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A versatile synthetic path to thiol containing polysiloxanes

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ABSTRACT

A synthetic strategy to polydimethylsiloxanes and polymethylsiloxanes containing thiol functions as end- or side-groups, respectively, is presented. Such polymers are important starting materials for elastomeric networks and for post-polymerization modifications. The synthesis starts either with vinyl end-functionalized polydimethylsiloxanes or with polymethylvinylsiloxanes. Their vinyl groups are reacted either with thioacetic acid or with a thioacetic acid/butanethiol mixture *via* a UV-initiated thiol-ene reaction to form the respective thioester quantitatively within few minutes. The thioesters are subsequently deprotected to the respective thiols by reduction with LiAlH₄. The resulting thiol containing polysiloxanes can be used for the formation of networks or for another functionalization.

KEYWORDS: polysiloxanes, thiols, thiol-ene addition

INTRODUCTION

The reaction of thiols to double bonds with formation of thioethers, also known as thiol-ene reaction, has been widely used for the synthesis of materials with advanced properties.¹ Due to its high conversion rate under mild conditions, it is not surprising that this reaction has been used in post-polymerizations as well as in polymer network formation.^{2,3} Additionally, it proceeds without the need of a metal catalyst, is tolerant to

many functional groups, resists oxygen inhibition and has practically no side reactions. Despite of all these positive facts, the greatest disadvantage of the thiol-ene reaction is the bad odour of thiols. This problem can be overcome when thiol containing polymers (polythiols) are used since they tend to have low volatility and therefore reduced odour.⁴ End-functionalized polythiols are accessible *via* an end-group functionalization and found applications in polymer network formation.² Side-functionalized polythiols are typically

We have recently used the thiol-ene reaction to prepare polar elastomer films in a post-polymerization starting from polymethylvinylsiloxane and mercaptopropionitrile.^{10,11} Apart from the bad odour of this mercapto reagent, the poor miscibility of this nonpolar polymer with the polar thiol was disadvantageous. Additionally, this post-polymerization modification required a large amount of solvent to achieve homogenous conditions. These problems might be overcome if the synthesis to the above mentioned polymer would be conducted in a reversed fashion, i.e. by starting from a polysiloxane containing thiol side groups and reacting these groups with allyl cyanide, again in a post-polymerization modification. Polysiloxanes containing thiol side-groups are commonly prepared by condensing the hydrolysis product of mercapto dialkylloxysilane **A** with octamethylcyclotetrasiloxane (**D₄**) in acidic conditions¹² or by condensing **A** with dialkylloxysilane **C** (Scheme 1, top). However, in this way polysiloxanes of rather low molar masses form.¹³ Thiol end-functionalized polysiloxanes were also previously prepared.¹⁴ In a three step process starting from a hydroxyl end-functionalized polydimethylsiloxane, the hydroxyl groups of which were converted to mesylates prior to their substitution with potassium thiolate followed by aminolysis (Scheme 1 bottom). Also in this case low molar mass polymers formed.

$$\begin{array}{c}
 \begin{array}{ccc}
 \begin{array}{c} \text{SH} \\ | \\ \text{RO-Si-OR} \\ | \\ \text{A} \end{array} & + & \begin{array}{c} \text{---} \text{Si-O} \text{---} \\ | \\ \text{D}_4 \end{array} \\
 \begin{array}{c} \text{SH} \\ | \\ \text{RO-Si-OR} \\ | \\ \text{A} \end{array} & + & \begin{array}{c} \text{RO-Si-OR} \\ | \\ \text{C} \end{array}
 \end{array}
 \xrightarrow{\text{H}^+}
 \begin{array}{c} \text{SH} \\ | \\ \text{HO} \text{---} \text{Si-O} \text{---} \text{---} \text{Si-O} \text{---} \text{H} \\ | \qquad \qquad | \\ \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \end{array}
 \end{array}$$

$$\begin{array}{c}
 \text{HO}(\text{H}_2\text{C})_6\text{O-Si-O} \text{---} \text{---} \text{Si-O} \text{---} \text{---} \text{Si-O}(\text{CH}_2)_6\text{OH} \\
 | \qquad \qquad | \qquad \qquad | \\
 \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---}
 \end{array}
 \xrightarrow{\text{CH}_3\text{SO}_2\text{Cl}}
 \begin{array}{c}
 \text{R}(\text{H}_2\text{C})_6\text{O-Si-O} \text{---} \text{---} \text{Si-O} \text{---} \text{---} \text{Si-O}(\text{CH}_2)_6\text{R} \\
 | \qquad \qquad | \qquad \qquad | \\
 \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---}
 \end{array}$$

$$\begin{array}{l}
 \text{R} = \text{OSO}_2\text{CH}_3 \\
 \text{R} = \text{SAC} \\
 \text{R} = \text{SH}
 \end{array}
 \begin{array}{c}
 \left. \begin{array}{c} \text{---} \\ \text{---} \end{array} \right\} \text{KSAC} \\
 \left. \begin{array}{c} \text{---} \\ \text{---} \end{array} \right\} \text{Pr}^-\text{NH}_2
 \end{array}$$

