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Novel cross-linkers for PDMS networks for controlled and well distributed grafting of functionalities by click chemistry†

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An azide-containing, trifunctional vinyl cross-linker for silicone networks has been synthesized. The cross-linker has through Cu(I) catalyzed 1,3-cycloaddition been reacted with six different alkyne-containing chemical groups which each possess a particular functionality. The functional cross-linkers have been utilized to prepare novel polydimethylsiloxane (PDMS) networks. All functional cross-linkers were successfully incorporated into the networks and were demonstrated to be well distributed within the PDMS films. This was substantiated by fluorescence microscopy of a film prepared with the 4-methylumbelliferone containing cross-linker. TGA showed that a ferrocene functionality increased the thermal degradation temperature of PDMS. It was furthermore shown that the incorporation of only 0.25 wt% of the push-pull dipole, ethynyl-4-nitrobenzene, increased the dielectric permittivity of PDMS by 35%. The contact angle of PDMS films was increased from 108° to 116° by the introduction of a small poly(pentafluorostyrene) chain. Finally, 17 α -ethynyl-1,3,5(10)-estratriene-3,17 β -diol and 1-ethynyl-3,5-bis(trifluoromethyl)benzene were incorporated as examples of other functional groups.

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Introduction

Polydimethylsiloxane (PDMS) is the most widely used siloxane polymer.¹ PDMS elastomers have numerous and widespread applications such as membranes,² adhesives,³ dielectric elastomers⁴ and biomedical applications. PDMS owes its many excellent properties to the presence of methyl groups along the flexible Si–O–Si backbone which gives the polymer high thermal stability, high gas permeability, low surface tension and chemical and biological inertness.⁵

Due to the many excellent properties of PDMS it is of great interest to extend the range of applications even further. The properties of PDMS are usually altered and improved by the application of fillers such as metal oxides or most frequently by silicates. However, such filler materials often agglomerate due to favorable particle–particle interactions and this leads to a deterioration of the properties locally instead of the desired macroscopic improvement. The possibility of incorporating evenly distributed functionalities into the PDMS elastomer networks without risking agglomeration could greatly improve and expand the application area of PDMS.⁶ The incorporation is

envisioned to be performed by covalent attachment of functional molecules to the network, which would provide a matrix with well distributed modifications that prevent leakage of the functional moieties from the PDMS network during use. Modification of the PDMS network by covalent grafting of functionality will change the properties and improve the applicability of PDMS within many areas such as electrical, optical and biomedical areas. The modification could furthermore improve properties such as oil and solvent resistance⁷ and current release problems encountered for thin PDMS films where the release forces between PDMS and the substrate easily exceed the tear strength of the material since the excellent wetting properties of PDMS may lead to strong substrate–PDMS interactions.⁸

The cross-linking of PDMS into an elastomer is frequently achieved by hydrosilylation where vinyl groups of one component react with hydrosilane groups of the other component in a platinum catalyzed reaction. In this work, a novel silicone compatible vinyl cross-linker containing an azide functionality is introduced. The vinyl groups allow for cross-linking reactions with hydride-terminated PDMS molecules whereas the azide group allows for modification of the PDMS network either before or after network cross-linking. The azide moiety opens up for click reactions, in this case the copper-catalyzed cycloaddition of an azide group and an alkyne (CuAAC) forming a 1,4-disubstituted-1,2,3-triazole.^{9–12} Click chemistry has previously been demonstrated to be successful for functionalization of polymers in general^{13–15} and in combination with

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polysiloxanes in particular.^{16–19} The azide group on the cross-linker therefore enables reactions with various types of alkyne functional molecules and thereby significantly widens the functionality that can be introduced into PDMS elastomers. Therefore a number of different functionalities are elaborated. Introduction of 4-methylumbelliferone will provide the PDMS network with a fluorescent tag at the cross-linking site that can not only be used to visualize the distribution of incorporated functionality but also create luminescent PDMS films. A push-pull dipole that potentially enhances the dielectric permittivity of the silicone elastomer can be inserted from an ethynyl-4-nitrobenzene and thus improve the dielectric elastomer performance.²⁰ The incorporation of ferrocene will provide PDMS films with potential applications within the optical, magnetic or electronic field²¹ and within the area of cancer research as certain ferricenium complexes are known to show anti-tumor activity.²² Ferrocene has also recently been positioned on surfaces of nanoparticles²³ or single-walled carbon nanotubes²⁴ by application of click chemistry and ethynylferrocene. Different kinds of drugs or therapeutics for biomedical applications will also be possible by the introduction of an estradiol functionality.²⁵ Recently, it has been shown that introduction of trifluoromethyl groups improve the oil and solvent resistance of PDMS films.⁷ With this in mind bis(trifluoromethyl)phenyl and a short poly(pentafluorostyrene) chain will be inserted into the PDMS network. Also possible improvements of the release properties of such fluorine containing PDMS films during processing will be investigated. An important property of the system is that the alkyne-functional molecule in principle can be clicked onto the azide cross-linker before or after the cross-linking reaction that leads to the PDMS network.

Here we present the preparation and characterization of novel PDMS networks containing the elaborated functionalities using the pre-cross-linking approach with the series of new silicone compatible cross-linkers. The pre-cross-linking procedure avoids the step of swelling the PDMS network for successful click reactions and furthermore allows for comprehensive characterization of the individual functional cross-linkers.

Experimental

Materials and methods

Hydride-terminated PDMS, DMS-H31 ($\bar{M}_n = 28\,000\text{ g mol}^{-1}$) and a vinyl functional PDMS cross-linker, VDT-431 ($\bar{M}_n = 28\,000\text{ g mol}^{-1}$, 16-functional) were acquired from Gelest Inc. The platinum cyclovinylmethyl siloxane complex catalyst (511) was purchased from Hanse Chemie AG. All other chemicals were acquired from Aldrich and used as received unless otherwise specified.

