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Synthesis of 1-ethyl-1,2,2-trimethyl-1,2-disilacyclobutane and its spontaneous polymerization and copolymerization with 1,1,2,2-tetramethyl-1,2-disilacyclobutane

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Dehalogenation of 1-[(chloro)(ethyl)(methyl)silyl]-2-[chloro(dimethyl)silyl]ethane with the alkali metal vapors gave 1-ethyl-1,2,2-trimethyl-1,2-disilacyclobutane. Its spontaneous ring-opening polymerization at room temperature afforded an amorphous linear polymer with T_g = –75 °C, M_w = 454 200—512 800, and M_w/M_n = 1.87—2.82. According to NMR data, the backbone of the polymer consists of alternating monomeric units linked in the "head-to-tail" ($SiMe_2CH_2CH_2SiMeEtSiMe_2CH_2CH_2SiMeEt$) and "head-to-head" ways ($SiMeEtCH_2CH_2SiMe_2SiMe_2CH_2CH_2SiMeEt$) in a ratio of 1 : 0.96. Spontaneous copolymerization of the above disilacyclobutane with 1,1,2,2-tetramethyl-1,2-disilacyclobutane gave partially crystalline copolymers with different glass transition and melting temperatures, depending on the ratio of the components in the reaction mixture. The compositions of the copolymers were examined by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy.

Key words: 1-ethyl-1,2,2-trimethyl-1,2-disilacyclobutane, spontaneous polymerization, copolymerization, organosilicon compounds.

1,2-Disilacyclobutanes (1,2-DSCB) still remain the scarcest class of compounds compared to other four-membered Si-C heterocycles, including isomeric 1,3-disilacyclobutanes. Unfortunately, 1,2-DSCB cannot be obtained by magnesium-assisted cyclization of 1-chloro-2-(β-chloroethyl)-1,2-disilanes or by the liquid-phase Würtz reaction from 1,2-bis[chloro(diorganyl)silyl]ethanes[1] because β-chloroethyl derivatives of silicon are unstable and decompose to organochlorosilanes and ethene in the presence of nucleophilic and electrophilic reagents.[2] In addition, the lower homologs of 1,2-DSCB are themselves unstable under normal conditions. All this makes them hardly accessible compounds. For this reason, the efforts of researchers were mainly focused on the synthesis of 1,2-DSCB with bulky substituents at all the endocyclic atoms that would be stable under normal conditions.[3—7] Gas-phase dehalogenation of 1,2-bis[chloro(dimethyl)silyl]ethane (**1**) with the alkali metal vapors afforded 1,1,2,2-tetramethyl-1,2-disilacyclobutane (**2**), a first representative of 1,2-disilacyclobutanes having no substituents at the ring C atoms.[8] This method succeeded because the reaction is highly selective in the gas phase at a low pressure (0.1—1.0 Torr) when the starting reagent **1** is continuously supplied to the reaction zone of a reaction tube; the resulting product **2** is stabilized by its prompt removal from the reaction zone into a frozen trap at 77 K. Unlike its 1,3-isomer (1,1,3,3-tetramethyl-1,3-disilacyclobutane), compound **2** is so reactive that its spontaneous room-temperature ring opening is accompanied by spontaneous polymerization. The backbone of the resulting regular polymer **3** consists of alternating bis(dimethylsilylene) and dimethylene groups ($Me_2Si—SiMe_2$ and CH_2CH_2, respectively[8—11]). Compound **2** can be isolated and characterized only at lowered temperatures (no higher than –40 °C). A study of its polymerization and copolymerization with styrene[11] has revealed that compound **2** spontaneously polymerizes *via* homolytic cleavage of the Si—Si bond; therefore, the process involves free radicals. The resulting highly crystalline homopolymer **3** (T_m = 113 °C) is insoluble in organic solvents below 55 °C (see Ref. 8); its molecular weight is 630 000 and M_w/M_n = = 4.4 (see Ref. 11).

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† Deceased.

