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Polysiloxane Elastomers via Room Temperature, Metal-Free Click Chemistry

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Introduction. Silicone (polysiloxane) elastomers are a class of polymers that have a broad utility in commerce.[1,2] Three routes are typically used to create silicone elastomers: platinum-catalyzed addition cure, tin- or titanium-catalyzed room temperature vulcanization (moisture cure), or radical cure, which is normally performed at higher temperatures.[1] All three methods of cure suffer from some deficiencies. These include the use of expensive metals such as platinum, the formation of elastomers that contain metal residues that can leach from the elastomer, and/or difficulties in processing the elastomer during and after cure. There is thus a need for a general, simple, efficient, catalyst-free system to prepare both functional and/or cross-linked silicones. In addition, it would be beneficial to be able to functionalize or cross-link silicones neat or in organic solvents and to have the possibility to control the cure rate over a wide range of temperatures.

The Huisgen 1,3-dipolar cycloaddition of azides to alkynes,[3−5] and its copper-catalyzed version, known as "click" chemistry, is a robust and reliable method for the functionalization of a wide variety of molecules because its sole product—the triazole ring—acts as a stable linker between the two precursors.[6−9] This latter process has been widely adopted for the functionalization and cross-linking of polymers.[10−14] However, to the best of our knowledge, the thermal cross-linking of azido- and alkyne-substituted polymers leading to elastomeric materials via dipolar cycloadditions has never been reported, likely because of the potential hazard associated with azido derivatives.[15]

Recently, we described the Cu-catalyzed and thermal functionalization of polysiloxanes and demonstrated that the thermal cycloaddition of azido-siloxanes to alkynes was a safe and highly efficient procedure:[16] small azido-modified siloxanes only began to undergo thermal degradation at ca. 115 °C, a temperature that increases with the molecular weight of the silicone; the Huisgen reaction occurs 20 °C below this temperature. Here we describe the first preparation of elastomeric polysiloxanes via uncatalyzed 1,3-dipolar cycloadditions (metal-free click chemistry). The synthesis of alkyne-terminated polysiloxanes, and their subsequent cross-linking with *graft*-poly(azidopropyl)siloxane, is first presented. We also show that the design of the alkyne cross-linker is integral to the process. The temperature at which the thermal reaction occurs is highly dependent on the electronic properties of the alkyne, with electron-deficient alkynes reacting at lower temperatures. Thus, it is possible to choose an offset temperature between room temperature and about 95 °C.

Experimental Section. *Materials and Methods.* (Chloropropyl)methylsiloxane−dimethylsiloxane copolymer (14−16 mol % (chloropropyl)methylsiloxane), octamethylcyclotetrasiloxane (D_4), and bis(hydroxybutyl)tetramethyldisiloxane were obtained from Gelest. Propiolic acid (95%), dicyclohexylcarbodiimide (DCC, 99%) and (dimethylamino)pyridine (DMAP, 99%) were obtained from Sigma-Aldrich. 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 were recorded at room temperature on a Bruker AC-200 spectrometer (at 200 MHz for ^{1}H and 50.3 MHz for ^{13}C) using deuterated solvents ($CDCl_3$). Solid-state ^{13}C and ^{29}Si NMR were performed on a Bruker AV300 spectrometer (at 75.5 MHz for ^{13}C and at 300 MHz for ^{29}Si). Pneumatically assisted electrospray ionization mass spectrometry (ESMS) was performed on a Micromass Quattro-LC triple quadrupole mass spectrometer. Mass spectra were reported as percent intensity (%) versus mass/charge (m/z) ratio. MALDI spectra were run on a Waters/Micromass Micro MX MALDI-ToF mass spectrometer operating in linear mode with an extraction voltage of 800 V (extraction delay 500 ns) and a source voltage of 15 000 V. A nitrogen laser (337 nm) was used at a setting of 150 μJ. Data were acquired at 2 GHz. Samples were dissolved in THF at a concentration of ~0.1 mg/mL and mixed with a solution of dithranol in THF (10 mg/mL). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC analysis) were performed using a Netzsch 409 PC Luxx station. Heating was performed at 10 °C min^{-1}.