FTIR was conducted on a PerkinElmer Spectrum One model 2000 Fourier Transform Infrared apparatus equipped with a universal attenuated total reflection accessory on a ZnSe-diamond composite. Spectra were recorded in the range of 4000–650 cm^{-1} with 4 cm^{-1} resolution and 16 scans. ¹H- and ¹³C-NMR experiments were performed on a Bruker 250 MHz

spectrometer. Solid state ¹³C-NMR was recorded on a Bruker Avance 500 MHz spectrometer. Thermogravimetric analysis (TGA) was performed on a Q500 from TA Instruments in a nitrogen atmosphere with a heating rate of 10 °C min⁻¹ from RT to 950 °C. Differential scanning calorimetry (DSC) measurements were performed on a DSC Q1000 from TA Instruments. The thermal analyses were performed with a heating and cooling rate of 10 °C min⁻¹ from 25–200 °C. Mechanical characterization of the prepared films was performed with a TA Instruments 2000 Rheometer set to a controlled strain mode at 1% strain, which was ensured to be within the linear viscoelastic regime. The measurements were performed at RT with a parallel plate geometry of 25 mm in the frequency range of 100–0.01 Hz. Optical characterization was performed on a Leica DMLB microscope with a Olympus Highlight 2000 light source. Fluorescence intensity measurements were performed on a BMG Labtech POLARstar Omega (excitation 355 nm, emission 460 nm). Size-exclusion chromatography (SEC) was performed on a Viscotek GPCmax VE-2001 instrument equipped with a Viscotek TriSEC Model 302 triple detector using two PLgel mixed-D columns from Polymer Laboratories. Samples were run in THF at 30 °C at a rate of 1 ml min⁻¹ and molar mass characteristics were calculated using polystyrene standards. Dielectric relaxation spectroscopy (DRS) was performed on a Novocontrol Alpha-A high performance frequency analyzer. Contact angle measurements with water were conducted on a Dataphysics OCA 20. A drop of 6 μl was placed on the surface of the film with the needle inside the drop. The drop was expanded at a rate of 0.125 ml s⁻¹. All reported contact angles are an average of 3 measurements on 3 drops.

Synthesis

All reactions were carried out under a nitrogen atmosphere.

Tris(allyloxy)(3-bromopropyl)silane (1). Allyl alcohol (4.24 g, 73.11 mmol) was dissolved in dry THF (120 ml) in a 250 ml 2-necked round bottomed flask. The mixture was cooled to 0 °C in an ice bath and triethylamine (9.87 g, 97.5 mmol) was added dropwise. (3-Bromopropyl)trichlorosilane (5 g, 19.5 mmol) was then added dropwise to the reaction mixture. The reaction was carried out for 17 hours at RT. The reaction mixture was filtered and the solvent and excess allyl alcohol and triethylamine were removed *in vacuo*. The product was obtained in the form of a light yellow oil (5.35 g, 86%). IR (cm^{-1}): 2870 (C–H stretch); 1645 (C=C stretch); 1070 (C–O stretch); 1035 (Si–O stretch). ¹H NMR (CDCl_3 , δ_{H} , ppm): 0.81 (m, 2H, $\text{CH}_2\text{--Si}$); 1.98 (m, 2H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 3.40 (t, ³ $J = 5.6\text{ Hz}$, 2H, Br--CH_2), 4.30 (m, 6H, O--CH_2), 5.12 (dd, ³ $J = 8.6\text{ Hz}$ and ² $J = 1.25\text{ Hz}$, 3H, CH=C), 5.27 (dd, 3H, ³ $J = 14.25\text{ Hz}$ and ² $J = 1.5\text{ Hz}$, CH=C), 5.92 (m, 3H, =CH--CH_2). ¹³C-NMR (CDCl_3 , δ_{C} , ppm): 9.55 (d); 26.48 (e); 36.51 (f); 63.60 (c); 114.84 (a); 136.30 (b).

Tris(allyloxy)(3-azidopropyl)silane (2). **1** (5.16 g, 16.06 mmol) and NaN_3 (1.39 g, 21.41 mmol) were dissolved in DMF (50 ml) in a 250 ml 2-necked round bottomed flask. The reaction mixture was stirred at RT for 17 hours. The reaction mixture was then quenched with H_2O (70 ml) and extracted with ethyl acetate (3 \times 70 ml). The organic phases were combined and washed with

H₂O (3 × 70 ml) and brine (1 × 70 ml), dried with MgSO₄, filtered and concentrated *in vacuo* to give the product in the form of an orange-yellow oil (3.91 g, 86%). IR (cm⁻¹): 2870 (C–H stretch); 2095 (–N₃ stretch); 1640 (C=C stretch); 1070 (C–O stretch); 1035 (Si–O stretch). ¹H NMR (CDCl₃, δ_H, ppm): 0.74 (m, 2H, CH₂–Si), 1.71 (m, 2H, CH₂–CH₂–CH₂), 3.26 (t, ³J = 5.75 Hz, 2H, N₃–CH₂), 4.30 (m, 6H, O–CH₂), 5.12 (dd, ³J = 8.5 Hz and ²J = 1.25 Hz, 3H, CH=C), 5.27 (dd, ³J = 14.5 Hz and ²J = 1.75 Hz, 3H, CH=C), 5.92 (m, 3H, =CH–CH₂). ¹³C-NMR (CDCl₃, δ_C, ppm): 7.60 (d); 27.47 (e); 53.69 (f); 63.58 (c); 114.77 (a); 136.29 (b).

