Inverse Vulcanization of Norbornenylsilanes: Soluble Polymers with Controllable Molecular Properties via Siloxane Bonds

J. M. Scheiger, M. Hoffmann, P. Falkenstein, Z. Wang, M. Rutschmann, V. W. Scheiger, A. Grimm, K. Urbschat, T. Sengpiel, J. Matysik, M. Wilhelm, P. A. Levkin*, P. Theato*
Author Contributions

M.H. Data curation: Lead
Table of Contents

Table of Contents .................................................................................................................. 2
Experimental Procedures ........................................................................................................ 2
Nomenclature of monomers .................................................................................................... 2
Nomenclature of polymers ........................................................................................................ 2
Chemicals ............................................................................................................................... 3
Synthesis of TMNBS ................................................................................................................ 3
Inverse vulcanization of Norbornenylsilanes ......................................................................... 3
Polycondensation of poly(S-r-NBS) in melt ............................................................................ 3
Precipitation of branched-poly(S-r-NBS) ............................................................................... 4
Polycondensation of poly(S-r-DENBS) in solution ................................................................. 4
Polycondensation of poly(S-r-DENBS) in melt with below stoichiometric amounts of H2O ....... 4
Preparation of poly(S50-r-Sty) and poly(S50-r-DIB) .............................................................. 4
Methods .................................................................................................................................. 5
Results and Discussion ............................................................................................................ 7
References ............................................................................................................................... 51
Author Contributions .............................................................................................................. 51

Experimental Procedures

Nomenclature of monomers

To improve the readability of the manuscript complex names of silane chemicals were simplified. The IUPAC names of silanes were simplified, and acronyms were formed. The simplified names were derived from the number (i.e., mono, di, and tri) and type of hydrolysable substituents (i.e., chloro- or ethoxy) of the silicon atom. Methyl substituents were excluded from the simplified names, except when three methyl substituents and no hydrolysable substituent were bound to the silicon atom. In case three methyl substituents were bound to the silicon atom, “trimethyl” was used as suffix. The bicyclo[2.2.1]hept-5-enyl substituent was referred to as “norbornenyl”.

Table S1. Nomenclature of ethoxy- and chlorosilanes used in this study.

| IUPAC | Simplified           | Acronym | Hydrolysable groups | Resulting siloxane |
|-------|----------------------|---------|---------------------|--------------------|
| Bicyclo[2.2.1]hept-5-en-2-yltrimethylsilane | Trimethylnorbornenylsilane | TMNBS   | 0                   | -                  |
| Bicyclo[2.2.1]hept-5-en-2-yl(ethoxy)dimethylsilane | Monoethoxy norbornenylsilane | MENBS   | 1                   | M                  |
| Bicyclo[2.2.1]hept-5-en-2-yl diethoxy(methyl) silane | Diethoxynorbornenylsilane | DENBS   | 2                   | D                  |
| Bicyclo[2.2.1]hept-5-en-2-yl dichloro(methyl) silane | Dichloronorbornenylsilane | DCNBS   | 2                   | D                  |
| Bicyclo[2.2.1]hept-5-en-2-yl triethoxysilane | Triethoxynorbornenylsilane | TENBS   | 3                   | T                  |
| Bicyclo[2.2.1]hept-5-en-2-yl trichlorosilane | Trichloronorbornenylsilane | TCNBS   | 3                   | T                  |

Nomenclature of polymers
The products of the inverse vulcanization were termed poly(S-x-NBS\(_x\)) in accordance with previous reports. NBS represents a norbornenylsilane, i.e., TMNBS, MENBS, DENBS, DCNBS, TENBS, or TCNBS. NBS, represents a binary mixture of a hydrolysable norbornenylsilane, i.e., MENBS, DENBS, DCNBS, TENBS, and TCNBS with TMNBS in which the index x denotes the mass fraction of the respective hydrolysable silane in the binary mixture. The sulfur content of polymers in this work was kept at 50 wt% unless stated differently. For example, poly(S-x-MENBS\(_x\)) refers to a polymer prepared via inverse vulcanization of 50 wt% sulfur and 50 wt% of a NBS mixture composed of 30 wt% MENBS and 70 wt% TMNBS. During the polycondensation of poly(S-x-NBS\(_x\)), siloxane bonds between poly(S-x-NBS\(_x\)) molecules form. The partial crosslinking of poly(S-x-NBS\(_x\)) with siloxane bonds results in branching. The products of the polycondensation of poly(S-x-NBS\(_x\)) are thus termed branch-poly(S-x-NBS\(_x\)). Insoluble or partially soluble products of branch-poly(S-x-NBS\(_x\)) are referred to as net-poly(S-x-NBS\(_x\)) analogue to our previous work on insoluble net-poly(S-x-StyTMS) polymers.

Chemicals

Elemental sulfur and dry THF were purchased from Alfa Aesar (Haverhill, USA) and used as received. Hydrolysable silanes were purchased from Gelest (Morrisville, USA) and used as received. Methyl lithium was purchased from Merck (Darmstadt, Germany).

Synthesis of TMNBS

Trimethylnorbornenylsilane (TMNBS) was synthesized from the reaction of methyl lithium (MeLi) with monoethoxy norbornenylsilane (MENBS). In brief, 7.14 g (0.036 mol, 1.00 eq.) of MENBS and 20 mL of dry THF were charged in a 50 mL Schlenck flask and fitted with an addition funnel. The air in the apparatus was replaced with a nitrogen atmosphere by three cycles of evacuation and purging with nitrogen. The addition funnel was then charged with 25 mL of MeLi solution (1.6 mol L\(^{-1}\), 0.04 mol, 1.10 eq.) in diethyl ether (DET) and the Schlenck flask was cooled down to 0°C using an ice bath. The MeLi solution was then added dropwise under stirring over the course of roughly 5 min. A slight yellow color can be observed upon addition of MeLi, presumably due to the reduction of the inhibitor MEHQ in MENBS. After the addition was completed, the reaction was stirred for 4 h at 0°C. The reaction mixture was poured onto 20 mL of ice water to quench excess MeLi. The phases were separated in a separation funnel and the organic phase was washed at least three times with 20 mL of deionized water and until the aqueous phase was pH neutral. The organic phase was dried over anhydrous magnesium sulfate and filtered. The volatiles of the filtrate were removed under reduced pressure. A slightly yellow, clear liquid was obtained in 77% yield. The product was characterized with ATR FT-IR, \(^1\)H, \(^13\)C, and \(^{29}\)Si NMR.

To ensure that MeLi could not hydrolyze prior to the reaction and to avoid storing bottles of MeLi with a punctured septum, the MeLi solution was purchased in bottles containing 25 mL MeLi solution and was used up entirely for one reaction. The use of THF as co-solvent is crucial to obtain a quantitative yield, presumably due to the presence of MeLi aggregates in pure DET.

Inverse vulcanization of Norbornenylsilanes

The following procedure was applied to all norbornenylsilanes (NBS), i.e., TMNBS, MENBS, DENBS, DCNBS, TENBS, and TCNBS. Equal masses of elemental sulfur and a norbornenylsilane or a mixture of norbornenylsilanes was charged into a 10 mL crimping vial with a stir bar. In a typical experiment, 500 mg of sulfur and 500 mg of NBS or 500 mg of a mixture of NBS were used. The crimping vial was sealed with a cap and a crimping tool and was heated to 150°C in an aluminum heating block. The temperature was controlled with a thermosensor reaching into a compartment of the heating block filled with silicon oil. Additionally, the temperature was confirmed using a thermometer. After putting the vials into the heating block, elemental sulfur was allowed to melt for roughly 5 min before stirring the reaction mixture at 400 rpm. The reaction was stopped after 5 h by cooling to room temperature. The resulting poly(S-x-NBS) were obtained as a red-black viscoelastic liquid. Reactions at 130 °C or 140 °C did not yield homogenous products after 5 h. The reaction did not produce significant amounts of H\(_2\)S since a tube from the reaction led into a lead acetate solution did not produce detectable quantities of lead sulfide and no pungent odor was present. The yield is assumed to be quantitative, since there are no traces of sulfur or NBS in the in the product, as confirmed by DSC and \(^1\)H NMR, respectively.

