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Synthesis and Functionalization of Poly[5,5′-(silylene)-2,2′-dithienylene]s Using Silyl Triflate Intermediates†

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Treatment of 5,5′-dilithio-2,2′-dithiophene with (dimethylamino)methylsily bis(triflate)- or α, ω-bis(triflate)-substituted trisilanes gave poly[5,5′-(silylene)-2,2′-dithienylene]s in high yields. The amino–silyl bond was cleaved selectively by triflic acid, leading to triflate-substituted derivatives. Conversion of these compounds with nucleophiles gave other functionalized polymers. Platinum-catalyzed hydrosilylation reactions between silicon–vinyl and silicon–hydrogen derivatives result in polymer networks which may serve as interesting preceramic materials. The structures of the polymers were proven by NMR spectroscopy (^{29}Si, ^{13}C, ^{1}H). Results of thermal gravimetric analysis (TGA), UV spectrometry and conductivity measurements are given.

Keywords: organosilicon polymer; poly(silylenedithienylene); silyl triflate

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INTRODUCTION

Organosilicon polymers containing a regular alternating arrangement of silylene or polysilylene units and π-electron systems, such as phenylene,[1–7] ethynylene,[8–15] diethynylene,[16–19] furylene[20,21] and oligothienylene[22–32] sequences, in the main chain have received increasing attention, because these polymers can be used as functional materials such as photoresists, semiconducting materials and precursors of silicon-containing ceramics.

Several routes to these materials, and particularly to polymers with alternating silylene and thienylene units, have been described. It is well known that the sodium condensation reaction of bis(chlorosilyl)-substituted compounds or the coupling reaction of dilithio compounds bearing a π-electron system with dichlorosilanes and α, ω-dichloro-oligosilanes offer a convenient route to various silicon-containing polymers. However, polymers prepared by these methods always involve a small proportion of siloxy units in the polymer backbone, which are formed from the hydrolysis of unreacted chlorosilyl units in the resulting polymer. Therefore, the search for alternative synthetic methods was intensified in the recent years. Novel convenient approaches to organosilicon polymers have been reported, for instance ring-opening polymerizations, rhodium- and palladium-catalyzed polymerizations and dehydrogenations by zirconium compounds. Electrochemical syntheses of poly[(silylene)-2,5-thiophene]s were also described.[33,34]

Recently, we investigated the chemistry of oligomeric and polymeric silyl triflates.[35–40] We found convenient approaches to numerous differently structured organosilicon polymers. These results stimulated us to investigate new synthetic routes to functional substituted and branched poly[5,5′-(silylene)-2,2′-dithienylene]s using silyl triflate intermediates.

RESULTS AND DISCUSSION

Systematic investigations of the reaction of compounds of the type R_2SiXY (R = alkyl) with triflic acid (Scheme 1) have shown that compounds $R_2SiXOTf$ can be synthesized readily by highly selective bond cleavages. The ease of replacement

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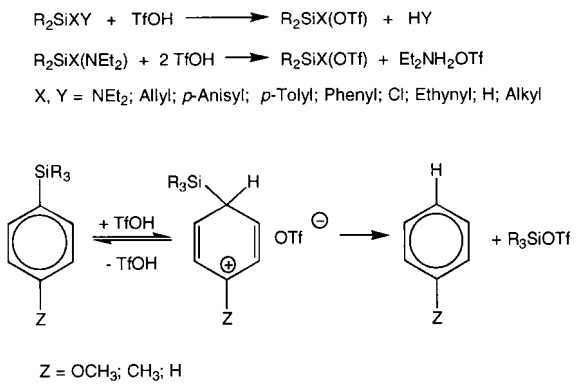
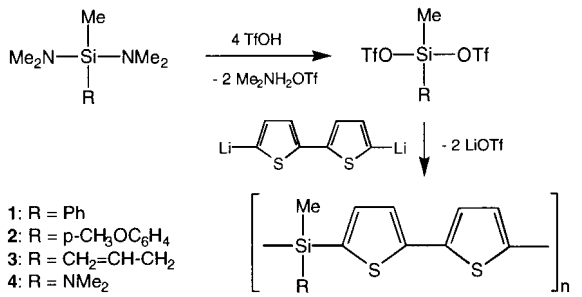