Synthesis

Synthesis of Diethynyl-Terminated Tetramethyldisiloxane 1. Small portions of DCC (4.13 g, 20 mmol) were added to a cooled (−40 °C; dry ice in acetone) solution of bis(hydroxybutyl)tetramethyldisiloxane (2.79 g, 10 mmol) and propiolic acid (1.75 g, 25 mmol) in dichloromethane (50 mL), after which was added a catalytic amount of DMAP (0.024 g, 0.2 mmol). The reaction was stirred at a temperature below −20 °C for 20 h. Then, dry ether was added (100 mL), and the solution was filtered. Following evaporation of the solvents, the crude product was purified by silica gel chromatography (from 95/5 to 75/25 hexanes/ethyl acetate as eluent) to yield 3.09 g (81%) of the dipropionic ester product. ^{1}H NMR ($CDCl_3$): δ 0.03 (s, 12H, $\mathrm{SiC}H_3$); 0.51 (t, 4H, J = 8.4 Hz, $\mathrm{SiC}H_2\mathrm{CH_2CH_2CH_2}$); 1.37 (m, 4H, $\mathrm{SiCH_2C}H_2\mathrm{CH_2CH_2}$); 1.69 (m, 4H, $\mathrm{SiCH_2CH_2C}H_2\mathrm{CH_2}$); 2.88 (s, 2H, $\mathrm{C{\equiv}C}H$); 4.18 (t, 4H, J = 6.6 Hz, $\mathrm{SiCH_2CH_2CH_2C}H_2$). ^{13}C NMR ($CDCl_3$): δ = 152.9 ($C\mathrm{{=}O}$), 74.9 ($C\mathrm{{\equiv}CH}$), 74.6 ($\mathrm{C{\equiv}}C\mathrm{H}$), 66.2 ($\mathrm{SiCH_2CH_2CH_2}C\mathrm{H_2O}$), 31.8 ($\mathrm{SiCH_2CH_2}C\mathrm{H_2CH_2O}$), 19.6 ($\mathrm{SiCH_2}C\mathrm{H_2CH_2CH_2O}$), 17.9 ($\mathrm{Si}C\mathrm{H_2CH_2CH_2CH_2O}$), 0.4 ($\mathrm{Si}C\mathrm{H_3}$). MS (ES-positive mode): m/z [M + H^+] calculated = 382.61; [M + H^+] found: 382.00.

Equilibration Reaction of 1 with Octamethylcyclotetrasiloxane (D_4): Synthesis of Ethynyl-Terminated Silicone 2. Octamethylcyclotetrasiloxane (D_4, 3.00 g, 100 mmol) and **1** (0.50 g, 1.31 mmol) were placed in a 50 mL round-bottomed flask fitted with a drying tube. The mixture was agitated with a magnetic stirrer, and then triflic acid (200 μL) was added. The mixture was stirred for 3 days at room temperature, after which was added magnesium oxide (0.40 g) followed by dry hexanes (40 mL). The slurry was stirred for 1 h and then filtered through

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Table 1. Outcome of the Cross-Linking Experiments between Polyazide 3 and Alkynes 1 and 2 (Scheme 1)

entry	alkyne	R^a	T (°C)	time (min)	resulting material	nominal hardness[b]
1	**1**	15.0	80	120	highly viscous oil	
2	**1**	7.50	80	120	soft elastomer	< 10
3	**1**	3.00	80	120	monolithic elastomer	40−50
4	**1**	1.00	80	20	monolithic elastomer	70−80
5	**1**	0.50	80	20	monolithic elastomer	
6	**1**	0.25	80	120	soft elastomer	10−20
7	**1**	0.10	80	120	viscous oil	
8	**1**	1.00	90	< 10	monolithic elastomer	70−80
9	**1**	1.00	rt	2880	monolithic elastomer	70−80
10	**2**	1.00	80	120	monolithic elastomer	60−70
11	**2**	1.00	50	240	monolithic elastomer	60−70
12	**2**	1.00	rt	1800	monolithic elastomer	60−70