Polycondensation of poly(S-x-NBS) in melt

A melt of poly(S-x-NBS) was formed by heating 1 g of poly(S-x-NBS) to 100°C in a crimping vial. To hydrolyze the ethoxy groups in poly(S-x-MENBS\(_x\)), poly(S-x-DENBS\(_x\)), or poly(S-x-TENBS\(_x\)), 20.0 eq. of HCl (pH 3) relative to the molar amount of ethoxy groups was added to the melt. For the hydrolysis of poly(S-x-DCNBS\(_x\)) and poly(S-x-TCNBS\(_x\)), 20.0 eq. of H\(_2\)O (pH 7) were added. After addition of HCl or water the crimping vial was sealed with a cap and a crimping tool. The heterogenous reaction was allowed to proceed for 18 h overnight. The vial was cooled to room temperature and excess water was rinsed of with methanol. The resulting branch-poly(S-x-NBS) were stored in an oven at 80°C without a cap for five days to drive the equilibrium towards the siloxane bond by removing water. The branch-poly(S-x-NBS) were dried in a vacuum oven at 40°C overnight.
Precipitation of branch-poly(S-r-NBS₉)

A solution of 25 mg mL⁻¹ branch-poly(S-r-NBS₉) in THF was added dropwise to a beaker with methanol at room temperature which was stirred vigorously at 1000 rpm. The mass of methanol was chosen to result in a concentration of 2 mg mL⁻¹ of branch-poly(S-r-NBS₉), neglecting the volume of THF. For multigram reactions, the concentration was increased to 50 mg mL⁻¹ branch-poly(S-r-NBS₉) in THF, and the mass of methanol was decreased to result in of 5 mg mL⁻¹ branch-poly(S-r-NBS₉), neglecting the volume of THF. After the addition of the branch-poly(S-r-NBS₉) the suspension was stirred for 5 min to encourage coagulation of particles into thick flakes, which were then allowed to settle for 10 min without stirring. The precipitate was filtered using a Buchner funnel. The filter cake was washed with methanol and ethanol and was dried in a vacuum oven at 40°C overnight to yield a grey solid. The yields for branch-poly(S-r-NBS₉) polymers were around 40 wt%. Upscaling of the reaction improved the yield (Table S2).

| Name               | Yield (%) - 1g scale | Yield (%) - 6g scale |
|--------------------|----------------------|----------------------|
| poly(S-r-TMNBS)    | 32                   | -                    |
| branch-poly(S-r-MENBS₁₀) | 40           | -                    |
| branch-poly(S-r-MENBS₂₀) | 41           | 42                   |
| branch-poly(S-r-MENBS₃₀) | 41           | -                    |
| branch-poly(S-r-DENBS₁₀) | 27           | -                    |
| branch-poly(S-r-DENBS₂₀) | 40           | -                    |
| branch-poly(S-r-DENBS₃₀) | 44           | -                    |
| branch-poly(S-r-DENBS₄₀) | 37           | -                    |
| branch-poly(S-r-DCNBS₁₀) | 41           | -                    |
| branch-poly(S-r-DCNBS₂₀) | 43           | 48                   |
| branch-poly(S-r-DCNBS₃₀) | 47           | -                    |
| branch-poly(S-r-TENBS₁₀) | 39           | -                    |
| branch-poly(S-r-TENBS₂₀) | 40           | -                    |
| branch-poly(S-r-TCNBS₁₀) | 32           | -                    |
| branch-poly(S-r-TCNBS₂₀) | 33           | 50                   |

Polycondensation of poly(S-r-DENBS) in solution

To a solution of 1 g poly(S-r-DENBS₁₀₀) in 5 mL of THF in a 10 mL crimping vial, 1 vol% of HCl (pH 4) solution was added. After addition of HCl or water the crimping vial was sealed with a cap and a crimping tool. The red and homogenous solution was stirred for 15 h at 60°C. The vial was cooled to room temperature and volatiles were removed under reduced pressure. The product was dried in a vacuum oven at 40°C overnight.

Polycondensation of poly(S-r-DENBS) in melt with below stoichiometric amounts of H₂O

A melt of poly(S-r-DENBS₁₀₀) was formed by heating 1 g of poly(S-r-DENBS₁₀₀) to 100°C in a crimping vial. To partially hydrolyze the ethoxy groups in poly(S-r-DENBS₁₀₀), 0.20 and 0.10 eq. of HCl (pH 3) relative to the molar amount of the ethoxy groups was added to the melt. After the addition of HCl the crimping vial was sealed with a cap and a crimping tool. The heterogeneous reaction was allowed to proceed for 18 h overnight. The vial was cooled to room temperature and excess water was rinsed off with methanol. The resulting branch-poly(S-r-NBS) were stored in an oven at 80°C without a cap for five days to drive the equilibrium towards the siloxane bond by removing water. The branch-poly(S-r-NBS) were dried in a vacuum oven at 40°C overnight.

Preparation of poly(S₉₀r-Sty) and poly(S₉₀r-DIB)

Polymers were prepared according to reported protocols, using 50 wt% of styrene or disopropenylbenzene, respectively. Inhibitors were removed prior to the reaction by passing the monomers through alumina.
**Supporting Information**

**Methods**

**ATR FT-IR**
Attenuated total reflection Fourier transform infrared spectra were recorded using a Vertex 80 spectrometer from Bruker Optik (Ettlingen, Germany) in 45° a geometry (single reflection) on a diamond/ZnSe crystal in a MiRacle ATR setup from PIKE Technologies (Madison, USA). ATR FT-IR spectra of norbornenylsilanes with 0-3 ethoxy-, 0-3 methyl-, and 2-3 chloro-substituents were investigated, thus, an unambiguous assignment of peaks to functional groups, e.g., Si-CH₃, Si-OCH₂CH₃ (Si-OEt), Si-CI, and norbornenyl (NB) can be provided. Assignment of norbornenyl peaks was further assisted by comparison with ATR FT-IR spectra of 2-norbornene from the NIST database and from the literature. Each peak is assigned by its wavenumber and the intensity is indicated with vs (very strong), s (strong), m (medium), w (weak), or vw (very weak). Broad signals are indicated as “br.”. Diagnostic signals are assigned in brackets. Indexes of assigned vibrations are abbreviated with “stretch” (stretching), “bend” (bending), “sym” (symmetrical), “anti” (anti-symmetrical) and “wag” (wagging).

**DLS**
Dynamic light scattering measurements were performed on a Zetasizer Nano ZS from Malvern Instruments (Malvern, United Kingdom) equipped with a 633 nm laser.

**DSC**
Thermal properties were measured on a DSC 2500 from TA Instruments (Newcastle, USA) with a heat rate of 10 K min⁻¹ between -40 and 130°C in Tzero sample holders from TA Instruments (Newcastle, USA). The glass transition temperature (T_g) was determined in the second heat run to eliminate possible interference from the polymer’s thermal history. The presence of residual sulfur was examined on the first heat run.

**EDX and SEM**
Energy dispersive X-ray spectroscopy a NORAN System SIX from Thermo Scientific (Waltham, USA) was used and scanning electron microscopy was conducted using a LEO 1530 scanning electron microscope from Leica (Hillsboro, USA) with an accelerating voltage of 5-10 kV. For SEM analysis, each specimen was sputtered with ca. 5 nm of carbon. Peaks were assigned according to the NIST Standard Reference Database 128.

**GPC**
Gel permeation chromatography was conducted using a Tosoh EcoSEC from Tosoh (Tokyo, Japan) equipped with a SDV 5 μm bead size guard column (50 × 8 mm) followed by three SDV 5 μm columns (300 × 7.5 mm, subsequently 100, 1000, and 105 Å pore size, PSS), a differential refractive index (DRI) detector, and a UV-vis detector set to 254 nm. THF was used as eluent at 35°C with a flow rate of 1.0 mL min⁻¹. The SEC system was calibrated by using linear poly(methyl methacrylate) standards ranging from 800 to 1.82 × 10⁶ g mol⁻¹. Samples were dissolved in THF (ca. 2 mg mL⁻¹) and filtered through 0.43 μm PTFE filters prior to injection into the system.

**Simulation of the chain length**
The script to simulate the chain length of poly(S-r-NB₃) in dependence of the MENBS:TMNBS ratio and the expected value of the chain length after the inverse Vulcanization was written in Python.

**Liquid-state NMR**
¹H and ¹³C nuclear magnetic resonance spectroscopy was conducted using a Bruker Avance III 400 MHz spectrometer from Bruker (Rheinstetten, Germany). ¹H NMR spectra were recorded using CDCl₃ (99.8 atom% D) from Merck (Darmstadt, Germany) as a solvent. For one spectrum between 32 and 128 scans were collected. ¹³C NMR spectra were recorded using CDCl₃ (99.8 atom% D) from Merck (Darmstadt, Germany) as a solvent. For one spectrum 1024 scans were collected. ²⁵Si NMR experiments were performed on a Bruker Avance Neo 400 MHz NB spectrometer equipped with a 5-mm BBO probe from Bruker (Rheinstetten, Germany). The spectra of TMNBS and MENBS were recorded with 512 scans. For the spectra of poly(S-r-MENBS) and net-poly(S-r-MENBS) 1024 and 4096 scans were accumulated, respectively. All samples were dissolved in CDCl₃ (99.8% D, 0.03 v/v% TMS) from ARMAR AG (Döttingen, Switzerland). The spectra were acquired at a read-out temperature of 298 K. The optimized ²⁵Si 90° pulse length was 10.5 μs and the recycle delay was set to 60 s. Heteronuclear decoupling during acquisition was achieved with WALTZ-16. The ²⁵Si chemical shifts were externally referenced to the ²⁵Si signal of TMS at 0 ppm. Processed data were analyzed using MestReNova 14.1.0 from Mestrelab Research S.L. (Santiago de Compostela, Spain).