4-Methyl-7-(prop-2-yn-1-yloxy)-2H-chromen-2-one (3). 4-Methylumbelliferone (3 g, 17.0 mmol) and K₂CO₃ (2.04 g, 20 mmol) were dissolved in acetone (85 ml). Propargyl bromide (2.43 g, 20 mmol) was added at a rate of 0.06 ml min⁻¹. The reaction was carried out under reflux for 24 hours. The reaction mixture was then quenched with H₂O (80 ml) and subsequently extracted 3 times with ethyl acetate. The organic phases were combined and washed with H₂O (3 × 80 ml) and brine (1 × 80 ml), dried with MgSO₄, filtered and concentrated *in vacuo*. The crude was recrystallized in an ethyl acetate–heptane mixture (1 : 0.75) to give the product in the form of a white solid in quantitative yield. IR (cm⁻¹): 3305 (C≡C–H stretch); 1720 (O–C=O stretch); 1605 (C=C stretch). ¹H NMR (CDCl₃, δ_H, ppm): 2.40 (s, 3H, Ar–CH₃), 2.57 (s, 1H, C≡C–H), 4.76 (d, ⁴J = 2 Hz, 2H, O–CH₂–), 6.16 (s, 1H, O=C–CH–), 6.95 (m, 2H, Ar–H), 7.52 (m, 1H, Ar–H). ¹³C-NMR (CDCl₃, δ_C, ppm): 18.58 (s); 56.09 (i); 76.43 (g); 77.34 (h); 102.07 (o); 112.31 (q); 112.59 (k); 114.16 (m); 125.56 (l); 152.56 (n); 154.93 (p); 160.27 (j); 160.99 (r).

General procedure for click reactions, 4-methyl-7-((1-(3-(tris(allyloxy)silyl)propyl)-1H-1,2,3-triazole-4-yl)methoxy)-2H-chromen-2-one (4). 2 (3.01 g, 10.6 mmol) and 3 (2.17 g, 10.0 mmol) were dissolved in THF (50 ml) in a 250 ml 2-necked round bottomed flask. CuI (0.206 g, 10.6 mmol) was subsequently added and Et₃N (1.61 g, 15.9 mmol) was added dropwise. The reaction was carried out at RT for 17 hours. The reaction mixture was extracted with ethyl acetate and washed with H₂O (3 × 40 ml) and brine (1 × 40 ml), dried with MgSO₄, filtered and concentrated *in vacuo* to give the product in the form of a light grey oil (2.66 g, 53%). IR (cm⁻¹): 2935 (C–H stretch); 1715 (O–C=O stretch); 1610 (C=C stretch); 1070 (C–O stretch); 1035 (Si–O stretch). ¹H NMR (CDCl₃, δ_H, ppm): 0.60 (m, 2H, CH₂–Si), 2.05 (m, 2H, CH₂–CH₂–CH₂), 2.40 (s, 3H, Ar–CH₃), 4.28 (m, 2H, N–CH₂–), 4.37 (m, 6H, O–CH₂–), 5.11 (dd, ³J = 8.5 Hz and ²J = 1.25 Hz, 3H, CH₂=C), 5.25 (s, 2H, O–CH₂–C–N), 5.26 (dd, ³J = 14.25 Hz and ²J = 1.5 Hz, 3H, CH=C), 5.92 (m, 3H, =CH–CH₂), 6.14 (s, 1H, O=C–CH–), 6.95 (m, 2H, Ar–H), 7.50 (m, 1H, Ar–H), 7.65 (s, 1H, –C=CH–N–). ¹³C-NMR (CDCl₃, δ_C, ppm): 7.39 (d); 18.54 (s); 23.93 (e); 52.39 (f); 62.20 (i); 63.70 (c); 101.98 (o); 112.08 (q); 112.27 (k); 113.89 (l); 114.90 (a); 122.95 (m); 125.60 (g); 136.10 (b), 142.69 (h); 152.39 (n); 154.99 (p); 161.02 (j); 161.07 (r).

4-Ferrocene-1-(3-(tris(allyloxy)silyl)propyl)-1H-1,2,3-triazole (5). The product was prepared according to the general click procedure using 2 (0.204 g, 0.71 mmol) and ethynylferrocene (0.145 g, 0.67 mmol), CuI (0.0134 g, 0.071 mmol) and Et₃N (0.107 g, 1.06 mmol) to give a brown oil (0.31 g, 94%). IR (cm⁻¹): 2955–2870 (C–H stretch); 1590 (C=C ring stretch); 1430 (C=C ring stretch); 1070 (C–O stretch); 1035 (Si–O stretch). ¹H NMR

(CDCl₃, δ_H, ppm): 0.68 (m, 2H, CH₂–Si), 2.07 (m, 2H, CH₂–CH₂–CH₂), 4.07 (m, 2H, N–CH₂–), 4.2–4.25 (m, 8H, Ar–H), 4.30 (m, 6H, O–CH₂–), 4.72 (m, 1H, Ar–H), 5.12 (dd, ³J = 8.75 Hz and ²J = 1.25 Hz, 3H, CH=C), 5.28 (dd, ³J = 14.25 Hz and ²J = 1.25 Hz, 3H, CH=C), 5.92 (m, 3H, =CH–CH₂), 7.46 (s, 1H, –C=CH–N–). ¹³C-NMR (CDCl₃, δ_C, ppm): 7.40 (d); 24.32 (e); 52.21 (f); 63.73 (c); 66.52 (k); 68.51 (j); 69.50 (i); 114.92 (a); 118.83 (g); 136.16 (b); 143.46 (h).