[a] R: molar ratio azide/alkyne. [b] By comparison with silicone elastomer reference standards of Shore A hardness that varied from 10 to 80.

a short pad of Celite. Volatiles were removed in vacuo to yield 3.10 g of crude product. This crude product was purified by Kugelrohr distillation (1 h at 120 °C, 2 h at 150 °C) to yield 2.28 g of a clear transparent oil. ^{1}H NMR spectroscopy indicates that the resulting polysiloxane chain was now constituted of 21 dimethylsiloxane units (relative integration of the 2H (alkynyl protons at 2.88 ppm) and 4H (CH_2 ester peak at 4.18 ppm) versus 126 for dimethylsiloxane ($SiCH_3$ at 0.03 ppm)), which correspond to a molecular weight of 1790 (yield: 65%).

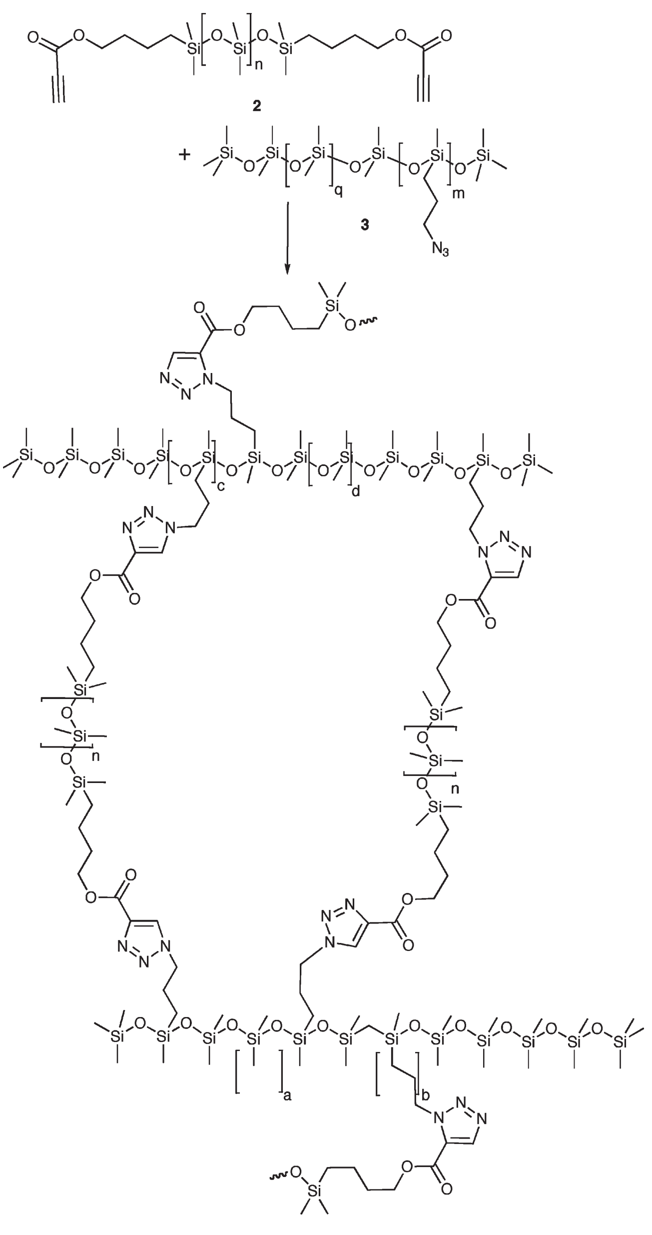
Synthesis of Poly(azidopropylmethyl)-co-(dimethylsiloxane) **3**. (Chloropropyl)methylsiloxane−dimethylsiloxane copolymer (14−16 mol % (chloropropyl)methylsiloxane, 10.0 g) was dissolved in 50 mL of a mixture of DMF and THF (1:1; v:v). Sodium azide (1.0 g, 15 mmol) was then added, and the mixture was heated at 70 °C for 24 h. At this stage, the reaction was found to be incomplete by ^{1}H NMR spectroscopy. Therefore, additional sodium azide (1.0 g, 15 mmol) was added, and the mixture was heated at 70 °C until completion (an additional 48 h, as indicated by the ^{1}H NMR spectrum). 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 g (99%) of the title compound. ^{1}H NMR ($CDCl_3$): δ = 3.24 (t, J = 6.9 Hz, 2H, $SiCH_2CH_2CH_2N_3$), 1.62 (m, 2H, $SiCH_2CH_2CH_2N_3$), 0.56 (m, 2H, $SiCH_2CH_2CH_2N_3$), 0.07 (br s, 36H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ = 54.2 ($SiCH_2CH_2CH_2N_3$), 22.9 ($SiCH_2CH_2CH_2N_3$), 14.6 ($SiCH_2CH_2CH_2N_3$), 1.2 ($SiCH_3$). IR (KBr, cm^{-1}): N_3 stretch = 2097 cm^{-1} (s). MS (MALDI-TOF): centered at 3400 (3000−5000). TGA and DSC analysis of compound **3**: showed the onset of decomposition is 211 °C (see Supporting Information).