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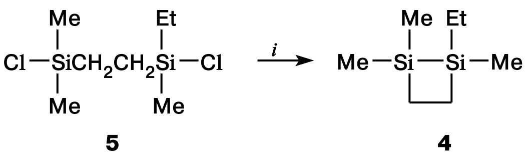
In the present work, we tried gas-phase dehalogenation with the alkali metal vapors for the synthesis of the nearest homolog of **2**, *viz.*, 1-ethyl-1,2,2-trimethyl-1,2-disilacyclobutane (**4**), and studied the tendency toward spontaneous polymerization in the series of 1,2-disilacyclobutanes to estimate how a homological difference (CH_2 group) and the resulting asymmetry of the molecule influence the reactivity of compound **4** and to compare the properties of the corresponding polymers.

Results and Discussion

Compound **4** was obtained by gas-phase dechlorination of 1-[(chloro)(ethyl)(methyl)silyl]-2-[chloro(dimethyl)silyl]ethane (**5**) (pre-degassed *in vacuo*) with the alkali metal vapors in a metal reaction tube using a flow vacuum system according to a known procedure[12] (Scheme 1).

Scheme 1



Reagents and conditions: *i*. K/Na, 300 °C, <1 Torr.

The yields of product **4** varied from 37 to 47%. The ^{1}H NMR spectrum recorded at –50 °C reflects the asymmetric differences of molecular structure **4** compared to **2**. The ^{1}H NMR spectrum exhibits singlets for the protons of the nonequivalent methyl groups at the Si atoms and a distinct triplet characteristic of the methyl protons in the ethyl substituent (see Experimental). The structure of compound **4** was confirmed by mass spectrometry. The mass spectrum contains, by analogy with **2**, a fairly intense molecular ion peak with *m/z* 158 ($[M]^{+\bullet}$, 28%), a peak with *m/z* 143 ($[M - Me]^+$, 38%), and an intense peak with *m/z* 130 ($[M - C_2H_4]^+$, 84%). The peak with *m/z* 129 ($[M - Et]^+$) indicates the presence of an ethyl group attached to the Si atom. The most intense peak with *m/z* 115 is due to the elimination of ethene and the methyl group from the molecular ion ($[M - C_2H_4 - Me]^+$).

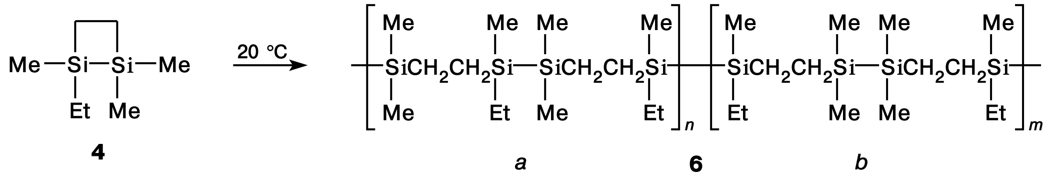
Monomer **4** is less reactive than compound **2**; the polymerization of the latter is completed in a few minutes,[12] while spontaneous polymerization of **4** at room temperature proceeded much more slowly. It took several days (usually, no less than a week) for the liquid to become thicker and turbid, finally transforming itself into a transparent solid polymer **6** (M_w = 454 200—512 800, M_w/M_n = 1.87—2.82) in 77—85% yield (Scheme 2).

Polymer **6** is more soluble than polymer **3**, forming at room temperature dilute solutions, *e.g.*, in toluene or THF (~0.01% and below). To obtain its more concentrated solutions for NMR and GPC experiments, heating to 40—55 °C is usually required. The better solubility of homopolymer **6** is consistent with its amorphism: a differential scanning calorimetry (DSC) study detects a distinct glass transition threshold (T_g = –75 °C) with no signs of crystallinity. Obviously, polymerization of asymmetric structure **4** can produce two types of arrangements of its monomeric units: "head-to-tail" (*a*) and "head-to-head" (*b*) (see Scheme 2). This in turn breaks the regular structure of the polymer chain, thus making polymer **6** amorphous.