Scheme 1

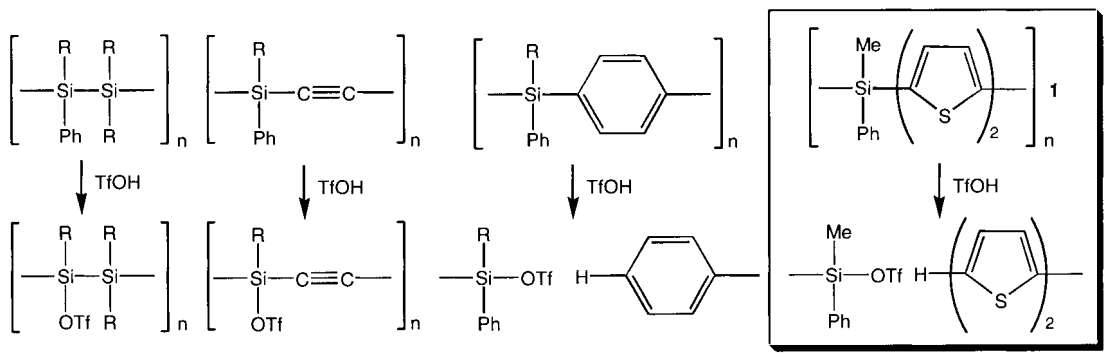


Scheme 2

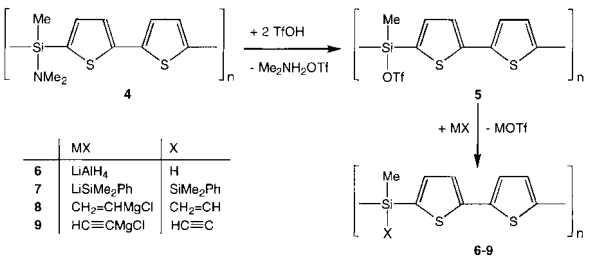
of Y by OTf decreases in the order (Y substituent) of NEt_2 > allyl > *p*-anisyl > α -naphthyl > *p*-tolyl > phenyl > Cl > ethynyl > H ≫ alkyl.[41–44] Phenylsilanes, which are highly reactive towards the protodesilylation reaction, are ideal starting materials for the synthesis of novel silyl triflates. Eaborn and coworkers[45] studied the effects of the substituents Z on the rate of acid cleavage of *p*-Z-$C_6H_4SiR_3$ (Scheme 1) and found that the reaction rates fell significantly in the order (Z substituent) of OCH_3 > CH_3 > H > Cl.

The excellent silylation properties[46,47] of these substances prompted us to elaborate syntheses for functional substituted and branched poly[5,5′-(silylene)-2,2′-dithienylene]s via silyl triflate intermediates. We obtained the parent compounds from silyl bis(triflates) and 5,5′-dilithio-2,2′-dithiophene (Scheme 2). The application of silyl triflates instead of the corresponding chlorosilanes was found to give polymers in higher yields under mild conditions and in shorter reaction times (60 min, 25 °C). Moreover, higher weight-average molecular weights in the region of $M_W \approx 2 \times 10^4$ g mol^{-1} were measured by GPC relative to polystyrene standards, if the stoichiometric ratio was kept at 1:1 exactly. (It is therefore necessary to determine the content of the organolithium compounds quantitatively before use). The molecular weights were determined only in the case of polymers **1** and **2**, which were hydrolytically stable. Otherwise, perturbations of the measurements by siloxane formation could not be excluded.