For the calculations of the azido (using the CH_2 adjacent to N_3 at 3.24 ppm) to alkyne (using the CH_2O adjacent to the ester at 4.18 ppm) ratios, we used the molecular weight of a repeating unit determined by ^{1}H NMR spectroscopy: for every azidopropyl chain, 36 protons were integrated from the methylsiloxane moieties, corresponding to a molecular weight of 512.

Elastomer Synthesis. The general procedure is illustrated by the cross-linking reaction between **1** and **3** (with an azide to alkyne ratio of 1) at 80 °C (Table 1, entry 4): polymer **3** (0.200 g, 0.39 mmol of repeating unit) was placed in a 5 mL scintillation vial followed by dialkyne **1** (0.074 g, 0.195 mmol). Then, 500 μL of 1,4-dioxane was added: on mixing, a homogeneous and transparent mixture results. The vial was then placed uncapped in an oven at 80 °C. Within 20 min, the original solution turned into a monolithic elastomer. The weight of this elastomer (274 mg) corresponds to the perfect addition of the two starting materials. The ^{29}Si NMR data are available in the Supporting Information.

The same procedure was used with the polymeric alkyne **2**: in this case, no added solvent was required as the two precursors are fully miscible.

Scheme 1. Synthesis of Alkynyl-Modified Siloxanes 1 and 2 and the Subsequent Cross-Linking of 2 with Polyazidosiloxane 3



