Thymine-functionalised siloxanes: model compounds and polymers

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Abstract

A novel, efficient synthetic method for the production of organosiloxane polymers functionalised with pendant DNA bases, typified by thymine, is reported. A condensation reaction between an $\alpha$-amino-$\omega$-alkylsilane or an amino-functionalised siloxane with aldehyde-functionalised thymine gave polymers in higher overall yields than the methods previously reported. Variation in the loading of thymine led to a range of material properties from a highly viscous fluid at 0.2% functionalization to a hard, brittle solid at 20% loading due to hydrogen bonding interactions.

Keywords: siloxane, thymine, hydrogen bonding, silicone, polymer

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Graphical abstract

Organosiloxane polymers functionalised with a pendant DNA base, thymine, have been prepared in high yield by condensation of amino-functionalised siloxanes with aldehyde-functionalised thymine.

Highlights

- Organosiloxanes functionalised with thymine have been prepared using a novel, efficient method
- Condensation of α-amino-ω-alkylsilanes or amino-functionalised siloxanes with aldehyde-functionalised thymine led to high molecular weight polymers
- Variation in thymine loading led to a range of material properties from highly viscous fluids to brittle solids
Introduction

We have previously reported an interest in the synthesis of organosiloxane polymers functionalised with pendant DNA (purine, pyrimidine) bases, as progress towards the production of ordered polymeric materials in which structure (and properties) are dictated by hydrogen bonding interactions between the DNA bases [1]. These well known complementary interactions have been exploited in forming supramolecular materials from several types of organic polymer [2, 3]. For example, Rowan et al. used [4] the nucleobase interactions to prepare liquid crystalline polymers that displayed thermoreversible phase behaviour. Other workers have prepared stimuli responsive surfaces [5, 6] which recognise the complementary nucleobases and also made use of the ability of thymine to form sandwich complexes with metals such as mercury for extraction and sensing. [7 - 9]

Thusfar, equivalent polymers with inorganic backbones have been relatively unexplored. However, the unique properties offered by a siloxane backbone [10] led us to explore the possibility of preparing silicones functionalised by nucleobases. Functional siloxanes can be prepared by anionic polymerization of small, three or four membered ring siloxanes carrying the functionality although a method with potentially wider applicability is to exploit a backbone carrying pendant vinyl groups onto which functionality can be added using hydrosilylation chemistry [11, 12].

Little work has been carried out involving nucleobase containing silicones although a number of amino acid-functionalised siloxanes have been reported. [13] Telechelic siloxanes terminated with quadruple hydrogen-bonding ureido-pyrimidone units which assembled into reversible high molecular weight polymers were reported by Meijer and co-workers. [14]

Our initial approach was either hydrosilylation of an alkenyl-substituted base or, alternatively, base-promoted coupling of a $\alpha$-bromo-$\omega$-alkylsilane and the appropriate heterocycle (thymine, cytosine, adenine or guanine). Although these approaches were successful, the synthetic sequences were complex and the overall yields low. Thus, alternative, more effective, coupling strategies are desirable and we report one such herein, namely a condensation reaction between a $\alpha$-amino-$\omega$-alkylsilane or an amino-functionalised siloxane and an aldehyde-functionalised base, typified by thymine.
Experimental

Experimental Procedures

Starting materials thymine, phenyldimethylsilane, chloroplatinic acid, benzaldehyde, p-tolualdehyde, α-bromo-p-tolualdehyde and the α,ω hydroxydimethylsiloxane oligomers were obtained from Sigma-Aldrich and (3-aminopropyl)diethoxymethylsilane, 3-bis-(3-aminopropyl)tetramethyldisiloxane from Fischer; all were used without further purification, while the α,ω hydroxydimethylsiloxanes and poly(dimethylsiloxane) functionalised at the 2 mol% level with 3-aminopropyl groups were gifts from Dow Corning.

Infra-red spectra were recorded as liquid films on NaCl plates using a Nexus Nicolet 510P FT-IR spectrometer in the region 4000 - 400 cm\(^{-1}\). \(^1\)H, \(^{13}\)C and \(^{29}\)Si spectra were recorded on Bruker Avance (300 or 400 MHz) Fourier transform spectrometers, using TMS as an internal reference. Elemental analyses were performed using a Carbo Erba Strumentazione E.A. mod 1106 analyser. The results were duplicated and the mean of the duplicated measurements was taken as the final result. Gel permeation chromatography, GPC, was carried out on 2 mg ml\(^{-1}\) samples in chloroform at a flow rate of 1 ml min\(^{-1}\) using refractive index detection and two ‘PLGel’ Mixed bed 30 cm columns with 10 μm packing at 30 °C. Molecular weights are reported relative to polystyrene calibration. DSC was carried out using a TA instruments calorimeter at a heating rate of 20 ° min\(^{-1}\) after cooling with liquid nitrogen.

