Supplementary Material (ESI) for Chemical Communications

Supporting Information

Versatile, efficient derivatization of polysiloxanes *via* Click technology

Ferdinand Gonzaga,* Gilbert Yu, and Michael A. Brook*

Department of Chemistry, McMaster University, 1280 Main St. W., Hamilton Ontario, L8S 4M1

* (E-mails: gonzaga@mcmaster.ca; mabrook@mcmaster.ca)

OUTLINE OF SUPPORTING INFORMATION

Experimental Section

1) Materials and methods

1,3-Bis(chloropropyl)tetramethyldisiloxane and (chloropropyl)- methylsiloxane-dimethyl-siloxane copolymer (14-16 mole% (chloropropyl) methylsiloxane) were obtained from Gelest/ABCR and Gelest, respectively. Sodium azide (95%) was purchased from J. T. Baker. Sodium iodide (99%), adipoyl chloride (97%), pyridine (99%), propargyl alcohol (99%), 3-butyn-2-methyl-2-ol (98%), phenylacetylene (98%), propargyl amine (98%), Boc-L-alanine (98%), Cbz-L-valine (99%) and dimethylacetylene dicarboxylate (99%), gluconolactone (99%) were obtained from Sigma-Aldrich. Triethylamine (99%) was purchased from EMD. Sodium ascorbate (98%) and EDC (98%) were obtained from Fluka, while copper(II) sulfate pentahydrate (99%) was purchased from Fisher Scientific. All materials were used as received.

IR analysis was made using a Bio-Rad Infrared Spectrometer (FTS-40). ^{1}H NMR and ^{13}C NMR was recorded at room temperature on a Bruker AC-200 spectrometer using $CDCl_3$ or DMSO as solvent. High-resolution mass spectrometry was performed with a Hi-Res Waters/Micromass Quattro Global Ultima (Q-TOF mass spectrometer). TGA analysis was performed using NETZCH STA 409 PC/PG.

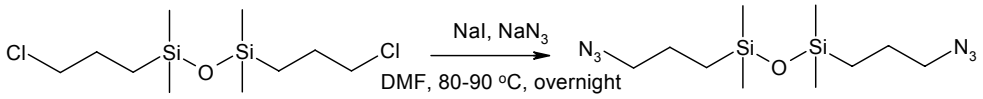
Precursors for click-reaction of silicones include azide- or alkyne-terminated siloxanes. Chloropropyl-terminated siloxanes are available in a wide range of molecular weights, and it was reasoned that a classical nucleophilic substitution by the azide anion would yield the corresponding azidopropyl derivative.

2) Synthesis and TGA Analysis of Azido-terminated siloxanes 1 and 2

BATPMDS **1** was obtained by dissolving sodium azide (6.2 g, 96 mmol, 3 equiv.), sodium iodide (9.3 g, 62 mmol, 2 equiv.), and 1,3-bis(chloropropyl)tetramethyldisiloxane (9.0 g, 31 mmol, 1 equiv.) in DMF (40 mL). The mixture was stirred until all reagents dissolved and then heated at 90 °C overnight. The reaction was stopped after ^{1}H NMR showed the absence of the 1,3-bis(chloropropyl)tetramethyldisiloxane starting material. The reaction mixture was

then partitioned between water and dichloromethane. The organic phase was separated, dried over sodium sulfate, then evaporated to give 9.7 g (96%) of the title compound as a light yellow liquid. ^{1}H NMR ($CDCl_3$): δ = 3.22 (t, *J* = 7.0 Hz, 4H), 1.59 (m, 4H), 0.539 (m, 4H), 0.056 (s, 12 H); ^{13}C NMR ($CDCl_3$): δ = 54.1, 22.9, 15.2, 0.3; IR (KBr, cm^{-1}): 2097 (N_3); HRMS (ESI): m/z calculated: $[M+Ag]^+$ = 407.0601, found: $[M+Ag]^+$ = 407.0620