4-(4-Nitrophenyl)-1-(3-(tris(allyloxy)silyl)propyl)-1H-1,2,3-triazole (6). The product was prepared according to the general click procedure using 2 (0.203 g, 0.72 mmol), 1-ethynyl-4-nitrobenzene (0.103 g, 0.68 mmol), CuI (0.0137 g, 0.072 mmol) and Et₃N (0.109 g, 1.07 mmol) to give a light yellow oil which crystallized upon cooling (0.156 g, 54%). *M*_p: 69 °C. IR (cm⁻¹): 2915–2860 (C–H stretch); 1645 (C=C stretch); 1605 (aromatic C=C stretch); 1505 (N=O asymmetric stretch); 1460 (aromatic C=C stretch); 1340 (N=O symmetric stretch); 1075 (C–O stretch); 1035 (Si–O stretch). ¹H NMR (CDCl₃, δ_H, ppm): 0.71 (m, 2H, CH₂–Si), 2.11 (m, 2H, CH₂–CH₂–CH₂), 4.31 (m, 2H, N–CH₂–), 4.44 (m, 6H, O–CH₂–), 5.13 (dd, ³J = 8.75 Hz and ²J = 1.25 Hz, 3H, CH=C), 5.28 (dd, ³J = 14.25 Hz and ²J = 1.25 Hz, 3H, CH=C), 5.92 (m, 3H, =CH–CH₂), 7.91–8.00 (m, 2H, Ar–H), 8.95 (m, 2H, NO₂–Ar–H), 8.30 (s, 1H, –C=CH–N–). ¹³C-NMR (CDCl₃, δ_C, ppm): 7.46 (d); 24.04 (e); 52.56 (f); 63.82 (c); 115.03 (a); 121.19 (g); 124.27 (k); 126.04 (j); 136.16 (b); 136.96 (i); 145.39 (l); 147.21 (h).

4-(3,5-Bis(trifluoromethyl)phenyl)-1-(3-(tris(allyloxy)silyl)propyl)-1H-1,2,3-triazole (7). The product was prepared according to the general click procedure using 2 (0.200 g, 0.706 mmol), and 1-ethynyl-3,5-bis(trifluoromethyl)benzene (0.17 g, 0.67 mmol), CuI (0.0138 g, 0.071 mmol) and Et₃N (0.107 g, 1.06 mmol) at 45 °C for 24 hours. Azide functional Merrifield resin (0.150 g, 0.21 mmol)²⁶ was added towards the end of the click reaction in order to remove excess 1-ethynyl-3,5-bis(trifluoromethyl)benzene. This reaction was carried out at 45 °C for 17 hours. The reaction mixture was thereafter filtered and extracted with ethyl acetate (3 × 60 ml) and washed with H₂O (3 × 60 ml), dried with MgSO₄, filtered and concentrated *in vacuo* to give the product in the form of an orange-brown oil (0.28 g, 80%). IR (cm⁻¹): 2930–2870 (C–H stretch); 1615 (aromatic C=C stretch); 1465 (aromatic C=C stretch); 1275 (C–F stretch), 1170 (C–F stretch), 1125 (C–F stretch), 1085 (C–O stretch); 1035 (Si–O stretch). ¹H NMR (CDCl₃, δ_H, ppm): 0.71 (m, 2H, CH₂–Si), 2.11 (m, 2H, CH₂–CH₂–CH₂), 4.31 (m, 2H, N–CH₂–), 4.45 (m, 6H, O–CH₂–), 5.12 (dd, ³J = 8.75 Hz and ²J = 1.25 Hz, 3H, CH=C), 5.27 (dd, ³J = 14.25 Hz and ²J = 1.5 Hz, 3H, CH=C), 5.93 (m, 3H, =CH–CH₂), 7.92 (s, 1H, Ar–H), 7.94 (s, 1H, –C=CH–N–), 8.28 (s, 2H, Ar–H). ¹³C-NMR (CDCl₃, δ_C, ppm): 7.45 (d); 24.07 (e); 52.59 (f); 63.74 (c); 114.96 (a); 120.78 (g); 121.55 (l); 125.54 (m); 132.03 (i); 132.47 (j); 132.89 (k); 136.27 (b); 144.93 (h).

4-(1,2,5(10)-Estratriene-1,17β-diol)-1-(3-(tris(allyloxy)silyl)propyl)-1H-1,2,3-triazole (8). The product was prepared according to the general click procedure using 2 (0.197 g, 0.71 mmol), 17α-ethynyl-1,3,5(10)-estratriene-3,17β-diol (0.203 g, 0.67 mmol), CuI (0.0134 g, 0.074 mmol) and Et₃N (0.107 g, 1.06 mmol) at RT for 17 hours then at 45 °C for 24 hours to give a light yellow oil (0.373 g, 96%). IR (cm⁻¹): 3310 (O–H stretch); 2930–2870 (C–H stretch); 1610 (aromatic C=C stretch), 1455

(aromatic C=C stretch), 1055 (C–O stretch); 1035 (Si–O stretch). ^1H NMR (CDCl_3 , δ_{H} , ppm): 0.68 (m, 2H, $\text{CH}_2\text{-Si}$), 1.04 (s, 3H, $-\text{CH}_3$), 1.41–2.82 (m, 15H, Al-H), 2.06 (m, 2H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 4.29 (m, 2H, N-CH_2), 4.39 (m, 6H, O-CH_2), 5.11 (dd, $^3J = 8.63$ Hz and $^2J = 1.38$ Hz, 3H, CH=C), 5.26 (dd, $^3J = 14.15$ Hz and $^2J = 1.5$ Hz, 3H, CH=C), 5.91 (m, 3H, $=\text{CH-CH}_2$), 6.56 (m, 2H, Ar-H), 7.04 (m, 1H, Ar-H), 7.42 (s, 1H, $-\text{C=CH-N}$). ^{13}C -NMR (CDCl_3 , δ_{C} , ppm): 7.41 (d); 14.19 (z); 23.29 (k); 23.97 (e); 26.16 (o); 27.17 (r); 29.58 (s); 32.91 (j); 37.85 (n); 39.35 (q); 43.28 (p); 47.27 (m); 48.47 (l); 52.31 (f); 63.77 (c); 82.29 (i); 112.77 (w); 115.15 (a); 115.30 (y); 121.40 (g); 126.22 (v); 132.00 (u); 136.21 (b); 137.96 (t); 153.39 (x); 153.75 (h).