**Solid-state NMR**
²⁵Si cross polarization (CP) magic-angle spinning (MAS) NMR spectra were recorded using a Bruker Avance III 400 MHz WB spectrometer from Bruker (Rheinstetten, Germany) equipped with a 4-mm double resonance MAS probe. The spectra were acquired at a read-out temperature of 298 K and a spinning frequency of 12 kHz using TMS at 0 ppm as external reference. For the ²⁵Si CP measurements, 1024 scans were accumulated. The optimized ¹H 90° pulse length was 2.5 μs and the recycle delay was set to 5 s. ¹H to ²⁵Si magnetization transfer was achieved by using linear 70–100% ¹H-ramped CP with a contact time of 8 ms to fulfill the Hartmann–Hahn condition. A swept-frequency two-pulse phase modulation (SW–TPPM) heteronuclear decoupling was used during the acquisition. Processed data were further analyzed using MestReNova 14.1.0 from Mestrelab Research S.L. (Santiago de Compostela, Spain).

**PXRD**
Powder X-ray diffraction was measured using a Stadi-P diffractometer (Stoe, Germany) with Ge-monochromatized Cu-Kα radiation operating in transmission geometry. All data were measured in the range 2-29°.
Rheometry
The mechanical properties of \textit{branch}-poly(S-\textit{r}-NBS\textsubscript{\textendash}) were investigated using an ARES G2 rheometer from TA instruments (New Castle, USA). Small oscillatory shear measurements were performed at different temperatures using strains from 0.5\% to 5\% in a frequency range from 0.1 to 100 rad s\textsuperscript{\textendash}1 using an 8 mm parallel plate geometry. The samples were punched out resulting in round disks with 13 mm in diameter and 1 mm in thickness.

Universal Tester
The mechanical properties of \textit{branch}-poly(S-\textit{r}-MENBS\textsubscript{\textendash}) were investigated using an AGS-X Universal tester from Shimadzu Inc. (Kyōto, Japan). Three samples were prepared for each tensile experiment. The tested samples were in a dumbbell shape with 1-2 mm thickness, 7.5 mm width and 5 mm length. The tensile speed was set at 50 mm/min.

UV-vis spectroscopy
Ultraviolet-visible spectra were recorded using a PerkinElmer Lambda 35 UV-vis spectrometer from PerkinElmer Ink. (Waltham, USA). A film of \textit{branch}-poly(S-\textit{r}-MENBS\textsubscript{25}) was measured by sandwiching the molten polymer between two glass slides. As a reference, water was sandwiched between to glass slides.
Results and Discussion

(A) Simplified reaction equation of the hydrolysis of a silane containing four hydrolysable functional groups to form orthosilicic acid. The orthosilicic acid undergoes polycondensation to yield quartz. Silanes do not have to be hydrolyzed quantitatively to undergo condensation. A silanol functional group can react directly with a hydrolysable functional group of another silane, resulting in a complex equilibrium of hydrolyzed and condensed species. (B) Depending on the number of hydrolysable groups at the silicon atom, different polycondensation products will be obtained. Silanes with one hydrolysable group form M siloxanes, whereas silanes with two hydrolysable groups form cyclic or linear D siloxanes. Silanes with three hydrolysable groups form T siloxanes, which can possess cage-like structures (silsesquioxanes) and network structures. When all four substituents of the silicon are hydrolysable, the final product is synthetic quartz with the general sum formula SiO₂.
Figure S2. (A) Reaction monitoring of the reaction between equal masses of sulfur and DENBS at 150 °C after different reaction times using ATR FT-IR ATR. (B) Inset of the normalized ethoxy bands between 1200 – 900 cm⁻¹ after different reaction times.

The characteristic peaks associated with the vibrations of the ethoxy groups in DENBS were assigned at 1164, 1103, 1074, and 948 cm⁻¹. The intensity and position of the characteristic ethoxy peaks does not change significantly, indicating a full retention of ethoxy groups even after 8 h. The intensity of peaks associated with the norbornene C=C double bond, i.e., 3057 cm⁻¹ (C-H stretching in C=C-H), 1568 (C=C stretching), 890 (C=CH bond), and 717 cm⁻¹ (C-H wag) were reduced drastically after 1 h and disappeared completely after 2 h, indicating full conversion of C=C double bonds.

ATR FT-IR DENBS: ν [cm⁻¹] = 3057 vw (C-H stretching in C=C-H), 2970 m and 2871 m (C-H stretching), 1568 vw (C=C stretching), 1388 w, 1333 w (C-H bond in C=C-H), 1256 s (Si-CH₃), 1164 m, 1103 vs, 1074 vs, and 948 s (Si-OEt), 891 s (C=CH bond), 816 s, 802 m, 785 s, 756 vs, 717 s (C-H wag), 696 s, 662 m.

ATR FT-IR poly(S-r-DENBS₁₀₀): ν [cm⁻¹] = 2966 m and 2872 m (C-H stretching), 1389 m, 1256 m (Si-CH₃ sym. stretch), 1163 m, 1101 vs, 1072 vs, and 945 s (Si-OEt), 905 s, 795 vs, 756 vs.
Figure S3. (A) Chemical structure of exo- and endo-isomers of MENBS and TMNBS. The highlighted H atoms could not be assigned unambiguously due to the complexity (multiplicity, exo- and endo-isomers, overlap of signals) of the spectra. However, the product (TMNBS) formation can be demonstrated by the disappearance of the ethoxy groups and the decrease from four SiCH$_3$ to two SiCH$_3$ peaks due to the chemical equivalence of the SiCH$_3$ groups in TMNBS. $^1$H NMR spectra of (B) MENBS and (C) TMNBS in CDCl$_3$.

The $^1$H NMR spectra of MENBS and TMNBS are complex due to the presence of exo- and endo-MENBS. The ratio of exo- and endo-MENBS was ca. 0.45 to 0.55, as deduced from the integral ratios of the four singlet peaks assigned to the Si-CH$_3$ groups at 0.12, 0.11, 0.04, and -0.04 ppm, i.e., two SiCH$_3$ peaks for both exo- and endo-MENBS, respectively. The alkene hydrogen atoms in the spectrum of MENBS were found at 6.15 and 5.95 ppm and the peaks of the ethoxy group were found at 3.66 and 1.18 ppm. In the spectrum of TMNBS, the alkene hydrogens were retained but experienced a mildly different chemical shift (6.15 and 5.94 ppm), whereas the peaks assigned to the ethoxy groups of MENBS disappeared quantitatively. Due to the substitution of the ethoxy group with a methyl group, all methyl groups became chemically identical and two (exo- and endo-TMNBS) instead of four SiCH$_3$ peaks were found (0.00 and -0.09 ppm). The integral ratio of the two SiCH$_3$ peaks in TMNBS confirmed an exo- and endo-TMNBS of 45 to 55 %, respectively.

MENBS
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ [ppm] = 6.15 and 5.95 (m, 2H, HC=CH), 3.66 (m, 2H, -OCH$_2$CH$_3$), 2.88 (m, 2H, CH$_{t}$), 1.88 (m, 1H), 1.62 (m, 1H), 1.37 (m, 1H), 1.18 (m, 3H, -OCH$_2$CH$_3$), 0.99 (m, 1 H), 0.42 (m, 1H), 0.12, 0.11, 0.04, -0.04 (s, 6H, Si-CH$_3$).

TMNBS
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ [ppm] = 6.15 and 5.94 (m, 2H, HC=CH), 2.87 (m, 2H, CH$_{t}$), 1.86 (m), 1.52 (m), 1.37 (m), 1.13 (m), 1.04 (m), 0.92 (m), 0.31 (m), 0.00 and -0.09 (s, 9H, SiCH$_3$).
Figure S4. (A) Chemical structure of exo- and endo-isomers of MENBS and TMNBS with numbered carbon atoms. $^{13}$C NMR spectra of (B) MENBS and (C) TMNBS in CDCl$_3$. The solvent peak of CDCl$_3$ was referenced to 77.0 ppm.

In the $^{13}$C NMR spectrum of MENBS, four peaks corresponding to alkene carbon atoms were found (138.2, 135.6, 134.1, and 133.4 ppm), i.e., two peaks for both exo- and endo-MENBS, respectively. For the two carbon atoms of the ethoxy group, only three peaks were found (58.4, 58.2, and 18.6 ppm), indicating that the difference in the chemical shift of exo- and endo-MENBS for the -CH$_3$ group is not detectable. Four peaks were found for the two SiCH$_3$ groups (-1.8, -2.0, -2.4, -2.6 ppm), i.e., two peaks for both exo- and endo-MENBS, respectively. In the spectrum of TMNBS, the alkene carbons were retained but experienced a mildly different chemical shift (138.5, 135.4, 134.0, and 133.2 ppm), whereas the peaks assigned to the ethoxy groups of MENBS disappeared quantitatively. Due to the substitution of the ethoxy group with a methyl group, all SiCH$_3$ groups became chemically identical and two (exo- and endo-TMNBS) instead of four SiCH$_3$ carbon peaks were found (-1.4 and -2.0).

MENBS
$^{13}$C NMR (CDCl$_3$, 400 MHz): δ [ppm] = 138.2, 135.6, 134.1, and 133.4 (C2, C3, C2’, C3’), 58.4 and 58.2 (C10, C10’), 51.3 and 47.0 (C7, C7’), 44.4, 42.6, 42.4, and 42.4 (C1, C1’, C4, C4’) 26.9 and 26.5 (C6, C6’), 25.3 and 25.2 (C5, C5’), 18.6 (C11, C11’), -1.8, -2.0, -2.4, -2.6 (C8, C9, C8’, C9’).