SCHEME 2



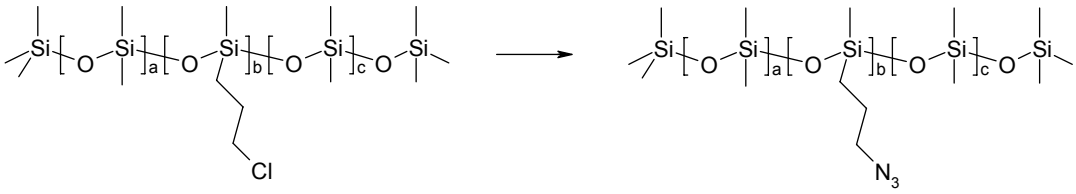
The reaction was followed by proton NMR, which shows the total disappearance of the triplet at 3.52 ppm (protons in α to chlorine) and their replacement by a triplet at 3.22 ppm (protons α to the azido moiety). It should be noted here that while most azides can be handled without any incident, some members of this class are explosives.[32] To establish the thermal stability of the model compound, Thermogravimetric Analysis (TGA) was performed (Figure 1A). TGA analysis did not reveal any sudden decomposition characteristic of an explosive behavior. Instead, a regular weight loss starting from about 105 °C was observed, despite the presence of 2 azido moieties in the model compound BAPTMDS. This slow decomposition occurs starting at temperatures well above those required to perform thermal click cycloadditions (from below room temperature to *ca*. 90 °C, depending on the alkyne reactivity).

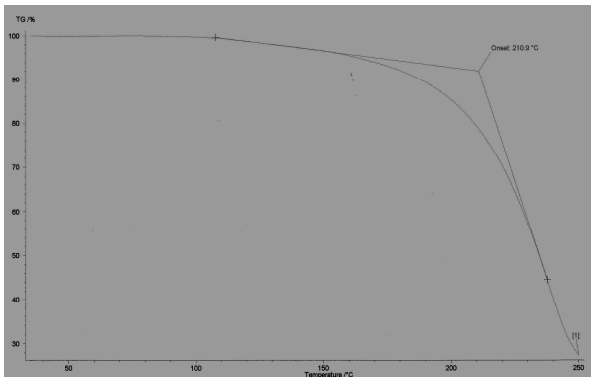
Polymeric azidoalkylsilicones can also be formed from chloroalkylsilicones. Commercially available dimethylsilicone-co-methylchloropropylsilicones were converted, in an analogous manner to that described above, to the polyazide **2** in DMF. The reaction worked very well particularly given the normal challenges of dissolving hydrophilic salts in hydrophobic media such as silicones (see Scheme 3). The product was isolated in a yield of nearly 100%: no residual chloropropyl groups could be observed by ^{1}H NMR. TGA analysis (Figure 1B) showed that the polyazido compound was even more thermally stable than the BAPTMDS (Figure 1A), with

onset of decomposition at about 211 °C. Thus, as confirmed below, these materials will undergo cycloaddition reactions at temperatures well below their decomposition temperatures.

The polymer of Scheme 3 was obtained by dissolving chloropropyl)methylsiloxane-dimethylsiloxane copolymer (14-16 mole% (chloropropyl)methylsiloxane, 10.0 g) in 40 ml of a mixture of DMF and THF (1:1; v:v). Sodium azide (1.0 grams, 15 mmol) was then added, and the mixture was heated at 70 °C for 24 h. At this stage, the reaction was found to be incomplete by proton NMR. Therefore, additional sodium azide (1.0 gram, 15 mmol) was added, and the mixture was heated at 70 °C until completion (48 additional hours, as indicated by proton NMR). The reaction medium was then cooled, added to 300 mL of water, and extracted twice with 100 mL of a mixture of hexanes and ethyl acetate (1:1; v:v). The combined organic phase was dried over Na_2SO_4. Volatiles were removed in vacuo to yield 9.9 grams (99%) of the title compound. ^{1}H NMR ($CDCl_3$): δ = 4.64 (d, J = 2.4 Hz, 18H), 2.44 (m, 2H), 2.32 (m, 2H), 1.66 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 54.2, 22.9, 14.6, 1.2; IR (KBr, cm^{-1}): N_3 stretch = 2097 cm^{-1}(s); MS (MALDI-TOF): 6000 (6188-6378), 10000 (10280-10642), 12000 (12318-12872)