It was therefore the aim of this work to develop a synthesis pathway to polysiloxanes containing thiols as end- or side-groups which would not only be fast, simple and highly efficient but would also provide access to low as well as to high molar mass products. Particularly the latter products would suggest themselves for applications in elastomeric networks. To achieve this, we started with polysiloxanes containing vinyl groups which were used in a post-polymerization modification to introduce protected thiol groups which are subsequently used to set free the thiols on demand. The molecular weight of the resulting polymers is predetermined by the starting polymer supposed the polymer backbone is not affected by

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the post-polymerization modifications. The UV-induced thiol-ene reaction employing thioacetic acid (**1**) and LiAlH₄ reduction of the formed thioesters are the key reactions used.

EXPERIMENTAL

Materials and methods

Unless otherwise stated all chemicals used were reagent grade and used as received. 2,2-dimethoxy-2-phenylacetophenone (DMPA), thioacetic acid (**1**), 1-butanethiol (**2**), LiAlH₄, sodium hydrogen carbonate, sodium sulfate, and benzene were purchased from Sigma-Aldrich. Methanol, dichloromethane, heptane, ethyl acetate, diethyl ether (Et₂O), and tetrahydrofuran (THF) were purchased from VWR. Tetramethylammonium hydroxide pentahydrate (TMAH), 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (**V**₄), and α,ω -vinyl dimethylsiloxane-polydimethylsiloxane of different M_w (**P**_t**V**_n, where **P**_t**V**₁: M_w = 500 g/mol, **P**_t**V**₂: M_w = 770 g/mol, **P**_t**V**₃: M_w = 6000 g/mol, or **P**_t**V**₄: M_w = 9700 g/mol) were purchased from ABCR. Poly(vinylmethylsiloxane) (**PV**) was prepared according to the literature.¹⁰ THF and Et₂O were dried over sodium and distilled prior use.

¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer using a 5 mm BBO Prodigy™ CryoProbe at 400.18 and 100.63 MHz, respectively. Chemical shifts (δ) in ppm are calibrated to residual solvent peaks (CDCl₃: δ = 7.24 and 77.00 ppm). IR spectra were recorded on a Bruker Tensor 27 ATR FT-IR. GPC in THF were taken with an Agilent 1100 Series HPLC (Columns: serial coupled PSS SDV 5 μ , 100A and PSS SDV 5 μ , 1000A, Detector: DAD, 235 nm and 360 nm; refractive index). The calibration was done with

polydimethylsiloxane (PDMS) standards, while toluene was used as internal standard.

1,3,5,7-tetramethyl-1,3,5,7-tetra-(2-(acetylthio)ethyl)-cyclotetrasiloxane (V**₄SAC)**

To a solution of **V**₄ (20.0 g, 58 mmol) in distilled THF (250 mL), **1** (21.2 g, 280 mmol) and DMPA (0.59 g, 2.3 mmol) were added. The reaction mixture was degassed by three freeze-pump-thaw cycles. It was then UV irradiated for 15 min. The reaction mixture was neutralized with a saturated solution of NaHCO₃, washed twice with water and extracted with dichloromethane. The combined organic layers were dried over Na₂SO₄, filtrated, and concentrated. The organic crude product was purified by flash chromatography using heptane and ethyl acetate as eluent.