**Synthesis of 1-amino-3-(phenyldimethylsilyl)propane (1).** Allylamine (2.30 g, 40 mmol), phenyldimethylsilane (2.50 g, 18.4 mmol) and a catalytic amount of chloroplatinic acid in propan-2-ol was heated at 90 °C for 18 h, after which the IR spectrum no longer displayed a peak at 2150 cm\(^{-1}\) corresponding to a Si-H stretching vibration. The volatiles were removed under reduced pressure and the resulting translucent grey liquid distilled under atmospheric pressure. The only product recovered was found to be (3-aminopropyl)phenyldimethylsilane (1) (55 %). Analysis, calcd for C\(_{11}\)H\(_{19}\)NSi: C 68.3, H 9.9, N 7.2 %, found C 67.8, H 9.9, N 7.2 %. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ = 7.48 (m, 2H, CH), 7.34 (m, 3H, CH), 2.64 (t, J = 7.0 Hz, 2H, CH\(_2\)NH\(_2\)), 1.43 (m, 2H, SiCH\(_2\)CH\(_2\)), 1.17 (s, 2H, NH\(_2\)), 0.73 (m, 2H, SiCH\(_2\)), 0.27 (s, 6H, Ph(CH\(_3\))\(_3\)Si)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): δ = 139.2 (CH), 133.5 (CH), 128.9 (CH), 127.7 (CH), 45.5 (CH\(_2\)NH\(_2\)), 28.2 (CH\(_2\)CH\(_2\)NH\(_2\)), 12.8 (SiCH\(_2\)), -3.1 (SiCH\(_2\)); \(^{29}\)Si NMR (60 MHz, CDCl\(_3\)): δ = -2.9.
Synthesis of 4-(5-Methyl-2,4-dioxo-3,4-dihydro-2H-pyrindin-1-ylmethyl)-benzaldehyde (2). A solution of thymine (0.63 g, 5 mmol), α-bromo-α-toluualdehyde (1.04 g, 5.2 mmol) and an excess of potassium carbonate (2.60 g, 18.8 mmol) in DMSO was stirred at room temperature for 18 h, after which a fine, voluminous precipitate had formed in the reaction mixture. The mixture was filtered and excess DMSO removed, affording a slightly oily yellow solid. The resulting solid was washed with water, dried in a dessicator, then finely divided with a pestle and mortar before being suspended in chloroform by vigorous stirring for 1 h. The suspension was filtered and dried to afford the air-stable product as a fine yellow powder (88 %, mp 177-9 °C). Analysis, calcd for C_{13}H_{12}O_3N_2: C 63.9, H 5.0, N 11.5 %, found C 63.5, H 4.9, N 11.1 %. 1H NMR (300 MHz, CDCl_3): δ = 10.02 (s, 1H, C-HO), 8.91 (bs, 1H, NH), 7.90 (d, J = 8.0 Hz, 2H, CH), 7.45 (d, J = 8.0 Hz, 2H, CH), 7.00 (s, 1H, CH), 4.97 (s, 2H, NC=CH), 1.91 (s, 3H, CC-H_3); 13C NMR (75 MHz, CDCl_3): δ = 191.5 (C-HO) 163.9 (C=O), 151.0 (C=O), 142.1 (CH), 139.6 (CH), 130.5 (CH), 128.3 (CH), 111.8 (CCH_3), 50.9 (NCH_2), 12.4 (CCH_3).