TMNBS
$^{13}$C NMR (CDCl$_3$, 400 MHz): δ [ppm] = 138.5, 135.4, 134.0, and 133.2 (C2, C3, C2’, C3’), 51.5 and 46.8 (C7, C7’), 44.8, 42.9, 42.5, and 42.4 (C1, C1’, C4, C4’) 27.1 and 27.0 (C6, C6’), 25.3 and 25.2 (C5, C5’), -1.4, -2.0 (C8, C9, C10, C8’, C9’, C10’).
Figure S5. (A) Chemical structure of exo- and endo-isomers of MENBS and TMNBS highlighting the silicon atom. $^{29}$Si NMR spectra of (B) MENBS and (C) TMNBS in CDCl$_3$.

In the $^{29}$Si NMR spectrum of MENBS two peaks at 17.8 and 17.1 ppm were detected, which correspond to the exo- and endo-isomers of MENBS. After the reaction with MeLi, both peaks shifted two 3.2 and 2.7 ppm. This is due to the exchange of the electronegative ethoxy group with a shielding methyl group.

MENBS
$^{29}$Si NMR (CDCl$_3$, 400 MHz): $\delta$ [ppm] = 17.8, 17.1.

TMNBS
$^{29}$Si NMR (CDCl$_3$, 400 MHz): $\delta$ [ppm] = 3.2, 2.7.
Figure S6. Digital image showing the products of the inverse vulcanization of sulfur with equal amounts of (A) TMNBS, (B) MENBS, (C) DENBS, and (D) TENBS for different reaction times. The mass of sulfur and the mass of the NBS was 500 mg.
Figure S7. $^{1}$H NMR spectra showing the consumption of norbornenyl C–C double bonds during the inverse vulcanization of sulfur with (A) TMNBS, (B) MENBS, (C) DENBS, and (D) TENBS for different reaction times. The mass of sulfur and the mass of the NBS was 500 mg.
Figure S8. DSC thermograms showing the conversion of crystalline sulfur during the inverse vulcanization of sulfur with (A) TMNBS, (B) MENBS, (C) DENBS, and (D) TENBS for different reaction times. The mass of sulfur and the mass of the respective NBS was 500 mg.
Figure S9. Digital images of the purification by precipitation of branch-poly(S-r-NBS). (A) Precipitation, (B) sedimentation, (C) vacuum filtration, (D) vacuum oven drying and (E) melting and shaping. The shown branch-poly(S-r-MENBS$_{20}$) were ductile but not sticky.
Figure S10. (A) GPC elugrams of poly(S-r-TMNBS) and (B) branch-poly(S-r-MENBS) before and after precipitation from THF into MeOH. The mass concentration of the polymer in THF was 20 mg mL$^{-1}$ and 1 mg mL$^{-1}$ MeOH in the precipitated suspension.
Figure S11. GPC elugrams showing the influence of the reaction time of the polycondensation of poly(S-r-MENBS$_{25}$) with HCl (pH 3) at 100°C. With increasing reaction time, the amount of low molar mass side products decreased, and the weight average molar mass ($M_w$) increased from 2 h to 4 h and to 18 h (3600, 4200, to 5200 g mol$^{-1}$, respectively).
Figure S12. (A) GPC traces and (B) analysis of the molar mass of poly(S-r-DENBS-100) after different reaction or work-up steps. The molar mass for the different steps were as follows: Inverse vulcanization ($M_N = 600$ g mol$^{-1}$, $M_W = 1300$ g mol$^{-1}$), hydrolysis ($M_N = 600$ g mol$^{-1}$, $M_W = 1400$ g mol$^{-1}$), removal of volatiles ($M_N = 800$ g mol$^{-1}$, $M_W = 1800$ g mol$^{-1}$), and vacuum drying ($M_N = 1200$ g mol$^{-1}$, $M_W = 5400$ g mol$^{-1}$).
Figure S13. (A) GPC traces and (B) analysis of the molar mass of poly(S-r-DENBS100) prepared in THF solution using different volume ratios of HCl (pH 4). An increase in the volume ratio of HCl led to a significant decrease in the molar mass. The molar mass for different volume ratios were as follows: 1 vol% (M$_{n}$ = 1200 g mol$^{-1}$, M$_{w}$ = 5400 g mol$^{-1}$), 10 vol% (M$_{n}$ = 900 g mol$^{-1}$, M$_{w}$ = 2000 g mol$^{-1}$), 15 vol% (M$_{n}$ = 800 g mol$^{-1}$, M$_{w}$ = 1500 g mol$^{-1}$), and 20 vol% (M$_{n}$ = 700 g mol$^{-1}$, M$_{w}$ = 1200 g mol$^{-1}$).
Figure S14. (A) GPC traces and (B) analysis of the molar mass of poly(S-r-DENBS$_{100}$) prepared in different solvents. For the polycondensation of poly(S-r-DENBS$_{100}$) in non-polar toluene at 100°C the lowest molar mass was obtained ($M_N = 300$ g mol$^{-1}$, $M_W = 400$ g mol$^{-1}$), which indicated polymer degradation. Use of the non-polar protic 1-butanol at 60°C yielded the second lowest molar mass ($M_N = 700$ g mol$^{-1}$, $M_W = 1600$ g mol$^{-1}$). Polar solvents yielded higher molar mass, as seen for the polar aprotic THF ($M_N = 1200$ g mol$^{-1}$, $M_W = 5400$ g mol$^{-1}$) and the polar protic 2-propanol ($M_N = 900$ g mol$^{-1}$, $M_W = 9000$ g mol$^{-1}$). However, the alcohols 1-butanol and 1-propanol suffered from a limited solubility of poly(S-r-DENBS$_{100}$).
Figure S15. (A) Digital image of the precipitation of poly(S-r-DENBS$_{100}$) from 2-propanol into water, resulting in a nanosized dispersion. A light source (not visible in the picture) was shined from above to demonstrate the light scattering characteristic for fine dispersion. The farther the light reaches into the dispersion, more blue and green light is absorbed and only yellow is scattered. (B) Differential light scattering of the poly(S-r-DENBS$_{100}$) dispersion. The average size of particles was 132.2 ± 0.06 nm.
Figure S16. (A) Digital images showing the preparation of a thin layer of \textit{branch-poly(S-r-MENBS_{20})} for UV vis spectroscopy. The transparency of the thin layer proves the homogeneity and \textit{branch-poly(S-r-MENBS_{20})}. First, (i) 10 mg of \textit{branch-poly(S-r-MENBS_{20})} were deposited on a glass slide and molten at 80°C for (ii) 2 min and (iii) 10 min. A second glass slide was placed on top of the \textit{branch-poly(S-r-MENBS_{20})} droplet and placed in an oven at 80°C for 15 min (iv).
**Figure S17.** UV-vis spectrum from 350 – 800 nm of a thin film of branch-poly(S-r-MENBS$_{20}$) in between two glass slides.
Supporting Information

Figure S18. (A) Insets of ATR FT-IR spectra of DCNBS and DENBS used as termonomers. The green areas highlight the bands corresponding to the hydrolysable substituents of silicon, i.e., the chloro- (DCNBS) and the ethoxy substituents (DENBS). Insets of the ATR FT-IR spectrum of (B) branch-poly(S-r-DENBS<sub>30</sub>) and (C) branch-poly(S-r-DCNBS<sub>30</sub>) showing the bands corresponding to the siloxane binding motifs (linear and ring-like molecules). The spectrum of PDMS (D) serves as a reference for a linear polysiloxane.
Pool of red (10 %) and grey (90 %) building blocks

Random assembly into chains with a chain lengths of 1-11 (Poisson distribution with $\mu = 4$)

60 % of chains "none"

40 % of chains "at least one"

Chains containing red blocks combine. The total number of chains reduces to 80%.

Chains containing two or more red blocks

Chains containing more than three red blocks recombine again once.