¹H NMR (400 MHz, CDCl₃, δ): 0.13 – 0.21 (m, 12 H, –Si–CH₃), 0.87 – 0.95 (m, 7.43 H, –Si–CH₂–CH₂–S–), 1.23 – 1.28 (m, 1.08 H, –Si–CHCH₃–S–), 2.28 (s, 10.83 H, –CH₂–CH₂–S–CO–CH₃), 2.31 (s, 1.15 H, –CHCH₃–S–CO–CH₃), 2.76 – 2.87 (m, 0.34 H, –Si–CHCH₃–S–), 2.88 – 2.95 (m, 7.34 H, –Si–CH₂–CH₂–S–); ¹³C NMR (100 MHz, CDCl₃, δ): -2.40 (–CH–Si–CH₃), -0.64 – -0.56 (–Si–CH₃), 16.15 (–Si–CHCH₃–S–), 17.66 – 17.86 (–Si–CH₂–CH₂–S–), 23.54 (–Si–CHCH₃–S–), 24.08 (–Si–CH₂–CH₂–S–), 30.48 (–CHCH₃–S–CO–CH₃), 30.59 (–CH₂–CH₂–S–CO–CH₃), 195.78 (–CHCH₃–S–CO–CH₃), 195.95 (–CH₂–CH₂–S–CO–CH₃); FTIR (KBr, ν , cm⁻¹): 2895 – 2960 (C–H stretch); 1658 (–C=O stretch); 1353 and 1410 (δ C–H), 1261 and 1277 (δ Si–CH₃); 1058 (Si–O–Si stretch); 790 (γ Si–CH₃); 622 (S–CO stretch); HRMS (ESI, m/z): [M+H⁺] calcd. for C₂₀H₄₁O₈S₄Si₄ 649.0756; found 649.0746. Anal. calcd. for C₂₀H₄₀O₈S₄Si₄: C 37.01, H 6.21; found: C 37.06, H 6.77.

Synthesis of 1,3,5,7-tetramethyl-1,3,5,7-tetra-(2-thioethyl)-cyclotetrasiloxane (V_4SH)

Reduction by $LiAlH_4$: To a degassed solution of V_4SAC (2.0 g, 3.08 mmol) in dry THF (40 mL) a degassed solution of $LiAlH_4$ (0.47 g, 12.32 mmol) in dry THF (20 mL) was added slowly. The reaction mixture was stirred for 1 h at 0 °C and for another 1 h at room temperature. Then a solution of acetic acid in water (10%) was added dropwise. The organic phase was separated and washed with a saturated solution of $NaHCO_3$, dried over Na_2SO_4 , and concentrated.

Aminolysis: To a degassed solution of V_4SAC (4.0 g, 6.16 mmol) in dry THF (10 mL), butyl amine (6 mL, 2.5-fold molar excess with respect to thioacetate moiety) was added and stirred for 18 h at room temperature. Then, the solution was concentrated and chromatographed (heptane : ethyl acetate = 4 :1) to give V_4SH as a colorless liquid.

1H NMR (400 MHz, $CDCl_3$, δ): 0.03 – 0.23 (m, 12 H, $-Si-CH_3$), 0.86 – 1.03 (m, 8.00 H, $-Si-CH_2-CH_2-SH$), 1.23 – 1.42 (m, 0.77 H, $-Si-CHCH_3-SH$), 1.49 – 1.56 (m, 4.03 H, $-CH_2-CH_2-SH$ and $-CHCH_3-SH$), 1.91 – 2.02 (m, 0.17 H, $-Si-CHCH_3-SH$), 2.48 – 2.69 (m, 7.73 H, $-Si-CH_2-CH_2-SH$); ^{13}C NMR (100 MHz, $CDCl_3$, δ): -0.39 – -0.33 ($-Si-CH_3$), 19.4 ($-Si-CH_2-CH_2-SH$), 23.03 – 23.17 ($-Si-CH_2-CH_2-SH$). The C signals for the Markovnikov product were too weak; FTIR (KBr, ν , cm^{-1}): 2889 – 2958 (C–H stretch); 2127 (S–H stretch); 1410 (δ C–H); 1259 and 1280 (δ Si–CH₃); 1055 (Si–O–Si stretch); 788 (ν Si–CH₃); HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{14}H_{32}NaO_4Si_4$, 503.0153; found 503.0153.

Synthesis of polysiloxanes containing thioacetate end-groups P_tSAC_n

P_tV_n (10.0 g) was dissolved in THF (200 mL) containing an appropriate amount of **1** (2 eq to the vinyl group in P_tV_n) and DMPA (0.01 eq). The

reaction mixture was degassed and irradiated with UV light for 15 min. Then, it was neutralized with a saturated aqueous solution of $NaHCO_3$, washed twice with water, and extracted with dichloromethane. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel using hexane:ethyl acetate 9:1 as eluent. P_tSAC_n were obtained as colorless viscous liquids.