Synthesis of [3-(Dimethyl-phenyl-silanyl)-propyl]-[1-phenyl-meth-(E)-ylidene]-amine (3). Benzaldehyde (0.32 g, 3.02 mmol) was added to a stirred suspension of anhydrous magnesium sulphate in dichloromethane. Once the benzaldehyde had dissolved, 1 was added and the mixture stirred at room temperature for 18 h, after which the IR spectrum revealed complete consumption of starting material. The mixture was filtered and the excess dichloromethane removed under reduced pressure to afford the slightly moisture sensitive imine product. Some degradation of the imine was noted with time so it was stored under dry nitrogen. Yield: 0.68 g, 80%. Analysis, calcd for C_{18}H_{23}NSi: C 76.8, H 8.2, N 5.0 %, found C 76.2, H 8.3, N 5.0 %. 1H NMR (300 MHz, CDCl_3): δ = 8.20 (s, 1H, HC=N), 7.70 (d, J = 8.0 Hz, 2H, CH), 7.51 (m, 2H, CH), 7.35 (m, 3H, CH), 7.33 (m, 3H, CH), 3.58 (t, J = 7.0 Hz, 2H, CH_2N=CH), 1.73 (m, 2H, SiCH_2CH_2), 0.78 (m, 2H, SiCH_2CH_2), 0.28 (s, 6H, Si(CH_3)_2); 13C NMR (75 MHz, CDCl_3): δ = 160.9 (HC=N), 139.2 (CH), 136.3 (CH), 133.6 (CH), 130.4 (CH), 128.8 (CH), 128.5 (CH), 128.0 (CH), 127.7 (CH), 65.0 (CH_2N=CH), 25.4 (SiCH_2CH_2), 13.3 (SiCH_2), -3.1 (SiCH_3); 29Si NMR (60 MHz, CDCl_3): δ = -2.9.

Also prepared by the same method were:
[3-(Diethoxy-methyl-silanyl)-propyl]-[1-phenyl-meth-(E)-ylidene]-amine (4): Using benzaldehyde (0.32 g, 3.02 mmol) and (3-aminopropyl)diethoxymethylsilane (1.00 g, 5.23 mmol). Yield: 0.51 g, 60%. Analysis, calcd for C_{18}H_{28}O_{2}NSi: C 64.5, H 9.0, N 5.0 %, found C 65.2, H 8.9, N 5.0 %. 1H NMR (300 MHz, CDCl₃): δ = 8.26 (s, 1H, HC=N), 7.72 (m, 2H, CH), 7.36 (m, 3H, CH), 3.76 (q, J = 7.0 Hz, 4H, SiOCH₂CH₃), 3.61 (t, J = 7.0 Hz, 2H, CH₂N=CH), 1.79 (m, 2H, SiCH₂CH₃), 1.21 (t, J = 7.0 Hz, 6H, SiOC₂H₃), 0.66 (m, 2H, SiCH₂CH₂), 0.13 (s, 3H, SiH₃); 13C NMR (75 MHz, CDCl₃): δ = 160.9 (HC=N), 136.4 (CH), 130.5 (CH), 128.6 (CH), 128.1 (CH), 64.6 (CH₂N=CH), 58.2 (SiOCH₂CH₃), 24.4 (SiCH₂CH₂), 18.5 (SiOCH₂CH₃) 11.6 (SiH₃), -4.9 (SiH₃); ²⁹Si NMR (60 MHz, CDCl₃): δ = -4.8.

1-(4-[[(E)-3-(Dimethyl-phenyl-silanyl)-propylimino]-methyl]-benzyl)-5-methyl-1H-pyrimidine-2,4-dione (5): Using 1 (0.26 g, 1.35 mmol) and 2 (0.21 g, 0.86 mmol):
Yield: 0.20 g, 55%. Analysis, calcd for C_{23}H_{30}N₂O₃Si: C 68.7, H 7.0, N 10.0 %, found C 68.2, H 6.9, N 9.9 %. 1H NMR (300 MHz, CDCl₃): δ = 8.21 (s, 1H, HC=N), 7.72 (d, J = 8.0 Hz, 2H, CH), 7.50 (m, 2H, CH), 7.33 (m, 5H, CH, overlapping signals), 6.95 (s, 1H, CH), 4.90 (s, 2H, CH₂N), 3.58 (t, J = 7.0 Hz, 2H, CH₂N=CH), 1.88 (s, 3H, CCH₃), 1.72 (m, 2H, SiCH₂CH₂), 0.74 (m, 2H, SiCH₂), 0.27 (s, 6H, SiH₃); 13C NMR (75 MHz, CDCl₃): δ = 161.9 (C=O), 160.1 (HC=N), 150.0 (C=O), 142.9 (CH), 139.6 (CH), 139.2 (CH), 136.6 (CH), 133.6 (CH), 130.0 (CH), 128.8 (CH), 128.2 (CH), 127.8 (CH), 111.4 (CCH₃), 64.5 (CH₂N=CH), 22.4 (SiCH₂CH₂), 12.8 (SiCH₂), 12.4 (CCH₃), -3.1 (SiH₃); ²⁹Si NMR (60 MHz, CDCl₃): δ = -2.8.