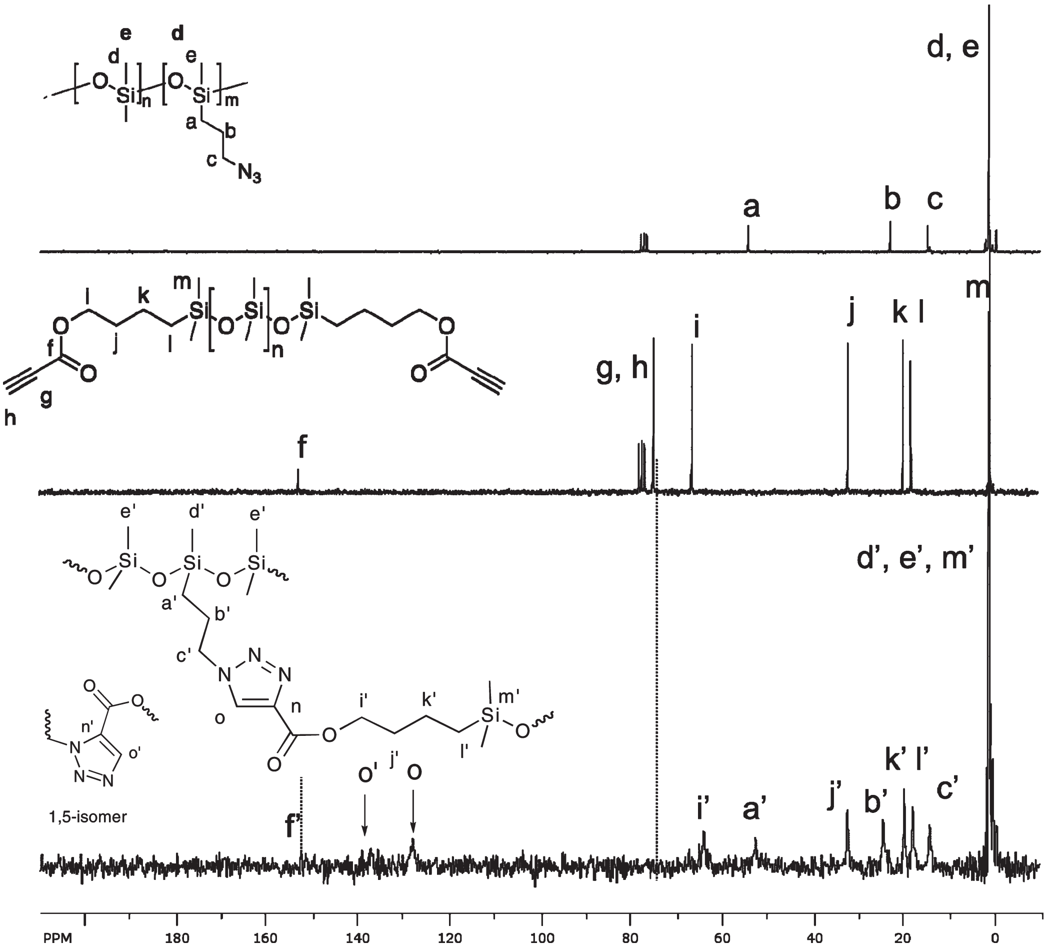


Figure 1. Comparison ^{13}C solution and solid-state ^{13}C NMR spectra of poly(azidopropyl)siloxane **3**, dialkynylsiloxane **2**, and of their cross-linked elastomer.

Room temperature cure was performed according the previously described procedure: vials containing the proper amount of precursors were aged at room temperature, and their physical status (solution, swollen gel, elastomer) was checked regularly. A control experiment was performed in the dark: gelation occurred in the same time as the light-exposed sample, indicating that the curing process results of a thermal cycloaddition and not through photochemical activation. The ^{13}C NMR spectrum is shown in Figure 1 (labels a–e and i–o are provided on the figure). Note that both 1,4- and 1,5-triazoles can result from thermal cycloadditions reactions of azides and alkynes, unlike copper-catalyzed click reactions that exclusively provide the 1,4-regioisomer.[16] ^{13}C NMR (CDCl$_3$): δ = 1.1 (d′, e′, m′), 14.2 (a′), 17.9 (l′), 19.8 (k′), 24.8 (b′), 32.3 (j′), 52.6 (c′), 64.0 (i′), 128.1 (o for the 1,4 isomer), 137.3 (o′ for the 1,5 isomer). The signals for the quaternary carbons (n, n′) are of lower sensitivity and are embedded in the spectral noise. The spectrum shown was obtained after 25 000 scans.

Hardness Measurements. The silicone elastomers prepared (Table 1) were unfilled. As is the normal case for such silicones, the polymers readily suffer cracking and tearing. As a consequence, it was not possible to use traditional techniques such as Shore hardness to characterize the polymers—they cracked. However, it was possible to manually compare the hardness of the polymers we prepared with those of silicone elastomer standards of known Shore A hardnesses, which ranged from 10 to 80. These numbers are provided as a guideline to the properties of the materials prepared.