P_tSAC_1 : 1H NMR (400 MHz, $CDCl_3$, δ): 0.05 – 0.06 (m, 3.68 H, $-Si-CH_3$), 0.10 – 0.13 (m, 6.07 H, $-CH_2-Si-CH_3$ and $-CH-Si-CH_3$), 0.86 – 0.91 (m, 1.83 H, $-Si-CH_2-CH_2-$), 1.24 – 1.28 (m, 0.31 H, $-Si-CHCH_3-S-$), 2.29 (s, 2.68 H, $-CH_2-CH_2-S-CO-CH_3$), 2.32 (s, 0.32 H, $-CHCH_3-S-CO-CH_3$), 2.77 – 2.80 (m, 0.11 H, $-Si-CHCH_3-S-CO-$), 2.87 – 2.91 (m, 1.80 H, $-Si-CH_2-CH_2-S-CO-$); ^{13}C NMR (100 MHz, $CDCl_3$, δ): -1.25 and -1.40 ($-CHCH_3-Si-CH_3$), 0.17 and 0.31 ($-CH_2-Si-CH_3$), 1.06 – 1.21 ($-Si-CH_3$), 16.29 and 16.32 ($-Si-CHCH_3-S-$), 18.86 and 18.95 ($-Si-CH_2-CH_2-S-$), 24.62 ($-Si-CHCH_3-S-$), 24.67 ($-Si-CH_2-CH_2-S-$), 30.55 ($-CHCH_3-S-CO-CH_3$), 30.61 ($-CH_2-S-CO-CH_3$), 196.26 ($-S-CO-CH_3$); FTIR (KBr, ν , cm^{-1}): 2959 (C–H stretch); 1688 (C=O stretch); 1351 and 1410 (δ C–H), 1255 (δ Si–CH₃); 1031 (Si–O–Si stretch); 792 (ν Si–CH₃); 623 (S–CO stretch).

P_tSAC_n : 1H NMR (400 MHz, $CDCl_3$, δ): 0.05 – 0.06 (m, $-Si-CH_3$), 0.10 – 0.13 (m, $-CH_2-Si-CH_3$ and $-CH-Si-CH_3$), 0.86 – 0.91 (m, $-Si-CH_2-CH_2-$), 1.24 – 1.28 (m, $-Si-CHCH_3-S-$), 2.29 (s, $-CH_2-CH_2-S-CO-CH_3$), 2.32 (s, $-CHCH_3-S-CO-CH_3$), 2.77 – 2.80 (m, $-Si-CHCH_3-S-CO-$), 2.87 – 2.91 (m, $-Si-CH_2-CH_2-S-CO-$); ^{13}C NMR (100 MHz, $CDCl_3$, δ): -14.8 – -1.24 ($-CHCH_3-Si-CH_3$), 0.15 – 0.31 ($-CH_2-Si-CH_3$), 0.67 – 1.11 ($-Si-CH_3$), 18.87 – 18.96 ($-Si-CH_2-CH_2-S-$), 24.68 ($-Si-CH_2-CH_2-S-$), 30.59 ($-CH_2-S-CO-CH_3$), 196.27 ($-S-CO-CH_3$). For the characteristics of the prepared polymers see Table 1.

Synthesis of polysiloxanes containing thiol end-group (P_tSH_n)

To a degassed solution of P_tSAc_n (6.0 g) in dry Et_2O (100 mL) a dispersion of $LiAlH_4$ (1.1 molar ratio to the thioacetate group) in dry Et_2O (100 mL) was added slowly under argon atmosphere at 0 °C. The reaction mixture was stirred at 0 °C for 20 min and at room temperature for an additional 1 h. Then, a solution of acetic acid (10%) was added. The phases were separated and the organic phase was washed with a saturated solution of $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated to give P_tSH_n as viscous liquids.

P_tSH_1 : 1H NMR (400 MHz, $CDCl_3$, δ): 0.01 – 0.15 (m, 21.84 H, $-Si-CH_3$, $-CH_2-Si-CH_3$ and $-CHCH_3-Si-CH_3$), 0.92 – 1.00 (m, 4.00 H, $-Si-CH_2-CH_2-$), 1.24 – 1.33 (m, 0.91 H, $-Si-CHCH_3-SH$ and $-Si-CHCH_3-SH$), 1.47 – 1.52 (m, 2.05 H, $-CH_2-CH_2-SH$), 1.90 – 1.99 (m, 0.19 H, $-Si-CHCH_3-SH$), 2.55 – 2.63 (m, 4.00 H, $-Si-CH_2-CH_2-SH$); ^{13}C NMR (100 MHz, $CDCl_3$, δ): -2.42 – -1.88 ($-CHCH_3-Si-CH_3$), 0.28 – 0.42 ($-CH_2-Si-CH_3$), 1.09 – 1.23 ($-Si-CH_3$), 19.80 ($-Si-CHCH_3-SH$), 19.95 ($-Si-CH_2-CH_2-SH$), 20.12 ($-Si-CHCH_3-SH$), 24.56 and 24.59 ($-Si-CH_2-CH_2-SH$); FTIR (KBr, ν , cm^{-1}): 2957 (C–H stretch); 1411 (δ C–H); 1254 (δ Si–CH₃); 1030 (Si–O–Si stretch); 791 (ν Si–CH₃);