1-(4-[[(E)-3-(Diethoxy-methyl-silanyl)-propylimino]-methyl]-benzyl)-5-methyl-1H-pyrimidine-2,4-dione (6):
Using (3-aminopropyl)diethoxymethylsilane (0.57 g, 3.02 mmol) and 2 (0.74 g, 3.02 mmol). Yield: 0.90 g, 71%. Analysis, calcd for C_{23}H_{30}N₂O₃Si: C 60.3, H 7.7, N 10.0 %, found C 60.1, H 7.7, N 9.9 %. 1H NMR (300 MHz, CDCl₃): δ = 8.26 (s, 1H, HC=N), 7.74 (d, J = 8.0 Hz, 2H, CH), 7.33 (d, J = 8.0 Hz, 2H, CH), 6.96 (s, 1H, CH), 4.91 (s, 2H, CH₂N), 3.76 (q, J = 7.0 Hz, SiOCH₂CH₃) 3.61 (t, J = 6.8 Hz, 2H, CH₂N=CH), 1.89 (s, 3H, CCH₃), 1.78 (m, 2H, SiCH₂CH₂), 1.21 (t, J = 7.0 Hz, 6H, SiOCH₂CH₃), 0.64 (m, 2H, SiCH₂), 0.13 (s, 3H, SiH₃); 13C NMR (75 MHz, CDCl₃): δ = 164.0 (C=O), 160.2 (HC=N), 151.1 (C=O), 143.4 (CH),...
139.6 (CH), 136.5 (CH), 128.2 (CH), 111.4 (CCH3), 64.6 (CH2N=CH), 58.1 (SiOCH2CH3), 45.1 (CH2N),
27.2 (SiCH2CH3), 18.4 (SiOCH2CH3), 11.0 (SiCH3), -4.9 (SiCH3); \(^{29}\)Si NMR (60 MHz, CDCl3): \(\delta = -4.6\).

Synthesis of \([3\text{-}[1,1,3,3\text{-Tetramethyl-3-}([1\text{-p-tolyl-meth-(E)-ylidene]}\text{-amino})\text{-propyl]}\text{-disiloxany}]\text{-propyl]}\text{-[1-p-tolyl-meth-(E)-ylidene]}\text{-amine}
(7). \(p\)-Tolualdehyde (0.25 g, 2.01 mmol) and 3-bis-(3-
aminopropyl)tetramethyldisiloxane (0.50 g, 2.01 mmol) were added to a stirred suspension of anhydrous
magnesium sulphate in dichloromethane and the reaction stirred at room temperature until the IR
spectrum revealed complete loss of starting material. The mixture was filtered and removal of excess
dichloromethane afforded (7) as an orange-brown oil (Yield: 92 %) with no further purification. Analysis,
calcd for C\(_{26}\)H\(_{30}\)N\(_2\)Si\(_3\)O: C 69.0, H 8.9, N 6.2 %, found C 68.8, H 8.8, N 6.2 %. \(^{1}\)H NMR (300 MHz, CDCl3):
\(\delta = 8.14 \text{ (s, 1H, HC=N)}, 7.54 \text{ (d, J = 8.0 Hz, 2H, CH)}, 7.14 \text{ (d, J = 8.0 Hz, 2H, CH)}, 3.50 \text{ (t, J = 7.0 Hz, 2H,}
CH\(_2\)N=CH), 2.30 \text{ (s, 3H, CCH\(_3\))}, 1.65 \text{ (m, 2H, SiCH\(_2\)CH\(_2\))}, 0.48 \text{ (m, 2H, SiCH\(_2\)CH\(_2\))}, 0.02 \text{ (s, 6H, SiCH\(_3\))};
\(^{13}\)C NMR (75 MHz, CDCl3): \(\delta = 160.2 \text{ (HC=N)}, 140.2 \text{ (CH)}, 133.4 \text{ (CH)}, 128.9 \text{ (CH)}, 127.7 \text{ (CH)}, 64.5
(CH\(_2\)N=CH), 24.5 (CCH\(_3\)), 21.1 (SiCH\(_2\)CH\(_2\)), 15.7 (SiCH\(_2\)CH\(_2\)), -0.4 (SiCH\(_3\)); \(^{29}\)Si NMR (60 MHz, CDCl3): \(\delta = 7.7\).

