Macromolecules

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Acid-Catalyzed Rearrangement of Azidopropyl-Siloxane Monomers for the Synthesis of Azidopropyl-Polydimethylsiloxane and Their Carboxylic Acid Derivatives

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Cite This: *Macromolecules* 2021, 54, 2921−2935

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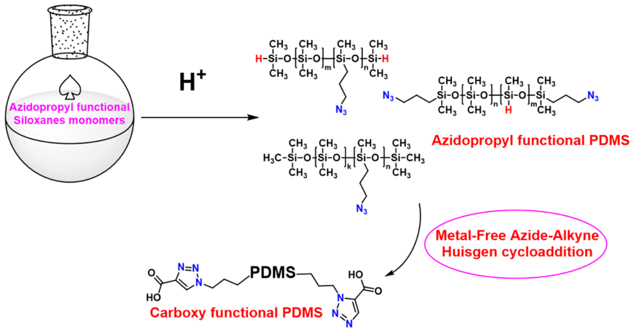
ABSTRACT: In this work, we were the first to show the possibility of synthesizing polydimethylsiloxanes (PDMSs) with azidopropyl-functional groups at the silicon atom by the classical methods for PDMS synthesis, that is, ring-opening polymerization (ROP) and catalytic rearrangement of siloxanes in the presence of a strong acid (CF_3SO_3H). The suggested method was used to obtain PDMSs containing azidopropyl-functional groups at both ends of the polymer chain (telechelics) as well as PDMSs with irregular structures containing different fractions (5−50%) of azidopropyl-functional groups in the main polymer chain. The suggested method also proved to be efficient for synthesizing PDMSs containing both azidopropyl- and hydridosilyl-functional groups simultaneously. As a result, PDMSs with different mutual arrangements of two types of functional groups along the PDMS chain were obtained. The method for the catalytic rearrangement of low-molecular-weight siloxanes that we used made it possible to obtain azidopropyl-functional PDMSs in a wide range of molecular weights from 2000 to 88,000 according to gel permeation chromatography (GPC) data. The possibility of further modification of the resulting azidopropyl-functional PDMS, as well as multifunctional PDMSs containing azidopropyl- and hydridosilyl-functional groups simultaneously, by azide-alkyne cycloaddition reactions was demonstrated. The polymers obtained were characterized by ^{1}H and ^{29}Si NMR spectroscopy and by GPC.

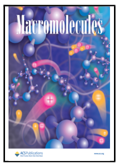


■ INTRODUCTION

Controlling the properties of organosilicon polymers, primarily polydimethylsiloxane (PDMS), by changing the polymer structure by well-controlled chemical modifications is a long-standing and well-established paradigm in silicon chemistry.[1] The efficiency of its implementation largely depends on the chemical tools used to control the structure of new polymers. Unfortunately, the scope of combinations of functional groups that allow one to control the structure of the polymer systems being created is quite limited. While for silicon-functional reagents, such as sodium salts reported by Andrianov,[1] new horizons in synthetic practice opened with the appearance of Rebrov's salts,[2] the majority of the other achievements are associated with hydride-vinyl systems that became the basis of numerous new structures, not to mention industrial applications.[3,4] Perhaps, only the unique process of siloxane bond formation by the Pierce−Rubinsztajn reaction[5] can be used as an exception that confirms the general rule. All the other achievements are associated with competent use of organofunctional reagents combined with reactions classical for silicones, that is, polymerization, telomerization, and equilibrium polymerization-depolymerization, which provide a statistical distribution of required functional groups along the PDMS chain.[6−13]

In general, linear polysiloxanes can be synthesized by both the anionic and cationic polymerization of cyclic siloxanes, which are usually called ″rearrangement″, ″equilibration″, or ″redistribution″ reactions. Rearrangement of siloxanes is the process where the (Si-O) linkages in a mixture of siloxanes (e.g., cyclic and linear) are continuously broken and reformed, in the presence of a catalyst, until the system reaches its thermodynamically most stable equilibrium state.[14,15] From this point of view, incorporation of new functions that ensure the creation of well-controlled structures and are compatible with synthetic methods traditional for organosilicon oligomers is quite an urgent task.

Received: December 17, 2020
Revised: January 21, 2021
Published: March 8, 2021



https://dx.doi.org/10.1021/acs.macromol.0c02790
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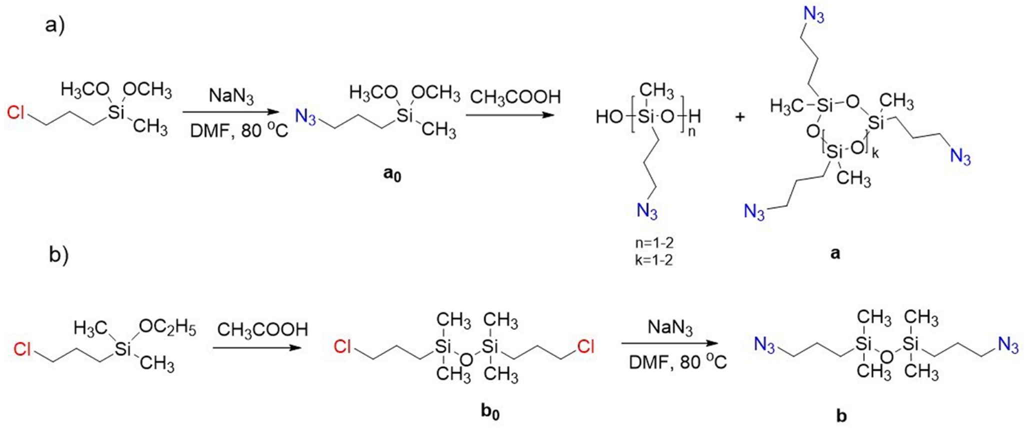
Scheme 1. Synthesis of the Starting Azido-Containing Siloxane Monomer Reagents



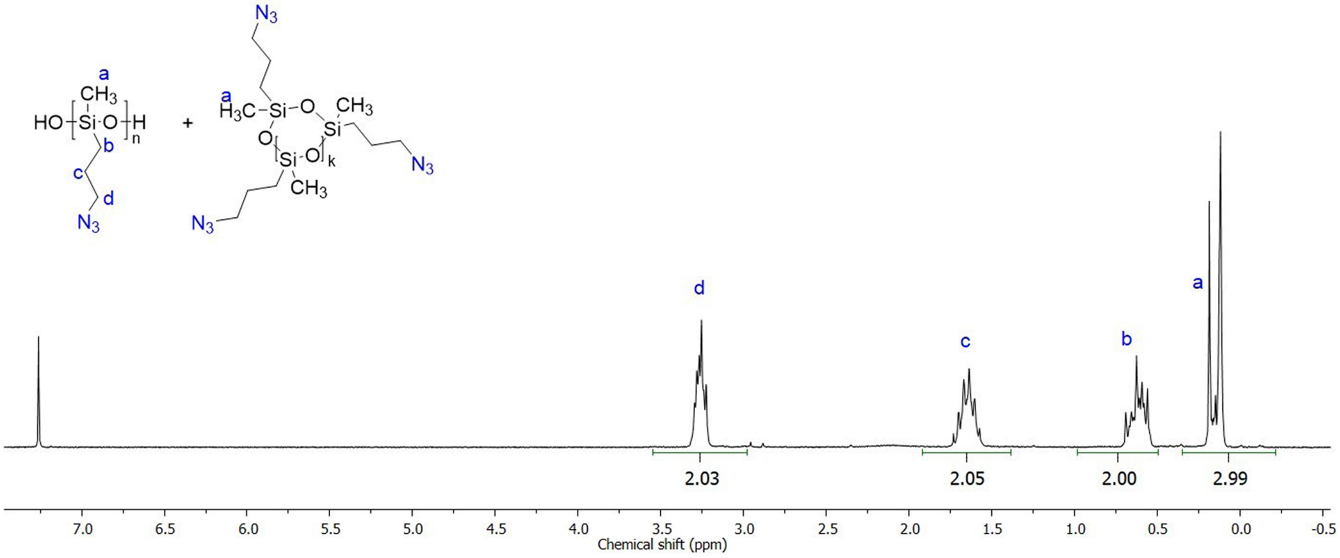
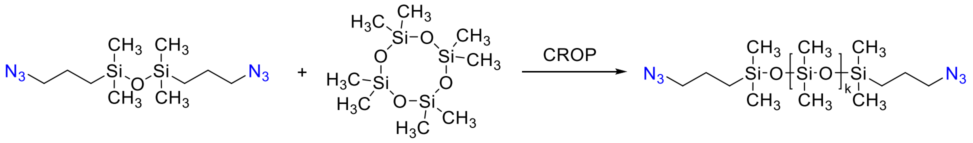


Figure 1. ^{1}H NMR spectrum of 3-azidopropylmethyldimethoxysilane hydrolysate.

Scheme 2. Synthesis of Azido-Containing Polymers N3-PDMS$_n$-N3 (b$_1$-b$_4$).



We noticed examples of successful application of click chemistry methods using PDMS polymer matrices[16−18] and decided to combine these functions with traditional reactions for synthesizing functional PDMS-oligomers and use the resulting oligomers to obtain carboxyl-containing PDMSs that have rich prospects for application in various technical fields.[19−32]

■ EXPERIMENTAL SECTION

Materials. All the reagents were used as received. Octamethylcyclotetrasiloxane (D$_4$), 3-chloropropylmethyldimethoxysilane, 3-chloropropyldimethylethoxysilane, propiolic acid, sodium azide, and undecene alcohol were supplied by ABCR, Germany. Polymethylhydrosiloxane (PMHS) (Penta-804) was obtained from Penta (Moscow).

Dry solvents, namely, toluene, 1,4-dioxane, and DMF, were prepared as follows: reflux for 3−5 h over calcium hydride followed by distillation under argon and then storage for 3 days over 3 Å molecular sieves.

Characterization. Nuclear magnetic resonance (NMR) spectra in solutions were acquired using a Bruker Avance AV-300 spectrometer (300 MHz for ^{1}H; 77.5 MHz for ^{13}C; 59.6 MHz for ^{29}Si). CDCl3 having a chemical shift of δ = 7.25 ppm was used as the internal standard.

Gel permeation chromatography (GPC) analysis was performed on a Shimadzu LC-10A series chromatograph (Japan) equipped with an RID-10A refractometer and SPD-M10A diode matrix detectors. Analytical separation was performed using a 7.8 mm × 300 mm Phenomenex column (USA) filled with Phenogel sorbent with a pore size of 15−500 Å. Toluene was used as the eluent.

High-resolution mass spectra were recorded with a Bruker Microtof II instrument by electrospray ionization (Germany).

Synthesis of bis-(3-chloropropyl)tetramethyldisiloxane (b$_0$). A solution of 20 g (0.11 mol) 3-chloropropyldimethylethoxysilane in 20 g (0.33 mol) acetic acid was stirred for 20 h at 118 °C.

https://dx.doi.org/10.1021/acs.macromol.0c02790
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The product was washed with water and then dried over Na_2SO_4. The solvent was distilled off under reduced pressure. The product was obtained as a colorless transparent liquid (19.14 g, yield 60.6%).^{1}H NMR (300 MHz, $CDCl_3$): δ 3.5 (t, J^2 = 7 Hz, 2H, CH_2-Cl), 1.62 (m, J^2 = 12 Hz, 2H, Si-CH_2-CH_2-), 0.56 (m, J^2 = 7 Hz, 2H, Si-CH_2-), 0.07 (t, J^2 = 10 Hz, 3H, Si-CH_3).