Results and Discussion. The synthesis of elastomeric polysiloxanes via 1,3-dipolar cycloaddition requires the preparation of azide- and alkyne-terminated siloxanes. The esterification reaction of 1,3-bis(hydroxybutyl)tetramethyl disiloxane with 2 equiv of propiolic acid, under conventional DCC coupling conditions, yielded the diethynyl-terminated disiloxane **1** (Scheme 1). An acid equilibration reaction of **1** with octamethylcyclotetrasiloxane yielded the ethynyl-terminated polysiloxane **2** in a 65% yield (MW of 1790). The synthesis of graft polyazidopropylsiloxane **3** involves a classical nucleophilic substitution of commercially available poly((dimethyldisiloxane)-*co*-(methylchloropropyl)siloxane) (MW: 7500–10 000; 14–16 mol % chloropropyl units) by azide anion in a THF:DMF solvent system: alternative approaches using the azide opening of epoxides have been described.[17]

Thermogravimetric analysis (see Supporting Information) demonstrated slow thermal decomposition for compound **3** (significantly slower than **1**) with an onset of decomposition at 227 °C, which may be explained by a dilution effect of the azido groups within the polymeric matrix: the decomposition took place over more than 5 min at a heating rate of 10 °C/min. This slow decomposition occurs at temperatures well above those required to perform thermal cycloadditions, and the compounds exhibit no characteristics of explosive behavior, confirming the viability of this generic synthetic approach. Explosive behavior is characterized by

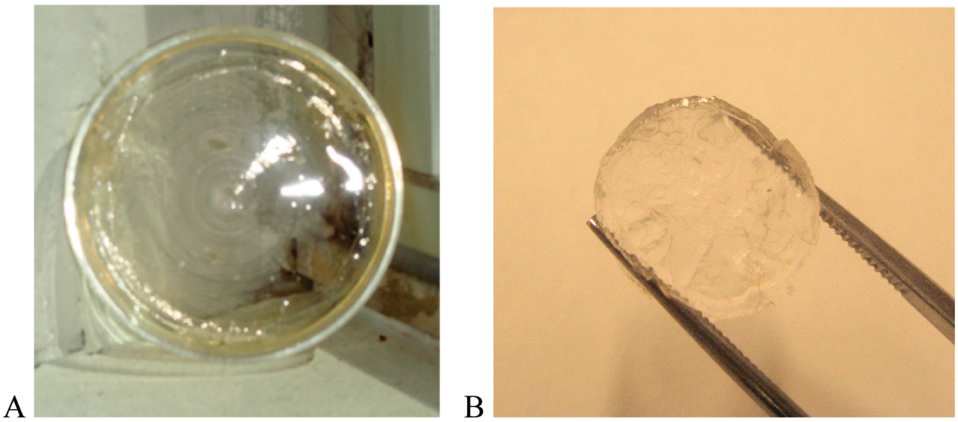


Figure 2. Click-cured: (A) 2 mm thick × 9 cm silicone film; (B) 1 cm × 5 mm thick silicone elastomer.

much shorter decomposition cycles, about 2 min at 10 °C/min.[18] The decomposition for the azidosilicone **3**, based on weight loss, is consistent with nitrogen loss.

The thermal click ligation between alkyne-terminated siloxanes **1** or **2** and polyazide **3** readily occurred. Cross-linking arises from the formation of triazole rings between the azide groups and the ethynyl moieties of **1** or **2**, as shown in Scheme 1. We decided to tune the molar ratio between azido and alkynyl moieties to determine which conditions would be the more suitable to obtain elastomers. The results are summarized in Table 1.

As compound **1** was not fully soluble in the polymeric azido derivative **3**, a small amount of 1,4-dioxane was used to homogenize the reaction medium. Under such conditions, the cross-linking reaction proceeded very efficiently. Monolithic elastomers were obtained through a wide range of azide/alkyne molar ratios (from ratios between 7.50 and 0.25; Table 1, entries 2−6). Most importantly, these elastomers were comparable in transparency and softness with conventional PDMS elastomers (e.g., Dow Corning Sylgard 184; platinum-cured PDMS) although occasionally the elastomer was tinged a very pale yellow (Figure 2). As no filler was included in the formulation, the elastomers that could be peeled from the mold could be easily torn (entries 3−5 and 8−12 in Table 1). The curing time could be efficiently tuned with respect of the temperature: only 20 min at 80 °C and less than 10 min at 90 °C (Table 1, entries 4 and 8). An even more remarkable result relies on the possibility to obtain a monolithic elastomer at room temperature: simple mixing of **1** and **3** with a minimum amount of 1,4-dioxane to homogenize the reaction medium results in gelation within 48 h. Further slow cross-linking and evaporation of the trapped dioxane over 4 more days leads to a monolithic elastomer of size comparable with the ones obtained by thermal cross-linking.