Synthesis of iminopropylthymine functionalised siloxane. (8) Reaction between 2 and poly(dimethyl-co-2%
aminopropylmethyl)siloxane. 2 (0.50 g, 2.05 mmol) was added to a stirred suspension of anhydrous
magnesium sulphate in dichloromethane and allowed to dissolve. To this was added PDMS incorporating
2 mol% aminopropyl functionality (7.75 g, 2.05 mmol), and the mixture was stirred at room temperature for
18 h, after which the mixture had visibly thickened and the IR spectrum indicated no further growth in the
C=N imine stretch (1600 – 1630 cm\(^{-1}\)). The mixture was diluted with dichloromethane before being filtered,
washed with a small amount of water and dried over anhydrous MgSO\(_4\). Upon removal of the volatiles a
very thick, air stable yellow rubber was recovered and found to be PDMS containing approximately 2
mol% iminopropylthymine functionality (8) via a propyl imine linkage. \(^{1}\)H NMR (300 MHz, CD\(_3\)\(_2\)CD\(_3\)): \(\delta = 8.05 \text{ (s, 1H, HC=N)}, 7.11 \text{ (m, 2H, CH)}, 7.02 \text{ (m, 2H, CH)}, 6.96 \text{ (s, 1H, CH)}, 3.60 \text{ (t, J = 7.0 Hz, 2H,}
CH\(_2\)N=CH), 1.90 \text{ (s, 3H, CCH\(_3\))}, 1.60 \text{ (m, 2H, SiCH\(_2\)CH\(_2\))}, 0.80 \text{ (m, 2H, SiCH\(_2\)CH\(_2\))}, 0.26 \text{ (s, ~ 300H,}
SiCH\(_3\)); \(^{13}\)C NMR (75 MHz, CD\(_3\)\(_2\)CD\(_3\)): \(\delta = 1.4 \text{ (SiCH\(_3\))}; \(^{29}\)Si NMR (60 MHz, CD\(_3\)\(_2\)CD\(_3\)): \(\delta = -21.5\); Analysis,
calcd for C\textsubscript{115}H\textsubscript{315}N\textsubscript{3}O\textsubscript{52}Si\textsubscript{50} i.e. full conversion of the 2mol% loading: C 34.7, H 8.0, N 1.1 %; found C 31.7, H 7.6, N 0.7 %; GPC (relative to polystyrene): Mn 21,000, Mw/Mn 3.6.

**Synthesis of poly(dimethyl-co-aminopropyl)methyl)siloxane.** (9) A equimolar mixture of \(\alpha,\omega\) hydroxydimethylsiloxane oligomer (with 5, 11 or \(~\)700 siloxane units) and 3-(diethoxymethylsilyl)propylamine was heated and stirred overnight with one drop of 10% HCl under a nitrogen atmosphere to give approximate loadings of aminopropyl sidechains of \(~\)20 mol%, \(~\)10 mol% and \(~\)0.2 mol%, respectively. In each case a clear, very viscous polymer was obtained. The NMR spectra were qualitatively identical: \(^1\)H NMR (300 MHz, C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3}): \(\delta = 2.60\) (m, CH\textsubscript{2}NH\textsubscript{2}), 1.40 (m, SiCH\textsubscript{2}CH\textsubscript{2} and CH\textsubscript{2}NH\textsubscript{2}), 0.45 (m, SiCH\textsubscript{2}CH\textsubscript{2}), 0.00 (s, SiCH\textsubscript{3}). \(^{13}\)C NMR (75 MHz, C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3}): \(\delta = 44.3\) (CH\textsubscript{2}NH\textsubscript{2}), 26.4 (SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 13.4 (SiCH\textsubscript{2}), 0.0-0.5 (SiCH\textsubscript{3}). \(^{29}\)Si (60 MHz, C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3}): \(\delta = -22.0, -22.6\).

The procedure described above for 8 was then used to add 2 to each of these propylamine-functionalised siloxanes (9) to give polymers functionalised with varying degrees of thymine (10).

**Crystallography**

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 1. Data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-K\(_x\) radiation (\(\lambda = 0.71073\) Å). Structure solution was followed by full-matrix least squares refinement and was performed using the WinGX-1.70 suite of programmes [15]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added in calculated positions which were located and freely refined, save H(1) which is involved in hydrogen bonding.
Table 1. Crystal data for 2

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Results and Discussion

1-amino-3-(phenyldimethylsilyl)propane (1) was prepared by the hydrosilylation of allylamine, catalysed by chloroplatinic acid, as a colourless, air-stable liquid (55% yield):

\[
\text{PhMe}_2\text{SiH} + \text{H}_2\text{C}=\text{C(H)CH}_2\text{NH}_2 \xrightarrow{[\text{H}\text{PtCl}_4\text{]}_{\text{propan-2-ol}}} \text{PhMe}_2\text{Si}(\text{CH}_2)_3\text{NH}_2
\]  

(1)

Only theω-silyl isomer was recovered, suggesting that the steric bulk of the silyl group has directed the regiochemistry of the reaction to produce exclusively the linear isomer of 1 by reacting at the terminal end of the olefin. Although briefly reported some years ago by others [16 - 18], 1 remains poorly characterised. The singlet at δ = -2.9 ppm in the ²⁹Si NMR, shows good agreement with the corresponding resonance of 4-(phenyldimethylsilyl)-1-bromobutane [δ = -3.0 ppm] [1].