The IR spectrum of polymer **6** exhibits intense narrow bands at 1050 and 1129 cm^{-1} ($SiCH_2CH_2Si$, see Refs 11, 12) and an intense band at 1244 cm^{-1} (to the Si—Me). The Raman spectrum of polymer **6** shows three medium-intensity bands at 450, 436, and 403 cm^{-1} (Si—Si stretches). In its IR spectrum, this range contains very weak ν(Si—Si) bands at 410, 419, and 437 cm^{-1} (with a shoulder at 431 cm^{-1}), which become perceptible only upon strong magnification. As expected, the high-intensity bands of the asymmetric vibrations in the IR spectrum, *e.g.*, at 2949 (ν(Me)), 2901 (ν(CH_2)), 1462 ($\delta^{as}(CH_2)$), and 829 cm^{-1} (δ^{as}(Si—C)) have close low-intensity analogs in the Raman spectrum (2951, 2894, 1460, and 830 cm^{-1}, respectively).

The ^{1}H NMR spectrum of polymer **6**, apart from the triplet-state signal for the Me group of the ethyl substituent (δ 1.12) and a narrow multiplet for all protons of the fragment CH_2Si (δ 0.78), shows two singlets for the $SiMe_2$ group (δ 0.25 and 0.23 in the "head-to-tail" and "head-to-head" arrangements, respectively) and two singlets for the protons of the fragment MeSiEt (δ 0.21 and 0.22 in the different arrangements). The integral intensity ratio for the pair signals (1 : 0.96) indicates the nearly equal con-

Scheme 2



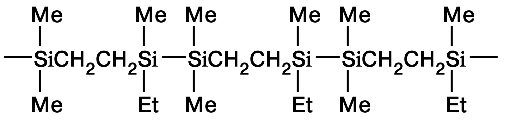
tents of the "head-to-tail" and "head-to-head" arrangements in the polymer chain and hence the nearly equal probabilities of linking the monomeric units in both ways.

The quantitative ^{13}C NMR spectrum of polymer **6** (Fig. 1) also contains two sets of signals with an integral intensity ratio of 1 : 0.96. Because all the signals in both the ^{1}H and ^{13}C NMR spectra appear in a narrow spectroscopic range, their unambiguous assignments were performed by recording a JMOD spectrum and a 2D $^{13}C-^{1}H$ HSQC spectrum with a *z*-gradient pulse. The resulting assignments of the ^{13}C NMR signals are as follows: for a series of the more intense signals, −5.95 ($\underline{Me}SiEt$), −3.26 ($\underline{Me}_2Si$), 5.76, 6.89, 6.97 ($Si\underline{C}H_2\underline{C}H_2Si$), 8.70 ($\underline{Me}CH_2Si$), and 9.40 ($Me\underline{C}H_2Si$); for a series of the less intense signals, −5.51 ($\underline{Me}SiEt$), −3.72 ($\underline{Me}_2Si$), 6.05, 7.22, 7.30 ($Si\underline{C}H_2\underline{C}H_2Si$), 8.70 ($\underline{Me}CH_2Si$), and 9.05 ($Me\underline{C}H_2Si$). Figure 1 displays a distinct splitting of the signal of one methylene carbon between the Si atoms.

Apparently, this splitting arises from the different environments of the Si atom in the vicinal position with respect to this carbon. Indeed, one can imagine three possible combinations of different arrangements of the monomeric units in the polymer chain **6**. When they are composed as triads, one can easily see that the dimethylene groups flanked by two Si atoms in the middle unit of the triad have three nonequivalent environments.