P_tSH_n : 1H NMR (400 MHz, $CDCl_3$, δ): 0.06 – 0.18 (m, $-Si-CH_3$, $-CH_2-Si-CH_3$ and $-CHCH_3-Si-CH_3$), 0.93 – 0.99 (m, $-Si-CH_2-CH_2-$), 1.30 – 1.33 (m, $-Si-CHCH_3-SH$), 1.47 – 1.52 (m, $-CH_2-CH_2-SH$), 1.92 – 1.99 (m, $-Si-CHCH_3-SH$), 2.56 – 2.64 (m, $-Si-CH_2-CH_2-SH$); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 0.24 – 0.42 ($-CH_2-Si-CH_3$), 0.74 – 1.23 ($-Si-CH_3$), 19.76 ($-Si-CHCH_3-SH$), 19.96 ($-Si-CH_2-CH_2-SH$), 24.57 and 24.61 ($-Si-CH_2-CH_2-SH$). For the characteristics of the prepared polymers see Table 1.

Polymethylsiloxanes containing thioacetate side-groups $PSAc_n$

PV (10.0 g, 116 mmol) was dissolved in THF (200 mL) containing an appropriate amount of **1** and **2** (20 mol% excess versus the vinyl group in **PV** was used) and DMPA (0.01 eq). The reaction mixture was degassed and irradiated with UV light for 15 min, and then concentrated. The residue was precipitated with methanol. The precipitate was redissolved in THF and precipitated again to give $PSAc_n$ as viscous liquids.

$PSAc_1$: 1H NMR (400 MHz, $CDCl_3$, δ): 0.07 – 0.16 (m, 6 H, $-Si-CH_3$), 0.85 – 0.92 (m, 8.79 H, $-Si-CH_2-CH_2-S-CO-$, $-Si-CH_2-CH_2-S-CH_2-$, and $-S-(CH_2)_3-CH_3$), 1.23 – 1.29 (m, 0.42 H, $-Si-CHCH_3-S-CO-$ and $-Si-CHCH_3-S-CH_2-$), 1.35 – 1.44 (m, 3.39 H, $-CH_2-CH_2-CH_3$), 1.50 – 1.58 (m, 3.85 H, $-CH_2-CH_2-CH_2-CH_3$), 2.28 (s, 0.73 H, $-CH_2-CH_2-S-CO-CH_3$), 2.33 (s, 0.09 H, $-CHCH_3-S-CO-CH_3$), 2.48 – 2.55 (m, 6.55 H, $-S-CH_2-(CH_2)_2-CH_3$ and $-Si-CH_2-CH_2-S-CH_2-$), 2.86 – 2.90 (m, 0.51 H, $-Si-CH_2-CH_2-S-CO-$); ^{13}C NMR (100 MHz, $CDCl_3$, δ): -0.07 ($-Si-CH_3$), 13.75 ($-S-(CH_2)_3-CH_3$), 18.36 ($-Si-CH_2-CH_2-S-CO-$ and $-Si-CH_2-CH_2-S-CH_2-$), 22.09 ($-CH_2-CH_2-CH_3$), 24.13 ($-Si-CH_2-CH_2-S-CO-$), 26.40 ($-Si-CH_2-CH_2-S-CH_2-$), 30.59 ($-CH_2-CH_2-S-CO-CH_3$), 31.67 and 31.73 ($-S-CH_2-(CH_2)_2-CH_3$, $-CH_2-CH_2-CH_2-CH_3$); FTIR (KBr, ν , cm^{-1}): 2872 – 2957 (C–H stretch); 1690 (C=O stretch); 1353 – 1464 (δ C–H), 1260 (δ Si–CH₃); 999 – 1087 (Si–O–Si stretch); 766 – 791 (ν Si–CH₃); 625 (S–CO stretch). For the characteristics of the prepared polymers see Table 2.

Polymethylsiloxanes containing thiol side-groups (PSH_n)

To a solution of $PSAc_n$ (10.0 g) in dry THF (200 mL) a dispersion of $LiAlH_4$ (1.1 molar ratio) in dry THF

(50 mL) was added slowly under argon atmosphere. The reaction was stirred at room temperature for 2 h. Then, a solution of acetic acid (10%) was slowly added to the reaction mixture. The two phases were separated, and the organic phase was washed with a saturated solution of NaHCO_3 . The organic layer was dried over Na_2SO_4 and concentrated to give **PSH_n** as viscous liquids. All polymers were synthesized using the same procedure except **PSH₁** where a mixture of Et_2O /THF was used as solvent.