Figure S19. Schematic explaining the theoretical considerations for the chain length distributions of branch-poly(S-r-MENBS) polymers and the working principle of the simulation. A pool of red and grey building blocks is randomly assembled into chains with a length of 1 – 11 blocks. The probability of chain lengths follows a Poisson distribution, with the expected value $\mu$ being four and $P(x=0)$ resembling a chain length of 1. Chains containing at least one red building block are then fused together. The resulting fused chains contain two or more red building blocks. Fused chains containing more than two red building blocks will fuse together again. Further fusing of chains, e.g., when a double fused chains contained more than six red building blocks were not considered. This is due the low probability of a single fused chain to contain three red building blocks and due to the possibility of intra-chain fusing, which could not explicitly be considered in this model. The distribution of chain lengths thus consists of primary chains (only grey building blocks), chains that fused together once (two red building blocks), and chains that fused together twice (six or more red building blocks).
Figure S20. Simulation results to mimic and calculate the chain length distribution of branch-poly(S-r-MENBS\textsubscript{x}) polymers (red) for different expected values $\mu$ for the primary chain length distributions (grey) and for different contents of MENBS in the NBS mixture. The primary distribution (grey) was approximated as a Poisson distribution with an expected value of (A) $\mu = 1$, (B) $\mu = 2$, (C) $\mu = 4$, and (D) $\mu = 8$ and is supposed to model the chain length distribution after the inverse vulcanization of the MENBS:TMNBS mixtures. The ratio of MENBS ("red blocks") in the NBS\textsubscript{x} mixture was chosen to be 0, 10, 20, 30, 40, and 50 %. An increase in the content of MENBS leads to an increase of the chain lengths and ultimately results in a multimodal distribution of the chain length. When the expected value $\mu$ of the chain length distribution after the inverse vulcanization is assumed to be small ($\mu = 1$ or $2$), a high content of MENBS is required to obtain branch-poly(S-r-MENBS\textsubscript{x}) with long chains. This is because a small average chain length after the inverse vulcanization decreases the chance of a chain to contain one or more MENBS units to condensate with other chains. When the primary distribution was chosen with higher expected values $\mu$ ($\mu = 4$ or $8$), i.e., assuming a higher average chain length after the inverse vulcanization, only a small content of MENBS is required to significantly shift the chain length distribution of branch-poly(S-r-MENBS\textsubscript{x}) to high chain lengths. This is because a higher average chain length after the inverse vulcanization increases the chance of a chain to contain one or more MENBS units to condensate with other chains. Experimental GPC data for branch-poly(S-r-MENBS\textsubscript{x}) has most resemblance with the simulated results for an expected value $\mu = 1$ or $\mu = 2$, which indicates that the inverse vulcanization of MENBS and TMNBS mostly leads to short chain oligomers with few repeating units. Such a behavior is typical for the inverse vulcanization of monoalkenes.
Figure S21. GPC traces of poly(S$_{50}$-r-Sty) and poly(S$_{50}$-r-DIB) prepared with 50 wt% of sulfur according to reported procedures. The resulting molar mass were $M_N = 100$ g mol$^{-1}$, $M_W = 200$ g mol$^{-1}$ for poly(S$_{50}$-r-Sty) and $M_N = 100$ g mol$^{-1}$, $M_W = 200$ g mol$^{-1}$ for poly(S$_{50}$-r-DIB). Sty is an abbreviation for styrene and DIB is an acronym for diisopropenylbenzene.
Figure S22. (A) Solubility of 20 mg of branch-poly(S-r-MENBS<sub>100</sub>) in 5 mL of THF after polycondensation of poly(S-r-MENBS<sub>100</sub>) with 0, 6, 7, and 10 mg of HCl (pH 3) corresponding to 0.13, 0.15, 0.22 eq. of HCl relative to MENBS. The solubility of branch-poly(S-r-MENBS<sub>100</sub>) decreased drastically with the amount of HCl used for polycondensation. Digital images of branch-poly(S-r-MENBS<sub>100</sub>) prepared using (B) 0.10 eq., (C) 0.20 eq., and net-poly(S-r-MENBS<sub>100</sub>) prepared using (C) 1.00 eq. of HCl (pH 3) relative to the amount of ethoxy groups for the polycondensation of poly(S-r-MENBS<sub>100</sub>). After multiple months, both (A) and (B) became brittle. This is presumably due to the polycondensation of remaining ethoxy groups because of moisture in the air, which converts branch-poly(S-r-MENBS<sub>100</sub>) to net-poly(S-r-MENBS<sub>100</sub>).
In the $^{13}$C NMR spectrum of MENBS four signals corresponding to alkene carbon atoms were found at 138.2, 135.6, 134.1, and 133.4 ppm. No alkene peaks were present in the spectrum of poly(S-r-MENBS$_{100}$), i.e., a quantitative consumption of C=C double bonds. Carbon atoms adjacent to the former alkene carbons experience an upfield shift, whereas peaks emerging between 46.6–41.3 ppm indicate the formation of C-S bonds. Since sulfur radicals could add to the norbornene C=C double bonds $syn$ or $anti$ as well as $exo$ or $endo$, many different isomer combinations are possible, explaining the various C-S bond peaks observed. The shifts from 75.4 – 67.8 ppm could be explained by partly oxidized sulfide chains or carbons bound to two polysulfide chains. The spectrum of branch-poly(S-r-MENBS$_{100}$) does not deviate much from the baseline. The decrease of peak intensities from the spectra of MENBS to poly(S-r-MENBS$_{100}$) to branch-poly(S-r-MENBS$_{100}$) is indicative for polymerizations and the increasingly restricted mobility of molecules.

MENBS
$^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ [ppm] = 138.2, 135.6, 134.1, and 133.4 (C2, C3, C2’, C3’), 58.4 and 58.2 (C10, C10’), 51.3 and 47.0 (C7, C7’), 44.4, 42.6, 42.4, and 42.4 (C1, C1’, C4, C4’) 26.9 and 26.5 (C6, C6’), 25.3 and 25.2 (C5, C5’), 18.6 (C11, C11’), -1.8, -2.0, -2.4, -2.6 (C8, C9, C8’, C9’).

Poly(S-r-MENBS$_{100}$)
$^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ [ppm] = 75.4, 73.3, 69.6, 69.3, 67.9, and 67.6 (S(-S=O)-C, (S$_2$)$_2$C) 58.6 and 58.5 (C10, C10’), 46.6, 45.6, 44.5, 43.6, 43.3, 41.7, and 41.3 (C2, C2’, C3, C3’), 38.4, 35.3, and 35.1 (C4, C4’, C7, C7’) 31.7, 29.3, 29.0, 28.9, 27.9, and 27.8 (C1, C1’, C5, C5’, C6, C6’), 18.7, 18.6 and 18.4 (C11, C11’), 0.0, -1.6, -1.8, -1.9, -2.8, -3.0 (C8, C8’, C9, C9’).

Branch-poly(S-r-MENBS$_{100}$) $^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ [ppm] = 69.6 (S(-S=O)-C, (S$_3$)$_2$C), 58.5 (C10, C10’), 45.6 (C2, C2’, C3, C3’), 38.4 (C4, C4’, C7, C7’), 18.4 (C11, C11’).
In the $^{29}$Si NMR spectrum of MENBS two peaks for $exo$-MENBS and $endo$-MENBS were found. In the spectrum of poly($S$-$r$-MENBS$_{100}$) the $exo$-MENBS and $endo$-MENBS peaks split into four signals and experience a slight upfield shift (15.2, 15.2, 14.9, and 14.7), which is attributed to the $syn$- and $anti$-addition of sulfur radicals to the norbornenyl $C=C$ double bond. A peak at 7.8 ppm is attributed to the premature formation of $M$-siloxane bonds due to the hydrolysis and condensation of the ethoxy group caused by water in the NMR solvent CDCls or from moisture in the air during the inverse vulcanization or during the shipping of the sample. In the $^{29}$Si spectrum of branch-poly($S$-$r$-MENBS$_{100}$) the intensity of peaks corresponding to $M$-siloxanes increased relative to the intensity of peaks corresponding to ethoxy silanes (16.6, 16.4, 16.2, 15.2, 14.9, 14.7). The presence of both $M$-siloxanes and ethoxy silane moieties is expected, since poly($S$-$r$-MENBS$_{100}$) was hydrolyzed only partially (0.20 eq. of water relative to ethoxy groups) to ensure solubility. The overall intensity of peaks is reduced because of polymer crosslinking via $M$-siloxane bonds. In the spectrum of branch-poly($S$-$r$-MENBS$_{100}$), different $M$ siloxane moieties rise above the noise level (8.6, 8.4, 8.2, 8.0, 7.8, 7.7, 7.4, 7.2 ppm) due to the increased amount of $M$-siloxane bonds in branch-poly($S$-$r$-MENBS$_{100}$) compared to poly($S$-$r$-MENBS$_{100}$), whereas the most intense peak is unchanged at 7.8.

MENBS
$^{29}$Si NMR (CDCls, 400 MHz): $\delta$ [ppm] = 17.8, 17.1.

Poly($S$-$r$-MENBS$_{100}$)
$^{29}$Si NMR (CDCls, 400 MHz): $\delta$ [ppm] = 15.2, 15.2, 14.9, 14.7, 7.8, 7.7, 7.4, 7.2.

Branch-poly($S$-$r$-MENBS$_{100}$)
$^{29}$Si NMR (CDCls, 400 MHz): $\delta$ [ppm] = $\delta$ [ppm] = 16.6, 16.4, 16.2, 15.2, 14.9, 14.7, 8.6, 8.4, 8.2, 8.0, 7.8.
Figure S25. ATR FT-IR spectra of branch-poly(S-r-MENBS100) for different amounts of HCl solution used for the polycondensation of poly(S-r-MENBS100). The red area highlights the characteristic region of Si-O vibrations. The spectrum with 0.00 eq. H2O is still poly(S-r-MENBS100) and serves as a reference.

