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(hydroxypthoxypropyl)-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 ¹H NMR, ¹³C NMR, and ²⁹Si 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(siloxaneurethane) copolymers.

Present address: Organosilicon Research Center, University of Wisconsin-Madison, 1101 University Avenue, Madison, 53706, USA

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 MDI₂-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

^{*}Corresponding author: Erika Pusztai, Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, 1111 Budapest, Szent Gellért tér 4, Hungary, e-mail: pusztaierika@hotmail.com

József Nagy: Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, 1111 Budapest, Szent Gellért tér 4, Hungary

Ödön Wagner: Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, 1111 Budapest, Szent Gellért tér 4, Hungary

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 $H_2PtCl_6 GH_2O$ (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, ¹H-NMR, ¹³C-NMR and ²⁹Si 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).

$$2 \begin{array}{c} CH_{3} \\ 2 \end{array} \begin{array}{c} CH_{3} \\ -O-CH_{2}-CH \\ CH_{3} \end{array} \begin{array}{c} CH_{2} \\ +\end{array} \begin{array}{c} CH_{3} \\ -O-CH_{2}-CH \\ CH_{2} \end{array} \begin{array}{c} CH_{3} \\ +\end{array} \begin{array}{c} CH_{3} \\ -\end{array} \begin{array}{c} CH_{3} \end{array} \begin{array}{c} CH_{3} \\ -\end{array} \begin{array}{c} CH_{3} \end{array} \begin{array}{c} CH_{3} \\ -\end{array} \begin{array}{c} CH_{3} \end{array} \begin{array}{c} CH_{3} \end{array} \begin{array}{c} CH_{3} \\ -\end{array} \begin{array}{c} CH_{3} \end{array} \end{array}{c} CH_{3} \end{array} \begin{array}{c} CH_{3} \end{array} \begin{array}{c} CH_{3} \end{array} \end{array}{c} CH_{3} \end{array} \begin{array}{c} CH_{3} \end{array} \begin{array}{c} CH_{3} \end{array} \end{array} \begin{array}{c} CH_{3} \end{array} \end{array}{c} CH_{3} \end{array} \end{array}{c} CH_{3} \end{array} \end{array} \begin{array}{c} CH_{3} \end{array} \end{array} \begin{array}{c} CH_{3} \end{array} \end{array} \begin{array}{c} CH_{3} \end{array} \end{array}{c} CH_{3} \end{array} \end{array}{c} CH_{3} \end{array} \end{array}{c} CH_{3} \end{array} \end{array}{c} CH_{3} \end{array} \end{array} \end{array}{c} CH_{3} \end{array} \end{array}{c} CH_{3} \end{array} \end{array} \\{c} CH_{3} \end{array} \end{array} \end{array}$$
{c} CH_{3} \end{array} \end{array}{c} CH_{3} \end{array} \end{array} \\{c} CH_{3} \end{array} \end{array} \\ CH_{3} \end{array} \end{array} \end{array} \\{c} CH_{

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

$$\begin{bmatrix} CH_3 & CH_3 \\ CH_3 - Si \\ CH_3 & CH_2CH_2CH_2 - Si \\ CH_3 & CH_3 \end{bmatrix}_2 O + H_2O \xrightarrow{\text{PTS}} \begin{bmatrix} HO-CH_2CH_2CH_2 - Si \\ CH_3 \end{bmatrix}_2 O + \begin{bmatrix} CH_3 \\ CH_3 - Si \\ CH_3 - Si \\ CH_3 - Si \end{bmatrix}_2 O + \begin{bmatrix} CH_3 \\ CH_3 - Si \\ CH_3 - Si \\ CH_3 - Si \end{bmatrix}_2 O + \begin{bmatrix} CH_3 \\ CH_3 - Si \\ CH_3 - Si \\ CH_3 - Si \\ CH_3 - Si \end{bmatrix}_2 O + \begin{bmatrix} CH_3 \\ CH_3 - Si \\ CH_3 - S$$

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

$$2 CH_{3} - Si - O - CH_{2}CH_{2} - O - CH_{2} - CH - CH_{2} + HSi - O - SiH - SiH - CH_{3} - S$$

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, salt catalyst is not frequently used in hydrosilylation. PtCl, is commercially available, and, with regard to efficient Pt-content, it is more cost-efficient than, for example, H₂PtCl₆. Additionally, PtCl₆ 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, 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.