Alkyne end-functionalized poly(pentafluorostyrene) (9). Alkyne functionalised poly(pentafluorostyrene) was synthesized according to a recently published procedure²⁷ by atom transfer radical polymerization (ATRP) of 2,3,4,5,6-pentafluorostyrene in bulk initiated with 3-bromo-1-(trimethylsilyl)-1-propyne. $T_g = 97$ °C. IR (cm^{-1}): 3316 ($\text{C}\equiv\text{C-H}$ stretch); 2960 (C–H stretch); 1496 (F-aromatic stretch); 981 (C–F-aromatic bend). ^1H NMR (CDCl_3 , δ_{H} , ppm): 1.70–3.00 ($\text{CH}_2\text{-C}\equiv\text{C} + \text{CH}_2\text{-CH} + \text{H-C}\equiv\text{C}$), 4.8 (m, 1H, CH-Br). ^{13}C -NMR (CDCl_3 , δ_{C} , ppm): 16.56 (i); 32.12 (j); 37.13–38.67 (k); 69.24 (g); 81.79 (h); 135.81 (l); 139.18 (n); 143.15 (o); 146.45 (m). SEC (THF): $\bar{M}_n = 3300$ Da, $\bar{M}_w/\bar{M}_n = 1.4$.

4-Poly(pentafluorostyrenyl)-1-(3-(tris(allyloxy)silyl)propyl-1H-1,2,3-triazole (10). The alkyne end-functional polymer **9** (0.6 g, 0.18 mmol) and CuI (0.031 g, 0.162 mmol) were mixed in THF (4 ml) followed by the addition of **2** (0.062 g, 0.216 mmol) and Et_3N (0.1 ml, 0.72 mmol). The click reaction proceeded at 35 °C for 20 h. The product was precipitated in methanol and dried *in vacuo*. Yield: 0.59 g (89%). $T_g = 112$ °C. IR (cm^{-1}): 2960–2870 (C–H stretch); 1653 (C=C stretch); 1498 (F-aromatic stretch); 981 (C–F-aromatic bend). ^1H NMR (CDCl_3 , δ_{H} , ppm): 0.70 (Si- CH_2), 1.70–3.00 (Si- $\text{CH}_2\text{-CH}_2 + \text{CH}_2\text{-CH} + \text{CH=C(N)-CH}_2$), 4.25 (Si-O- $\text{CH}_2 + \text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$), 5.15 ($\text{CH}_2=\text{CH}$), 5.87 ($\text{CH}_2=\text{CH}$), 7.60 (N- CH=C(N)-CH_2). ^{13}C -NMR (CDCl_3 , δ_{C} , ppm): 7.51 (d); 24.07 (e); 25.52 (i); 32.12 (j); 37.05–38.79 (k); 52.85 (f); 63.26 (c); 114.15 (a); 125.27 (g); 135.93 (l); 136.11 (b); 139.32 (n); 143.42 (o); 146.24 (m); 153.16 (h). $\bar{M}_n = 3300$ Da, $\bar{M}_w/\bar{M}_n = 1.4$.

Procedure for stability measurements

The hydrolytic stability of the Si–O–C linkage in **2** was determined using a previously described method.²⁸ 30 mg of sample was dissolved in 0.8 ml CDCl_3 in an NMR tube to which 50 μl D_2O was added. The ^1H -NMR of the mixture was recorded over time for 72 h. The silyl ether cleavage was evaluated by integration and comparison of the O- CH_2 peak and the $\text{CH}_2\text{-Si}$ peak.

Preparation of polymer films

Cross-linkers (**2**, **4–8** and **10**) (0.043 mmol) were dissolved in dry THF (0.3 ml) and mixed with a 16-functional cross-linker (VDT-431) (0.0027 mmol) and hydride-terminated PDMS (DMS-H31) (0.086 mmol). The platinum cyclovinylmethyl siloxane complex catalyst (511) (10–30 ppm) in dry THF was thereafter added and the mixture was mixed on a vortex mixer for 2 minutes. The mixture was thereafter degassed *in vacuo* to remove solvent and

air bubbles. The mixture was poured into 1 mm thick steel molds on a fluorinated ethylene propylene (FEP) release liner and cured at 60 °C for 24 h.

Swelling experiments

The gel fractions were determined using two methods. The first method, Soxhlet extraction with chloroform for 48 hours, was used to pull out all extractables. The samples were thereafter dried for 24 h and the gel fraction was determined as the weight after extraction and drying (m_e) to the initial weight of the sample (m_0) as $W_{\text{gel}} = m_e/m_0$.

The second method consisted of swelling experiments used to pull out leachables from the prepared films. Samples were swelled in chloroform for 48 hours at RT. The solvent was replaced after 24 hours. The solvent was then decanted and the films were washed several times with chloroform. The samples were thereafter dried for 24 h. Gel fractions were determined as the weight after extraction and drying (m_e) to the initial weight of the sample (m_0) as $W_{\text{gel}} = m_e/m_0$.

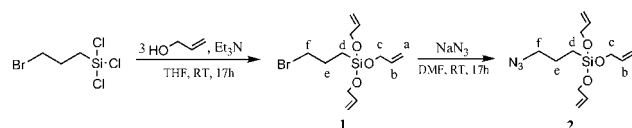
Results and discussion

The azide functional, silicone compatible vinyl cross-linker (**2**) was synthesized in two steps *via* the silyl ether reaction between (3-bromopropyl)trichlorosilane and allyl alcohol and subsequent substitution of bromine with azide as illustrated in Scheme 1.

The azide cross-linker was isolated as an orange-yellow oil with a high yield and high purity. The vinyl cross-linker proved to be hydrolytically stable under the utilized synthesis conditions which included several extraction procedures with water. The stability of the formed silyl ether bond was evaluated using ^1H -NMR in D_2O . Spectra were recorded over time and integration of the O- CH_2 peak compared to integration of other peaks indicated that no detectable cleavage of the Si–O–C bond had taken place in the stability test during the 72 hours.

The alkyne functional molecules used in the click reactions with **2** are shown in Table 1. A general reaction scheme for the click reaction is illustrated in Scheme 2.