Synthesis of bis-(3-azidopropyl)tetramethyldisiloxane (b). A solution of 10.7 g (0.0373 mol) bis-(3-chloropropyl)-tetramethyldisiloxane and 4.97 g (0.0765 mol) sodium azide in 80 mL DMF was stirred for 15 h at 90 °C in the presence of tetrabutylammonium iodide as the catalyst (0.1% mass.). The solvent was distilled off under reduced pressure. The product was obtained as a colorless transparent liquid (10.6 g, yield 99%).^{1}H NMR (300 MHz, $CDCl_3$): δ 3.24 (t, J^2 = 7 Hz, 2H, CH_2-N_3), 1.62 (m, J^2 = 12 Hz, 2H, Si-CH_2-CH_2), 0.56(m, J^2 = 7 Hz, 2H, Si-CH_2-) 0.08 (t, J^2 = 10 Hz ,3H, Si-CH_3).

Table 1. Siloxane Characterization Data

siloxane polymer	M_{NMR}[a]	M_n	M_w	M_w/M_n	yield, %
B_1	878	1588	2223	1.4	90
B_2	1800	1950	3315	1.7	98
B_3	6500	4700	10,810	2.3	90
B_4	80,000	55,000	88,000	1.6	73
B_5	2060	1900	3420	1.8	70
B_6	8950	8000	15,200	1.9	81
B_7	13,000	7500	16,500	2.2	71
B_8	10,000	10,526	20,000	1.9	78
B_9	3800	5294	9000	1.7	77
A_1	2400	2625	4200	1.6	94
A_2	4300	5526	10,500	1.9	95
A_3	19,200	9316	17,700	1.9	84
A_4	23,200	18,747	28,120	1.5	84
A_5		28,036	78,500	2.8	84
C_0		4260	6010	1,4	99
C_1		28,057	78,560	2.8	99
C_2		5526	10,500	1.9	99
C_3		9316	17,700	1.9	99
C_4		1950	3315	1.7	99

[a] The masses of the products are calculated from the data of ^{1}H NMR spectroscopy.

Synthesis of (3-azidopropyl)methyldimethoxysilane (a_0). A solution of 30 g (0.164 mol) (3-chloropropyl)methyldimethoxysilane and 11.22 g sodium azide (0.172 mol) in 120 mL DMF was stirred for 10 h at 80 °C in the presence of tetrabutylammonium iodide as the catalyst (0.1% mass.). The product was washed with water and then dried over Na_2SO_4. The solvent was distilled off under reduced pressure to give 23 g (77% yield) of 3-azidopropylmethyldimethoxysilane. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.5 (m, 3,25, 3H, O−CH_3), 3.25 (t, 2H, CH_2−N_3), 1.64 (m, 2H, Si−CH_2−CH_2−), 0.62 (m, 2H, Si−CH_2−), 0.08 (m, 3H, Si−CH_3).

Hydrolysis and Condensation of (3-azidopropyl)-methyldimethoxysilane in Acetic Acid (a). A mixture of 10 g (0.029 mol) 3-azidopropylmethyldimethoxysilane, 31.7 g (0.059 mol) dry acetic acid, and 4.8 g (0.265 mol) water was stirred for 13 h at room temperature. The resulting product was washed with toluene, and then the solvent was distilled off under reduced pressure. 7.34 g (97%) of a hydrolysis product of 3-azidopropylmethyldimethoxysilane was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.25 (t, 2H, CH_2−N_3), 1.64 (m, 2H, Si−CH_2−CH_2−), 0.62 (m, 2H, Si−CH_2−), 0.08 (m, 3H, Si−CH_3). ^{29}Si NMR: δ −9.43, −11.32, −12.25-(−12.64), −20.16, −21.84-(−22.63).

Synthesis of bis-(3-azidopropyl)dimethylsiloxane Polymers N_3-$PDMS_n$-N_3 by the Cationic Mechanism (b_1-b_4). A mixture of bis-(3-azidopropyl)tetramethyldisiloxane, octamethylcyclotetrasiloxane, and trifluoromethanesulfonic acid was stirred for 13 h at 60 °C. The conversion was monitored using GPC, based on the depletion of the reaction mixture with D4. The catalyst was removed by adding Na_2CO_3 into toluene solution followed by stirring at room temperature for 1 h and subsequent filtration. The product was isolated by reprecipitation from a toluene/ethanol system followed by evaporation of the volatiles (p = 0.5 bar and 100 °C).

N_3-$PDMS_{10}$-N_3 (b_1). N_3-$PDMS_{10}$-N_3 (b_1) was obtained from 1.33 g (0.0048 mol) bis-(3-azidopropyl)tetramethyldisiloxane, 2.84 g (0.0096 mol) octamethylcyclotetrasiloxane, and 0.006 g (0.1% mass.) trifluoromethanesulfonic acid as the catalyst. 3.7 g (90% yield) of a colorless transparent liquid was obtained. M_n, GPC (toluene) = 1500 g/mol, and M_w/M_n = 1.4 relative to PS standards. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.23 (m, 2H, CH_2−N_3), 1.62 (m, 2H, Si−CH_2−CH_2−), 0.57 (m, 2H, Si−CH_2−), 0.07 (m, 3H, Si−CH_3).

N_3-$PDMS_{20}$-N_3 (b_2). N_3-$PDMS_{20}$-N_3 (b_2) was obtained from 0.4 g (0.0014 mol) bis-(3-azidopropyl)tetramethyldisiloxane, 2.07 g (0.0070 mol) octamethylcyclotetrasiloxane, and 0.0060 g (0.1% mass.) trifluoromethanesulfonic acid. 2.42 g (yield 98%) of a colorless transparent liquid was obtained. M_n, GPC (toluene) = 1950 g/mol, and M_w/M_n = 1.7 relative to PS standards. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.23 (m, 2H, CH_2−N_3),1.62 (m, 2H, Si−CH_2−CH_2−), 0.57 (m, 2H, Si−CH_2−), 0.07 (m, 3H, Si−CH_3).

N_3-$PDMS_{80}$-N_3 (b_3). N_3-$PDMS_{80}$-N_3 (b_3) was obtained from 0.09 g (0.00033 mol) bis-(3-azidopropyl)tetramethyldisiloxane, 1.95 g (0.0666 mol) octamethylcyclotetrasiloxane, and 0.006 g (0.1% mass.) trifluoromethanesulfonic acid. 1.84 g (yield 90%) of a colorless transparent liquid was obtained. M_n, GPC (toluene) = 4700 g/mol, and M_w/M_n = 2.3 relative to PS standards. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.23 (m, 2H, CH_2−N_3),1.62 (m, 2H, Si−CH_2−CH_2−), 0.57 (m, 2H, Si−CH_2−), 0.07 (m, 3H, Si−CH_3).

N_3-$PDMS_{1349}$-N_3 (b_4). N_3-$PDMS_{1349}$-N_3 (b_4) was obtained from 0.0272 g (0.0001 mol) bis-(azidopropyl)tetramethyldisiloxane, 9.97 g (0.0337 mol) octamethylcyclotetrasiloxane, and 0.006 g (0.1% mass.) trifluoromethanesulfonic acid as the catalyst. 9.30 g (93% yield) of a colorless transparent liquid was obtained. M_n, GPC (toluene) = 55,000 g/mol, and M_w/M_n = 1.6 relative to PS standards. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.23 (m, 2H, CH_2−N_3),1.62 (m, 2H, Si−CH_2−CH_2−), 0.57 (m, 2H, Si−CH_2−), 0.07 (m, 3H, Si−CH_3).

Synthesis of Hydrido(Dimethyl)Siloxane Copolymers (N_3-$PDMS(CH_3)_n(H)_m$-N_3) (b_5-b_9). A mixture of bis-(3-azidopropyl)-tetramethyldisiloxane, octa-methylcyclotetrasiloxane, PMHS, and trifluoromethanesulfonic acid was stirred for 15 minutes at room temperature and then for 20 hours at 80 °C. The conversion was monitored by GPC based on the depletion of the reaction mixture with octamethylcyclotetrasiloxane. The catalyst was removed by adding Na_2CO_3 into toluene solution followed by stirring at room temperature for 1 h and filtration. The product was isolated by reprecipitation from a toluene/ethanol system followed by evaporation of the volatiles (p = 0.5 bar and 100 °C).

N_3-$PDMS(CH_3)_{20}(H)_1$-N_3 (b_5). N_3-$PDMS(CH_3)_{20}(H)_1$-N_3 (b_5) was obtained from 4 g (0.0130 mol) bis-(3-azidopropyl) tetramethyldisiloxane, 20 g (0.0670 mol) octamethylcyclotetrasiloxane, 0.84 g (0.0002 mol) PMHS, and 0.12 g (0.1% mass.) trifluoromethanesulfonic acid. 17.5 g (70% yield) of a clear yellowish liquid was obtained. M_n, GPC (toluene) = 1900 g/mol, and M_w/M_n = 1.8 relative to PS standards. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.68 (br.s., 1H, Si−H), 3.23 (m, 2H, CH_2−N_3), 1.62 (m, 2H, Si−CH_2−CH_2−), 0.57 (m, 2H, Si−CH_2−), and 0.07 (m, 3H, Si−CH_3).

N_3-$PDMS(CH_3)_{85}(H)_{10}$-N_3 (b_6). N_3-$PDMS(CH_3)_{85}(H)_{10}$-N_3 (b_6) was obtained from 0.15 g (0.0005 mol) bis-(3-azidopropyl)-tetramethyldisiloxane, 3.1 g (0.0104 mol) octamethylcyclotetrasiloxane, 0.4 g (0.0001 mol) PMHS, and 0.005 g (0.1% mass.) trifluoromethanesulfonic acid. 2.5 g (yield 81%) of a clear yellowish liquid was obtained. M_n, GPC (toluene) = 8000 g/mol, and M_w/M_n = 1.9 relative to PS standards. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.68 (br.s., 1H, Si−H), 3.23 (m, 2H, CH_2−N_3),1.62 (m, 2H, Si−CH_2−CH_2−), 0.57 (m, 2H, Si−CH_2−), 0.07 (m, 3H, Si−CH_3). ^{29}Si NMR: δ 7.13, −20.61, −21.96, −37.55.