The required purine-substituted tolualdehyde (2) was synthesised in very good yield from 1-bromo-p-tolualdehyde and thymine:

\[
\begin{align*}
\text{Br} & \quad \begin{array}{c}
\text{CHO} \\
\text{H} \\
\text{O} \\
\text{N}
\end{array} & \xrightarrow{\text{K}_2\text{CO}_3\text{, DMF}} & \begin{array}{c}
\text{CHO} \\
\text{H} \\
\text{O} \\
\text{N}
\end{array}
\end{align*}
\]  

(2)

The peak due to the methylene protons α to nitrogen in the ¹H NMR of 2 compares well with the analogous peak in benzylthymine [δ = 4.87 ppm] [19], suggesting similar N¹-substitution. The asymmetric unit of the crystal of 2 (Figure 1) is formed of a single molecule in which 1-bromo-p-tolualdehyde has added to thymine at the N-1 position [N(2)-C(6) 1.475(2) Å], at a distance which compares well with N¹-Cα distances in similar molecules such as (trimethylsilyl)-1-allylthymine [1.474(2) Å] and (4-phenyldimethylsilyl)butylthymine [1.4778(19) Å] [1]. The C=C double bond [C(2)-C(3) 1.342(3) Å], the endocyclic N¹-C bonds [N(1)-C(1) 1.386(2) Å, N(1)-C(4) 1.375(2) Å] and the endocyclic N¹-C bonds [N(2)-C(3) 1.383(2) Å, N(2)-C(4) 1.367(2) Å] in the thymine ring each compare well in length to the analogous bonds in thymine [C(2)-C(3) 1.343(4), N(1)-C(1) 1.401(5), N(1)-C(4) 1.361(4), N(2)-C(3) 1.384(5), N(2)-
C(4) 1.358(4) Å, [20] showing that little or no ring distortion has taken place in 2 to accommodate the \( \rho \)-tolualdehyde group. The angle at bridging C(6) [N(2)-C(6)-C(7) 112.23(14)°] is relatively wide, to accommodate the bulk of the two rings, though the heterocyclic bond angles around the two nitrogen atoms [C(3)-N(2)-C(4) 121.62(14), N(1)-C(4)-N(2) 115.01(14), C(1)-N(1)-C(4) 126.85(15)°] are again similar to the analogous angles in thymine [C(3)-N(2)-C(4) 122.5(3), N(1)-C(4)-N(2) 115.5(2), C(1)-N(1)-C(4) 126.3(3)°] [20]. The angles around the N\(^1\)-C\(_\alpha\) bond [C(3)-N(2)-C(6) 119.26(14)°, C(4)-N(2)-C(6) 119.10(14)°, C(3)-N(2)-C(4) 121.62(14)°] compare well with those in (4-phenyldimethylsilyl)-butylthymine [C(3)-N(2)-C(6) 119.59(13)°, C(4)-N(2)-C(6) 118.77(13)°, C(3)-N(2)-C(4) 121.48(13)°].