SCHEME 3



A 

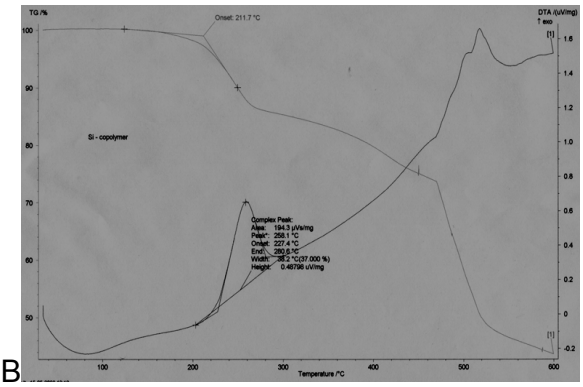
B 

Figure 1A shows a Thermogravimetric Analysis (TGA) of **1**; and Figure 1B shows a Thermogravimetric Analysis (TGA) of a polyazidopropylsilicone, **2**.

3) Synthesis of Alkynyl derivatives

Alkynylgluconamide[38] (**Error! Reference source not found.** 1, Entry 7), *N*-(tert-Butoxycarbonyl)-L-alanine-*N*'-propargylamide[39] (**Error! Reference source not found.** 1, Entry 9) were prepared following literature procedures and *N*-Cbz-L-valine-*N*'-propargylamide (**Error! Reference source not found.** 1, Entry 8) was characterized as follows: ^{1}H NMR ($CDCl_3$): δ = 8.40 (t, J = 5.0 Hz, 1H), 7.35 (s, 5H), 4.95 (s, 2H), 3.85 (m, 2H), 3.10 (s, 1H), 1.91 (m, 1H), 0.82 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ = 171.1, 156.1, 137.1, 128.3, 127.7, 81.0, 72.9, 65.4, 60.1, 30.3, 27.8, 19.1, 18.3; IR (KBr, cm^{-1}) = 3314 (≡C-H (stretch), 3275 (NH), 1685 (C=ONH), 1650 (Ar stretching); HRMS (ESI): m/z $[M+H]^+$ calculated = 289.1552. $[M+H]^+$ found: 289.1552.

4) General procedures for thermal Huisgen cycloadditions

The thermal Huisgen cycloaddition reaction of BAPTMDS was carried out at 90 °C with two common alkynes, propargyl alcohol and phenylacetylene, respectively. The alkyne was used as both reagent and solvent for the reaction. Both reactions occurred efficiently: click ligation with propargyl alcohol was complete within only 3 hours, while phenylacetylene required a longer reaction time (*ca.* 16 to 20 hours). In the two cases, simple removal of the excess alkyne under reduced pressure yielded the click adduct in quantitative yield (Table 1).

The reaction was repeated with both alkynes at room temperature and no reaction was evident after 1 day of reaction. Thus, thermally-catalyzed click ligation was found to be slow/undetectable at low temperature, but efficacious at higher temperatures. Such a reaction profile is ideal for the processing of a silicone elastomer, which could be sold as a two part or one part mixed system that will not cure until exposed to elevated temperatures.

The general procedure for the thermal reaction of BAPTMDS with alkynes is illustrated by the thermal reaction between BAPTMDS with propargyl alcohol (Table 1, entry 1): In a 5 mL round-bottomed flask, 1,3-bis(azidopropyl)-tetramethyldisiloxane (300 mg, 1.00 mmol) and propargyl alcohol (1.0 mL, 17.18 mmol) were stirred at 90 °C under a nitrogen atmosphere. Proton NMR indicated that the reaction was complete within 3 h. The resulting mixture was then subjected to vacuum to remove the excess volatile alkyne to yield 412 mg of the product (100% yield). This product was composed of 3 regioisomers (bis-1,4 click addition; bis-1,5 click addition; mixed 1,4-and 1,5-click additions). No attempts were made to separate these regioisomers: ^{1}H NMR ($CDCl_3$): δ = 7.57 (s, 1.1H), 7.50 and 7.48 (2 singlets, 0.9H). The first signal at 7.57 ppm is attributed to the regioisomer having the 2 hydroxymethyl in position 4 of the triazolyl ring (55% of the addition), while the 2 other singlets correspond to the bis (5-hydroxymethyl) or mixed (4-and 5-hydroxymethyl) regioisomers (45%). 4.75 (br s, 4H), 4.43 (br s, 2H), 4.28 (m, 4H), 1.92 (m, 4H), 0.47 (m, 4H), 0.03 (br s, 12H); ^{13}C NMR ($CDCl_3$): δ = 147.9, 136.4, 132.7, 122.1, 122.0, 56.2, 53.1, 52.9, 51.1, 24.8, 24.7, 24.4, 15.2, 15.1 -0.3 ; HRMS (ESI): $[M+H]^+$ calculated = 413.2153, $[M+H]^+$ found: 413.2147. NMR spectra of the pure 1,3-bis((4-hydroxymethyl-1,2,3-triazol-1-yl)propyl)tetramethyldisiloxane, prepared using the copper(I)-catalyzed procedure, are reported below.