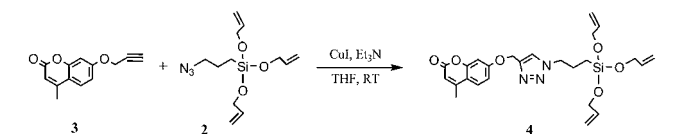
The click reaction was used to prepare a variety of different functional cross-linkers as shown in Table 1. Two of the employed alkynes, **3** and **9**, were not commercially available but prepared for this study. **3** was prepared through a Williamson ether synthesis of 4-methylumbelliferone and propargyl bromide using K_2CO_3 as the base catalyst. **9** was polymerized under controlled ATRP conditions using a previously published procedure²⁷ yielding an alkyne functional poly(pentafluorostyrene). The functionalized cross-linkers were all prepared under similar click reaction conditions in THF using a CuI– Et_3N catalytic system. In the case



Scheme 1 Preparation of the azide-functional vinyl cross-linker **2**.

Table 1 Alkynes and functional cross-linkers from click reactions. Letters are used in assignment of ^{13}C -NMR spectra

Alkyne	Click-product



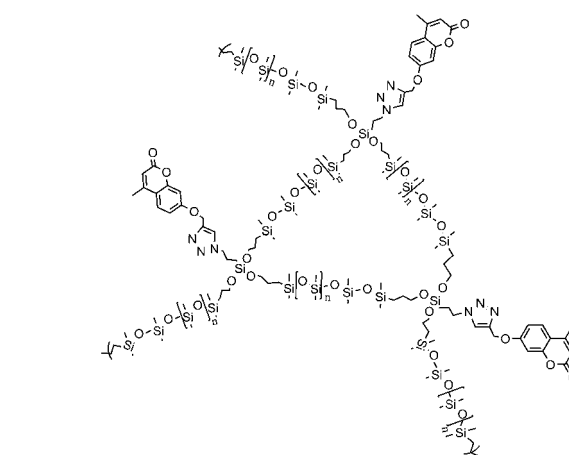
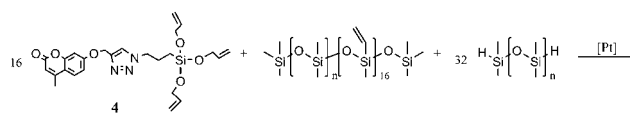
Scheme 2 General reaction scheme for click reaction between the azide cross-linker (2) and alkyne exemplified by 3.

of 5, 8 and 10 yields were high (~90%) but in the case of 4 and 6 the yields were in the order of 50%. This was assessed to be acceptable and was not attempted optimized.

The synthesized alkynes and all novel vinyl cross-linkers, 4–8 and 10, were thoroughly characterized by FTIR and ^1H - and ^{13}C -NMR. FTIR was used to confirm the completion of the click reactions by the disappearances of the alkyne band at approximately 3300 cm^{-1} and the very distinct azide band at approximately 2100 cm^{-1} . The presence of the triazole proton in ^1H -NMR points to the successful formation of reaction products. The triazole proton appears from $\delta_{\text{H}} = 7.42\text{ ppm}$ to $\delta_{\text{H}} = 8.30\text{ ppm}$ depending on the electron density of the triazole. Representative spectra can be found as ESI.† If small residues of azide/alkyne can be detected, they are easily removed by use of resins which facilitates a simple purification procedure. In connection with the synthesis of 7, a small alkyne band was detected by FTIR and a peak for the alkyne proton was also detected by ^1H -NMR at $\delta_{\text{H}} = 3.26\text{ ppm}$. 7 was consequently treated with an azide functional Merrifield resin in order to remove the residual alkyne reactant by additional click reaction and resulting attachment of the alkyne reactant to the resin. The azide resin with the excess alkyne attached could thereafter be removed from the reaction mixture by simple filtration.

The PDMS networks were prepared from cross-linkers 2, 4–8 and 10, hydride terminated PDMS and a platinum catalyst according to Scheme 3.

A commercially available 16-functional silicone vinyl cross-linker was used to reinforce the network since networks prepared solely from three-functional cross-linkers are known to be very soft and have low mechanical breakdown strength.²⁹ The molar ratio between the three-functional synthesized cross-linkers and the 16-functional commercial silicone cross-linker were 16 : 1 to ensure a high concentration of the functionalized cross-linkers and minimize possible competition from the 16-functional cross-linker. The networks were prepared with equimolar amounts, meaning that the number of functional hydride groups of the polymer corresponds to the total number



Scheme 3 Cross-linking reaction between 4 and hydride terminated PDMS.

of vinyl groups on the two cross-linkers. The PDMS films ranged from light yellow in color for films with **6** and **8** to light brown for films with **5** and **7** and dark brown for **10**. The film with **2** was completely transparent whereas the film with **4** was light grey and opaque. Images of all films can be found in the ESI.†

All prepared films were characterized by FTIR. There was, however, no differences between the films with different functional cross-linkers since the concentrations of cross-linkers in the films were found to be too low to be detected by this technique. A solid state ^{13}C -NMR spectrum of the elastomer with **4** obtained over 20 h reveals the dominating Si-CH₃ resonance at ~1 ppm. In addition three small resonances at ~4, ~8, ~24 ppm can be assigned to CH₂ close to Si atoms. Weak signals in the 100–160 ppm range indicate the presence of aromatic carbons. The solid state ^{13}C -NMR analysis thus strongly supports the presence of the silyl-based cross-linker in the network.