The characteristic peaks associated with the vibrations of the ethoxy groups in poly(S-r-MENBS100) were assigned at 1163, 1101, 1076, and 943 cm⁻¹. Upon reaction with 0.20 eq. of H2O, the intensity of ethoxy peaks at 1163, 1101, and 943 cm⁻¹ reduced drastically and the ethoxy peak at 1076 cm⁻¹ was covered by the emerging Si-O-Si vibration band centered at 1049 cm⁻¹. For 3.00 eq. of H2O all peaks related to ethoxy groups disappeared and a siloxane band was observed at 1028 cm⁻¹.

ATR FT-IR poly(S-r-MENBS100): ν [cm⁻¹] = 2951 m and 2868 m (C-H stretch), 1449 w, 1389 w, 1250 s (Si-CH₃), 1163 m, 1101 s, 1076 s, and 943 m (Si-OEt), 907 m, 824 vs, 779 vs, 702 m, 679 m, 634 m, 501 w.

ATR FT-IR branch-poly(S-r-MENBS100) (3.00 eq. H2O): ν [cm⁻¹] = 2949 m and 2864 m (C-H stretch), 1449 w, 1404 vw, 1252 s (Si-CH₃), 1028 vs, br. (Si-O-Si) 907 m, 815 vs, 775 vs, 725 m, 679 m, 642 m, 501 w.
Figure S26. GPC traces of commercial polydimethylsiloxane (PDMS, 100 cSt).
Figure S27. GPC traces for \textit{branch-poly(S-r-NBS)} prepared using different amounts of (A) DENBS or (B) DCNBS termonomer as D siloxane precursor and (C) TENBS or (D) TCNBS termonomer as T siloxane precursor. Polymers using 30 wt\% of a T siloxane precursor (TENBS or TCNBS) were not fully soluble in THF and thus not analyzed.
Figure S28. GPC traces for three independently prepared samples of branch-poly(S-r-DENBS<sub>20</sub>) to investigate the reproducibility of the molar mass. The average molar mass was 7600 ± 700 g mol<sup>-1</sup>. 
Figure S29. ATR FT-IR spectra of (A) TMNBS and (B) poly(S-r-TMNBS). The characteristic region for siloxane vibrations is highlighted in grey.

The characteristic peaks associated with the vibrations of the norbornene C=C double bond in TMNBS were assigned at 3059, 1568, 1333, 891, and 714 cm\(^{-1}\). The spectrum of poly(S-r-TMNBS\(_{100}\)) does not contain peaks of norbornene C=C double bonds, indicating full conversion of TMNBS. From the absence of strong peaks between 1100 – 1000 cm\(^{-1}\) it can be concluded that there are no ethoxy silane groups in TMNBS and no siloxane bonds in poly(S-r-TMNBS\(_{100}\)).

ATR FT-IR TMNBS: \(\nu\) [cm\(^{-1}\) = 3059 \text{vw (C-H stretch in C=C-H)}, 2953 \text{ m}, 2864 \text{ w (C-H stretch)}, 1568 \text{ vv (C=C stretch)}, 1406 \text{ br. vv (Si-CH\textsubscript{3} anti. deform)}, 1388 \text{ w}, 1333 \text{ w (C-H bend in C=C-H)}, 1246 \text{ s (Si-CH\textsubscript{3} sym. deform)}, 945 \text{ w}, 912 \text{ w}, 891 \text{ s (C=O band)}, 827 \text{ vs (Si-CH\textsubscript{3})}, 802 \text{ s}, 785 \text{ s}, 746 \text{ w}, 714 \text{ vs (C-H wag)}, 689 \text{ s}, 631 \text{ w}.

ATR FT-IR poly(S-r-TMNBS): \(\nu\) [cm\(^{-1}\) = 2948 \text{ s}, 2864 \text{ m (C-H stretch)}, 1449 \text{ m}, 1404 \text{ w (Si-CH\textsubscript{3} anti. deform)}, 1246 \text{ s (Si-CH\textsubscript{3} sym. deform)}, 1100 \text{ w}, 1052 \text{ w}, 1030 \text{ w}, 990 \text{ w}, 962 \text{ w}, 906 \text{ m}, 827 \text{ vs (Si-CH\textsubscript{3})}, 746 \text{ s}, 688 \text{ s}, 620 \text{ m}. 
Figure S30. ATR FT-IR spectra of (A) MENBS and (B) branch-poly(S-r-MENBSx) prepared using a NBS mixture containing 10, 20, and 30 wt% of MENBS and 90, 80, and 70 wt% of TMNBS, respectively. The characteristic ethoxy (A) and siloxane (B) vibrations are highlighted in red.

The characteristic peaks associated with the vibrations of the norbornene C=C double bond were assigned at 3059, 1568, 1333, 889, and 716 cm⁻¹ (MENBS) and at 3059, 1568, 1333, 891, and 714 cm⁻¹ (TMNBS). Diagnostic peaks associated with the vibrations of the ethoxy group of MENBS were assigned at 1164, 1107, 1078, and 945 cm⁻¹. The spectra of branch-poly(S-r-MENBSx) do not contain peaks of norbornene C=C double bonds, indicating full conversion of TMNBS and MENBS. Further, spectra of branch-poly(S-r-MENBSx) do not contain peaks assigned to ethoxy groups but instead a new broad siloxane peaks emerged at 1044 cm⁻¹.

ATR FT-IR TMNBS: ν [cm⁻¹] = 3059 vw (C-H stretching in C=C-H), 2953 m, 2864 w (C-H stretching), 1568 vw (C=C stretching), 1406 br. vw (Si-CH₃ anti. deform), 1388 w, 1333 w (C-H bend in C=C-H), 1246 s (Si-CH₃ sym. deform), 945 w, 912 w, 891 s (C-O bond), 827 vs (Si-CH₃), 802 s, 785 s, 746 w, 714 vs (C-H wag), 689 s, 631 w.

ATR FT-IR MENBS: ν [cm⁻¹] = 3059 vw (C-H stretching in C=C-H), 2966 m, 2866 m (C-H stretching), 1568 vw (C=C stretching), 1447 vw, 1391 w, 1333 w (C-H bend in C=C-H), 1250 s (Si-CH₃ sym. deform), 1164 w, 1107 vs, 1078 vs, and 945 s (Si-OEt), 889 s (C-O bond), 827 vs (Si-CH₃), 802 s, 771 vs, 716 vs (C-H wag), 691 s, 646 m.

ATR FT-IR branch-poly(S-r-MENBSx): ν [cm⁻¹] = 2949 m, 2862 w (C-H stretching), 1449 w, 1405 w (Si-CH₃ anti. deform), 1300 w, 1248 s (Si-CH₃ sym. deform), 1044 s, br. (Si-O-Si), 990 w, 912 w, 829 vs (Si-CH₃), 783 s, 748 s, 688 m.
The characteristic peaks associated with the vibrations of the norbornene C=\( \text{C} \) double bond in were assigned at 3057, 1568, 1333, 891, and 714 cm\(^{-1}\) (DENBS) and at 3059, 1568, 1333, 891, and 714 cm\(^{-1}\) (TMNBS). Diagnostic peaks associated with the vibrations of the ethoxy group of DENBS were assigned at 1164, 1103, 1074, and 948 cm\(^{-1}\). The spectra of branch-poly(S-r-DENBS\(_x\)) do not contain peaks of norbornene C=\( \text{C} \) double bonds, indicating full conversion of TMNBS and DENBS. Further, spectra of branch-poly(S-r-DENBS\(_x\)) do not contain peaks assigned to ethoxy groups, but instead new broad siloxane peaks emerged at 1069, 1052, and 1012 cm\(^{-1}\).

ATR FT-IR TMNBS: \( \nu \text{[cm}^{-1}] = 3059 \text{vw (C-Hstretch in } \text{C=H)} , 2953 \text{ m, 2864 w (C-Hstretch)}, 1568 \text{ vw (C=Ostretch)}, 1406 \text{ br. vw (Si-CH}_3\text{ anti. deform)}, 1388 \text{ w, 1333 w (C-Hbond in C=H)}, 1246 \text{ s (Si-CH}_3\text{ sym. deform), 945 w, 912 w, 891 s (C=Cbond), 827 vs (Si-CH}_3), 802 s, 785 s, 746 w, 714 vs (C-H\text{wig}), 689 s, 631 w. \)

ATR FT-IR DENBS: \( \nu \text{[cm}^{-1}] = 3057 \text{ vw (C-Hstretch in } \text{C=H)} , 2970 m and 2871 m (C-H\text{stretch}), 1568 \text{ vw (C=Ostretch)}, 1445 \text{ vw, 1388 w, 1333 w (C=CH}}_2\text{ bond}), 1256 \text{ s (Si-CH}_3\text{ sym. deform), 1164 m, 1103 vs, 1074 vs, and 948 s (Si-\text{OEt}}), 891 s (C=C\text{bond), 816 s, 802 m, 785 s, 756 vs, 717 s (C-H\text{wig}), 696 s, 662 m. \)

ATR FT-IR branch-poly(S-r-DENBS\(_x\)): \( \nu \text{[cm}^{-1}] = 2950 \text{ m, 2864 w (C-H\text{stretch})}, 1449 \text{ w, 1403 w (Si-CH}_3\text{ anti. deform)}, 1301 \text{ w, 1246 s (Si-CH}_3\text{ sym. deform), 1069 s, br., 1052 s, 1012 s (Si-O-Si), 912 w, 849 s, 829 vs (Si-CH}_3), 786 s, 747 s, 688 m. \)
The characteristic peaks associated with the vibrations of the norbornene C=C double bond in were assigned at 3060, 1570, 1335, 891, and 718 cm\(^{-1}\) (DCNBS) and at 3059, 1568, 1333, 891, and 714 cm\(^{-1}\) (TMNBS). Diagnostic peaks associated with the vibrations of the chloro group of DCNBS were assigned at 537 cm\(^{-1}\). The spectra of branch-poly(S-r-DCNBS\(_x\)) do not contain peaks of norbornene C=C double bonds, indicating full conversion of TMNBS and DCNBS. Further, spectra of branch-poly(S-r-DCNBS\(_x\)) do not contain peaks assigned to chlorine groups, but instead new broad siloxane peaks emerged at 1071, 1052, and 1014 cm\(^{-1}\).