5) General procedures for copper(I)-catalyzed Click cycloadditions

For purposes of comparison, the copper(I)-catalyzed reaction was examined. It was observed that generally, copper catalyzed reactions occurred more quickly than the thermal reactions but the thermal reactions obtained superior yields. The copper catalyzed reaction between BAPTMDS and propargyl alcohol or phenylacetylene took only 1 hour to go to completion at room temperature. A variety of other functional groups were investigated as shown in Table 1 entries 1-9. All reactions were carried using 2% molar copper(II) catalyst, and 10% molar sodium ascorbate, in solvent systems such as THF:water (1:1; v:v) or DMF:water (5:1; v:v). This catalyst system was simpler (and also cheaper) than use of a copper(I) source, and allows one to avoid the unwanted oxidative coupling usually observed with Cu(I) catalysts.[11, 12] All of the alkynes tested were successfully incorporated into 1,3-BAPTMDS to

form the bis-triazole product. The latter show characteristic peaks between 120 and 150 ppm in ^{13}C NMR, attributed to the two carbons in the triazole ring. Moreover, in cases where terminal alkynes were used, the proton in the triazole ring was also visible in ^{1}H NMR (7-8 ppm). The copper catalyzed reaction was found to be regioselective: only one regioisomer was formed from this reaction with terminal alkynes as indicated by the presence of a singlet for the proton in the triazole ring.

One interesting outcome of these experiments was the 'click' reaction involving an internal alkyne, dimethylacetylene dicarboxylate (DMAD), (Table 1, entry 6). It has been reported in the literature[16, 17, 26, 33] that the copper(I) catalyzed (copper(II)sulfate and sodium ascorbate catalyst system) Huisgen cycloaddition reaction is not practical with internal alkynes such as DMAD because only terminal alkynes can form the copper-acetylide complex, a complex that is generally accepted to be a crucial component in the step-wise mechanism of the copper(I) catalyzed click reaction, which may also be responsible for the regiospecificity of this process.[4-7,34] To establish if DMAD is an exception to this rule, or whether the thermally mediated azide-DMAD cycloaddition reactions with this molecule can occur at very low temperatures (thermal click reactions are usually performed at elevated temperatures, i.e., 70 °C or above),[11, 12, 34] the thermal 1,3-BAPTMDS-DMAD cycloaddition reaction was attempted at room temperature in the absence of copper catalyst. The non-catalyzed (metal free) reaction was completed in the same time frame as the copper-mediated reaction. This observation opens up potentially interesting opportunities, showing that it is possible to perform thermal click reactions of mono- or disubstituted electron-deficient alkynes at ambient temperature.

As a further demonstration of this effect, the reaction of phenylacetylene and propargyl alcohol, respectively, with the diazidosilicone BAPTMDS were compared. The thermal reaction of phenylacetylene occurred more slowly than that of propargyl alcohol, as noted above. By contrast, in water with copper catalysis, phenylacetylene reacted faster than propargyl alcohol. While not wishing to be bound the theory, the origins of this observation may lie in the relative hydrophobicities of both BAPTMDS and the alkyne: phenylacetylene is miscible with BAPTMDS whereas propargyl alcohol, soluble in water, is much less so. The compatibility of 1,3-BAPTMDS and phenylacetylene towards each other and their

mutual hydrophobicity (relative insolubility in water) may drive them to be as close as possible together (an enforced hydrophobic interaction[36]) in the reaction environment, thereby increasing the chance of contact and subsequent coupling. Previous research has noted that such interactions occur in both the Huisgen cycloaddition and Diels-Alder reactions when run in aqueous environments.[11, 12, 36, 37] This proposal is also supported by the slow reaction of 1,3-BAPTMDS with propargyl alcohol due to problems of miscibility: no reaction had taken place in the copper(I) catalyzed reaction of propargyl alcohol and BAPTMDS after 2 hours.