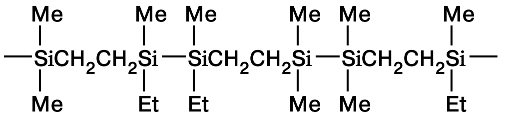
The quantitative ^{29}Si NMR spectrum of polymer **6** exhibits four peaks in the resonance range characteristic of the fragment $C_3Si-SiC_3$ (δ −12.55 and −12.60 ($\underline{Si}MeEt$) and δ −16.15 and −16.23 ($\underline{Si}Me_2$)). As expected, the integral intensity ratio of these two pairs of signals is 1 : 1.

To further estimate the relative reactivities of monomers **4** and **2** in spontaneous polymerization at room temperature and estimate the possibility of varying the properties of poly(ethylenedisilylene) polymers, we carried out the copolymerization of these neat monomers at three different ratios (Scheme 3, Table 1). Monomers **4** and **2** were placed in an evacuated (at 77 K) tube, which was sealed and kept at room temperature until an immobile block was formed (usually for no more than a week). Copolymers **7—9** were isolated, purified by reprecipitation, dried in a vacuum desiccator at 50 °C, and analyzed by NMR spectroscopy, GPC, and DSC. The DSC curves of each sample of polymers **7—9** show only one glass transition temperature. The substantial difference of copolymers **7—9** in T_g values from both homopolymers in combination with the unimodal character of these samples (GPC data) provides evidence for the copolymerization of monomers **4** and **2**.



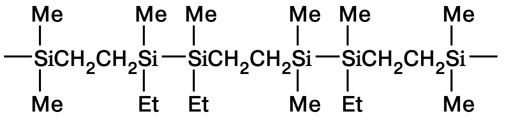
$$-\underset{Me}{\overset{Me}{Si}}CH_2CH_2\underset{Et}{\overset{Me}{Si}}-\underset{Me}{\overset{Me}{Si}}CH_2CH_2\underset{Et}{\overset{Me}{Si}}-\underset{Me}{\overset{Me}{Si}}CH_2CH_2\underset{Et}{\overset{Me}{Si}}-$$

6A



$$-\underset{Me}{\overset{Me}{Si}}CH_2CH_2\underset{Et}{\overset{Me}{Si}}-\underset{Et}{\overset{Me}{Si}}CH_2CH_2\underset{Me}{\overset{Me}{Si}}-\underset{Me}{\overset{Me}{Si}}CH_2CH_2\underset{Et}{\overset{Me}{Si}}-$$

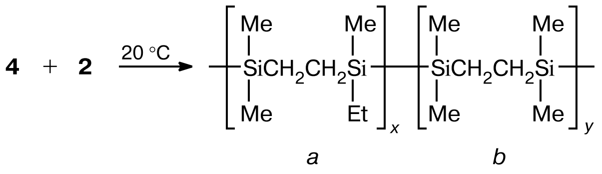
6B



$$-\underset{Me}{\overset{Me}{Si}}CH_2CH_2\underset{Et}{\overset{Me}{Si}}-\underset{Et}{\overset{Me}{Si}}CH_2CH_2\underset{Me}{\overset{Me}{Si}}-\underset{Et}{\overset{Me}{Si}}CH_2CH_2\underset{Me}{\overset{Me}{Si}}-$$

6C

Scheme 3



$$4 + 2 \xrightarrow{20\ °C} \left[\underset{Me}{\overset{Me}{Si}}CH_2CH_2\underset{Et}{\overset{Me}{Si}}\right]_x\left[\underset{Me}{\overset{Me}{Si}}CH_2CH_2\underset{Me}{\overset{Me}{Si}}\right]_y$$

7—9

7: *x* : *y* = 1 : 0.41; **8**: *x* : *y* = 1 : 1.20; **9**: *x* : *y* = 1 : 2.40