¹H and ¹³C NMR experiments were performed on a Bruker DRX-300, and ²⁹Si NMR experiments were performed on a Bruker DRX-500 spectrometer. All compounds were dissolved in CDCl₃. Compound **1** and **2** were purified before analysis on a semi-preparative HPLC column with Perkin Elmer Series 200 equipment; methanolwater 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 CaCl₂ overnight. After the ether was evaporated, 1,3-bis(dichloromethyl)tetramethyl disiloxane was distilled under reduced pressure. Bp. 85°C/20 Torr, n_p^{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 Na₂SO₄. 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_d²⁵=1.455, 65% yield. ¹H NMR (300.133 MHz, CDCl₂, δ): 3.78 (s, -O-C<u>H</u>₂-Si-), 3.53 (t, J=6.8 Hz, HO-C<u>H</u>₂-), 2.35 (t, J=7.3 Hz, -CH,-COO-), 1.57 (m, HO-CH,-CH,-CH,-CH,-), 1.49 (m, HO-CH,-CH₂-), 1.28 (m, HO-CH₂-CH₂-CH₂-), 0.136 (s, -Si-CH₂). ¹³C NMR (75.403 MHz, CDCl., δ): 178.27 (-<u>C</u>OO-), 62.08 (HO-<u>C</u>H₂-), 58.74 (-<u>C</u>H₂-Si-), 34.21 (<u>CH</u>₂-COO-), 31.36 (HO-CH₂-<u>C</u>H₂-), 25.04 (-<u>C</u>H₂-CH₂-COO-), 24.70 (HO-CH₂-CH₂-<u>C</u>H₂-), -2.45 (-Si-<u>C</u>H₃). ²⁹Si NMR (99.314 MHz, CDCl₃, 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 C₁₈H₃₈Si₂O₇: 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 SO. After diethyl ether was evaporated, the product was distilled under reduced pressure. Bp. 140°C/0.4 Torr, n_p²³=1.442, 74% yield. ¹H NMR (300.133 MHz, CDCl₂, δ): 4.37 (q, J=7.0 Hz, CH₂-CH-(OH)-), 3.89 (d, J=14.3 Hz, -CH^aH^b-Si-), 3.84 (d, J=14.3 Hz, -CH^aH^b-Si-), 1.34 (d, J=7.3 Hz, CH,-CH(OH)-), 0.14 (s, -Si-CH₂). ¹³C NMR (75.403 MHz, CDCl., δ): 177.56 (-<u>C</u>OO-), 67.30 (CH.,-<u>C</u>H(OH)-), 59.41 (<u>CH</u>₂-CH(OH)-), -2.52 (-Si-<u>C</u>H₂). ²⁹Si NMR (99.314 MHz, CDCl₂, 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 C₁₂H₂₂Si₂O₂: 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_p^{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_0^{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. ¹H NMR (300.13 MHz, CDCl₃, δ): 3.48 (t, J=6.9 Hz, HO-C<u>H</u>₂-CH₂-), 1.52 (m, J=6.9, 8.5 Hz, -HO-CH₂-C<u>H</u>₂-), 0.46 (t, J=8.5 Hz, -C<u>H</u>₂-Si-), 0.01 (s, -Si-CH₃). ¹³C NMR (75.40 MHz, CDCl₃, δ): 65.07 (HO-<u>C</u>H₂-CH₂-), 26.34 (HO-CH₂-<u>C</u>H₂-), 13.95 (-<u>C</u>H₂-Si-), 0.20 (-Si-<u>C</u>H₃). ¹³C NMR (99.31 MHz, CDCl₃, 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 C₁₀H₂₆Si₂O₃: 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, $n_{\rm D}^{25}$ =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 PtCl₄ 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(6trimethylsiloxyethoxypropyl)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. ¹H NMR (300.13 MHz, CDCl₃, δ): 3.47 (t, J=5.0 Hz, HO-C \underline{H}_2 -CH₂-), 3.30 (t, J=5.0 Hz, HO-CH₂-C \underline{H}_2 -), 3.21 (t, J=6.9 Hz, -O-C \underline{H}_2), 1.39 (m, -O-CH₂-C \underline{H}_2 -CH₂-), 0.29 (t, J=8.5 Hz, -C \underline{H}_2 -Si-), -0.16 (s, -Si-C \underline{H}_2). ¹³C NMR (75.40 MHz, CDCl₃, δ): 73.41 (HO-CH₂-C \underline{H}_2 -), 71.45 (-O-C \underline{H}_2 -CH₂-), 60.76 (HO-C \underline{H}_2 -CH₂-), 22.77 (-O-CH₂-CH₂-), 13.61 (- \underline{C} H₂-Si-), -0.24 (-Si- \underline{C} H₃). ³²Si NMR (99.31 MHz, CDCl₃, 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 C₁₄H₃₄Si₂O₄: 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 Na₂SO₄. After diethyl ether was evaporated, the product

