) chloromethyl dimethylchlorosilane was added dropwise to 450 ml water and 600 ml petroleum ether, under constant, vigorous stirring and cooled in a cold water bath. The mixture was stirred for a further 2 h. The organic layer was separated, washed with water and dried with $CaCl_2$ overnight. After the ether was evaporated, 1,3-bis(dichloromethyl)tetramethyl disiloxane was distilled under reduced pressure. Bp. 85°C/20 Torr, n_D^{25}=1.437, 86% yield.

Preparation of 1,3-bis(5-hydroxyhexanoylmethyl) tetramethyl disiloxane (1)

1.00 mol (231.0 g) of 1,3-bis(chloromethyl)tetramethyl disiloxane, 2.00 mol (340.0 g) potassium caprolactate (obtained from 2.00 mol ε-caprolactone and 2.00 mol KOH in aqueous solution from which water was evaporated in vacuum, following which the salt was dried at 80°C for a day) and 600 g dimethyl formamide was refluxed for 5 h. The precipitated potassium chloride was removed by filtration, and the solvent was distilled. The product was dissolved in diethyl ether and washed with water. The organic layer was separated and dried with Na_2SO_4. After diethyl ether was evaporated, the product was filtered. No distillation occurred because this compound decomposes below its boiling point. $T_{decomp.}$=200°C (in air, determined with thermogravimetric analysis); n_d^{25}=1.455, 65% yield. ^{1}H NMR (300.133 MHz, $CDCl_3$, δ): 3.78 (s, -O-C$\underline{H}_2$-Si-), 3.53 (t, J=6.8 Hz, HO-C$\underline{H}_2$-), 2.35 (t, J=7.3 Hz, -C$\underline{H}_2$-COO-), 1.57 (m, HO-CH$_2$-CH$_2$-CH$_2$-C$\underline{H}_2$-), 1.49 (m, HO-CH$_2$-C$\underline{H}_2$-), 1.28 (m, HO-CH$_2$-CH$_2$-C$\underline{H}_2$-), 0.136 (s, -Si-C$\underline{H}_3$). ^{13}C NMR (75.403 MHz, $CDCl_3$, δ): 178.27 (-$\underline{C}$OO-), 62.08 (HO-$\underline{C}$H$_2$-), 58.74 (-$\underline{C}$H$_2$-Si-),

34.21 (<u>C</u>H_2-COO-), 31.36 (HO-CH$_2$-<u>C</u>H_2-), 25.04 (-<u>C</u>H_2-CH$_2$-COO-), 24.70 (HO-CH$_2$-CH$_2$-<u>C</u>H_2-), -2.45 (-Si-<u>C</u>H_3). ^{29}Si NMR (99.314 MHz, $CDCl_3$, δ): 3.42 ppm. IR 756, 798, 836, 1050, 1163, 1254, 1285, 1364, 1418, 1458, 1731, 2864, 2937, 3365 cm^{-1}. Elemental analysis calculated for $C_{18}H_{38}Si_2O_7$: C, 51.15; H, 9.06. Found: C, 51.66; H, 9.33.

Preparation of 1,3-bis(2-hydroxypropanoylmethyl)-tetramethyl disiloxane (2)

1.00 mol (231.0 g) of 1,3-bis(chloromethyl)tetramethyl disiloxane, 2.00 mol (256.0 g) potassium lactate (obtained from lactic acid and potassium carbonate in aqueous solution from which water was evaporated in vacuum, following which salt was dried at 80°C for a day) and 535 g dimethyl formamide were refluxed for 5 h. The precipitated potassium chloride was removed by filtration, and the solvent was distilled. The product was dissolved in diethyl ether and washed with water. The organic layer was separated and dried with Na_2SO_4. After diethyl ether was evaporated, the product was distilled under reduced pressure. Bp. 140°C/0.4 Torr, n_D^{23}=1.442, 74% yield. ^{1}H NMR (300.133 MHz, $CDCl_3$, δ): 4.37 (q, J=7.0 Hz, CH_3-C<u>H</u>-(OH)-), 3.89 (d, J=14.3 Hz, -C<u>H</u>^{a}H^b-Si-), 3.84 (d, J=14.3 Hz, -CH^a<u>H</u>^{b}-Si-), 1.34 (d, J=7.3 Hz, C<u>H</u>$_3$-CH(OH)-), 0.14 (s, -Si-C<u>H</u>$_3$). ^{13}C NMR (75.403 MHz, $CDCl_3$, δ): 177.56 (-<u>C</u>OO-), 67.30 (CH_3-<u>C</u>H(OH)-), 59.41 (<u>C</u>H_3-CH(OH)-), -2.52 (-Si-<u>C</u>H_3). ^{29}Si NMR (99.314 MHz, $CDCl_3$, δ): 3.36 ppm. IR 721, 762, 798, 835, 874, 1042, 1126, 1198, 1253, 1287, 1373, 1418, 1451, 1730, 2909, 2960, 3468 cm^{-1}. Elemental analysis calculated for $C_{12}H_{26}Si_2O_7$: C, 42.58; H, 7.74. Found: C, 42.96; H, 8.05.