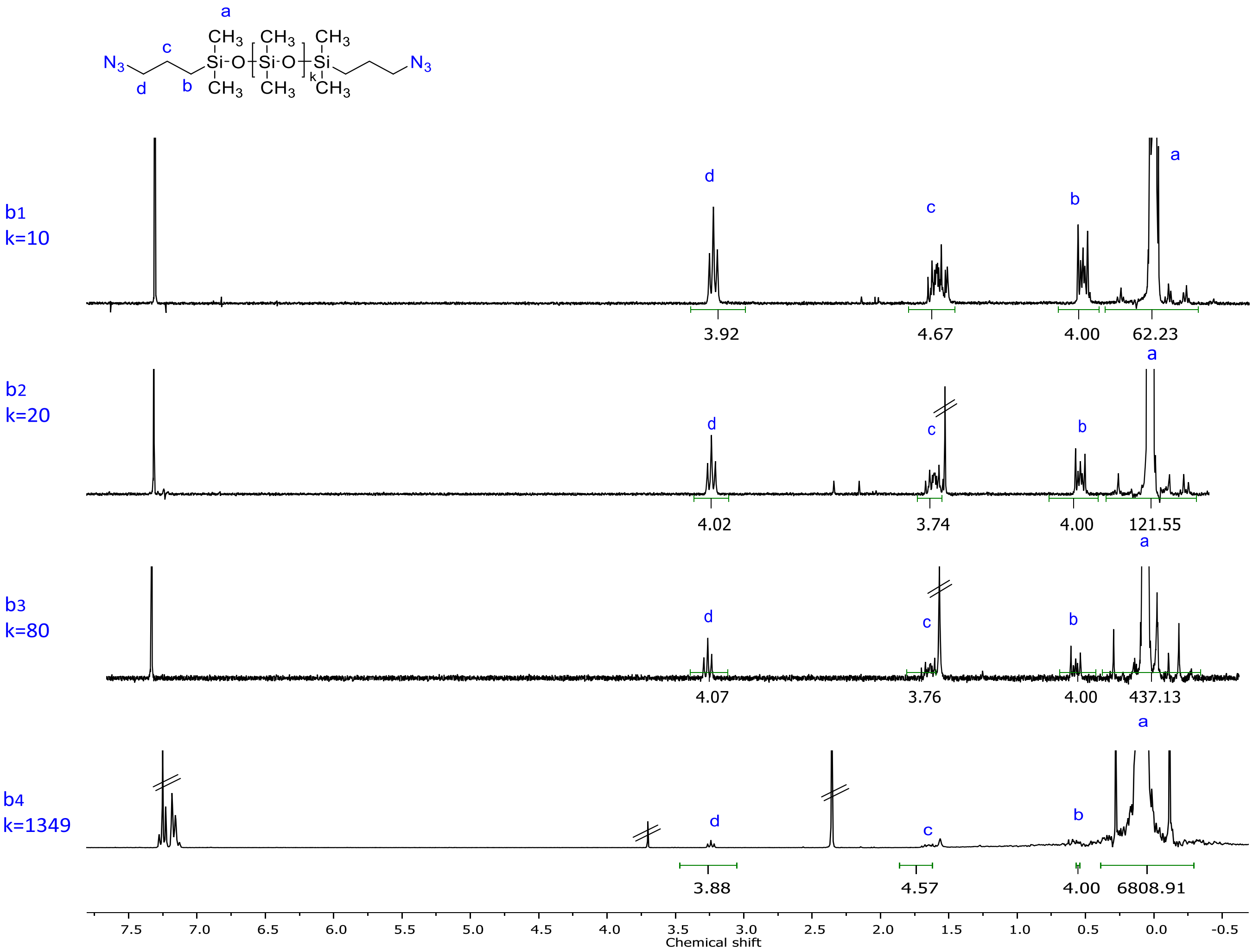


Figure 2. ^{1}H NMR spectra of azido-containing polymers N_3-PDMS$_n$-N_3.

N_3-PDMS$(CH_3)_{50}(H)_{50}$-N_3 (b_7). N_3-PDMS$(CH_3)_{50}(H)_{50}$-N_3 (b_7) was obtained from 0.30 g (0.0010 mol) bis-(3-azidopropyl)-tetramethyldisiloxane, 3.70 g (0.00063 mol) (0.0125 mol) octamethylcyclotetrasiloxane, 2.35 g PMHS, and 0.005 g (0.1% mass.) trifluoromethanesulfonic acid. 4.45 g (71% yield) of a clear yellowish liquid was obtained. M_n, GPC (toluene) = 7600 g/mol, and M_w/M_n = 2.1 relative to PS standards.^{1}H NMR (300 MHz, $CDCl_3$): δ 4.68 (br.s.,1H, Si−H), 3.23 (m, 2H, CH_2−N_3), 1.62 (m, 2H, Si−CH_2−CH_2−), 0.57 (m, 2H, Si−CH_2−), 0.07 (m, 3H, Si−CH_3).

N_3-PDMS$(CH_3)_{100}(H)_{10}$-N_3 (b_8). N_3-PDMS$(CH_3)_{100}(H)_{10}$-N_3 (b_8) was obtained from 0.3 g (0.0010 mol) bis-(3-azidopropyl)-tetramethyldisiloxane, 7.39 g (0.025 mol) octamethylcyclotetrasiloxane, 0.47 g (0.00013 mol) PMHS, and 0.005 g (0.1% mass.) trifluoromethanesulfonic acid. 6.3 g (yield 78%) of a clear yellowish liquid was obtained. M_n, GPC (toluene) = 10,500 g/mol, and M_w/M_n = 1.9 relative to PS standards. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.68 (br.s.,1H, Si−H), 3.23 (m, 2H, CH_2−N_3), 1.62 (m, 2H, Si−CH_2−CH_2−), 0.57 (m, 2H, Si−CH_2−), 0.07 (m, 3H, Si−CH_3).

N_3-PDMS$(CH_3)_{45}(H)_3$-N_3 (b_9). N_3-PDMS$(CH_3)_{45}(H)_3$-N_3 (b_9) was prepared from 0.6 g (0.0020 mol) bis-(3-azidopropyl)-tetramethyldisiloxane, 7.72 g (0.022 mol) octamethylcyclotetrasiloxane, 0.46 g (0.0012 mol) PMHS, and 0.005 g (0.1% mass.) trifluoromethanesulfonic acid. 5.9 g (yield 77%) of a clear yellowish liquid was obtained. M_n, GPC (toluene) = 5500 g/mol, and M_w/M_n = 1.6 relative to PS standards. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.68 (br.s., 1H, Si−H), 3.23 (m, 2H, CH_2−N_3), 1.62 (m, 2H, Si−CH_2−CH_2−), 0.57 (m, 2H, Si−CH_2−), 0.07 (m, 3H, Si−CH_3).

Synthesis of (3-azidopropyl)dimethylsiloxane Copolymer with Hydridosilyl/Methyl Terminal Groups (H-PDMS$(CH_3)_n(N_3)_n$-H/H_3C-PDMS$(CH_3)_n(N_3)_n$-CH_3) (a_1-a_5). A mixture of the 3-azidopropylmethyldimethoxysilane hydrolysis product, octamethylcyclotetrasiloxane, tetramethyldisiloxane/hexamethyldisiloxane, and trifluoromethanesulfonic acid was stirred for 15 minutes at room temperature and then for 15 h at 60 °C. The conversion was monitored by GPC based on the depletion of the reaction mixture with D4. The catalyst was removed by addition of Na_2CO_3 in toluene solution followed by stirring at room temperature for 1 h followed by filtration. The product was isolated by reprecipitation from a toluene/ethanol system followed by evaporation of the volatiles (p = 0.5 bar and 100 °C).

H-PDMS$(CH_3)_{20}(N_3)_1$-H (a_1). H-PDMS$(CH_3)_{20}(N_3)_1$-H (a_1) was obtained from 0.81 g (0.0057 mol) of the hydrolysis product of (3-azidopropyl)methyldimethoxysilane, 8.42 g (0.028 mol) octamethylcyclotetrasiloxane, 0.76 g (0.0056 mol) tetramethyldisiloxane, and 0.01 g (0.1% mass.) trifluoromethanesulfonic acid. 9.0 g (yield 94%) of a clear yellowish liquid was obtained. M_n, GPC (toluene) = 4200 g/mol, and M_w/M_n = 1.6 relative to PS standards. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.68 (br.s.,1H, Si−H), 3.23 (m, 2H, CH_2−N_3), 1.62 (m, 2H, Si−CH_2−CH_2−), 0.57 (m, 2H, Si−CH_2-), 0.07 (m, 3H, Si−CH_3).

H-PDMS$(CH_3)_{45}(N_3)_5$-H (a_2). H-PDMS$(CH_3)_{45}(N_3)_5$-H (a_2) was obtained from 1.71 g (0.0112 mol) of the hydrolysis product of (3-azidopropyl) methyldimethoxysilane, 7.97 g (0.027 mol) octamethylcyclotetrasiloxane, 0.32 g (0.0023 mol) tetramethyldisiloxane, and 0.01 g (0.1% mass.) trifluoromethanesulfonic acid. 9.6 g (yield 95%)

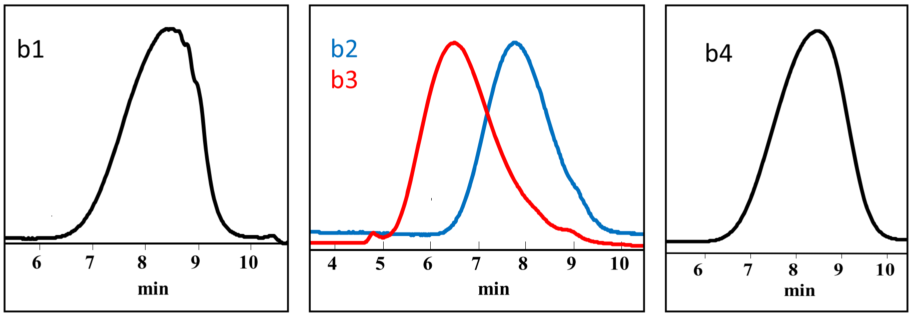
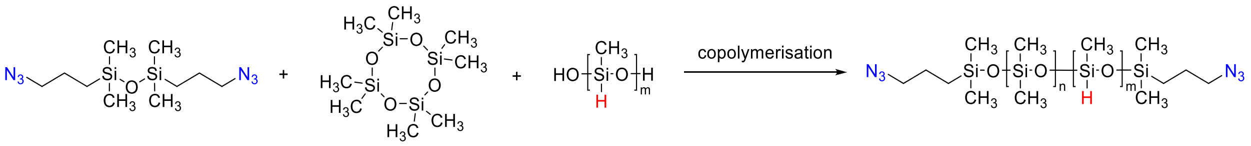


Figure 3. GPC curves of azido-containing polymers N$_3$-PDMS$_n$-N$_3$.

Scheme 3. Synthesis of Hydridodimethylsiloxane Copolymers with Terminal Azidopropyl Groups (b5-b9)



of a clear yellowish liquid was obtained. M_n, GPC (toluene) = 5400 g/mol, and M_w/M_n = 1.9 relative to PS standards. ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.68 (br.s.,1H, Si−H), 3.23 (m, 2H, CH$_2$−N$_3$),1.62 (m, 2H, Si−CH$_2$−CH$_2$−), 0.57 (m, 2H, Si−CH$_2$−), 0.07 (m, 3H, Si−CH$_3$).

H-PDMS(CH$_3$)$_{100}$(N$_3$)$_{10}$-H (a$_3$). H-PDMS(CH$_3$)$_{100}$(N$_3$)$_{10}$-H (a$_3$) was obtained from 1.59 g (0.011 mol) of the hydrolysis product of 3-azidopropylmethyldimethoxysilane, 8.26 g (0.027 mol) octamethylcyclotetrasiloxane, 0.143 g tetramethyldisiloxane (0.001 mol), and 0.01 g (0.1% mass.) trifluoromethanesulfonic acid. 8.6 g (yield 84%) of a clear yellowish liquid was obtained. M_n, GPC (toluene) = 9500 g/mol, and M_w/M_n = 1.9 relative to PS standards. ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.68 (br.s.,1H, Si−H), 3.23 (m, 2H, CH$_2$−N$_3$),1.62 (m, 2H, Si−CH$_2$−CH$_2$−), 0.57 (m, 2H, Si−CH$_2$−), 0.07 (m, 3H, Si−CH$_3$). ^{29}Si NMR: δ −22.09.