The characterization of 1,3-bis((4-phenyl-1,2,3-triazol-1-yl)propyl)tetramethyldisiloxane (Table 1, entries 2, 5):

Thermal version contained this isomer and also the isomer reported below for the copper catalyzed reaction: ^{1}H NMR ($CDCl_3$): δ = 7.81 (m, 6H), 7.37 (m, 6H), 4.32 (m, 4H), 1.90 (m, 4H), 0.44 (m, 4H), 0.04 (m, 12); ^{13}C NMR ($CDCl_3$): δ = 147.7, 137.8, 133.12, 130.8, 129.5, 129.2, 128.9, 128.1, 127.4, 125.7, 119.7, 68.0, 53.2, 51.1, 24.8, 24.4, 15.1, 0.3; HRMS (ESI): m/z $[M+H]^+$ calculated = 505.2567, $[M+H]^+$ found: 505.2559.

Copper-catalyzed version: ^{1}H NMR ($CDCl_3$): δ = 7.82 (m, 6H), 7.37 (m, 6H), 4.36 (t, *J* = 7.2 Hz, 4H), 1.94 (m, 4H), 0.52 (m, 4H), 0.06 (s, 12); ^{13}C NMR ($CDCl_3$): δ = 147.6, 130.8, 128.9, 128.1, 125.7, 119.8, 53.1, 24.8, 15.2, 0.3; HRMS (ESI): m/z $[M+H]^+$ calculated = 505.2567, $[M+H]^+$; found: 505.2584.

The general procedure for the copper-catalyzed reaction of BAPTMDS with alkynes is illustrated by the thermal reaction between BAPTMDS with propargyl alcohol (Table 1, entries 1,3): 1,3-bis(azidopropyl)tetramethyldisiloxane (300 mg, 1.0 mmol) and propargyl alcohol (168 mg, 3.0 mmol, 1.5 equiv. for each azide) were solubilized in 2 mL of THF. Sodium ascorbate (49 mg, 0.25 mmol, in 1.00 mL of water) was added, followed by copper(II) sulfate pentahydrate (13 mg, 0.05 mmoles, in 1.00 mL of water). The mixture was stirred vigorously for two days, at which stage ^{1}H NMR indicated the complete consumption of the starting materials. The reaction mixture was fractionated between water and dichloromethane. The aqueous phase was extracted three times with dichloromethane. The combined organic phase was dried over sodium sulfate, filtered, evaporated then passed through a short pad of neutral

alumina to afford 94% of the click adduct. For alkynyl amino acids, DMF was used in lieu of THF. See thermal section, above for spectra.

The following compounds have been prepared in accordance to the general procedure and characterized as follows :

1,3-Bis((4-(1,1-dimethyl)hydroxymethyl-1,2,3-triazol-1-yl)propyl)tetramethyldisiloxane (Table 1, entry 4)

1,3-Bis(azidopropyl)tetramethyldisiloxane (300 mg, 1.0 mmol); 3-butyn-2-methyl-2-ol (252 mg , 3.0 mmol, 1.5 equiv. for each azide); Yield: 95% (468 mg). ^{1}H NMR ($CDCl_3$): δ = 7.50 (s, 2H), 4.26 (t, *J* = 7.4 Hz, 4H), 3.49 (s, 2H), 1.89 (m, 4H), 1.64 (s, 12), 0.509 (m, 4H), 0.04 (s, 12); ^{13}C NMR ($CDCl_3$): δ = 155.8, 119.4, 68.5, 53.0, 30.5, 24.7, 15.2, 0.3; MS (ESI): m/z $[M+H]^+$ calculated = 469.2779, $[M+H]^+$; found: 469.2770, $[M+Na]^+$ found: 492.2617.