Swelling and extraction experiments were used to determine the gel fraction of the films. This was done in order to further elucidate if the synthesized cross-linkers had reacted with the PDMS chains and were incorporated covalently in the network. Possible problems that such modified networks could encounter include poor compatibility with the matrix and steric hindrance of the three-functional cross-linker leading to dangling chains and extractable substructures containing primarily the triazole cross-linkers. Some of the produced films had indeed large sol fractions especially from the Soxhlet extraction data (Table 2). It is, however, not common practice to perform this type of extractions when investigating PDMS network gel fractions as it is a very aggressive method. The swelling experiments performed are therefore more suitable for comparison with previously performed PDMS swelling experiments.^{30,31} Optimized PDMS elastomers usually have gel fractions of 95–97% whereas stoichiometrical PDMS networks usually have gel fractions around 90%. This can be explained by the optimized PDMS elastomers having a stoichiometry of 1.1–1.4 which means that the cross-linker is in excess and that all cross-linker sites do not need to react thus reducing steric hindrance.³² The networks prepared in this study are all stoichiometric such that gel fractions of less than 90% are anticipated.

A visual evaluation of the dry sol and gel fraction revealed that all films (gel fractions) retained their initial colors which are due to the presence of the functional cross-linkers. Furthermore all sol fractions bore little or no evidence of color from cross-linkers. In order to further investigate the nature of the gel and sol

fraction, the fluorescence intensity was measured of both the dried sol and the gel fraction of the film prepared with the fluorescence cross-linker **4** after the Soxhlet extraction experiment. The fluorescence intensity was also measured for the film with **4** before the Soxhlet extraction. Results are shown in Fig. 1.

It was observed that the fluorescence intensity of the film prepared with **4** only decreases by 4% after extraction. This indicates that cross-linker **4** is indeed incorporated into the PDMS network gel fraction and is thus covalently bound to the network. The sol fraction exhibits very low fluorescence intensity and therefore most likely consists of PDMS substructures not connected to the network such as inert or mono-functional PDMS chains. It can hence be concluded, that the synthesized cross-linkers can be successfully incorporated into PDMS networks.

To investigate the distribution of the grafted functionalities, fluorescence microscopy was performed on the film prepared with cross-linker **4** which acts as a fluorescent tag in the network as seen in Fig. 2.

It is seen that the film with **4** is indeed fluorescent and that the fluorescent cross-linker is evenly distributed throughout the network. This indicates that the synthesized triazole cross-linkers can successfully be incorporated into PDMS networks in a well distributed manner.

Mechanical characterization was performed by determining the storage and loss moduli for all films. In Fig. 3 the results for films prepared with **2** and **4** are presented. A similar plot for films with **5–8** and **10** can be found in the ESI.†

It is seen in Fig. 3 that both networks are well cross-linked as the storage modulus for both networks are of an order of 10 to 100 times that of the loss modulus for the investigated frequency regime.³² The elastomer containing cross-linker **4** is seen to have slightly lower moduli than the film with cross-linker **2**. This can be explained by the bulkier group attached on **4** which thereby creates a small diluting effect in the network creating a less elastic film. All other films showed similar mechanical behavior. The elastomer with cross-linker **10** has lower moduli than the other films. This corresponds with the results seen from the extraction experiments which showed that the film with **10** has a significantly smaller gel fraction than the other networks. The large poly(pentafluorostyrene) groups thereby creates a soft network with a large portion of extractable

Table 2 Gel contents of samples as results from Soxhlet extractions and swelling experiments (%)

Cross-linker	Gel fraction (Soxhlet extraction)	Gel fraction (swelling)
2	78.5	84.1
4	57.3	92.2
5	52.8	82.7
6	56.8	68.5
7	74.1	90.1
8	55.9	59.3
10	41.5	69.1

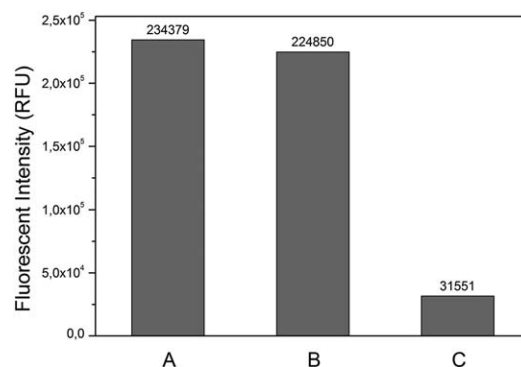


Fig. 1 Fluorescent intensity of A: film with **4** before Soxhlet extraction; B: dried film with **4** after Soxhlet extraction (gel fraction) and C: dried sol fraction of film with **4**.

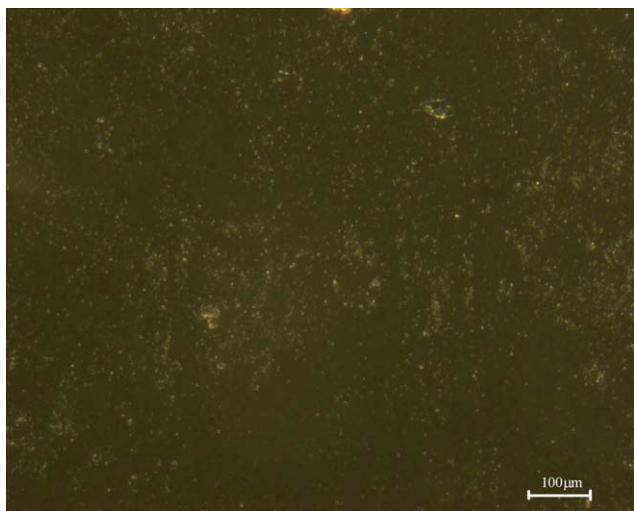


Fig. 2 Fluorescent microscopy image of the film prepared with cross-linker 4.

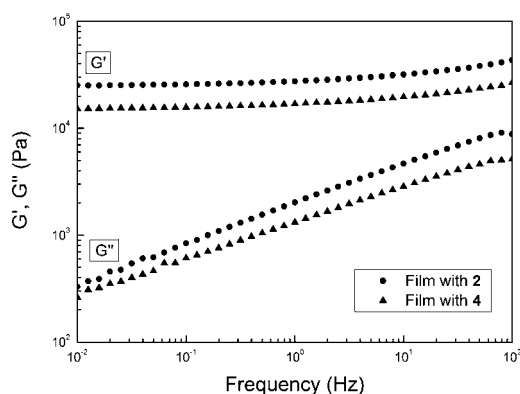


Fig. 3 Storage modulus (G') and loss modulus (G'') as functions of frequency for films prepared with 2 and 4.

substructures. This can be due to incompatibility between the two polymers leading to phase separation which is also visually evident from the darker domains formed in the film.