References

- Adhikari, R.; Gunatillake, P. A.; McCarthy, S. J.; Meijs, G. F. Effect of chain extender structure on the properties and morphology of polyurethanes based on H₁₂MDI and mixed macrodiols (PDMS-PHMO). *J. Appl. Polym. Sci.* **1999**, *74*, 2979–2989.
- Adhikari, R.; Gunatillake, P. A.; McCarthy, S. J.; Meijs, C. F. Mixed macrodiol-based siloxane polyurethanes. Effect of the comacrodiol structure on properties and morphology. J. Appl. Polym. Sci. 2000, 78, 1071–1082.
- Adhikari, R.; Gunatillake, P. A.; McCarthy, S. J.; Meijs, G. F.
 Low-modulus siloxane-based polyurethanes. I. Effect of the chain extender 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethyidis-iloxane (BHTD) on properties and morphology. J. Appl. Polym. Sci. 2002, 83, 736–746.
- Adhikari, R.; Gunatillake, P. A.; McCarthy, S. J.; Bown, M.; Meijs, G. F. Low-modulus siloxane-polyurethanes. Part II. Effect of chain extender structure on properties and morphology. J. Appl. Polym. Sci. 2003, 87, 1092–1100.
- Benrashid, R.; Nelson, G. L. Flammability improvement of polyurethanes by incorporation of a silicone moiety into the structure of block-copolymers. In *Fire and Polymers II* - *Materials and Tests for Hazard Prevention*; Nelson, G. L. Ed. American Chemical Society: Washington, 1995; pp. 217–235.
- Braun, F.; Willner, L.; Hess, M.; Kosfeld, R. Synthesis of disiloxanes containing hydroxyalkyl groups. *J. Organomet. Chem.* **1987**, *332*, 63–68.
- Braun, F.; Willner, L.; Hess, M.; Kosfeld, R. Synthesis and characterization of oligosiloxanes with hydroxyalkyl substituents. J. Organomet. Chem. 1989, 366, 53–56.
- Briganti, E.; Losi, P.; Raffi, A.; Scoccianti, M.; Munao, A.; Soldani, G. Silicone based polyurethane materials: a promising biocompatible elastomeric formulation for cardiovascular applications. J. Mat. Sci. – Mat. Med. 2006, 17, 259–266.
- Chen, X. L.; Jiao, C. M. Synergistic effects of hydroxy silicone oil on intumescent flame retardant polypropylene system. *J. Polym. Res.* **2009**, *16*, 537–543.
- Chrusciel, J. J.; Lesniak, E. Preparation of flexible, self-extinguishing silicone foams. J. Appl. Polym. Sci. 2011, 119, 1696–1703.
- Chu, H. K.; Frye, C. L. Cyclohydrosilylation dimer formationevidence for Pt(0) – Pt(II) – Pt(IV) catalysis. J. Organomet. Chem. **1993**, 446, 183–189.

was distilled under reduced pressure. Bp. 95°C/0.3 Torr, n_D^{25} = 1.435, 68% yield. ¹H NMR (300.13 MHz, CDCl₃, δ): 3.20 (s, HO-C<u>H</u>₂-Si-), 0.05 (s, -Si-C<u>H</u>₃). ¹³C NMR (75.40 MHz, CDCl₃, δ): 55.71 (HO-<u>C</u>H₂-Si-), 1.61 (-Si-<u>C</u>H₃). ²⁹Si NMR (99.31 MHz, CDCl₃, δ): 3.72 ppm. IR 714, 752, 793, 833, 1046, 1178, 1252, 1411, 1726, 2875, 2959, 3312 cm⁻¹. Elemental analysis calculated for C₆H₁₈Si₂O₃: C, 37.08; H, 9.33. Found: C, 37.84; H, 9.67.

Acknowledgement: The authors thank Pál Kolonits for NMR, József Nagy jr. and Gyulané Timkó for FT-IR, Jenő Fekete and Péter Jenei for HPLC assistance. The authors also thank Robert West for the language help.