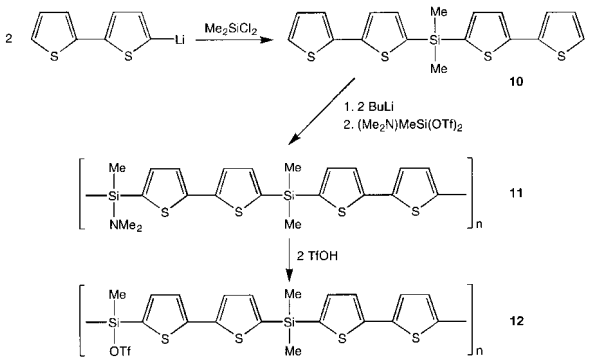
The protodesilylation of the polymers **1** and **2** with triflic acid is confronted by difficulties. The attack by the strong electrophile CF_3SO_3H of both aromatic side-groups and dithienylene units is followed by backbone cleavage. Recently, we investigated the protodesilylation of poly[(silylene)-phenylene]s and made a similar observation. The behavior of phenylated poly(silylene)s,[43], poly-[(silylene)alkyne]s,[12,48], poly[(silylene)phenylene]s,[7] and poly[5,5′-(methylphenylsilylene)-2,2′-dithienylene] **1** during protodesilylation reactions with triflic acid is compared in Scheme 3. Therefore, the functionalization of poly[5,5′-(silylene)-2,2′-dithienylene]s without backbone cleavage requires better leaving groups at the silicon atom.



Scheme 3



Scheme 4



Scheme 5

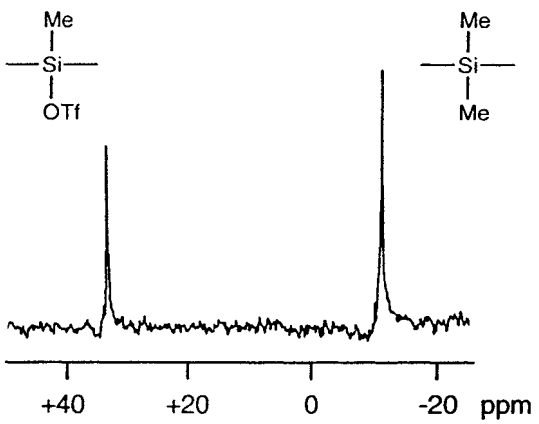
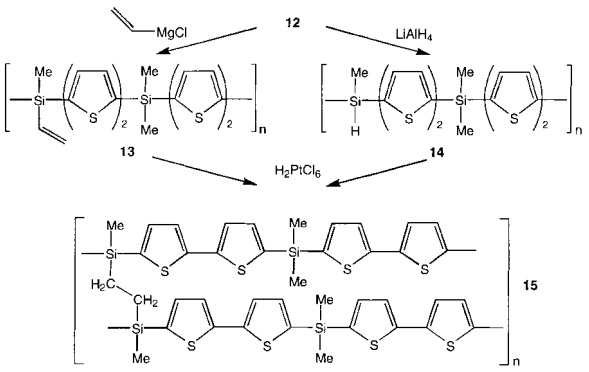


Figure 1 ^{29}Si{H} NMR spectrum of polymer **12**.

Allyl[49] and amino[41] substituents attached to silicon are better leaving groups than aromatic units are. Therefore, the polymers **3** and **4** should be suitable starting materials for functionalized and branched poly[5,5′-(silylene)-2,2′-dithienylene]s. Normally, we used the amino-substituted compound **4** as starting material because the by-product dimethylammonium triflate, which is insoluble in common organic solvents, separates as a solid. Progress and the end of the reaction may, therefore, be observed by the increase in the salt phase. As indicated in Scheme 4, the conversion of **4** with triflic acid leads to the triflate-substituted derivative **5**, which can be isolated as a red-brown, hydrolytically sensitive and viscous oil. The product shows only one relatively narrow signal in the ^{29}Si NMR spectrum. The regular alternating arrangement of silicon atoms and dithienyl units can be verified by this spectrum. Signals of terminal silicon atoms were not found, but this is not unusual for compounds with polymerization degrees of $n \approx 60$–100. Novel functionalized poly[5,5′-(silylene)-2,2′-dithienylenes] **6–9** could be synthesized in high yields from **5** and nucleophiles under mild conditions (Scheme 4). The compounds were characterized by ^{29}Si, ^{13}C and ^{1}H NMR spectroscopy and elemental analysis. The molecular weights of **6–9** were found to be similar to those of **1** and **2**. From this observation we conclude that no backbone cleavages occur during the protodesilylation and substitution processes.