ATR FT-IR TMNBS:  \(\nu\) [cm\(^{-1}\)] = 3059 vs (C-H\(_{\text{branched}}\) in C=C-H), 2970 m, 2864 w (C-H\(_{\text{branched}}\)), 1568 vw (C=C\(_{\text{branched}}\)), 1406 br. vw (Si-CH\(_3\)\(_{\text{anti}}\)\_deform.), 1388 w, 1333 w (C-H\(_{\text{bend in C-C-H}}\)), 1246 s (Si-CH\(_3\)\(_{\text{sym. deform.}}\)), 945 w, 912 w, 891 s (C=C\(_{\text{bend}}\)), 827 vs (Si-CH\(_3\)), 802 s, 785 s, 746 w, 714 vs (C-H\(_{\text{wag}}\)), 689 s, 631 w.

ATR FT-IR DCNBS:  \(\nu\) [cm\(^{-1}\)] = 3600-3100 vw br. (O-H), 3060 vw (C-H\(_{\text{branched}}\) in C=C-H), 2970 m, 2869 m (C-H\(_{\text{branched}}\)), 1570 vw (C=C\(_{\text{branched}}\)), 1447 vw, 1404 w (Si-CH\(_3\)\(_{\text{anti}}\)_deform.), 1335 w (C-H\(_{\text{bend in C-C-H}}\)), 1260 s (Si-CH\(_3\)\(_{\text{sym. deform.}}\)), 1226 m, 1079 m br., 1034 m, 965 m, 954 m, 891 s (C=C\(_{\text{bend}}\)), 815 m, 786 vs, 741 s, 718 vs (C-H\(_{\text{wag}}\)), 687 s, 623 m, 537 s, br. (Si-Cl).

ATR FT-IR branch-poly(S-r-DCNBS\(_x\)):  \(\nu\) [cm\(^{-1}\)] = 2951 m, 2866 w (C-H\(_{\text{branched}}\)), 1449 w, 1405 w (Si-CH\(_3\)\(_{\text{anti}}\)_deform.), 1301 w, 1249 s (Si-CH\(_3\)\(_{\text{sym. deform.}}\)), 1071 m br., 1052 m, 1014 s (Si-O-Si), 791 m, 748 s, 688 m.
Figure S33. ATR FT-IR spectra of (A) TENBS and (B) branch-poly(S-r-TENBSx) prepared using a NBS mixture containing 10, 20, and 30 wt% of TENBS and 90, 80, and 70 wt% of TMNBS, respectively. The characteristic siloxane vibrations are highlighted in blue.

The characteristic peaks associated with the vibrations of the norbornene C=C double bond in were assigned at 3057, 1568, 1335, 891, and 706 cm⁻¹ (TENBS) and at 3059, 1568, 1333, 891, and 714 cm⁻¹ (TMNBS). Diagnostic peaks associated with the vibrations of the ethoxy groups of TENBS were assigned at 1164, 1101, 1074, and 953 cm⁻¹. The spectra of branch-poly(S-r-TENBSx) do not contain peaks of norbornene C=C double bonds, indicating full conversion of TMNBS and TENBS. Further, spectra of branch-poly(S-r-TENBSx) do not contain peaks assigned to ethoxy groups, but instead new broad siloxane peaks emerged at 1100, 1077, and 1026 cm⁻¹.

ATR FT-IR TMNBS: ν [cm⁻¹] = 3059 vw (C-Hstretch in C=C-H), 2953 m, 2864 w (C-Hstretch), 1568 vw (C=Cstretch), 1406 br. vw (Si-CH₃, anti. deform), 1388 w, 1333 w (C-Hbond in C=C-H), 1246 s (Si-CH₃, sym. deform), 945 w, 912 w, 891 s (C=Cbend), 827 vs (Si-CH₃), 802 s, 785 s, 746 w, 714 vs (C-Hwag), 689 s, 631 w.

ATR FT-IR TENBS: ν [cm⁻¹] = 3059 vw (C-Hstretch in C=C-H), 2972 m and 2880 w (C-Hstretch), 1568 vw (C=Cstretch), 1445 w, 1389 w, 1335 w (C-Hbond in C=C-H), 1292 w, 1246 w, 1164 m, 1101 vs, 1074 vs, and 953 s (Si-OEt), 891 m (C=Cbend), 813 w, 802 m, 773 s, 744 m, 706 s (C-Hwag), 671 w, 613 m.

ATR FT-IR branch-poly(S-r-TENBSx): ν [cm⁻¹] = 2950 m, 2866 w (C-Hstretch), 1449 w, 1403 br. vw (Si-CH₃, anti. deform), 1389 w, 1301 w, 1247 s (Si-CH₃, sym. deform), 1164 w, 1100 s, 1077 s, 1026 s (Si-O-Si), 962 m, 912 m, 850 s, 830 vs (Si-CH₃), 774 s, 689 s, 620 m.
The characteristic peaks associated with the vibrations of the norbornene C=C double bond were assigned at 3065, 1572, 1335, 890, and 710 cm$^{-1}$ (TCNBS) and at 3059, 1568, 1333, 891, and 714 cm$^{-1}$ (TMNBS). Diagnostic peaks associated with the vibrations of the chloro groups of TCNBS were assigned at 563 cm$^{-1}$. The spectra of branch-poly(S-r-TCNBS$_x$) do not contain peaks of norbornene C=C double bonds, indicating full conversion of TMNBS and TENBS. Further, spectra of branch-poly(S-r-TCNBS$_x$) do not contain peaks assigned to chloro groups, but instead new broad siloxane peaks emerged at 1098, 1051, and 1028 cm$^{-1}$.

ATR FT-IR TMNBS: v [cm$^{-1}$] = 3059 vw (C-H$_{\text{stretch}}$ in C=CH$_2$), 2953 m, 2864 w (C-H$_{\text{stretch}}$), 1568 vw (C=C$_{\text{stretch}}$), 1406 br. vw (Si-CH$_3$ anti. deform.), 1388 w, 1333 w (C-H$_{\text{bend}}$ in C=CH$_2$), 1246 s (Si-CH$_3$ sym. deform.), 945 w, 912 w, 891 s (C-O$_{\text{bend}}$), 827 vs (Si-CH$_3$), 802 s, 785 s, 746 w, 714 vs (C-H$_{\text{wag}}$), 689 s, 631 w.

ATR FT-IR TCNBS: v [cm$^{-1}$] = 3500-3000 vw br. (O-H), 3065 vw (C-H$_{\text{stretch}}$ in C=CH$_2$), 2975 m, 2870 w (C-H$_{\text{stretch}}$), 1572 vw (C=C$_{\text{stretch}}$), 1447 w, 1335 w (C-H$_{\text{bend}}$ in C=CH$_2$), 1252 w, 1126 m, 1097 m, 1034 m, 955 m, 890 vs (C-O$_{\text{bend}}$), 826 m, 813 m, 777 vw, 738 m, 723 s, 710 s (C-H$_{\text{wag}}$), 698 s, 641 s, 627 m, 563 br. (Si-Cl).