Preparation of (2-propenyloxy)trimethylsilane (3a)

0.730 mol (79.6 g) trimethyl chlorosilane and 0.730 mol (118.1 g) hexamethyl disilazane were mixed and 2 mol (116.0 g) of allyl alcohol was added dropwise to the mixture with vigorous stirring and cooling in an ice-water bath. The mixture was then heated and refluxed for 3 h. The salt formed was filtered off, and the filtrate was distilled. Bp. 100–101°C, n_D^{25}=1.394, 62% yield.

Preparation of 1,3-bis(3-trimethylsiloxypropyl) tetramethyl disiloxane (3b)

0.550 mol (73.7 g) 1,1,3,3-tetramethyldisiloxane was slowly added to 1.21 mol (157.3 g) (2-propenyloxy)trimethylsilane containing a catalytic amount of anhydrous $PtCl_4$ (1 ml of 1% 2-propanol solution) at 80°C. The mixture was stirred further for 2.5 h at 120°C. Subsequent distillation under reduced pressure yielded the desired compound. Bp. 127°C/1.0 Torr, n_D^{24}=1.424, 81% yield.

Preparation of 1,3-bis(3-hydroxypropyl)tetramethyl disiloxane (3) by hydrolysis of 1,3-bis(3-trimethylsiloxypropyl)tetramethyl disiloxane (3b)

0.127 mol (50.0 g) 1,3-bis(3-trimethylsiloxypropyl)tetramethyldisiloxane and 0.278 mol (2.0 g) water were heated and stirred with 0.1 g of p-toluenesulfonic acid for 2 h. The mixture was distilled. Bp. 70°C/20 Torr, n_D^{23}=1.442, 88% yield. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 3.48 (t, J=6.9 Hz, HO-C<u>H</u>$_2$-CH$_2$-), 1.52 (m, J=6.9, 8.5 Hz, -HO-CH$_2$-C<u>H</u>$_2$-), 0.46 (t, J=8.5 Hz, -C<u>H</u>$_2$-Si-), 0.01 (s, -Si-C<u>H</u>$_3$). ^{13}C NMR (75.40 MHz, $CDCl_3$, δ): 65.07 (HO-<u>C</u>H$_2$-CH$_2$-), 26.34 (HO-CH$_2$-<u>C</u>H$_2$-), 13.95 (-<u>C</u>H$_2$-Si-), 0.20 (-Si-<u>C</u>H_3). ^{29}Si NMR (99.31 MHz, $CDCl_3$, δ): 7.95 ppm. IR 704, 773, 793, 835, 1010, 1046, 1178, 1251, 1411, 1437, 2874, 2930, 2955, 3315 cm^{-1}. Elemental analysis calculated for $C_{10}H_{26}Si_2O_3$: C, 47.95; H, 10.46. Found: C, 48.14; H, 10.23.

Preparation of (6-hydroxyethoxypropyl)trimethylsilane (4a)

0.370 mol (40.1 g) trimethyl chlorosilane and 0.370 mol (59.6 g) hexamethyl disilazane were mixed and 1 mol (102.0 g) of allyloxyethanol was added dropwise to the mixture with vigorous stirring and cooling in an ice-water bath. The mixture was then heated and refluxed for 3 h. The salt formed was filtered off, and the filtrate was distilled. Bp. 60°C/20 Torr, n_D^{25}=1.421, 76% yield.

Preparation of 1,3-bis(6-trimethylsiloxyethoxypropyl) tetramethyl disiloxane (4b)

0.268 mol (35.9 g) 1,1,3,3-tetramethyldisiloxane was slowly added to 0.590 mol (102.7 g) (6-hydroxyethoxypropyl)trimethylsilane containing a catalytic amount of anhydrous $PtCl_4$ at 80°C. The mixture was stirred for a further 3 h at 120°C. Subsequent distillation under reduced pressure yielded the desired compound. Bp. 174°C/0.6 Torr, n_D^{24}=1.432, 76% yield.