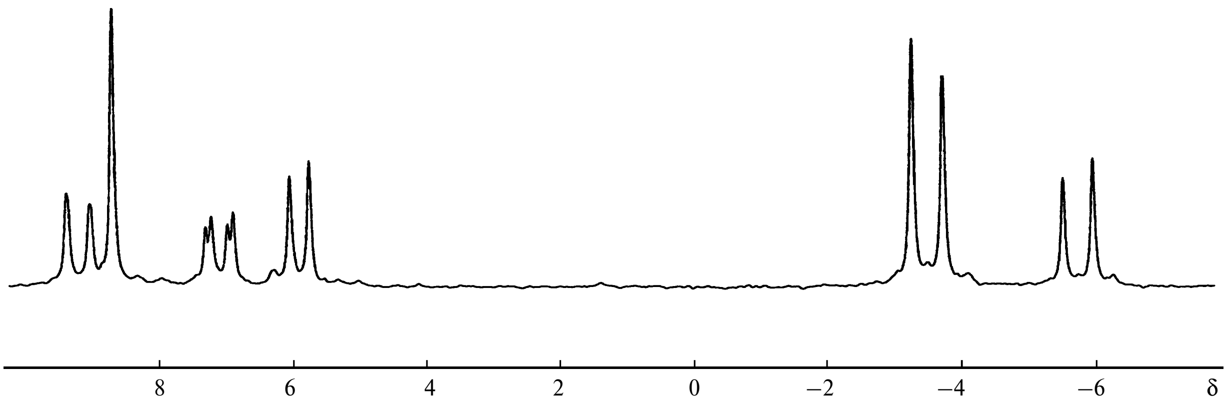


Fig. 1. ^{13}C NMR spectrum of homopolymer **6**.

Table 1. Properties of copolymers **7**—**9** obtained by room-temperature bulk copolymerization of 1-ethyl-1,2,2-trimethyl-1,2-disilacyclobutane (**4**) with 1,1,2,2-tetramethyl-1,2-disilacyclobutane (**2**)

Copolymer	**4** : **2**	Yield (%)	Ratio *a* : *b* (NMR)			GPC		DSC*	
			^{1}H	^{13}C	^{29}Si	$M_w \cdot 10^{-5}$	M_w/M_n	T_g/°C	T_m/°C
7	1 : 0.26	77	1 : 0.41	1 : 0.47	1 : 0.54	4.52	2.76	−69.7 (−71)	38.7 (44.2)
8	1 : 1.06	85	1 : 1.20	1 : 1.19	1 : 1.12	4.47	2.66	−46 (−52)	62.8 (62.2)
9	1 : 2.02	80	1 : 2.40	1 : 2.20	1 : 2.80	6.57	2.48	−37 (−42)	87.8 (78.4)

* The glass transition (T_g) and melting temperatures (T_m) determined for the reheated samples are given in parentheses.

The NMR spectra of copolymers **7**—**9** show the same signals as the spectra of homopolymer **6**; however, the integral intensity ratio of the signals depends on the relative fractions of the homopolymeric blocks *a* and *b* with consideration that asymmetric monomer **4** can, as in the case of homopolymerization, be inserted into growing macromolecules according to "head-to-tail" and "head-to-head" arrangements, which results in two different copolymers (see Scheme 3). The compositions of the copolymers (namely, the ratio of monomeric units *a* and *b* in them) can fairly accurately be determined from their NMR spectra.

The *a* : *b* ratios calculated from the ^{1}H (most accurate values), ^{13}C, and ^{29}Si NMR spectra and other properties of copolymers **7**—**9** are given in Table 1.

Copolymers **7**—**9** are partially crystalline, which is evident from DSC curves. It can be seen in Table 1 that the melting and glass transition temperatures of the copolymers show symbatic variations with the content of the monomeric units of symmetric monomer **2**: the higher the number of symmetric units *b* in the copolymer, the higher its melting temperature; the lower the number of symmetric units *b* in the copolymer, the lower its glass transition temperature.

All copolymer samples contain fewer units with the SiEt group obtained from monomer **4** than does the starting monomer feed, which confirms the aforementioned lower polymerizability of compound **4** compared to symmetric monomer **2**.