(b) 1,3-Bis((4-phenyl-1,2,3-triazol-1-yl)propyl)tetramethyldisiloxane (Table 1, entry 5)

1,3-Bis(azidopropyl)tetramethyldisiloxane (300 mg, 1.0 mmol) and phenylacetylene (306 mg , 3.0 mmol, 1.5 equiv. for each azide) were reacted using the same conditions as above to give 484 mg (96%) of the product. *See thermal section, above for spectra*

(c) 1,3-Bis((4,5-dimethylcarboxy-1,2,3-triazol-1-yl)propyl)tetramethyldisiloxane (Table 1, entry 6)

1,3-Bis(azidopropyl)tetramethyldisiloxane (300 mg, 1.0 mmol); dimethylacetylene-dicarboxylate (426 mg, 3.0 mmol, 1.5 equiv. for each azide); yield: 92% (554 mg). ^{1}H NMR ($CDCl_3$): δ = 4.56 (t, *J* = 7.2 Hz, 4H), 3.99 (s, 6H), 3.97 (s, 6H), 1.90 (m, 4H), 0.48 (m, 4H), 0.03 (s, 12); ^{13}C NMR ($CDCl_3$): δ = 160.6, 159.1, 139.9, 129.9, 53.5, 53.2, 24.6, 15.0, 0.2; MS (ESI): m/z $[M+H]^+$ calculated = 585.2161, $[M]^+$ found: 585.2158, $[M+NH_4]^+$ found: 602.2595.

1,3-Bis((4-N-methylenegluconamide-1,2,3-triazol-1-yl)propyl)tetramethyldisiloxane (Table 1, entry 7)

1,3-Bis(azidopropyl)tetramethyldisiloxane (300 mg, 1.0 mmol); gluconoamide (700 mg, 3.0 mmol, 1.5 equiv. for each azide); yield: 94% (721 mg). ^{1}H NMR ($CDCl_3$): δ =

8.10 (t, *J* = 5.6 Hz, 2H), 7.86 (s, 2H), 5.46 (d, *J* = 4.0 Hz, 2H), 4.26 (m, 24H), 1.77 (m, 4H), 0.43 (m, 4H), 0.025 (s, 12); ^{13}C NMR ($CDCl_3$): δ = 173.1, 145.4, 123.2, 74.1, 72.7, 71. 9, 70.6, 63.7, 52.4, 34.6, 24.6, 14.9, 0.7; MS (ESI): m/z $[M+H]^+$ calculated = 767.3427, $[M+H]^+$ found: 767.3398.

1,3-Bis((4-N-methylene-Cbz-valineamide-1,2,3-triazol-1-yl)propyl)tetramethyldisiloxane (Table 1, entry 8)

1,3-Bis(azidopropyl)tetramethyldisiloxane (300 mg, 1.0 mmol);d *N*-Cbz-L-valine-*N*'-propargylamide (867 mg, 3.0 mmol, 1.5 equiv. for each azide); in lieu of THF, DMF was the co-solvent used; yield: 100% (877 mg). ^{1}H NMR ($CDCl_3$): δ = 8.43 (t, *J* = 5.6 Hz, 2H), 7.85 (s, 2H), 7.27 (m, 12H), 5.09 (s, 4H), 4.30 (m, 8H), 3.82 (t, *J* = 7.4 Hz, 2H), 1.87 (m, 2H), 1.74 (m, 4H), 0.78 (d, *J* = 6.6 Hz, 12H), 0.39 (m, 4H), 0.004 (s, 12); ^{13}C NMR ($CDCl_3$): δ = 171.7, 156.7, 145.1, 137.6, 128.8, 128.1, 123.3, 65.9, 60.7, 52.4, 34.7, 30.8, 24.7, 19.7, 18.8, 14.9, 0.7; MS (ESI): m/z $[M+]^+$ calculated = 877.4576, $[M]^+$ found: 877.4539.

1,3-Bis((4-N-methylene-Boc-alanineamide-1,2,3-triazol-1-yl)propyl)tetramethyldisiloxane (Table 1 , entry 9)

1,3-Bis(azidopropyl)tetramethyldisiloxane (300 mg, 1.0 mmol); *N*-(tert-butoxycarbonyl)-L-alanine-*N*'-propargylamide (732 mg, 3.0 mmol, 1.5 equiv. for each azide); in lieu of THF, DMF was utilized as the co-solvent; yield: 95% (715 mg). ^{1}H NMR ($CDCl_3$): δ = 8.26 (t, *J* = 4.8 Hz, 2H), 7.82 (s, 2H), 6.90 (d, *J* = 7.0 Hz, 2H), 4.26 (m, 8H), 3.96 (m, 2H), 1.71 (m, 4H), 1.24 (s, 24H), 1.12 (d, *J* =7.6Hz, 6H), 0.41 (m, 4H), 0.005 (s, 12H); ^{13}C NMR ($CDCl_3$): δ = 172.9, 169.7, 145.0, 122.6, 78.0, 52.0, 49.8, 34.4, 28.0, 24.2, 18.1, 14.5, 0.2; MS (ESI): m/z $[M+H]^+$ calculated = 753.4263, $[M+H]^+$ found: 753.4241.