H-PDMS(CH$_3$)$_{100}$(N$_3$)$_{100}$-H (a$_4$). H-PDMS(CH$_3$)$_{100}$(N$_3$)$_{100}$-H (a$_4$) was obtained from 1.96 g (0.0137 mol) of the hydrolysis product of (3-azidopropyl)methyldimethoxysilane, 1.01 g (0.0034 mol) octamethylcyclotetrasiloxane, 0.024 g (0.00014 mol) tetramethyldisiloxane, and 0.005 g (0.1% mass.) trifluoromethanesulfonic acid. 2.7 g (yield 84%) of a clear yellowish liquid was obtained. M_n, GPC (toluene) = 19,000 g/mol, and M_w/M_n = 1.5 relative to PS standards. ^{1}H NMR (300 MHz, CDCl3): δ 4.68 (br.s., 1H, Si−H), 3.23 (m, 2H, CH$_2$−N$_3$), 1.62 (m, 2H, Si−CH$_2$−CH$_2$−), 0.57 (m, 2H, Si−CH$_2$−), 0.07 (m, 3H, Si−CH$_3$). ^{29}Si NMR: δ −22.39-(−21.20).

H$_3$C-PDMS(CH$_3$)$_{910}$(N$_3$)$_{227}$-CH$_3$ (a$_5$). H$_3$C-PDMS(CH$_3$)$_{910}$(N$_3$)$_{227}$-CH$_3$ (a$_5$) was obtained from 1.62 g (0.0135 mol) of the hydrolysis product of (3-azidopropyl) methyldimethoxysilane, 3.37 g (0.114 mol) octamethylcyclotetrasiloxane, 0.0081 g (0.0005 mol) hexamethyldisiloxane, and 0.005 g (0.1% mass.) trifluoromethanesulfonic acid. 4.2 g (yield 84%) of a transparent yellowish liquid was obtained. M_n, GPC (toluene) = 27,700 g/mol, and M_w/M_n = 2.8 relative to PS standards. ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.23 (m, 2H, CH$_2$−N$_3$),1.62 (m, 2H, Si−CH$_2$−CH$_2$−), 0.57 (m, 2H, Si−CH$_2$−), 0.07 (m, 3H, Si−CH$_3$).

Procedures for the Hydrosilation Reaction. *UT-PDMS-(CH$_3$)$_{20}$(N$_3$)$_1$-UT (c$_0$).* A solution of 0.3 g (6.5*10−5 mol) (3-azidopropyl)dimethylsiloxane copolymer with hydridosilyl terminal groups H-PDMS(CH$_3$)$_{20}$(N$_3$)1-H (a$_1$), 0.044 g (0.00014 mol) undecene tosylate, and 20 μL (0. 5% mass.) platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in 3.5 mL toluene was stirred for 15 h at room temperature. Upon completion of the reaction, the solvent was evaporated. The polymer was evacuated under reduced pressure (p = 0.5 bar and 100 °C). M_n, GPC (toluene) = 4258 g/mol, M_w/M_n = 1.41 relative to PS standards. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.77−7.781 (m, 1H, C−H of the benzene ring), 7.31−7.37 (m, 1H, C−H of the benzene ring), 4.01 (m, 2H, CH$_2$−O), 3.23 (m, 2H, CH$_2$−N$_3$), 2.45 (m,3H, CH$_3$-benzene ring), 1.62 (m, 2H, Si−CH$_2$−CH$_2$−), 1.21 (m, 2H, Si−CH$_2$−CH$_2$−CH$_2$), 0.57 (m, 2H, Si−CH$_2$−), 0.07 (m, 3H, Si−CH$_3$). ^{13}C NMR:1.01, 1.15, 18.22, 21.61, 23.20, 25.30, 28.76, 28.86, 28.92, 29.03, 29.29, 29.38, 29.54, 33.45, 33.77, 70.68, 127.88, 129.78, 144.60.

Procedures for the "Click" Reactions. *H$_3$C-PDMS(CH$_3$)$_{910}$(1,4-Triazole-COOH)$_{227}$-CH$_3$ (c$_1$).* A solution of 0.5 g (0.00005 mol) (3-azidopropyl)dimethylsiloxane copolymer with methyl terminal groups H$_3$C-PDMS(CH$_3$)$_{910}$(N$_3$)$_{227}$-CH$_3$ (a5) and 0.039 g (0.0011 mol) propiolic acid in 10 mL dioxane was stirred for 10 h at 60 °C. Upon completion of the reaction, the solvent was evaporated. The polymer was evacuated under reduced pressure (p = 0.5 bar, 100 °C). 0.4 g (yield 90%) of a strong transparent insoluble film was obtained. ^{1}H NMR (300 MHz, CDCl$_3$): 8.18 (m, 1H, C−H of triazole ring), 4.70 (m, 2H, CH$_2$−N), 4.28 (m, 2H, CH$_2$-N), 1.95 (m, 2H, Si−CH$_2$−CH$_2$), 0.52 (m, 2H, Si−CH$_2$), 0.07 (m, 3H, Si−CH$_3$).

H-PDMS(CH$_3$)$_{45}$(1,4-Triazole-COOH)$_5$-H (c$_2$). A solution of 0.5 g (0.00012 mol) (3-azidopropyl)dimethylsiloxane copolymer with hydridosilyl terminal groups H-PDMS(CH$_3$)$_{45}$(N$_3$)$_5$-H (a2) and 0.042 g (0.0006 mol) propiolic acid in 10 mL dioxane was stirred for 10 hours at 60 °C. Upon completion of the reaction, the solvent was evaporated. The polymer was evacuated under reduced pressure (p = 0.5 bar, 100 °C). 0.35 g (yield 70%) of an insoluble film material was obtained. ^{1}H NMR (300 MHz, CDCl3): 8.18 (m, 1H, C−H of triazole ring), 4.70 (m, 2H, CH$_2$−N), 4.28 (m, 2H, CH$_2$−N), 1.95 (m, 2H, Si−CH$_2$−CH$_2$), 0.52 (m, 2H, Si−CH$_2$), 0.07 (m, 3H, Si−CH$_3$).

H-PDMS(CH$_3$)$_{100}$(1,4-Triazole-COOH)$_{10}$-H (c$_3$). A solution of 0.5 g (0.00056 mol) (3-azidopropyl)dimethylsiloxane copolymer with hydridosilyl terminal groups H-PDMS(CH$_3$)$_{100}$(N$_3$)$_{10}$-H (a3) and 0.039 g (0.00056 mol) propiolic acid in 10 mL of dioxane was stirred for 10 h at 60 °C. Upon completion of the reaction, the solvent was evaporated. The polymer was evacuated under reduced pressure (p = 0.5 bar, 100 °C). 0.37 g (yield 74%) of an insoluble film material was obtained. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.18 (m, 1H, C−H of triazole ring), 4.70 (m, 2H, CH$_2$−N), 4.28 (m, 2H, CH$_2$−N), 1.95 (m, 2H, Si−CH$_2$−CH$_2$), 0.52 (m, 2H, Si−CH$_2$), 0.07 (m, 3H, Si−CH$_3$).

HOOC-1,3-Triazole-PDMS-1,4-Triazole-COOH (c$_4$). A solution of 0.4 g (0.00021 mol) bis-(3-azidopropyl)dimethylsiloxane polymer N$_3$-PDMS$_{20}$-N$_3$ and 0.030 g (0.00041 mol) propiolic acid in 4 mL dioxane was stirred for 6 h at 60 °C. After completion of the reaction, the solvent was evaporated. The polymer was evacuated under reduced pressure (p = 0.5 bar, 100 °C). 0.3 g (75% yield) of a very viscous liquid was obtained. M_n, GPC (toluene) = 1950 g/mol, and M_w/M_n = 1.7 relative to PS standards. ^{1}H NMR (300 MHz, CDCl$_3$): δ 10.15 (m, 1H, COOH), 8.18 (m, 1H, C−H of triazole ring), 4.70

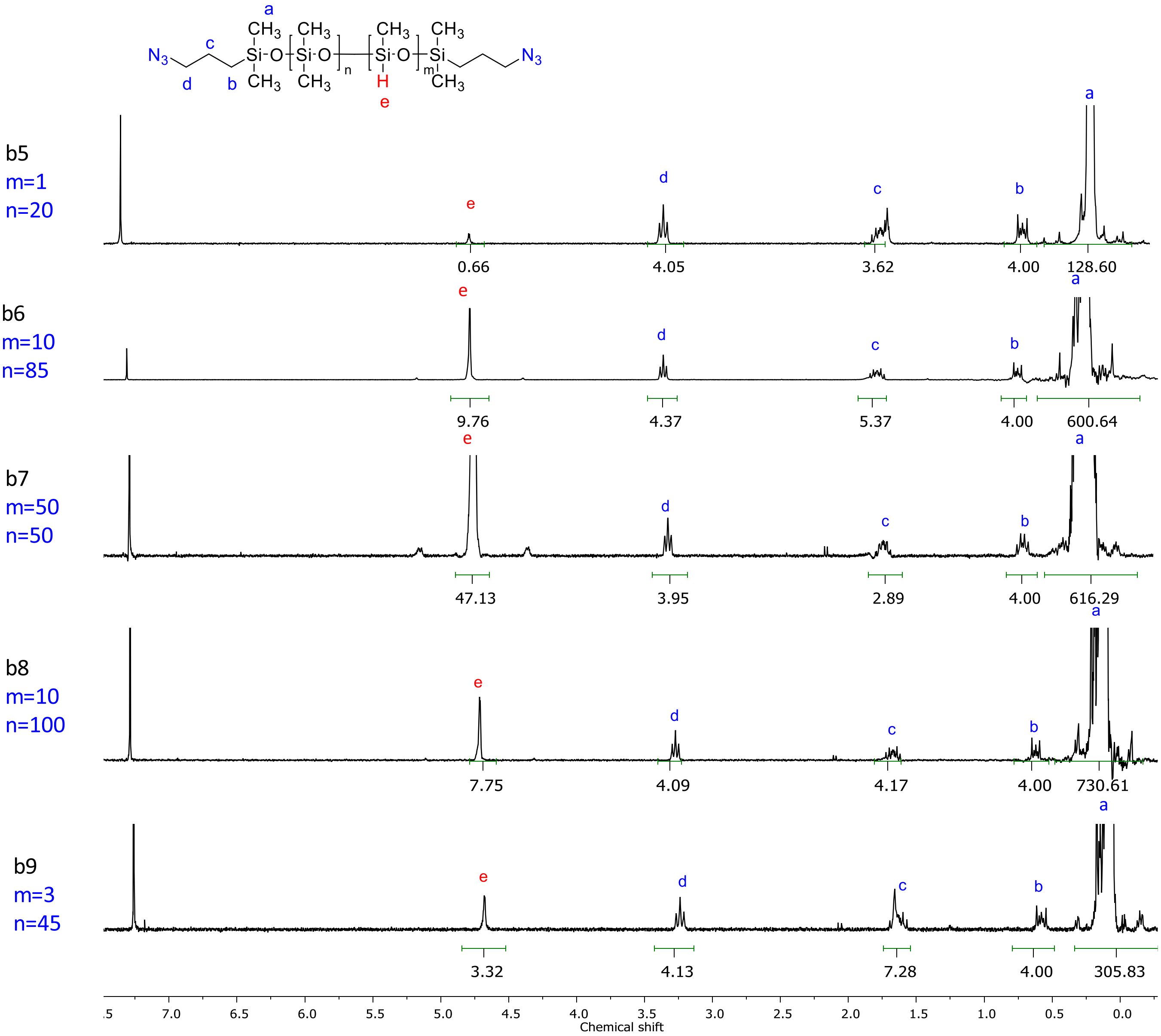


Figure 4. ^{1}H NMR spectra of hydridodimethylsiloxane copolymers N_3-PDMS(CH_3)n(H)m-N_3.