Thus, 1-ethyl-1,2,2-trimethyl-1,2-disilacyclobutane can spontaneously polymerize under normal conditions to give amorphous high-molecular-weight poly[ethylene-(ethyltrimethyl)disilylene]. Its copolymerization with 1,1,2,2-tetramethyl-1,2-disilacyclobutane affords copolymers with different crystallinity degrees and different glass transition and melting temperatures.

Experimental

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DPX-400 spectrometer (400, 100.6, and 79.5 MHz, respectively). The recording parameters of the quantitative ^{13}C NMR spectra were as follows: 45° pulse, relaxation delay 8 s, and proton decoupling during data sampling. The mass spectrum (EI) was recorded on a Finnigan 4021 GC/MS instrument. IR spectra were recorded on Specord M-80 (400—4000 cm^{-1}) and IFS 66v/s instruments (Bruker) (350—500 cm^{-1}). The Raman spectrum was recorded on a LabRAM 300 laser Raman spectrometer (100—4000 cm^{-1}, He—Ne laser (λ = 632.81 nm), ouput power 6 mW). The molecular mass distributions of the polymers were determined by gel permeation chromatography (GPC) on a Waters setup (column 7.8×300 mm, Phenogel sorbent (5 μm, 10—4 Å), 2% THF in toluene (1 mL min^{-1})) calibrated against polystyrene standards. Calorimetric measurements were carried out on a Mettler TA-4000 differential scanning calorimeter with a DSC-30 heating cell (heating rate 10 deg min^{-1}, argon).

Toluene, THF, MeOH, and EtOH for dissolution and precipitation of the polymers were used freshly distilled.

1,2-Bis[chloro(dimethyl)silyl]ethane (**1**) and 1-[(chloro)-(ethyl)(methyl)silyl]-2-[chloro(dimethyl)silyl]ethane (**5**) were prepared according to a known procedure.[13] Monomer **2** was prepared as described earlier.[8]

1-Ethyl-1,2,2-trimethyl-1,2-disilacyclobutane (4). Dechlorination of compound **5** with the alkali metal vapors was carried out in a flow vacuum system according to a known procedure.[11] The starting dichloride **5** was pre-degassed *in vacuo*. A tube containing compound **5** was heated in such a way that its vapor were supplied to the reaction tube over a K/Na melt (300 °C, 0.1—1 Torr). The supply rate was regulated so that the reaction temperature was no higher than 330 °C and the pressure was no higher than 1 Torr. Dechlorination products were collected in a flow trap cooled with liquid nitrogen. After the reaction was completed, the stopcock was closed and the trap was warmed to ambient temperature. The dechlorination products melted and flowed down into a distillation flask fitted with a Vigreux column. The dechlorination products were distilled under dry argon bubbled through a capillary. Monomer **4** was collected in cooled calibrated tubes, which were sealed and kept in liquid nitrogen before use. In a typical experiment, the yield of pure disilacyclobutane **4** from dichloride **5** (12.00 g) was 3.05 g (37%), b.p. 28—30.5 °C (~5 Torr). Found (%): C, 53.14; H, 11.53; Si, 35.73. $C_7H_{18}Si_2$. Calculated (%): C, 53.08; H, 11.45; Si, 35.46. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 158 $[M]^{+\cdot}$ (28.1), 143 $[M - Me]^+$ (38.2), 130 $[M - C_2H_4]^+$ (84.2), 129 $[M - C_2H_5]^+$ (25.6), 127 (15.9), 115 $[M - Me - C_2H_4]^+$ (100), 113 (8.0), 102 $[M - 2\ C_2H_4]^+$ (31.2), 97 (12.0), 85 $[M - Me_2SiCH_2 - H]^+$ (24.0), 83 (10.1), 73 $[Me_3Si]^+$ (20.7), 59 (34.2), 45 (11.2), 43 (15.9), 28 (7.0). ^{1}H NMR (CDCl$_3$, –45 °C), δ: –0.13, –0.15, –0.24 (all s, 9 H, MeSi); 0.73 (m, 6 H, SiCH$_2$); 0.95 (t, 3 H, MeC, J = 7.8 Hz).