6) Polymeric derivatives: synthesis and characterizations

The polyazide was also amenable to click chemistry in analogy with the model disiloxane compound **1**. Two reactions demonstrated the efficacy of this functionalization reaction. In the first reaction, an excess of phenylacetylene was reacted with the polysiloxane-azide in the absence of solvent, at 90 °C. The reaction

was complete within one day and gave a pale yellow-orange, higher viscosity oil. Simple removal of the excess phenylacetylene under reduced pressure afforded the corresponding coupling product in quantitative yield, demonstrating the ease and efficiency of the thermal approach. NMR studies indicated complete conversion of azido groups to triazole rings (easily monitored by the olefinic protons in the α position).

For comparison, an example of a copper-catalyzed click reaction was also performed with the polyazide, using a highly polar alkyne: ethynyl gluconamide (entry 11 of Table 1). Reaction for 2 days, under standard copper-catalyzed conditions (in a binary solvent water:THF, 1:1, vol:vol), afforded the polymeric glucose-siloxane composite product in 84% yield. A simple filtration was performed to isolate a pure product: after reaction, the reaction medium was slowly added to 100 mL of water under stirring. The functionalized-polymeric product precipitated, while copper and ascorbate salts remained in solution.

The functionalized polymer of Table 1, entry 10 was prepared by stirring, in a 5mL round-bottomed flask, poly(azidopropyl)-co-poly(dimethyl)siloxane (0.706 g; 1.2 mmol of repeating unit) and phenylacetylene (1.0 g; 9.8 mmol) at 90 °C under a nitrogen atmosphere for 24 h. Volatiles were then removed in vacuo to yield 0.860 g (quantitative yield) of poly(phenyl-triazolyl) derivatives as a viscous yellow-orange oil. ^{1}H NMR ($CDCl_3$): δ = 7.55 (s, 1H), 7.51 (s, 1H), 4.71 (m, 4H), 4.24 (m, 4H), 3.69 (m, 2H), 1.82 (m, 4H), 0.43 (m, 4H), 0.01 (m, 12H); ^{13}C NMR ($CDCl_3$): δ = 147.9, 136.6, 132.6, 122.1, 67.9, 55.9, 53.0, 52.6, 51.0, 25.5, 24.6, 24.3, 15.0, 0.2; MS (ESI): $[M+H]^+$ calculated = 413.2153, $[M+H]^+$ found: 413.2147.

The functionalized polymer of Table 1, entry 11 was prepared by dissolving, in a 5mL round-bottomed flask, poly(azidopropyl)-co-poly(dimethyl)siloxane (0.723 g, 1.2 mmol of repeating unit) in 1mL of THF. Ethynylgluconamide (500 mg, 2.1 mmol) dissolved in 3mL water was added. Sodium ascorbate (49 mg, 0.25 mmol) was then added, followed by copper(II) sulfate pentahydrate (13 mg, 0.05 mmoles). The mixture was stirred vigorously for two days. It was then slowly added to 100mL of water, which resulted in precipitation of a fluffy solid. The solid was filtered, dissolved again in a minimum amount of water/THF (1:1, vol:vol), and precipitated again in 100mL of water. The solid was filtrated, and dried in vacuo to yield 0.848 g

(84%) of the click-adduct. ^{1}H NMR (DMSO-d_6): δ = 7.55 (s, 1H), 7.51 (s, 1H), 4.71 (m, 4H), 4.24 (m, 4H), 3.69 (m, 2H), 1.82 (m, 4H), 0.43 (m, 4H), 0.01 (m, 12H); ^{13}C NMR ($CDCl_3$): δ = 147.9, 136.6, 132.6, 122.1, 67.9, 55.9, 53.0, 52.6, 51.0, 25.5, 24.6, 24.3, 15.0, 0.2; MS (ESI): $[M+H]^+$ calculated = 413.2153, $[M+H]^+$ found: 413.2147.