Figure 1. The structure of 2 showing the labelling scheme of the asymmetric unit and intermolecular hydrogen bonding interactions; thermal ellipsoids are at the 50% level. Selected geometric data: N(1)-C(1) 1.386(2), N(1)-C(4) 1.375(2), N(2)-C(3) 1.383(2), N(2)-C(4) 1.367(2), N(2)-C(6) 1.475(2), C(1)-O(1) 1.226(2), C(4)-O(2) 1.226(2), C(2)-C(3) 1.342(3), C(6)-C(7) 1.510(2), C(13)-O(3) 1.202(2) Å; C(1)-N(1)-C(4) 126.85(15), C(3)-N(2)-C(6) 119.26(14), C(3)-N(2)-C(4) 121.62(14), C(4)-N(2)-C(6) 119.10(14), C(2)-C(3)-N(2) 123.11(15)°. Symmetry operations: ’ 1-x,1-y, -z; ”-x-1/2, ½+y, ½-z
The molecule forms a dimer via two symmetry related N-H---O hydrogen bonds \([H(1)---O(2) 1.89(3) \text{ Å}; N(1)-H(1)---O(2) 176(2)]\), the same length within experimental error as hydrogen bonds in (4-phenyldimethylsilyl)butylthymine \([1.97(2) \text{ Å}; 172(2)^\circ] [1]\). \(2\) further interacts via a C-H---O hydrogen bond \([H(3)---O(3) 2.30 \text{ Å}]\) to form a supramolecular chain of dimers, longer than analogous bonds in compounds such as 1-methylcytosine \([H(1)---O(2) 2.04(2) \text{ Å}] [21]\), but similar in length to that found in (trimethylsilyl)-1-allylthymine \([2.29, 2.34 \text{ Å}] [1]\). Notably, this hydrogen bond involves the carbonyl group of the aldehyde, not the second exocyclic C=O of the heterocycle. The bond in \(2\) is, however, considerably closer to linearity \([C(3)-H(3)---O(3) 172.8^\circ]\) than the analogous bond in (trimethylsilyl)-1-allylthymine \((158.8, 164.0^\circ) [1]\). Analogous C-H---O hydrogen bonds are also seen in the lattice structures of uracil \([22]\) and 1-methylcytosine \([21]\). Despite the differing hydrogen bond interactions in \(2\), the two C=O bond lengths associated with the thymine residue are identical \([1.226(2) \text{ Å}]\) despite the fact that O(1) is not involved in any intermolecular interaction, while weakly hydrogen bonded C=O(3) retains significant double-bond character \([C(13)-O(3) 1.202(2) \text{ Å}]\). This is in marked contrast to, for example, thymine \([20]\) and uracil \([22]\), where a marked lengthening of the carbonyl bond involved in C=O---H-N bonding \([ca. 1.245 \text{ Å}]\) is seen in comparison to the passive C=O \([ca. 1.215 – 1.225 \text{ Å}]\). In both thymine and uracil, one C=O is long \((ca 1.244 \text{ Å})\) and is associated with a strong C=O---HN hydrogen bond, while a shorter C=O \((ca 1.22 \text{ Å})\) is associated with a much weaker C=O---HC hydrogen bond. In \(2\), the non-H bonded C=O, at 1.226Å, is similar to the latter while some lengthening of the other, relatively short, C=O (also 1.226Å) associated with the C=O---HN hydrogen bond might be anticipated. There is no obvious electronic reason for this not occurring, so it is presumably a consequence of packing factors.

Having established that \(2\) could be synthesised in high yield and purity, the next stage involved coupling of the aldehyde (or, as a model reaction, of benzaldehyde) with an aminosilane to form precursors for siloxanes via imine formation. The reactions were monitored until there was no further observable increase in the intensity of the IR band due to \(\nu(C=N)\) at 1600 – 1630 cm\(^{-1}\) or no further decrease in the \(\nu(C=O)\) stretch at 1710 cm\(^{-1}\).

The imines were isolated as slightly moisture sensitive solids in 55 – 80% yield. In addition to \(^1\)H and \(^{13}\)C NMR spectra which confirm imine formation \([\delta(HC=N)): 8.20 – 8.26 \text{ ppm}; \delta(HC=N): 160.1 – 160.9 \text{ ppm}]\), \(3 – 6\) display singlet \((\delta \text{ } ^{29}\text{Si})\) peaks with shifts in the range -2.8 - -4.6 ppm.
was reacted with

Commercially available poly(dimethylsiloxane) functionalised with ~2 mol% of 3-aminopropyl sidechains was reacted with 2 to afford, after solvent removal, polymer 8 as an air-stable rubbery material.
The low polymer loading of functionalised side-chains means that the NMR spectra of 8 are essentially those of the siloxane backbone i.e. $^1$H $\delta = 0.26$; $^{13}$C $\delta = 1.4$; $^{29}$Si $\delta = -21.5$ ppm, corresponding to the dominant Me$_2$Si group; the loading of functionalised silyl groups is too low for a distinct signal to be observable. However, 8 also displays weak signals at $\delta = 0.80$, 1.60 and 3.60 ppm, corresponding to the methylene protons $\alpha$, $\beta$ and $\gamma$ to silicon respectively, while resonances at $\delta = 1.90$ and 6.96 ppm were assigned to the methyl group attached to thymine and the heterocyclic ring proton, respectively, and those at $\delta = 7.02$ and 7.11 ppm were assigned to the protons in the pendant phenyl group; a signal at $\delta = 8.05$ was observed for the imine proton.

The number average molecular weight of 8, measured by gel permeation chromatography relative to polystyrene, was 21,000, with a polydispersity of 3.6, indicating that the grafting of 2 onto the aminopropyl functionalised PDMS resulted in a stable siloxane polymer. The molecular weight of the repeat unit of PDMS is 74, suggesting a chain backbone containing the order of a few hundred repeat units although it should be noted that the GPC calibration with polystyrene rules out a fuller quantitative analysis. The end-group signals in the NMR were too weak to allow accurate quantification of chain lengths.