Received April 2, 2012; accepted May 29, 2012; previously published online July 12, 2012

- Chuang, F. S.; Tsen, W. C.; Shu, Y. C. The effect of different siloxane chain-extenders on the thermal degradation and stability of segmented polyurethanes. *Polym. Degrad. Stab.* 2004, 84, 69–77.
- Ebdon, J. R.; Hourston, D. J.; Klein, P. G. Polyurethane-polysiloxane simultaneous interpenetrating polymer networks. *Adv. Chem. Ser.* **1986**, *211*, 171–193.
- Ekin, A.; Webster, D. C.; Daniels, J. W.; Stafslien, S. J.; Casse, F.; Callow, J. A.; Callow, M. E. Synthesis, formulation, and characterization of siloxane-polyurethane coatings for underwater marine applications using combinatorial high-throughput experimentation. J. Coat. Tech. Res. 2007, 4, 435–451.
- Feng, S. Y.; Cui, M. Z. Study of polysiloxanes containing epoxy groups. I. Synthesis and characterization of polysiloxanes containing 3-(2,3-epoxypropoxy)propyl groups. *React. Funct. Polym.* 2000, 45, 79–83.
- Frampton, M. B.; Subczynska, I.; Zelinsko, P. M. Biocatalytic synthesis of silicon polyesters. *Biomacromolecules* 2010, 11, 1818–1825.
- Greber, G.; Jager, S. Über oligomere Siliciumverbindungen mit funktionellen Gruppen. 12. Mitt. Über Herstellung von oligomeren siliciumorganischen Diolen und Diaminen und ihre Umsetzungen mit organischen Diisocyanaten. *Makromol. Chem.* **1962**, *57*, 150–191.
- Gunatillake, P. A.; Meijs, G. F.; McCarthy, S. J.; Adhikari, R. Poly(dimethylsiloxane)/poly(hexamethylene oxide) mixed macrodiol based polyurethane elastomers. I. Synthesis and properties. J. Appl. Polym. Sci. **2000**, *76*, 2026–2040.

Hamdani, S.; Longuet, C.; Perrin, D.; Lopez-Cuesta, J. M.; Ganachaud, F. Flame retardancy of silicone-based materials. *Polym. Degrad. Stab.* **2009**, *94*, 465–495.

- Hofmann, N.; Bauer, A.; Frey, T.; Auer, M.; Stanjek, V.; Schulz, P. S.; Taccardi, N.; Wasserscheid, P. Liquid-liquid biphasic, Platinumcatalyzed hydrosilylation of allyl chloride with trichlorosilane using an ionic liquid catalyst phase in a continuous loop reactor. Adv. Synth. Cat. 2008, 350, 2599–2609.
- Ioan, S.; Grigorescu, G.; Stanciu, A. Effect of segmented poly(estersiloxane)urethanes compositional parameters on differential scanning calorimetry and dynamic-mechanical measurements. *Eur. Polym. J.* 2002, *38*, 2295–2303.

Jankowiak, M.; Maciejewski, H.; Gulinski, J. Catalytic reactions of hydrosiloxanes with allyl chloride. *J. Organomet. Chem.* **2005**, *690*, 4478–4487.

Kossmehl, G.; Neumann, W.; Schafer, H. Polymeric and oligomeric dimethylsiloxanes with alcoholic groups and their conversions into polymers with dimethylsiloxane and urethane moieties. *Makromol. Chem.-Macromol. Chem. Phys.* **1986**, *187*, 1381–1388.

Kozakiewicz, J. Polysiloxaneurethanes, new polymers for potential coating applications. *Prog. Org. Coat.* **1996**, *27*, 123–131.

Krol, P. Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers. *Prog. Mat. Sci.* 2007, *52*, 915–1015.

Krol, P.; Pielichowska, K.; Byczynski, L. Thermal degradation kinetics of polyurethane-siloxane anionomers. *Thermochim. Acta* **2010**, *507–08*, 91–98.

Lappert, M. F.; Scott, F. P. A. The reaction pathway from Speier's to Karstedt's hydrosilylation catalyst. J. Organomet. Chem. 1995, 492, C11–C13.

Lin, M. F.; Tsen, W. C.; Shu, Y. C.; Chuang, F. S. Effect of silicon and phosphorus on the degradation of polyurethanes. J. Appl. Polym. Sci. 2001, 79, 881–899.

Losi, P.; Briganti, E.; Magera, A.; Spiller, D.; Ristori, C.; Battolla, B.; Balderi, M.; Kull, S.; Balbarini, A.; Stefano, R.; Soldani, G. Tissue response to poly(ether)urethane-polydimethylsiloxane-fibrin composite scaffolds for controlled delivery of pro-angiogenic growth factors. *Biomaterials* **2010**, *31*, 5336–5344.