Polymer 6. A sealed tube containing compound **4** (1.60 g, 0.01 mol) was kept at room temperature for a week until a transparent immobile block was formed. The tube was opened, the contents was dissolved in toluene, and polymer **6** was precipitated with ethanol. The resulting precipitate of polymer **6** was reprecipitated, washed with ethanol, and dried in a vacuum desiccator at 50 °C to a constant weight. The yield was 1.36 g (85%). Found (%): C, 53.47; H, 11.22; Si, 35.69. $(C_7H_{18}Si_2)_x$. Calculated (%): C, 53.08; H, 11.45; Si, 35.46. ^{1}H NMR (CD$_3$C$_6$D$_5$), δ: 0.21, 0.22 (both s, MeSiEt, "head-to-head" and "head-to-tail"); 0.23, 0.25 (both s, SiMe$_2$, "head-to-head" and "head-to-tail"); 0.78 (m, CH$_2$Si); 1.12 (t, MeCSi, J = 7.8 Hz). ^{13}C NMR (CDCl$_3$), δ: –5.95 ($\underline{\mathrm{Me}}$SiEt); –3.26 ($\underline{\mathrm{Me}}_2$Si); 5.76, 6.89, 6.97 (Si$\underline{\mathrm{C}}$H$_2\underline{\mathrm{C}}$H$_2$Si); 8.70 ($\underline{\mathrm{Me}}$CH$_2$Si); 9.40 (Me$\underline{\mathrm{C}}$H$_2$Si) for the more intense series; –5.51 ($\underline{\mathrm{Me}}$SiEt); –3.72 ($\underline{\mathrm{Me}}_2$Si); 6.05, 7.22, 7.30 (Si$\underline{\mathrm{C}}$H$_2\underline{\mathrm{C}}$H$_2$Si); 8.70 ($\underline{\mathrm{Me}}$CH$_2$Si); 9.05 (Me$\underline{\mathrm{C}}$H$_2$Si) for the less intense series. ^{29}Si NMR (CDCl$_3$), δ: –12.55; –12.60 (SiMeEt); –16.15; –16.23 (SiMe$_2$). IR, ν/cm^{-1}: 2949 (ν^{as}(Me)), 2901 (ν^{as}(CH$_2$)), 2870 (ν^s(Me)), 2780 (ν^s(CH$_2$)), 1462 (δ^{as}(CH$_2$)), 1404 (δ(MeC)), 1370 (δ(MeC)), 1244 (δ^s(MeSi)), 1129, 1090, 1050 (fragment SiCH$_2$CH$_2$Si), 1000, 950, 829, 770, 730 (δ(Si—C)), 680, 610 (δ(Si—C)), 590. Raman spectrum, ν/cm^{-1}: 2951, 2894, 2811, 2790, 2728, 1460, 1403, 1378, 1237, 1130, 1054, 1008, 982, 971, 853, 830, 810, 779, 738, 710, 682, 637, 612, 450, 436, 403, 359, 335, 312, 277, 180, 144.

Copolymer 7. Monomers **4** (1.58 g, 0.01 mol) and **2** (0.37 g, 0.0026 mol) were recondensed into a tube precalcined *in vacuo*. The tube was sealed and kept at room temperature for eight days until an immobile block was formed. The tube was opened and the copolymer was dissolved in toluene at ~50 °C and precipitated with hot ethanol. Then the copolymer was reprecipitated under the same conditions, washed with ethanol, and dried in a vacuum desiccator at 50 °C to a constant weight. The yield of copolymer **7** was 1.51 g (77%). Found (%): C, 51.64; H, 11.14; Si, 37.42. ^{1}H NMR (CD$_3$C$_6$D$_5$, 40 °C), δ: 0.21, 0.22 (both s, $\underline{\mathrm{Me}}$SiEt, I* = 3.00); 0.23, 0.25 (both s, SiMe$_2$, I = 12.72); 0.78 (m, CH$_2$Si, I = 7.64); 1.12 (t, MeCSi, I = 3.00, J = 7.8 Hz). ^{13}C NMR (CDCl$_3$), δ: –3.70 (Me$_2$Si$_b$); –3.24, –3.70 (both Me$_2$Si$_a$, I = 4.88); 5.76, 6.05 (both SiCH$_2$CH$_2$Si$_a$, I = 0.88); 6.98, 7.31 (both SiCH$_2$CH$_2$Si$_a$, I = 0.96); 8.72 ($\underline{\mathrm{Me}}$CH$_2$Si, I = 1.00); 8.89 (SiCH$_2$CH$_2$Si$_b$, I = 1.36); 9.07 (Me$\underline{\mathrm{C}}$H$_2$Si, I = 1.00). ^{29}Si NMR (CDCl$_3$), δ: –11.69 (SiMeEt, I = 1.00), –15.48 (SiMe$_2$, I = 2.08).