In order to vary the amount of thymine available for hydrogen bonding within the material, polymers with variable amine content were needed. These (9) were produced by acid-catalysed reaction of 3-(diethoxymethylsilyl)propylamine with a poly(dimethyl siloxane) diol of various chain lengths ($x = 5, 11, \sim 700$), where loss of ethanol afforded the amine-functionalised co-polymers with varying amine loadings ($\sim 0.2, \sim 10, \sim 20\%$). The co-polymers were soluble in toluene and the NMR spectra were unremarkable with peak assignments similar to those of 1 and 8.
Functionalisation of 9 with 2 proceeded as described earlier (Eqn. 6). The resulting polymers (10) were very sparingly soluble although NMR characterisation confirmed the nature of the materials and inclusion of 2. In each case, marked physical changes were noted. Prior to reaction with 2, the amino-functionalised polymers 9 were clear fluids which, while viscous, retained flow characteristics. Inclusion of ~0.2 mol% 2 gave a material which was more viscous but retained the ability to flow. Higher levels of 2 gave rubbery materials, each pale yellow in colour (Figure 2) while the 20 mol% polymer formed a powdery, brittle solid. These changes are suggestive of increasing interaction between the chains, most likely between the pendant thymine molecules forming hydrogen-bonded links analogous to those reported in the model compound (2) above (Figure 1). While it is not possible to state definitively whether hydrogen bonding interactions are intra-polymer or crosslinks between different polymer strands, such crosslinks would most readily explain the very limited solubility of these materials which has hampered fuller characterisation, particularly by GPC. A preliminary small-angle X-ray scattering experiment on samples of 8 suggested that there may be some degree of order in the material with a repeat distance of 7.8 Å. However, further work is required to confirm this and to identify the precise nature of the interactions.

Figure 2. Siloxane polymers functionalised with varying levels of 2.
Figure 3 shows DSC thermograms recorded on the materials. Prior to functionalization with 2, the polymers with low amine loadings (< 10 mol%) show a PDMS melting transition around ~ -40°C, consistent with literature values [23]. The same transition was noted in the thymine modified materials although it was less prominent. These materials also show a second, broad melting transition around 70 – 100 °C. This is significantly below the melting point of 2 (177-9 °C) but does provide further evidence for some interchain interactions. The transition becomes more prominent as the amount of thymine in the polymer increases. At the highest loading, some interaction between the aminosiloxanes is apparent even in the absence of thymine.

Figure 3. DSC thermograms of amino- and thymine functionalised polysiloxanes.
Conclusions

While the intractable nature of the materials containing high concentrations of thymine make complete characterisation difficult, we have established a reliable methodology for functionalising polysiloxanes with thymine. Related chemistry with other purine and pyrimidine bases should follow the same procedures allowing a fuller exploration of the potential for these polymers to form materials with interesting and useful properties.

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References

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Figure captions

Figure 1. The structure of 2 showing the labelling scheme of the asymmetric unit and intermolecular hydrogen bonding interactions; thermal ellipsoids are at the 50% level. Selected geometric data: N(1)-C(1) 1.386(2), N(1)-C(4) 1.375(2), N(2)-C(3) 1.383(2), N(2)-C(4) 1.367(2), N(2)-C(6) 1.475(2), C(1)-O(1) 1.226(2), C(4)-O(2) 1.226(2), C(2)-C(3) 1.342(3), C(6)-C(7) 1.510(2), C(13)-O(3) 1.202(2) Å; C(1)-N(1)-C(4) 126.85(15), C(3)-N(2)-C(6) 119.26(14), C(3)-N(2)-C(4) 121.62(14), C(4)-N(2)-C(6) 119.10(14), C(2)-C(3)-N(2) 123.11(15)°. Symmetry operations: ′ 1-x,1-y, z; ″ -x+1/2, ½+y, ½-z

Figure 2. Siloxane polymers functionalised with varying levels of 2.

Figure 3. DSC thermograms of amino- and thymine functionalised polysiloxanes.
Fig 2.

0.2 mol%  2 mol%  20 mol%
Fig. 3

0.2 mol% aminosiloxane

0.2 mol% aminosiloxane + thymine

2 mol% aminosiloxane

2 mol% aminosiloxane + thymine

20 mol% aminosiloxane

20 mol% aminosiloxane + thymine

Temperature / °C