Thermal gravimetric analysis (TGA) was used to investigate the effects of the different functional cross-linkers on the thermal stability of the PDMS films (Fig. 4).

All TGA curves show a two step mass loss process. The first degradation step occurring from 390 °C to 540 °C (mass loss of 1.8–12.7 wt%) depending on functionality corresponds to the cleavage of Si–CH₃ bonds. In the case of 10 it is noted that at 510 °C all the poly(pentafluorostyrene) has degraded.³³ The second decomposition step occurring from 590 °C to 690 °C (mass loss of 32.5–86.4 wt%) can be attributed to structural rearrangements followed by mineralization of the material.³⁴ The decomposition temperatures are taken as the peak temperature of the first derivative of the temperature with time. The TGA curves show that the PDMS samples have different decomposition temperatures depending on the incorporated functionality with 5 giving the highest initial degradation temperature (540 °C) due to higher thermal stability of ferrocene³⁵ which increases the degradation temperature of the PDMS film. It is

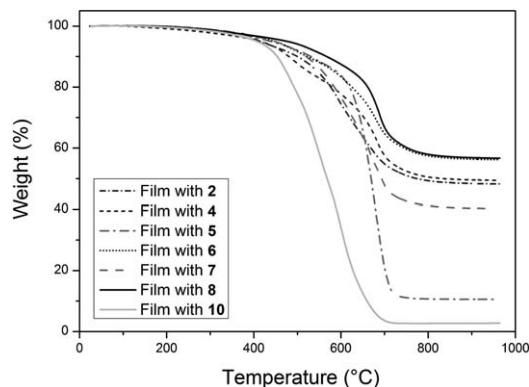


Fig. 4 TGA measurements of PDMS films prepared with cross-linkers 2, 4–8 and 10.

hypothesized that the ferrocene cross-linker, however, also catalyzes the PDMS degradation such that mineralization occurs to a larger extent. The catalytic effect can also be observed for the film with 10 (poly(pentafluorostyrene)). It is moreover noted that all films with a functional cross-linker except for 10 induced a higher decomposition temperature than films with a non-functional cross-linker (2).

The dielectric properties were determined by dielectric relaxation spectroscopy (DRS) for the films prepared with the 2 and 6 cross-linkers, see Fig. 5.

It was found, that the dipolar nature of the 6 cross-linker, due to the nitro group, increases the dielectric properties of the film from 2.3 for films with 2 to 3.1 for films with 6 which corresponds to an increase of 35%. This increase is remarkable since the content of this dipolar cross-linker is only around 0.75 wt% corresponding to 0.25 wt% of the pure dipole molecule. It is therefore likely that by increasing the amount of dipolar cross-linker it would be possible to achieve a large increase in the dielectric permittivity which could improve the performance of dielectric elastomers to a very great extent.

The impact of the fluorine containing cross-linkers on the release properties of the PDMS films was determined using contact angle measurements. The contact angle was found to increase from 108° ± 2.5 for the film with cross-linker 2 to

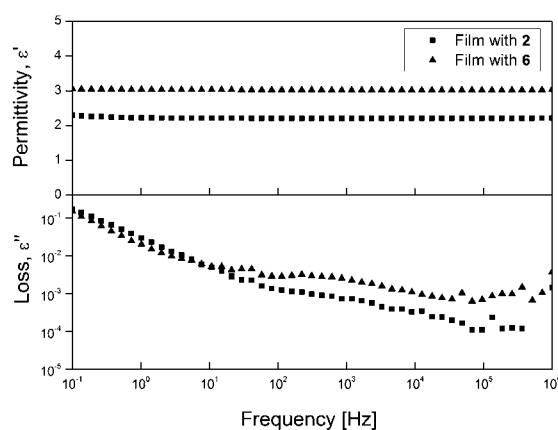


Fig. 5 Permittivity spectra of films prepared with the 2 and 6 cross-linkers showing both the frequency dependence on the permittivity (ϵ') and the dielectric loss (ϵ'').

116° ± 2.5 for the PDMS film with cross-linker **10**. This is due to the hydrophobic nature of the poly(pentafluorostyrene) which causes a migration of the fluorinated polymer to the PDMS surface³⁶ and thus increasing the contact angle and thereby also a possible improvement of release properties for PDMS films during processing.⁸ The film with **7** showed no increase in contact angle compared to the film with **2**. This is probably due to the low concentration of fluorine on this cross-linker which allows the cross-linker to be encapsulated within the PDMS network and no migration to the surface will consequently occur.

Conclusions

A novel silicone compatible cross-linker that allows for click reactions and thereby grafting of various molecular functionalities into PDMS networks has been developed. The developed system opens up for a wide variety of possible reactions and network functionalizations which can expand the application area of PDMS networks greatly. The functionalization of PDMS networks was demonstrated by the successful synthesis of a number of diverse functional cross-linkers that were used to create PDMS films. It was shown that all functional cross-linkers had been successfully incorporated into the network and that only minute amounts of the functionality could be extracted from the network. It was also demonstrated by fluorescence microscopy that the functional cross-linkers were well distributed within the PDMS network. Thermal gravimetric analysis (TGA) showed that the incorporation of a ferrocene functionality increased the thermal degradation temperature of the PDMS network. Furthermore it was shown that the incorporation of a dipolar cross-linker could improve the dielectric permittivity of PDMS by a factor of 35% at only 0.25 wt% of dipole-functionality and that the contact angle of the PDMS films could be increased from 108° to 116° by the incorporation of a small poly(pentafluorostyrene) chain.

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