Evidence that cross-linking occurs through 1,3-dipolar cycloaddition reactions was demonstrated by ^{13}C and ^{29}Si solid-state NMR. The ^{29}Si solid-state NMR spectrum shows a unique resonance at −22.37 ppm, characteristic of dimethylsiloxane units ($-OSiMe_2O-$; see Supporting Information). Figure 1 shows the comparable ^{13}C NMR of the starting polyazide **1**, the dialkyne **3**, and the elastomeric material obtained with a 1:1 ratio of alkyne/azide (from entry 12 of Table 1).

First, the two signals corresponding to the ethylenic carbons at 74.6 and 74.9 ppm are not present in the elastomer, showing complete conversion of the alkyne into triazole rings. The triazole rings can also be seen from the presence of the two characteristic new signals at 128.1 and 137.3 ppm, respectively. Moreover, the signal attributed to the carbon in α of the azido groups (at 54.2 ppm) is lacking in the elastomer and is replaced by a signal at 52.5 ppm, corresponding to the carbon in the α-position of the triazole ring: that small but significant shift was also observed in the click ligation synthesis of several alkynes with azidopropyltetramethyldisiloxane or poly(azidopropyl)methyl-*co*-dimethylsiloxane copolymer.[16] Taken together, these results unambiguously demonstrate that cross-linking occurs from the uncatalyzed click ligation of the alkyne- and azido-siloxane precursors.

In order to eliminate the need of a solvent, cross-linking experiments were performed with the polymeric alkyne-terminated siloxane **3**: this derivative is fully miscible with polyazide **1**. Once again, the cross-linking via 1,3-dipolar cycloaddition proved successful: elastomers were obtained within 2 h at 80 °C, in 4 h at 50 °C, and in 30 h at room temperature (Table 1, entries 10−12).

The hardness of the resulting polymers directly correlated with cross-link density and had a maximum at $R = 1$ (Table 1). After a short period of time at elevated temperature (entry 8), the material was tack-free but had not completely cured. Ultimately, all materials with $R = 1$ exhibited the same hardness. Because of the poor tear strength of unfilled silicones, it was not possible to measure Shore A hardness: the elastomers cracked during measurement. However, comparison with reference standards using lower levels of pressure permitted a relative hardness scale to be described (Table 1).

To the best of our knowledge, this is the first uncatalyzed, metal-free, room temperature synthesis of elastomeric silicones. The strategy benefits from the unique reactivity of propiolic esters **1** and **2**. It has previously been demonstrated that electron-deficient alkynes such as dimethyl acetylenedicarboxylate or cyclic α-difluorinated alkynes could "click" at room temperature, within a few hours and without catalyst.[19−22] By virtue of the electronic demand of the carbonyl group, esters of propiolic acid such as **1** and **2** are activated alkynes: the $3 + 2$ cycloaddition reaction elastomers will occur through a slow room temperature cross-linking process or in just a few minutes at a more elevated temperature (80 °C). Thus, it should be possible to thermally tune the cross-linking reaction to control pot life and/or the desired onset temperature.

Conclusions. The cross-linking of silicone polymers is challenged by the need of noble (expensive) or potentially toxic metal catalysts that can remain in the product and/or by high-temperature requirements. The simple uncatalyzed 1,3-dipolar cycloaddition of activated alkynes with polyazido-siloxanes obviates all these problems, leading easily to elastomeric materials. An efficient curing process results from that uncatalyzed click process, neat or in organic solvent, at room temperature or with heating, at the will of the experimentator. This strategy is currently being applied to the synthesis of other composite materials.

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Supporting Information Available: DSC and TGA analysis of polyazidosiloxane **3**; ^{29}Si NMR spectra of the elastomeric polysiloxane derived from **2** + **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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