Maciejewski, H.; Szubert, K.; Marciniec, B. New approach to synthesis of functionalized silasesquioxanes via hydrosilylation. *Cat. Comm.* **2012**, *24*, 1–4.

Majumdar, P.; Webster, D. C. Surface microtopography in siloxanepolyurethane thermosets. The influence of siloxane and extent of reaction. *Polymer* **2007**, *48*, 7499–7509.

Merker, R. R. Hydroxyester substituted siloxanes. US Patent 2,770,631; November 1956.

Nishihara, H.; Suda, Y.; Sakuma, T. I. Halogen- and phosphorusfree flame retardant PC plastic with excellent moldability and recyclability. *J. Fire Sci.* **2003**, *21*, 451–464.

Prabu, A. A.; Alagar, A. Mechanical and thermal studies of intercross-linked networks based on siliconized polyurethaneepoxy/unsaturated polyester coatings. *Prog.Org. Coat.* 2004, 49, 236–243.

Rath, S. K.; Chavan, J. G.; Sasane, S.; Srivastava, A.; Patri, M.; Samui, A. B.; Chakraborty, B.C.; Sawant, S. N. Coatings of PDMS-modified epoxy via urethane linkage: segmental correlation length, phase morphology, thermomechanical and surface behaviour. *Prog. Org. Coat.* **2009**, *65*, 366–374.

Ryan, J. W.; Menzie, G. K.; Speier, J. L. The addition of silicon hydrides to olefinic double bonds. 5. The addition to allyl and metallyl chlorides. J. Am. Chem. Soc. 1960, 82, 3601–3604.

Sabourault, N.; Mignani, G.; Wagner, A.; Mioskowski, C. Platinum oxide (PtO2). A potent hydrosilylation catalyst. *Org. Lett.* **2002**, *4*, 2117–2119.

Singh, H.; Jain, A. K. Ignition, combustion, toxicity, and fire retardancy of polyurethane foams: a comprehensive review. J. Appl. Polym. Sci. 2009, 111, 1115–1143.

Soldani, G.; Losi, P.; Bernabei, M.; Burchielli, S.; Chiappino, D.; Kull, S.; Briganti, E.; Spiller, D. Long term performance of small-diameter vascular grafts made of a poly(ether)urethanepolydimethylsiloxane semi-interpenetrating polymeric network. *Biomaterials* **2010**, *31*, 2592–2605.

Speier, J. L. A study of the chlorination of methylchlorosilanes. J. Am. Chem. Soc. **1951**, 73, 824–826.

Speier, J. L.; Daubert, B. F; McGregor, R. R. Acetoxymethyl and hydroxymethyldisiloxanes. J. Am. Chem. Soc. 1949, 71, 1474–1475.

Speier, J. L.; Zimmerman, R.; Webster, J. The addition of silicon hydrides to olefinic double bonds. 1. The use of phenylsilane; diphenylsilane; phenylmethylsilane; amylsilane and tribromosilane. J. Am. Chem. Soc. 1956, 78, 2278–2281.

Speier, J. L.; Webster, J. A.; Barnes, G. H. The addition of silicon hydrides to olefinic double bonds. 2. The use of group-VIII metal catalysts. J. Am. Chem. Soc. 1957, 79, 974–979.

Spiller, D.; Losi, P.; Briganti, E.; Sbrana, S.; Kull, S.; Martinelli, I.; Soldani, G. PDMS content affects in vitro hemocompatibility of synthetic vascular grafts. *J. Mat. Sci.-Mat. Med.* 2007, *18*, 1097–1104.

Stanciu, A.; Airinei, A.; Timpu, D.; Ioanid, A.; Ioan, C.; Bulacovschi,
V. Polyurethane/polydimethylsiloxane segmented copolymers. *Eur. Polym. J.* 1999a, *35*, 1959–1965.

Stanciu, A.; Bulacovschi, V.; Lungu, M.; Vlad, S.; Balint, S.; Oprea, S. Mechanical behaviour of crosslinked poly(ester-siloxane) urethanes. *Eur. Polym. J.* **1999b**, *35*, 2039–2044.

Zhu, X. L.; Zhang, M.; Zhang, Q. S.; Feng, S. Y.; Kong, X. Z. Synthesis and characterization of bis(methoxyl hydroxyl)-functionalized disiloxane and polysiloxane oligomers derivatives therefrom. *Eur. Polym. J.* 2005, 41, 1993–2001.