PSH₄: ^1H NMR (400 MHz, CDCl_3 , δ): 0.08 – 0.22 (m, 6 H, $-\text{Si}-\text{CH}_3$), 0.86 – 0.92 (m, 5.26 H, $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_2-$, and $-\text{S}-(\text{CH}_2)_3-\text{CH}_3$), 0.95 – 0.99 (t, 1.72 H, $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{SH}$), 1.23 – 1.29 (m, 0.27 H, $-\text{Si}-\text{CHCH}_3-\text{SH}$ and $-\text{Si}-\text{CHCH}_3-\text{S}-$), 1.32 – 1.44 (m, 2.46 H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.51 – 1.58 (m, 3.04 H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$, and $-\text{CH}_2-\text{SH}$), 1.83 – 0.92 (m, 0.12 H, $-\text{Si}-\text{CHCH}_3-\text{SH}$ and $-\text{Si}-\text{CHCH}_3-\text{S}-$), 2.48 – 2.55 (m, 4.28 H, $-\text{S}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ and $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_2-$), 2.58 – 2.62 (m, 1.56 H, $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{SH}$); ^{13}C NMR (100 MHz, CDCl_3 , δ): -0.06 – 0.06 ($-\text{Si}-\text{CH}_3$), 13.75 ($-\text{S}-(\text{CH}_2)_3-\text{CH}_3$), 18.34 ($-\text{Si}-\text{CH}_2-$

$\text{CH}_2-\text{S}-\text{CH}_2-$), 19.41 ($-\text{Si}-\text{CH}_2-\text{CH}_2-\text{SH}$), 22.09 ($-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 23.69 ($-\text{Si}-\text{CH}_2-\text{CH}_2-\text{SH}$), 26.38 ($-\text{Si}-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_2-$), 31.67 ($-\text{S}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$), 31.78 ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$); FTIR (KBr, ν , cm^{-1}): 2895 – 2960 (C–H stretch); 2126 (S–H stretch); 1378 – 1464 (δ C–H); 1259 (δ Si–CH₃); 999 – 1084 (Si–O–Si stretch); 765 and 790 (γ Si–CH₃). For the characteristics of the prepared polymers see Table 2. The ^1H NMR, ^{13}C NMR and 2D spectra of all polymers can be found in SI.

RESULTS AND DISCUSSION

To achieve the goal mentioned in introduction, it was of utmost importance to prove that vinylsiloxanes can successfully be employed into UV-induced thiol-ene reactions and by this way protected thiol groups can be introduced to these silicones in a virtually quantitative manner. We thus studied the UV-induced thiol-ene addition of **1** to vinylsiloxane and the subsequent reduction of the thioester formed (Scheme 2).

SCHEME 2 Synthesis of a thiol containing cyclosiloxane (top), of polydimethylsiloxanes containing thiol end-groups (middle), and polymethylsiloxanes containing thiol side-groups (bottom).

For all thiol-ene reactions, the DMPA UV-initiator and a slight excess of **1** were used. The thermally induced thiol-ene reaction of **V₄**¹⁶ and 1,3-divinyltetramethyldisiloxane¹⁷ with **1** and the thermally activated radical initiator azobisisobutyronitril is known.¹⁸ The main disadvantages of the reported synthesis are the long reaction time and the high temperature used. Our first orienting experiments conducted on **V₄** showed that the vinyl groups are consumed in a relatively short time with formation of two addition products: the anti-Markovnikov (major) and the Markovnikov (minor, less than 10 mol%) products (Scheme 2).^{19,20} The disappearance of the vinyl protons signals between $\delta = 5.75 - 6.15$ ppm and the appearance of a new signal $\delta = 2.31$ ppm characteristic for the methyl group from thioester are clear indications for the complete reaction (See SI). The formation of **V₄SAC** was further supported by the mass spectrum which shows the $[M+H]^+$ ion at $m/z = 649$. Next, the deprotection of **V₄SAC** to the thiol **V₄SH** was conducted by reducing with $LiAlH_4$ and found to be quantitative. The disappearance of the singlet at $\delta = 2.31$ ppm characteristic for the acetyl group and the appearance of a new peak between $\delta = 1.50 - 1.65$ ppm characteristic for the thiol groups in the ¹H NMR spectra are clear indications that the reduction of the thioester to thiol was successful. Furthermore, the presence of $[M+Na]^+$ ion at $m/z = 503$ in the MS spectrum also supports the product. Having in hand the two cyclic siloxanes (**V₄SAC** and **V₄SH**), their anionic and cationic polymerizations were attempted, however with only limited success. Either a low viscosity product formed, a clear indication that the polymerization was not

successful, or a highly viscous polymer ($M_w = 234$ kDa) with an unacceptable high polydispersity ($D = 6.94$) formed when **V₄SAC** was polymerized in cationic conditions.