ATR FT-IR branch-poly(S-r-TCNBS$_x$): v [cm$^{-1}$] = 2950 m, 2866 w (C-H$_{\text{stretch}}$), 1449 w, 1404 w (Si-CH$_3$ anti. deform.), 1301 w, 1248 s (Si-CH$_3$), 1098 s, 1051 s, 1028 s (Si-O-Si), 991 s, 913 m, 850 s, 831 vs (Si-CH$_3$ sym. deform.), 748 s, 689 m.
Figure S35. DSC thermograms of the first heat ramp of branch-poly(S-r-NBSx) to 130°C. The presence of crystalline sulfur would be apparent within the displayed area from a melting peak at ca. 115°C. (A) poly(S-r-TMNBS) (B) branch-poly(S-r-MENBSx) (C) branch-poly(S-r-DENBSx) (D) branch-poly(S-r-DCNBSx) (E) branch-poly(S-r-TENBSx), and (F) branch-poly(S-r-TCNBSx).
Figure S36. PXRD patterns of branch-poly(S-r-NBS) powders. The presence of sulfur would be apparent by characteristic and sharp reflexes. (A) poly(S-r-TMNBS) (B) branch-poly(S-r-MENBS) (C) branch-poly(S-r-DENBS) (D) branch-poly(S-r-DCNBS) (E) branch-poly(S-r-TENBS), and (F) branch-poly(S-r-TCNBS).
Figure S37. (A) SEM images of precipitated powders of (i) branch-poly(S-r-MENBS₈), (ii) branch-poly(S-r-DENBS₈), (iii) branch-poly(S-r-DCNBS₈), (iv) branch-poly(S-r-TENBS₈), and (v) branch-poly(S-r-TCNBS₈). Each powder was allowed to age for at least one month prior to the measurement. (B) EDX spectra of precipitated powders of (i) branch-poly(S-r-MENBS₈), (ii) branch-poly(S-r-DENBS₈), (iii) branch-poly(S-r-DCNBS₈), (iv) branch-poly(S-r-TENBS₈), and (v) branch-poly(S-r-TCNBS₈). For each powder, a spectrum of the background and two spectra of grains or other outstanding features on the surface were taken to examine the surface for signs of polymer degradation into sulfur crystals. For all EDX spectra, the Kα peaks for C, and Si were found at 0.27 and 1.74 keV. The peaks corresponding to sulfur were found at 0.15 (Lα), 2.3 (Kα), and 2.47 (Kβ) keV.
Figure S38. GPC traces of branch-poly(Sx-r-DENBS20) with different feed ratios of sulfur, i.e., 60, and 70 wt% (A-B). The relative mass ratio of the silanes DENBS (20 wt%) and TMNBS (80 wt%) was kept constant. (C) Molar mass $M_N$, $M_W$, and dispersity $D$ of branch-poly(Sx-r-DENBS20) in dependence of the sulfur feed ratio ranging from 30, 40, 50, 60, to 70 wt%. The molar masses were obtained as follows: branch-poly(S30-r-DENBS20) ($M_N = 2400$, $M_W = 6000$, $D = 2.5$), branch-poly(S40-r-DENBS20) ($M_N = 2700$, $M_W = 13900$, $D = 5.2$), branch-poly(S50-r-DENBS20) ($M_N = 1200$, $M_W = 8650$, $D = 7.2$), branch-poly(S60-r-DENBS20) ($M_N = 700$, $M_W = 5800$, $D = 8.3$), and branch-poly(S70-r-DENBS20) ($M_N = 600$, $M_W = 2900$, $D = 4.8$).
Figure S39. DSC thermograms of (A) poly(S-r-TMNBS) and the M-siloxane containing polymer (B) branch-poly(S-r-MENBS)x with different mass ratios of MENBS. The $T_G$ of poly(S-r-TMNBS) is 6°C. The $T_G$ of branch-poly(S-r-MENBS10), branch-poly(S-r-MENBS20), branch-poly(S-r-MENBS30), and branch-poly(S-r-MENBS50) are 10, 14, 18, and 27°C.
Figure S40. DSC thermograms of the D-siloxane containing polymers (A) poly(S-r-DENBS) and (B) branch-poly(DCNBS) with different mass ratios of DENBS and DCNBS, respectively. The Tg of branch-poly(S+r-DENBS), branch-poly(S+r-DENBS), and branch-poly(S+r-DENBS), are 15, 26, and 35°C. The Tg of branch-poly(S+r-DENBS), branch-poly(S+r-DENBS), and branch-poly(S+r-DENBS), are 1, 12, and 35°C.
Figure 41. DSC thermograms of the T-siloxane containing polymers (A) poly(S-r-TENBS) and (B) branch-poly(TCNBS) with different mass ratios of TENBS and TCNBS, respectively. The T_g of branch-poly(S-r-TENBS) and branch-poly(S-r-TENBS) are 17 and 22°C. The T_g of branch-poly(S-r-TCNBS), branch-poly(S-r-TCNBS) are 11 and 20°C.
Figure S42. Small amplitude oscillatory shear rheology measurements of branch-poly(S-r-MENBS$_{20}$) at different temperatures. (A) branch-poly(S-r-MENBS$_{20}$) displays a higher loss than storage modulus which indicates a dominant viscous behavior at 40 and 60°C. The same behavior is found for (B) branch-poly(S-r-NBS$_{20}$) at 40, 60, and 80°C. The viscoelastic behavior is indicated by the loss modulus being greater than the storage modulus (G'' > G'). (C) At 60°C branch-poly(S-r-TCNBS$_{20}$) showed a dominant elastic behavior for frequencies until a cross over at 0.17 rad s$^{-1}$ upon which the viscous behavior dominated. At 80°C and 100°C, the cross overs for branch-poly(S-r-TCNBS$_{20}$) were 6.5 and 74.5 rad s$^{-1}$, respectively. At 120°C, branch-poly(S-r-TCNBS$_{20}$) viscous behavior dominated below 0.22 rad s$^{-1}$ and elastic behavior dominated at least until 100 rad s$^{-1}$. Elastic properties are generally indicated by the storage modulus being independent of the frequency and being greater than the loss modulus (G > G’). After the measurement of branch-poly(S-r-TCNBS$_{20}$) at 120°C the polymer chemically changed, as indicated by a shift of the cross over (G’ = G’’) at 80°C from 6.51 to 0.89 rad s$^{-1}$. A decrease of the cross over time relates to a lower relaxation time and indicates cleaved sulfur chains due to the dynamic covalent nature of sulfur chains at elevated temperatures.
Figure S43. Small amplitude oscillatory shear rheology measurements of branch-poly(S-r-NBS20) to investigate the complex viscosity at different temperatures in dependence of the termonomer type and content. (A) The complex viscosity of branch-poly(S-r-MENBSx) at 40 and 60°C for x = 15, 20, and 25 wt%. Increasing the content of MENBS increased the complex viscosity. For all polymers, i.e., (A) branch-poly(S-r-MENBSx), (B) branch-poly(S-r-DCNBS20), and (C) branch-poly(S-r-TCNBS20), the complex viscosity decreased with the temperature. (D) Comparison of the complex viscosity of branch-poly(S-r-NBS20) at 60°C. The complex viscosity for branch-poly(S-r-TCNBS20) was the highest for all frequencies, and the complex viscosity of branch-poly(S-r-MENBS20), was the lowest for all frequencies.
Figure S44. (A) Tensile test measurements of branch-poly(S-r-MENBS$_{15}$), branch-poly(S-r-MENBS$_{20}$), and branch-poly(S-r-MENBS$_{25}$). Curves are the average of three experiments. Error bars are the standard error (N = 3). The maximum force required to stretch branch-poly(S-r-MENBS$_{15}$) increased in the order 1.83 ± 0.05 N for branch-poly(S-r-MENBS$_{15}$), 3.98 ± 1.26 N for branch-poly(S-r-MENBS$_{20}$), and 6.28 ± 0.82 N for branch-poly(S-r-MENBS$_{25}$). (B) Digital microscopy image of a branch-poly(S-r-MENBS$_{20}$) thread laying on cellulose after being elongated to 1000 % of its original length without breaking.
References

[1] Y. Zhang, J. J. Griebel, P. T. Dirlam, N. A. Nguyen, R. S. Glass, M. E. Mackay, K. Char, J. Pyun, J. Polym. Sci. A 2017, 55, 107.
[2] W. J. Chung, J. J. Griebel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen et al., Nat. chem. 2013, 5, 518.
[3] I. W. Levin, W. C. Harris, Spectrochim. Acta A 1973, 29, 1815.
[4] V. K. Tomazetti, W. G. Santos, B. S. Lima-Neto, React. Kinet. Mech. Cat. 2017, 120, 663.
[5] P. Linstrom, NIST Chemistry WebBook, NIST Standard Reference Database 69, National Institute of Standards and Technology, 1997.
[6] A. Groza, A. Surmeian, J. Nanomat. 2015, 1.
[7] L. M. Johnson, L. Gao, C. W. Shields IV, M. Smith, K. Ellimenko, K. Cushing, J. Genzer, G. P. López, J. nanobiotechnology 2013, 11, 22.
[8] L. Hudson, X-ray Transition Energies, NIST Standard Reference Database 128, National Institute of Standards and Technology, 2003.
[9] Shaka, A., Keeler, J., Freeman, R., J. Magn. Reson. 1983, 53, 313–340.
[10] Metz, G., Wu, X. L. & Smith, S. O., J. Magn. Reson. Ser. A 1994, 110, 219–227.
[11] Thakur, R. S., Kurur, N. D., Madhu, P. K. Chem. Phys. Lett. 2006, 426, 459–463.
[12] Vinod Chandran, C., Madhu, P. K., Kurur, N. D., Bräuniger, T. Magn. Reson. Chem. 2006, 46, 943–947

Author Contributions

J. M. S. proposed the original idea, performed the experiments, curated, and analyzed the data, and wrote the paper (lead). M. H. acquired rheometry data (lead). P. F. acquired 29Si NMR data (lead). Z. W. acquired data for mechanical analysis (lead). M. R. acquired pXRD data (lead). V. W. S. wrote the script to model the chain growth mechanism (lead). A. G., K. U., and T. S. helped with experiments and analysis of data (supporting). J. M., M. W., P. A. L., and P. T. acquired funding and corrected the paper (lead).