(m, 2H, CH_2−N), 4.28 (m, 2H, CH_2−N), 1.95 (m, 2H, Si−CH_2−CH_2), 0.52 (m, 2H, Si−CH_2), 0.07 (m, 3H, Si−CH_3).

HOOC-1,4-Triazole-Si-O-Si-1,4-Triazole-COOH (c_5). A solution of 0.3 g (0.0010 mol) bis-(3-azidopropyl)tetramethyldisiloxane and 0.14 g (0.0020 mol) propiolic acid in 3.2 mL dioxane was stirred for 6 h at 60 °C. The isomers were separated by recrystallization of a mixture of reaction products in the dioxane/hexane system. After completion of the reaction, the solvent was evaporated. The polymer was evacuated under reduced pressure (p = 0.5 bar, 100 °C). 0.13 g of a very viscous liquid was obtained.^{1}H NMR (300 MHz, CDCl3): δ =8.69 (m, 1H, C−H of the triazole ring), 4,36 (m, 2H, CH_2−N), 1.82 (m, 2H, Si−CH_2−CH_2), 0.39 (m, 2H, Si−CH_2), 0.01 (m, 3H ,Si−CH_3). ^{13}C NMR: 0, 14, 24, 39.5, 53, 128, 139, 183. ^{29}Si NMR: δ 9.7.

■ RESULTS AND DISCUSSION

The general route for synthesizing linear polysiloxanes from silicone monomers used industrially includes two steps. The first step involves the hydrolytic polycondensation of a bifunctional silane precursor. This process results in a mixture of linear and cyclic oligosiloxanes, often referred to as the

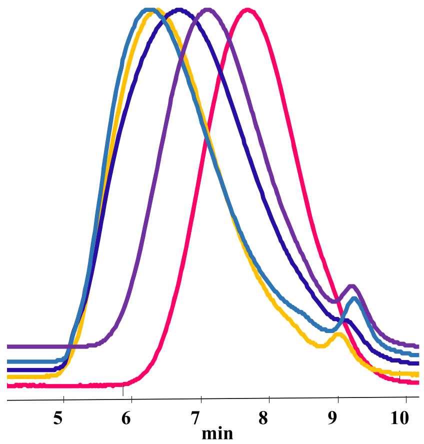
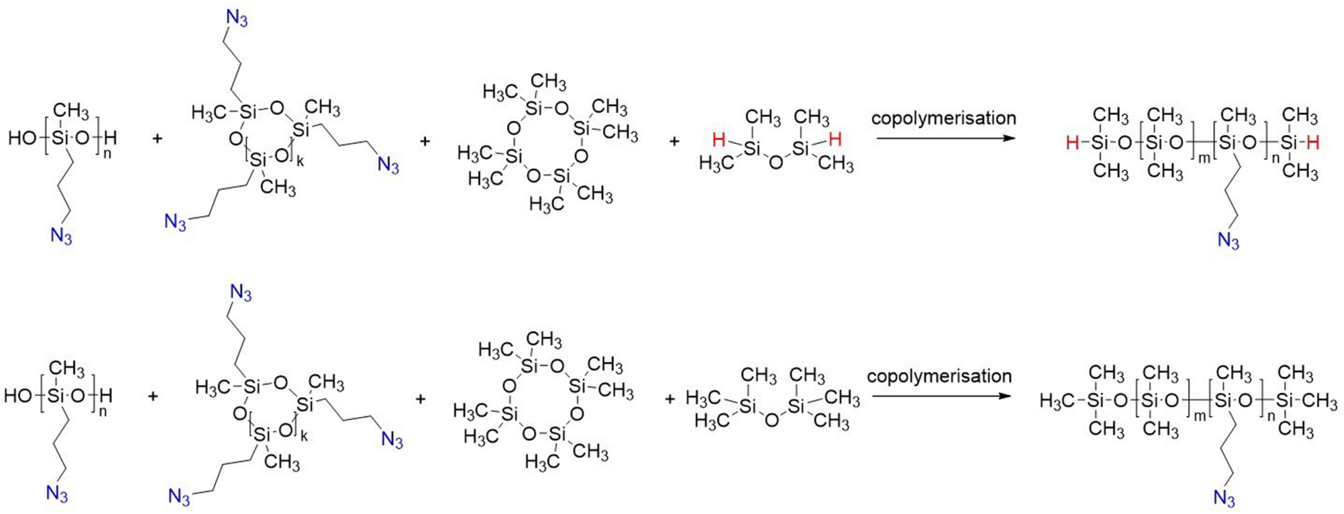


Figure 5. GPC curves of hydridodimethylsiloxane copolymers N_3-PDMS$(CH_3)_n(H)_m$-N_3(b_5-b_9).

Scheme 4. Synthesis of (3-Azidopropyl)Dimethylsiloxane Copolymers H-PDMS(CH$_3$)$_n$(N$_3$)M-H/H$_3$C-PDMS(CH$_3$)$_n$(N$_3$)$_m$-CH$_3$ (a$_1$-a$_5$)



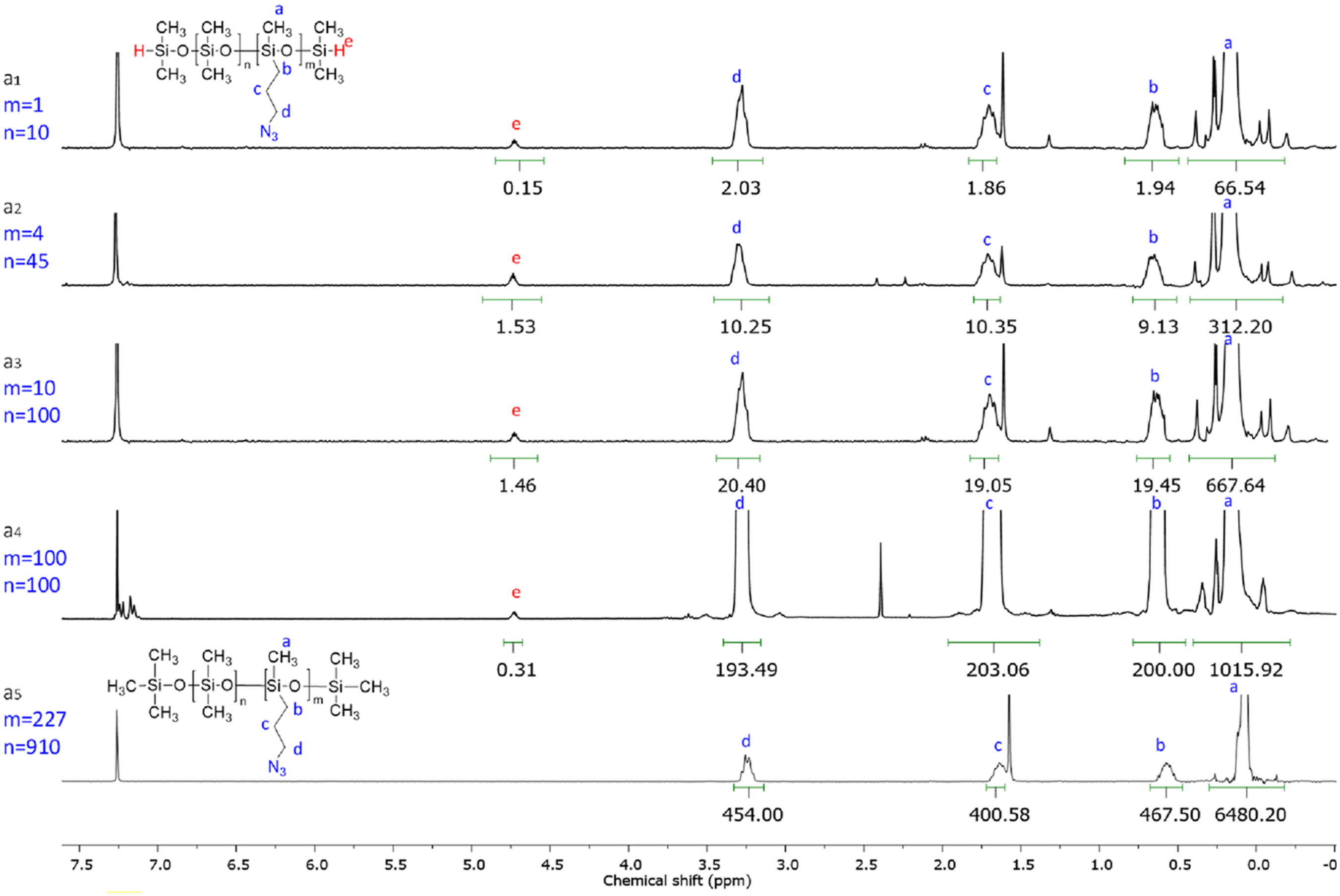


Figure 6. ^{1}H NMR spectra of (3-azidopropyl)dimethylsiloxane copolymers H-PDMS(CH$_3$)$_n$(N$_3$)$_n$-H (a$_1$-a$_4$) and H$_3$C-PDMS(CH$_3$)$_n$(N$_3$)$_n$-CH$_3$(a$_5$).

hydrolysate. The second step involves the conversion of oligomers into a high-molecular-weight polymer. The synthesis of the high-molecular-weight polymer is performed either by polycondensation of the hydroxy-terminated short-chain polysiloxanes or by ring-opening polymerization (ROP) of cyclic oligomers.[33,34] Depending on the starting monomers, both *α*,*ω*-difunctional polysiloxanes and side group-modified polysiloxanes can be obtained. The ROP of cyclosiloxanes allows high-molecular-weight polysiloxanes to be synthesized with better accuracy than polycondensation methods. The starting monomers, the type of functional groups they contain, and the polymerization method determine the properties and chemical reactivity of the final polymers, and consequently, their industrial usability.

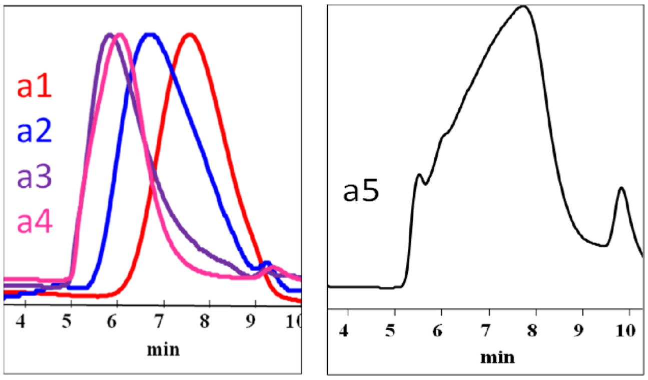


Figure 7. GPC curves of (3-azidopropyl)dimethylsiloxane copolymers H-PDMS$(CH_3)_n(N_3)_n$-H(a_1-a_4) and H_3C-PDMS$(CH_3)_n(N_3)_n$-CH_3(a_5).