Copolymer 8 was obtained as described for copolymer **7** from monomers **4** (1.62 g, 0.0102 mol) and **2** (1.57 g, 0.0108 mol). The yield was 2.70 g (85%). Found (%): C, 51.28; H, 11.12; Si, 37.44. ^{1}H NMR (CD$_3$C$_6$D$_5$, 40 °C), δ: 0.21, 0.22 (both s, $\underline{\mathrm{Me}}$SiEt, I = 3.00); 0.23, 0.25 (both s, SiMe$_2$, I = 21.16); 0.78 (m, CH$_2$Si, I = 10.85); 1.12 (t, MeCSi, I = 3.00, J = 7.8 Hz). ^{13}C NMR (CDCl$_3$), δ: –3.70 (Me$_2$Si$_b$); –3.24, –3.70 (both Me$_2$Si$_a$, I = 7.76); 5.76, 6.05 (both SiCH$_2$CH$_2$Si$_a$, I = 0.92); 6.98, 7.31 (both SiCH$_2$CH$_2$Si$_a$, I = 1.00); 8.72 ($\underline{\mathrm{Me}}$CH$_2$Si, I = 1.00); 8.89 (SiCH$_2$CH$_2$Si$_b$, I = 2.46); 9.07 (Me$\underline{\mathrm{C}}$H$_2$Si, I = 1.00). ^{29}Si NMR (CDCl$_3$), δ: –11.69 (SiMeEt, I = 1.00), –15.48 (SiMe$_2$, I = 3.36).

Copolymer 9 was obtained as described for copolymer **7** from monomers **4** (1.34 g, 0.0085 mol) and **2** (2.49 g, 0.0172 mol). The yield was 3.08 g (80%). Found (%): C, 52.22; H, 11.38; Si, 36.39. ^{1}H NMR (CD$_3$C$_6$D$_5$, 40 °C), δ: 0.21, 0.22 (both s, MeSiEt, I = 3.00); 0.23, 0.25 (both s, SiMe$_2$, I = 37.80); 0.78 (m, CH$_2$Si, I = 15.92); 1.12 (t, 3 H, MeCSi, I = 3.00, J = 7.8 Hz). ^{13}C NMR (CDCl$_3$), δ: –3.70 (Me$_2$Si$_b$); –3.24, –3.70 (both Me$_2$Si$_a$, I = 12.28); 5.76, 6.05 (both SiCH$_2$CH$_2$Si$_a$, I = 1.04); 6.98, 7.31 (both SiCH$_2$CH$_2$Si$_a$, I = 1.08); 8.72 ($\underline{\mathrm{Me}}$CH$_2$Si, I = 1.00); 8.89 (SiCH$_2$CH$_2$Si$_b$, I = 4.76); 9.07 (Me$\underline{\mathrm{C}}$H$_2$Si, I = 1.00). ^{29}Si NMR (CDCl$_3$), δ: –11.69 (SiMeEt, I = 1.00); –15.48 (SiMe$_2$, I = 6.24).

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* Hereafter, I is the integral signal intensity.