The thiol-ene reaction of **AcSH** was further explored on commercially available vinyl end-functionalized polydimethylsiloxane **P_tV_n** of different molar masses (Table 1) as shown in Scheme 2. Also here the conversion of vinyl groups was quantitative. Figure 1 shows the ¹H NMR spectra of **P_tV₁**, **P_tSAC₁**, as well as of the **P_tSH₁**. This last polymer was obtained from the reduction of **P_tSAC₁** with $LiAlH_4$. The presence of thiol protons between 1.52 - 1.47 ppm is a clear indication of a successful reaction. While for the conversion of **P_tSAC** to **P_tSH** hydrolysis in acidic or basic conditions at elevated temperatures could in principle be used, the instability of polysiloxanes under these conditions was a concern since depolymerization can occur with formation of shorter silicone chains which have uncontrolled end groups (vinyl, hydroxyl or both). To assess if there was any change in the molar mass, GPC investigations were conducted which showed a slight shift of the elugrams for **P_tSH_n** products to higher molar masses which might be due to the fact that some of the low molar mass compounds are lost during washing (Figure 2). The M_n calculated using ¹H NMR spectra are in the same order of magnitude as those found by GPC. For the characteristics of the prepared polymers see Table 1.

TABLE 1 Molecular characteristics of **P_tV_n**, **P_tSAC_n**, and **P_tSH_n**.

Sample Code	M_w [g/mol]	2M_n [g/mol]	2d	3M_n NMR [g/mol]
P_iV₁	500 ¹	-	-	300
P_iSAC₁	-	-	-	450
P_iSH₁	-	-	-	390
P_iV₂	770 ¹	-	-	1030
P_iSAC₂	-	-	-	1140
P_iSH₂	-	-	-	1190
P_iV₃	6000 ¹ 8840 ²	3300	2.7	5700
P_iSAC₃	7000 ²	2000	3.47	6460
P_iSH₃	10100 ²	5400	1.89	7840
P_iV₄	9400 ¹ 14200 ²	8700	1.64	8580
P_iSAC₄	12300 ²	7200	1.71	8650
P_iSH₄	16500 ²	10900	1.51	10510

¹As given by the provider; ²as determined by GPC, ³calculated from the ¹H NMR spectra.

FIGURE 1 ^1H NMR spectra of P_tV_1 (bottom), P_tSAC_1 (middle), and P_tSH_1 (top).

FIGURE 2 GPC elugrams of P_tV_4 , P_tSAC_4 , and P_tSH_4 (left) and of PV , PSAC_1 , and PSH_1 (right) in THF.

For the introduction of thiols as side groups, **PV** ($M_w = 170'000$ g/mol, $M_n = 77'000$ g/mol, $D = 2.2$) was used. **PV** was prepared starting from **V**₄ via anionic polymerization in presence of TMAH.⁹ To tune the ratio of thioester side groups in **PSAC**_n, **PV** which by structure carries at every repeat unit a vinyl group was reacted with different molar ratios of **1** : **2**. The thioacetic acid **1** allowed us introducing protected thiol groups to the silicone

chains, while **2** was used to ensure the same overall conversion of the vinyl groups and can in principle be replaced by any other functional thiol. Table 2 gives the amount of reagents used, the composition of all copolymers, as well as the molecular weights and distributions. The expected increase in the molar mass for the addition products **PSAC**_n was confirmed by GPC (Figure 2). As can be seen in Figure 3, the conversion of vinyl

groups was quantitative and new signals appeared due to the addition of **1** and **2** to the vinyl groups, however, the amount of **1** was slightly higher than expected and shows that the **1** adds faster to the vinyl groups than **2**. The assignments of proton and carbon signals were possible with the help of 2D NMR spectra (Figure 4 and SI). The reduction of **PSAc_n** with LiAlH₄ allowed formation of polysiloxanes containing different mol% of thiol side groups. The signal of the thiol protons overlaps with the one of the methylene protons of butyl groups as well as with the water signal and therefore, the integral of the signal between $\delta = 1.70 - 1.45$ was in all cases higher than expected. The signal intensity of the C atom connected to the thiol in the ¹³C NMR spectra rises with increasing content of thiol groups in **PSH_n** (see SI). Furthermore, the coupling of SH protons with the methylene groups in CH₂-SH in the COSY spectrum as well as the coupling of thiol protons with the two carbons from the CH₂-CH₂-SH group in HMBC spectra are further supporting the presence of thiols (see SI). GPC investigations show that the molar mass of the resulting polymers **PSH_n** decreased. Although a decrease in molar mass after the thiol formation was expected, the molar mass was lower than that of the starting polymer