Numerous examples of the preparation of siloxanes by the ROP method, including those with various functional groups in the substituent at the silicon atom, have been published to date.[35−39] The ROP of cyclic siloxanes is classified as anionic (AROP) or cationic (CROP), depending on the structure of the reactive propagation center. Cationic polymerization is usually catalyzed by Brønsted and Lewis acid catalysts.[35−39]

The ROP, as well as the catalytic rearrangement of a mixture containing predominantly cyclic products in the presence of a cationic catalyst, can be used for the synthesis of polysiloxanes with various substituents, provided that they do not react with the basic initiator or the silanolate center. This method is particularly useful for synthesizing siloxane polymers and copolymers with substituents that are unstable in the presence of strong bases such as SiH, SiCl, $Si(CH_2)_nCl$, and $Si(CH_2)_nCOOH$.[40−42] Protic acids are the most common initiators used in the CROP of siloxanes. Their initiating power increases with the acid strength. In fact, CF_3SO_3H and $HClO_4$ are particularly efficient, while the majority of kinetic studies dealt with the polymerization of D_3 and D_4 initiated by CF_3SO_3H (TfOH).[43−46]

Preparation of Azidopropyl-Functional Monomeric Siloxanes by Condensation of the Corresponding Alkoxysilanes in Acetic Acid. Previously, only a few studies for incorporation of azido functions into PDMS were performed. The first work on the preparation of azidopropyl-functional PDMS appeared in 2000.[46] Only one sample was obtained in two stages, namely, hydrosilylation of allyl bromide followed by replacement of the bromine atom with an azido group by the reaction of the substrate with sodium azide. The polymer was characterized by FT-IR only. The resulting functional PDMS was subsequently used to create a fullerene-containing polysiloxane as a stationary phase for capillary gas chromatography. Brook et al. approached the problem of synthesizing azidopropyl-substituted siloxanes more thoroughly: they obtained azidopropyl-containing PDMS by replacing the chlorine atom in a chloropropyl-containing PDMS by the reaction with sodium azide (NaN_3). However, the method was found to be rather laborious.[16] Bretzle et al. obtained PDMS with functional azido groups from epoxides preliminarily incorporated into the PDMS structure by the hydrosilylation reaction.[16] It should also be noted that at the moment, work has been carried out on the synthesis of azidoalkylsiloxanes of nonlinear structure.[47−49]

The drawbacks of the previously described methods of incorporating a functional azido group into the polydimethylsiloxane chain are: multiple stages are needed and expensive catalysts (Pt, $B(C_6F_5)_3$) are used, as well as high-boiling solvents (DMF) at the stage of replacing the chlorine atom in the alkyl substituent with an azido group in the final polymer.[16,18]

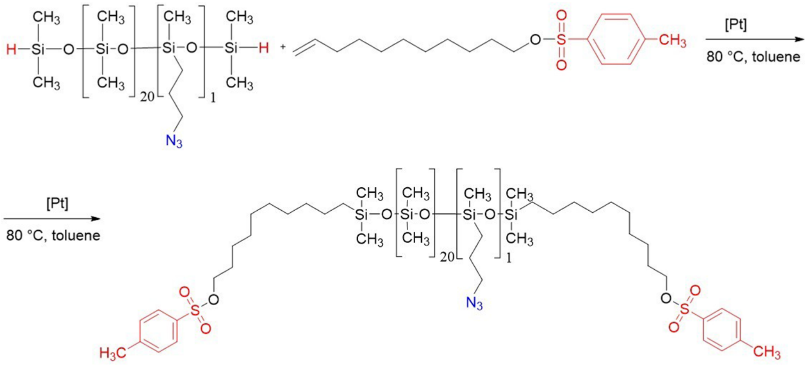
The process we suggested for synthesizing functional azidopropyl polydimethylsiloxanes consists of two major stages: the preparation of the starting functional azidopropyl monomers (difunctional disiloxane and hydrolysis products of (3-azidopropyl)methyldimethoxysilane) and copolymerization of the resulting functional azidopropyl monomers with other starting siloxane compounds (D_4, Si-H functional compounds) in the presence of CF_3SO_3H as the catalyst.

Scheme 1 shows a general pathway for the preparation of bis-3-azidopropyltetramethyldisiloxane and 3-azidopropyl)-methyldimethoxysilane hydrolysis products. The azido group was incorporated into the monomer structure by the technique reported previously.[16] The hydrolytic condensation of functional alkoxy monomers with azidopropyl-functional groups was carried out in an active medium (30% solution in acetic acid) until complete disappearance of alkoxy groups in the ^1H NMR spectra.[50−53]

Figure 1 shows the ^1H NMR spectrum of the product of (3-azidopropyl)methyldimethoxysilane hydrolysis. The spectrum contains no signals from the methoxy group (3.5 ppm), which indicates that they are converted completely, and siloxane products are formed. At the same time, signals of all organic substituents characteristic of the starting monomer are present.

Synthesis of PDMS Containing an Azidopropyl-Functional Terminal Group (Telechelics) (b_1-b_4). First of all, we demonstrated that it is possible to obtain α,ω-

Scheme 5. Undecantentosylate Hydrosilylation with a Hydridosiloxane PDMS.



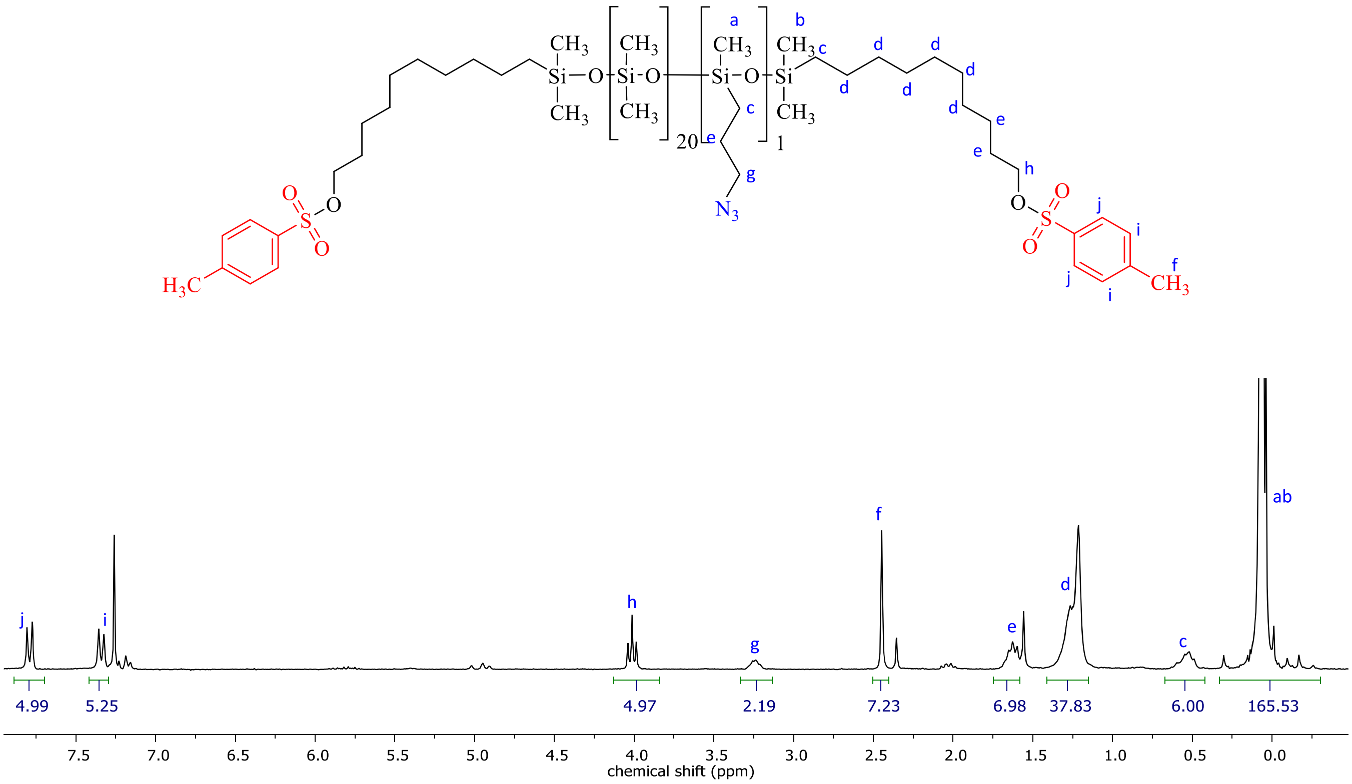


Figure 8. ^{1}H NMR spectra of the undecantentosylate hydrosilylation with a hydridosiloxane PDMS (C_0).

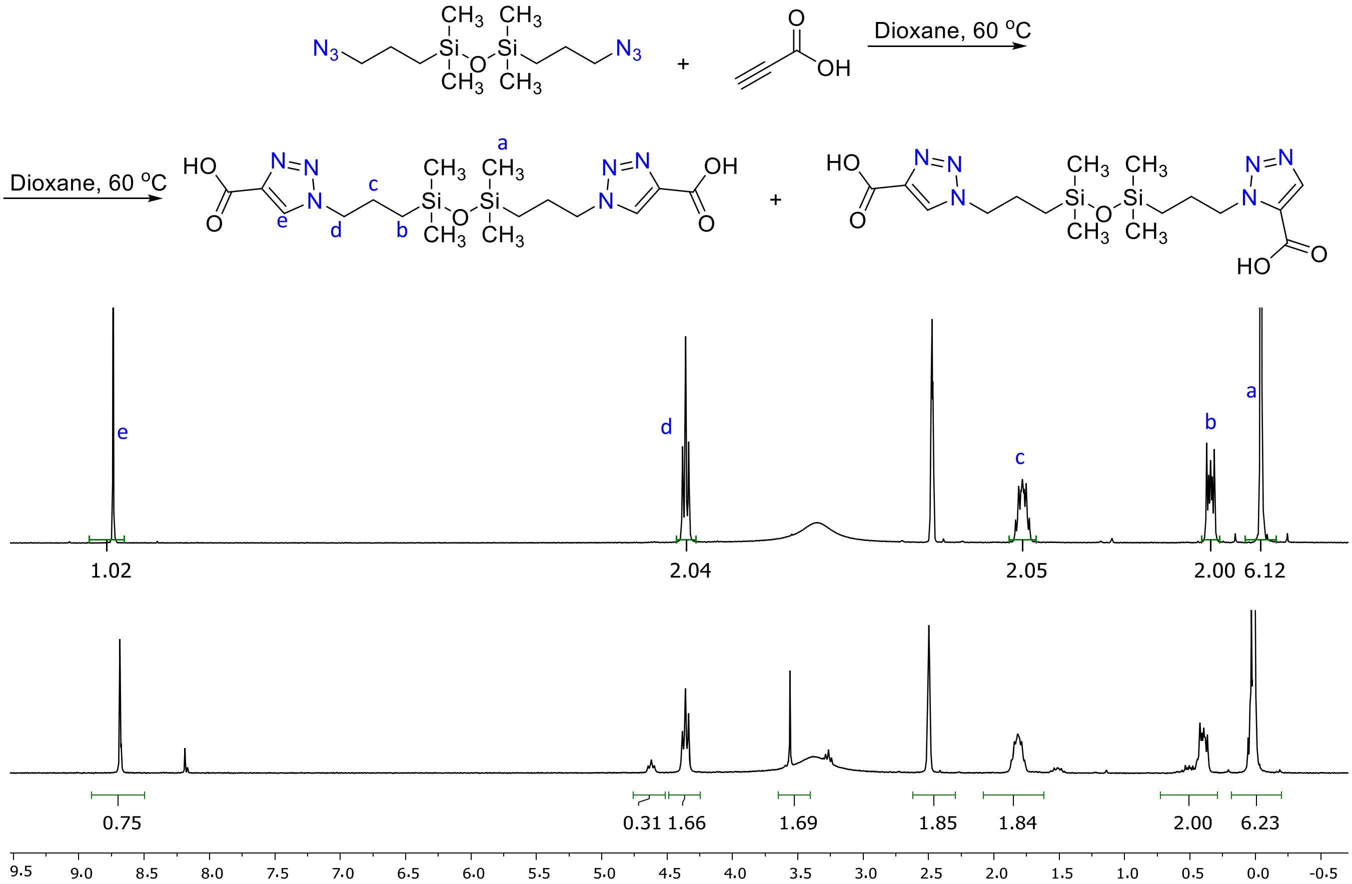


Figure 9. ^{1}H NMR spectra of an isolated isomer (c_5) (upper spectrum) and a mixture of isomers (lower spectrum).