Preparation of 1,3-bis(6-hydroxyethoxypropyl)-tetramethyl disiloxane (4) by hydrolysis of 1,3-bis(6-trimethylsiloxyethoxypropyl)tetramethyl disiloxane (4b)

0.202 mol (97.1 g) 1,3-bis(6-trimethylsiloxyethoxypropyl)tetramethyl disiloxane, 0.556 mol (10.0 g) water were heated and stirred with 0.1 g of p-toluenesulfonic acid for 2 h. The mixture was distilled. Bp. 65°C/20 Torr, n_D^{25}=1.452, 86% yield. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 3.47 (t, J=5.0 Hz, HO-C<u>H</u>$_2$-CH$_2$-), 3.30 (t, J=5.0 Hz, HO-CH$_2$-C<u>H</u>$_2$-), 3.21 (t, J=6.9 Hz, -O-C<u>H</u>$_2$-), 1.39 (m, -O-CH$_2$-C<u>H</u>$_2$-CH$_2$-), 0.29 (t, J=8.5 Hz, -C<u>H</u>$_2$-Si-), -0.16 (s, -Si-C<u>H</u>$_3$). ^{13}C NMR (75.40 MHz, $CDCl_3$, δ): 73.41 (HO-CH$_2$-<u>C</u>H$_2$-), 71.45 (-O-<u>C</u>H$_2$-CH$_2$-), 60.76 (HO-<u>C</u>H$_2$-CH$_2$-), 22.77 (-O-CH$_2$-<u>C</u>H$_2$-), 13.61 (-<u>C</u>H$_2$-Si-), -0.24 (-Si-<u>C</u>H_3). ^{29}Si NMR (99.31 MHz, $CDCl_3$, δ): 7.46 ppm. IR 705, 773, 795, 835, 899, 943, 1044, 1098, 1117, 1186, 1250, 1358, 1411, 1456, 2865, 2929, 2953, 3446 cm^{-1}. Elemental analysis calculated for $C_{14}H_{34}Si_2O_5$: C, 49.66; H, 10.12. Found: C, 49.83; H, 10.48.

Preparation of 1,3-bis(acetoxymethyl)tetramethyl disiloxane (5a)

0.965 mol (223.0 g) 1,3-bis(chloromethyl)tetramethyl disiloxane and 2.00 mol (196.0 g) potassium acetate were added to 450 ml dimethyl formamide. The mixture was refluxed for 6 h. The precipitated potassium chloride was filtered, the solvent distilled, the residue

solved in diethyl ether, washed with water and dried with $CaCl_2$. After the diethyl ether was evaporated, the product was distilled under reduced pressure. Bp. 85°C/0.3 Torr, n_D^{25}=1.422, 85% yield.

Preparation of 1,3-bis(hydroxymethyl)tetramethyl disiloxane (5)

0.766 mol (210.0 g) 1,3-bis(acetoxymethyl)tetramethyl disiloxane was dissolved in 560 ml methanol containing 5% HCl. The mixture was refluxed for 1.5 h then 2/3 of the methanol was distilled away. The same amount of abs. methanol was added to the residue which was refluxed again for 1.5 h. These two steps were repeated two further times. The third time, all the methanol was distilled, and the residue was dissolved in diethyl ether, washed with water and dried with Na_2SO_4. After diethyl ether was evaporated, the product was distilled under reduced pressure. Bp. 95°C/0.3 Torr, n_D^{25}= 1.435, 68% yield. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 3.20 (s, HO-C$\underline{H}_2$-Si-), 0.05 (s, -Si-C$\underline{H}_3$). ^{13}C NMR (75.40 MHz, $CDCl_3$, δ): 55.71 (HO-$\underline{C}H_2$-Si-), -1.61 (-Si-$\underline{C}H_3$). ^{29}Si NMR (99.31 MHz, $CDCl_3$, δ): 3.72 ppm. IR 714, 752, 793, 833, 1046, 1178, 1252, 1411, 1726, 2875, 2959, 3312 cm^{-1}. Elemental analysis calculated for $C_6H_{18}Si_2O_3$: C, 37.08; H, 9.33. Found: C, 37.84; H, 9.67.

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