PV (Table 2). The reason behind this might be the presence of hydroxyl end-groups in **PSAc_n** which are converted to silanolates active centres and undergo backbiting. It is known that the cyclosiloxane monomers can be polymerized in acidic and basic conditions and that the polymerization proceeds until an equilibrium is reached between polymers and cycles.²¹ The position of the equilibrium is however shifted to cycles when solvents and elevated temperatures are used. Despite using low temperatures for the deprotection, it was not possible to completely suppress the depolymerization which is favoured by the presence of silanolates end groups and tetrahydrofuran solvent. Nevertheless, hydroxyl end-groups functionalized polysiloxanes **PSH_n** of appreciable molar mass and containing varying amounts of thiol side groups were prepared. Interestingly, the polydispersity of the polymers was rather low ($D < 1.8$) (Table 2). One concern was the stability of the deprotected thiols which can rather easily form disulfides which leads to cross-linking. Fortunately, **PSH_n** were stable for several months when stored in the deep fridge in dark and no change in the NMR spectra was detected.

TABLE 2 The amounts of reagents used for the synthesis of **PSAc_n** and their composition, molecular weights and distributions.

Sample	PV		1		2		1 : 2^{a)}	1 : 2^{b)}	$M_w^{c)}$	$M_n^{c)}$	$PDI^{c)}$
	[g]	[mmol]	[g]	[mmol]	[g]	[mmol]			[g/mol]	[g/mol]	
PSAc₁	10	116	1.06	13.9	11.3	125.0	1 : 9	1 : 6.4	270000	85000	3.18
PSAc₂	10	116	2.12	27.8	10.0	111.4	2 : 8	2 : 6.3	281000	89200	3.15
PSAc₃	10	116	3.18	41.8	8.79	97.5	3 : 7	3 : 6.1	220400	65200	3.38
PSAc₄	10	116	4.24	55.7	7.53	83.5	4 : 6	4 : 5.2	295100	105800	2.79
PSAc₅	5	58	2.65	34.8	3.14	34.8	1 : 1	1 : 0.64	279400	89400	3.13
PSH₁	10	5.73	-	-	-	-	-	-	26800	14900	1.80
PSH₂	10	11.55	-	-	-	-	-	-	7500	4400	1.70
PSH₃	10	17.48	-	-	-	-	-	-	9900	5700	1.72
PSH₄	10	23.47	-	-	-	-	-	-	11900	7300	1.63
PSH₅	6	17.75	-	-	-	-	-	-	11400	6800	1.68

^{a)}Feed ratio of **1** : **2**, ^{b)}ratio of 1:2 incorporated into **PSAc_n** as calculated from the ¹H NMR spectra, ^{c)} M_w , M_n , and D as determined by GPC.

FIGURE 3 ^1H NMR spectra of **PV** (bottom), **PSAc_4** (middle), and **PSH_4** (top).

FIGURE 4 HMBC spectrum of **PSH_4** .

Preliminary results show aminolysis to be an alternative way to deprotect the thioesters to thiols, as it is known that butyl amine does not attack the polysiloxane chain. The signal of the methyl group from thioester in ^1H NMR spectrum was completely removed after 48 h at 65 °C (See SI). Special care has to be however taken during this reaction to avoid formation of disulfides which leads to cross-linking. This problem might be overcome, when sacrificial 1,4-dithioerythritol is used which allows intramolecular cyclization to disulphide, which is energetically favoured since a six member ring is formed.²²

CONCLUSIONS

In conclusion, the thiol-ene addition of thioacetic acid to polymethylsiloxanes containing vinyl as end- or side-groups is an efficient reaction which allows introduction of protected thiols as end- or side-groups quantitatively within few min. The amount of protected thiol side-groups into the polymers was tuned by reacting polymethylvinylsiloxane with different ratios of thioacetic acid/butanethiol, whereby butanethiol ensured a complete conversion of vinyl groups. The reduction of the thioester containing polysiloxanes by LiAlH_4 allows access to polymethylsiloxanes that carry thiols either as end- or side-groups. Such polymers offer themselves for a second functionalization event whereby thiol-ene reaction can be used. Furthermore, since the butanethiol can in principle be replaced by other functional thiols, the described procedure suggests the broad applicability of the method.

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GRAPHICAL ABSTRACT

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The thiol-ene addition of thioacetic acid to vinyl containing polysiloxanes allows introduction of protected thiols as end- or side-groups quantitatively within few min. The thioesters are subsequently deprotected to the respective thiols by reduction with LiAlH_4 . The resulting thiols can be used for another functionalization.