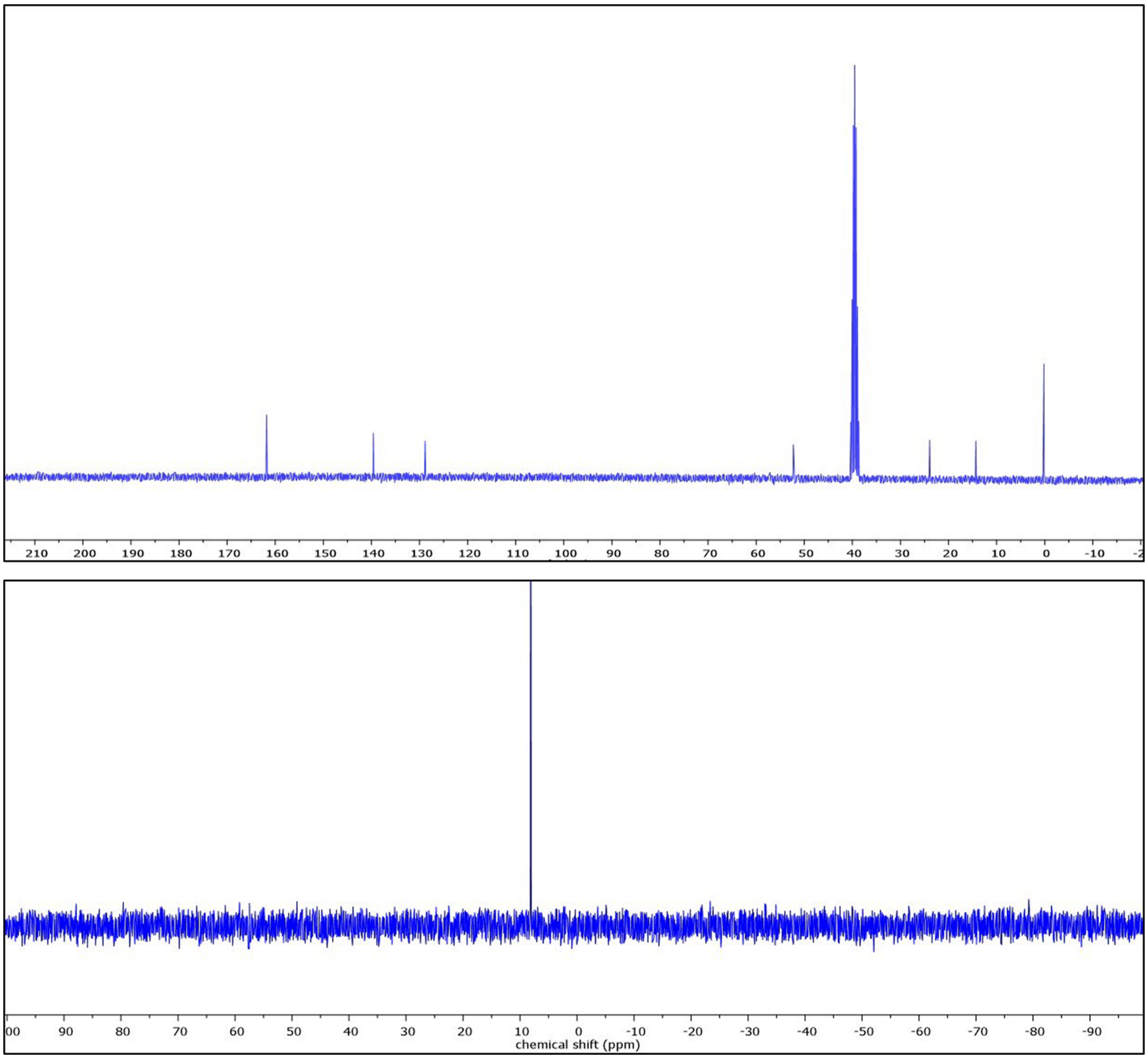


Figure 10. ^{13}C and ^{29}Si NMR spectra of the isolated isomer.

difunctional polysiloxanes with azidopropyl-functional groups. The reaction of octamethylcyclotetrasiloxane was carried out by the CROP mechanism with bis-(3-azidopropyl)-tetramethyldisiloxane as the stopper and CF_3SO_3H as the catalyst (Scheme 2). The general formula of the resulting polymers was N_3-PDMS$_n$-N_3. The polymerization process was carried out at 60 °C, usually for 15 h, until the maximum amount of high-molecular-weight products was formed according to GPC monitoring (Figure 3). The calculated and determined molecular weights of the polymers studied are presented in Table 1.

The presence of azidopropyl groups in the final polymer, as well as the fact that the ratio of the signal intensities of the propyl bridge protons and dimethylsiloxane moieties coincides with the theoretical value, allows us to conclude that bis-(3-azidopropyl)tetramethyldisiloxane is indeed incorporated into the structure of polydimethylsiloxane and plays the role of a stopper (Figure 2).

The yield of polymers b_1-b_3 ranged from 90 to 98%. The yield of the high-molecular-weight polymer was about 70% (according to GPC) (Figure 3).

Synthesis of Hydrido-Containing Dimethylsiloxane Copolymers N_3-PDMS(CH3)$_n$(H)$_m$-N_3 (b_7-b_{11}). Utilizing a set of independent functional groups in the structure of a polymer allows one to adjust its properties in a broader range. Examples of this kind are available in the literature.[17,53,54] We succeeded in obtaining hydridodimethylsiloxane copolymers with azidopropyl side groups by cationic copolycondensation of bis-(3-azidopropyl)tetramethyldisiloxane with D_4 and PMHS (Scheme 3):

Like in the previous cases, the reaction was carried out until an equilibrium was established. After standard workup, the polymers were analyzed by ^1H NMR and ^{29}Si spectroscopy (see the Supporting Information). The polymers showed characteristic signals of the hydrido group at 4.70 ppm (Si−H) and all signals corresponding to the azidopropyl group (Figure 4). The GPC curves of the obtained polymers are shown in Figure 5. The yield of the high-molecular-weight polymer ranged from 70 to 81% (according to GPC).

Synthesis of 3-(Azidopropyl)Dimethylsiloxane Copolymers H-PDMS$(CH_3)_n(N_3)_n$-H (a_1-a_4)/H_3C-PDMS-$(CH_3)_n(N_3)_m$-CH_3 (a_5). (3-Azidopropyl)dimethylsiloxane copolymers with side hydrido/methyl groups (a_1-a_5) were

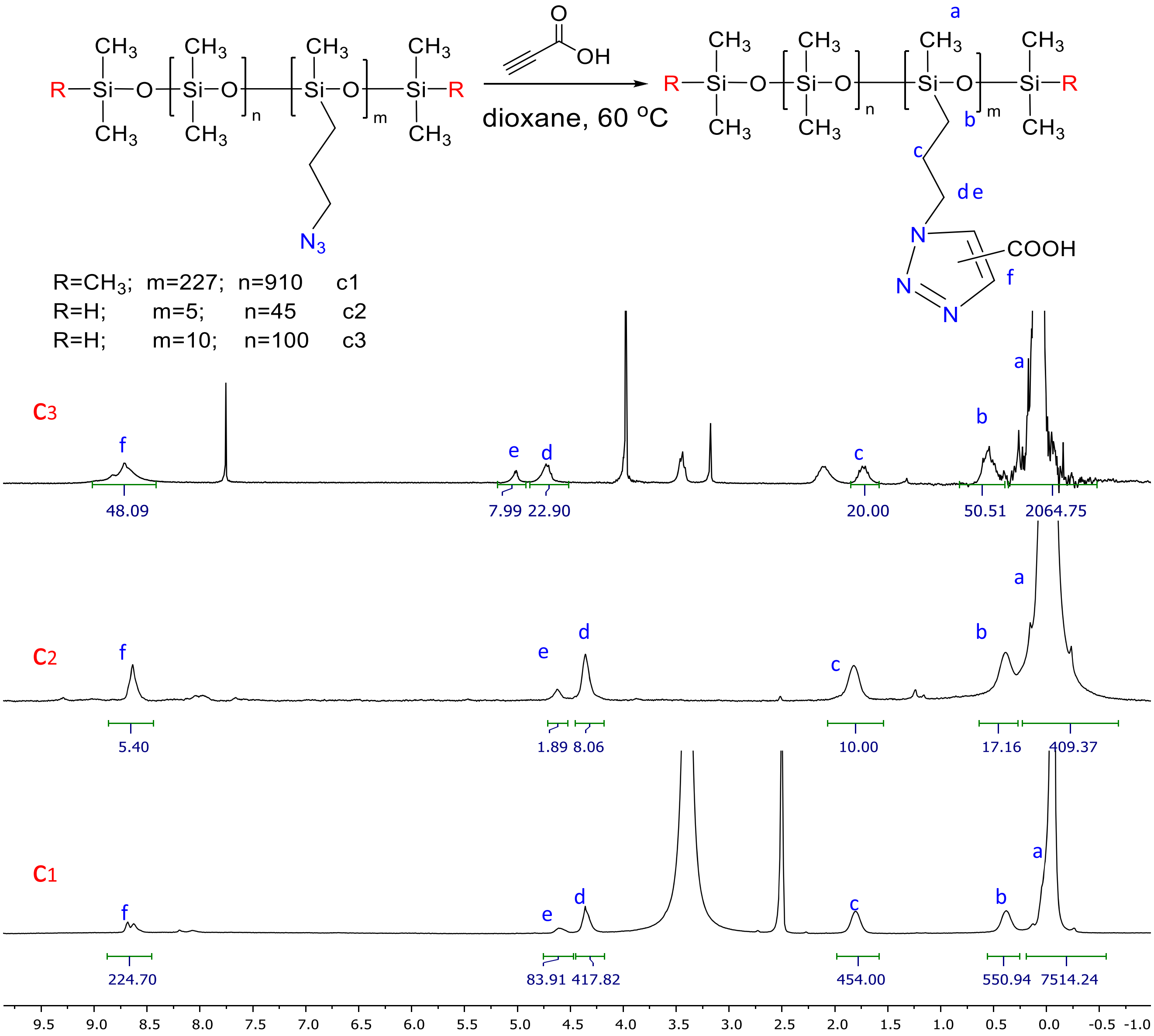


Figure 11. ^{1}H NMR spectra of the click reaction products (c_1-c_3).

obtained from the (3-azidopropyl)methyldimethoxysilane hydrolysis product by the cationic copolymerization mechanism (Scheme 4) :

The progress of the reaction is demonstrated by NMR data, in particular, by the presence of weak signals of hydride groups along with the corresponding signals of the azidopropyl group in the given ratio, as well as by GPC data (Figures 6 and 7).

Hydrosilation Reaction. We have demonstrated the possibility of easy introduction of other functional fragments by the hydrosilylation reaction into the structure of PDMS with hydride- and azide-functional groups. Thus, 10-undecene-1-tosylate was hydrosilylated with PDMS H-PDMS-$(CH_3)_{20}(N_3)_1$-H (a_1) with terminal hydride groups and azidopropyl groups in the side chain in the presence of Karsted's catalyst at room temperature (Scheme 5). The reaction proceeded overnight at room temperature. The progress of the reaction was monitored by NMR, by the disappearance of signals from the proton of the Si−H group. The NMR spectrum of the final product after the hydrosilylation reaction is shown in Figure 8. Polymers with tosylate-functional groups on a long alkyl spacer can be an effective macroinitiator of the polymerization of oxazoline cycles, which was demonstrated in our earlier studies.[55,56] Thus, we wanted to demonstrate the potential of the obtained PDMS with hydride and azide groups for the creation of complex polymer structures.

Azide-Alkyne Cycloaddition (AAC) Click Reactions. It was shown in early studies on the addition of propiolic acid to a functional azido group that this reaction occurs ambiguously and gives isomers, namely, 1,4- and 1,5-substituted triazoles, and the carboxy group can be eliminated to give a simple 1,2,3-triazole ring.[57,58] Earlier, Zheng et al. showed that the use of boronic acid derivatives to activate unsaturated carboxylic acids proved to be an efficient method for the classical dipolar [3 + 2]-cycloaddition involving azides and unsaturated carboxylic acids.[59]

First, we decided to perform a model reaction of bis-(3-azidopropyl)tetramethyldisiloxane with propiolic acid without any catalysts. The reaction was carried out in dioxane as the solvent. The reaction started at a temperature of about 60 °C

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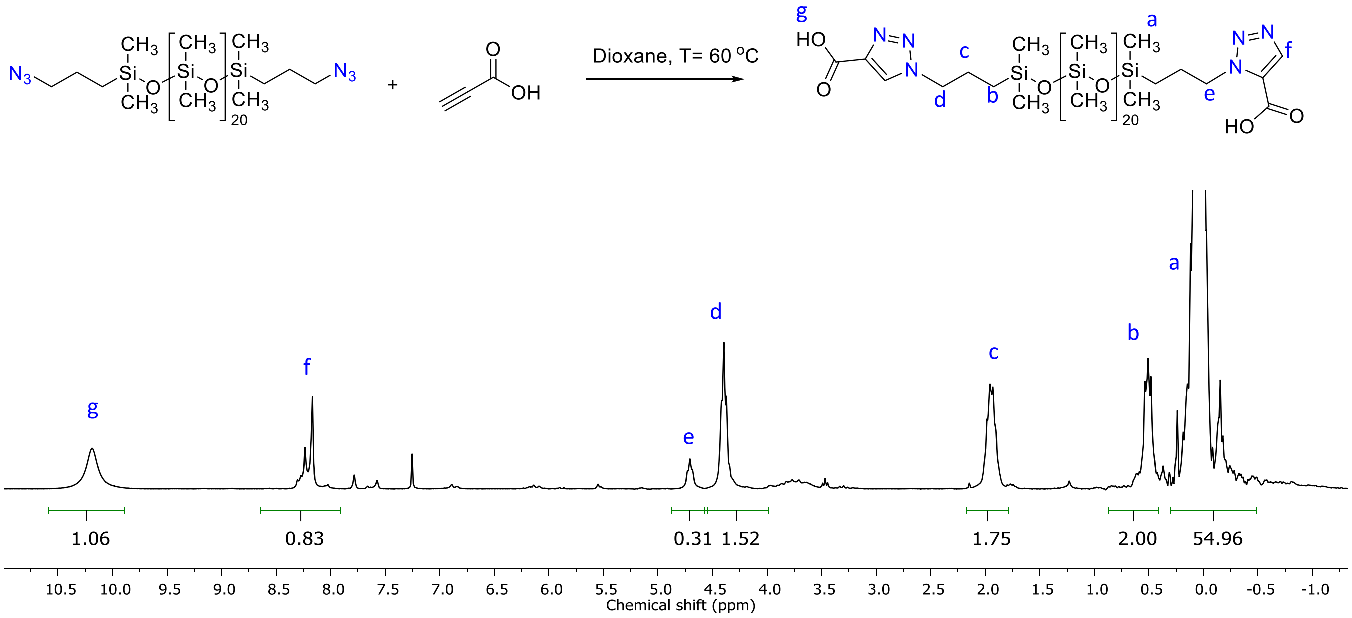


Figure 12. ^{1}H NMR spectrum of the isomer mixture (c_4).

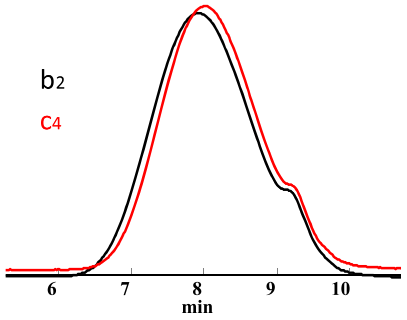
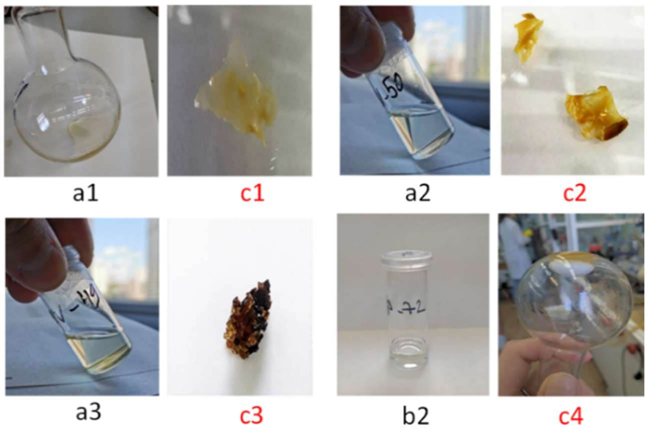


Figure 13. GPC curves of b_2 and c_4 (AAC reaction with an acetylenic acid product).


a1 c1 a2 c2

a3 c3 b2 c4

Figure 14. Photographs of the starting polymers (a_1, a_2, a_3, and b_2) and the resulting AAC reaction products (c_1−c_4).

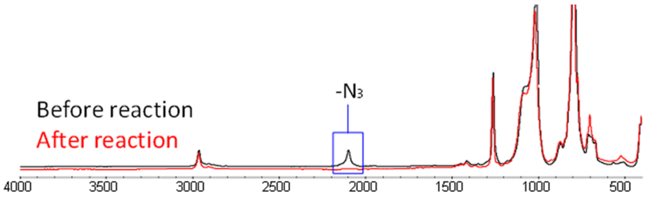


Figure 15. IR spectrum of the reaction product of the AAC of phenylacetylene to a bis-(3-azidopropyl) dimethylsiloxane polymer (C_4).

and required about 6 h until the total conversion of azido groups. The conversion of azido groups was monitored by ^{1}H NMR spectroscopy. The results are presented in Figure 9. The progress of the reaction is demonstrated by the appearance of signals corresponding to the triazole ring (^{1}H NMR, $\delta = 8.75$, 8.20 ppm − C−H of the triazole ring). As a result, 1,4- and 1,5-cycloaddition products were obtained, mainly 1,4-substituted ones. Analysis of the reaction products did not reveal products of carboxy group elimination or other side processes.

The isomers were separated by recrystallization of a mixture of reaction products in the dioxane/hexane system. In this case, we easily isolated the 1,4-substitution product. The resulting symmetric disiloxane as a white powder was characterized by ^{1}H (Figure 9, upper spectrum)), ^{13}C, and ^{29}Si NMR spectroscopy (Figure 10) as well as high-resolution mass spectroscopy (HRMS) (Supporting information).

Thus, we suggested a new method for the incorporation of a carboxy-functional group into siloxane structures. At the same time, the presence of small isomeric structural defects nearly does not affect the properties of the resulting polymeric carboxy-containing polysiloxane structures. The AAC between 3-(azidopropyl)dimethyl siloxane copolymer and hydridosilyl/methyl terminal groups (H-PDMS$(CH_3)_n(N_3)_n$-H / H_3C-PDMS$(CH_3)_n(N_3)_n$-CH_3) and propiolic acid (c_1-c_3) was carried out without a catalyst at 60 °C for 10 hours in dioxane. The AAC between siloxane telechelics with azidopropyl-functional groups and propiolic acid (c_4) was carried out without a catalyst at 60 °C for 6 h in dioxane. The reaction was carried out until the azido groups were converted completely. ^{1}H NMR of the obtained functionalized polymers are shown in Figures 11 and 12. The reaction gave 1,4- and 1,5-substituted siloxanes with added propiolic acid, predominantly 1,4-substituted ones, like in the case of the model disiloxane. It is also important to note that the GPC curves of the starting siloxane telechelics and propiolic acid addition products practically do not differ, which indicates that no molecular degradation processes occur (Figure 13). Moreover, the appearance of the material changed considerably up to the formation of a solid (Figure 14). The reaction is perfectly monitored by IR spectroscopy. The completion of the reaction is confirmed by the absence of characteristic bands of azido groups at 2135−2090 cm^{-1} in the IR spectrum (Figure 15).

■ CONCLUSIONS

Based on our studies, we suggested a simple method for synthesizing PDMSs with azidopropyl-functional groups. Such PDMSs are prepared from azidopropylalkoxysilanes that were shown to be easily converted into the corresponding low-molecular-weight siloxanes by condensation in acetic acid. The subsequent catalytic rearrangement of the condensation products of azidopropylalkoxysilanes and dimethylsiloxanes in the presence of trifluoromethanesulfonic acid allowed us to obtain PDMS products containing azidopropyl-functional groups. The method also allows one to obtain PDMSs containing both azidopropyl and hydridosilyl-functional groups. Such polymers were not obtained before. As a result, we have synthesized and characterized a number of new functional PDMS in the range of molecular weights from 2000 to 88,000. In our work, we also demonstrated the possibility of postpolymerization functionalization of azidopropyl-functional PDMS with propiolic acid by the metal-free azide-alkyne Huisgen cycloaddition reaction. We believe that the suggested new method for the simple preparation of azidopropyl-containing functional PDMSs and atom-economy catalyst-free carboxy derivatives may contribute to the development of the chemistry and technology of PDMS-based hybrid materials and their practical implementation.

The addition of propiolic acid to the azidopropyl-functional PDMS by the metal-free azide-alkyne Huisgen cycloaddition reaction is an atom-economy process that also proved to be a convenient method for the incorporation of a polar carboxy group into the PDMS structure. The new prospects of PDMS modification demonstrated in the example with incorporation of carboxy groups can significantly expand the combinatorial capabilities of PDMS modification by simple well-controlled processes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c02790.

NMR spectra, GPC curves, and HRMS (PDF)

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Notes

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■ ACKNOWLEDGMENTS

This work was supported by RFBR (19-29-05227MK). The studies on the modification of copolymers by the ″click″ reaction were made with support of the Russian-Vietnamese Tropical Center (Grant Ecolan T-2.5). We acknowledge funding from the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2020-794). NMR and GPC were performed with financial support from the Ministry of Science and Higher Education of the Russian Federation (No. 0086-2019-0005) and using the equipment of the “Collaborative Access Center for Polymer Research” of ISPM RAS.

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