The platinum-catalyzed hydrosilylation reaction between the polymers **6** and **8** should give a intermolecular branched compound. Unfortunately, the product was insoluble in common organic solvents and could not be characterized by spectroscopic methods. This should be caused by the high degree of cross-linking. Therefore, we attempted to 'dilute' the reactive groups in the starting materials. The reaction of **4** with triflic acid in a molar ratio of 1:1 led to a polymer containing 50% MeSi(NMe_2)- and 50% MeSi(OTf) units. Broad NMR signals, however, indicated a statistical distribution of the substituents in the resulting polymer. Therefore, we tried to prepare the poly[5,5′-(silylene)-2,2′-dithienylene] with an alternating arrangement of Me_2Si and MeSi(OTf) units by a stepwise chain construction. First, we obtained bis[5-(2,2′-dithienyl)]dimethylsilane **10** from 5-lithio-2,2′-bithiophene and dimethyldichlorosilane as indicated in Scheme 5. Metallation of **10** with butyl-lithium was followed by polycondensation with (dimethylamino)methylsilyl bis(triflate) to give polymer **11** containing MeSi(NMe_2) and Me_2Si units by turns. The partially triflate-substituted poly[5,5′-(silylene)-2,2′-dithienylene] **12** was prepared from **11** with triflic acid. The ^{29}Si NMR spectrum of **12** shows two narrow signals indicating the regular arrangement of the polymer backbone (Fig. 1).

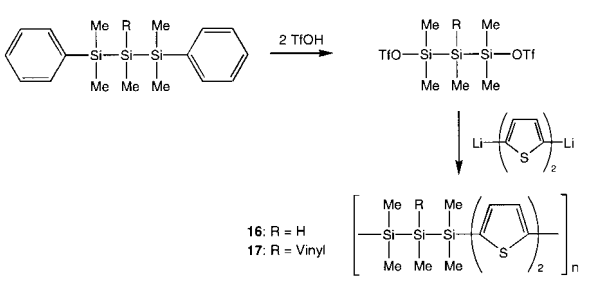
Nucleophilic substitutions of the triflate derivative **12** with vinylmagnesium chloride and lithium tetrahydridoaluminate respectively gave the partially functionalized polymers **13** and **14**, which are



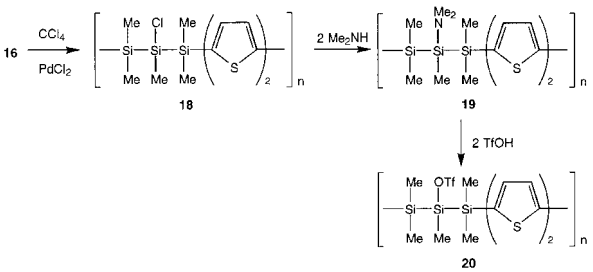
Scheme 6

suitable for cross-linking reactions. The platinum-catalyzed hydrosilylation was carried out in chlorobenzene by the method of Corriu.[50] As indicated in Scheme 6, we obtained the branched polymer **15**, which is soluble in chlorinated hydrocarbons and toluene. The NMR spectra are consistent with the purely β-hydrosilylation product.

Recently, we studied another convenient approach to functional substituted organosilicon polymers containing dithienylene units. The polymer chain was prepared by polycondensation of 5,5′-dilithio-2,2′-dithiophene and α, ω-bis(triflate)-substituted trisilanes containing a functional group in the 2-position. The trisilanes were obtained by protodesilylation of the corresponding α, ω-diphenyltrisilanes with triflic acid as shown in Scheme 7. The substituents in the 2-position may be vinyl groups or hydrogen atoms. The hydrogen-substituted derivative **16** can be used as the starting material for further modification reactions. Treatment of **16** with a catalytic amount of palladium dichloride in refluxing carbon tetrachloride for 4 h afforded the corresponding chloro compound **18**. The amino derivative **19** can be prepared from **18** and an excess of dimethylamine. The triflate-



Scheme 7



Scheme 8

substituted polymer **20** was obtained by protodesilylation of **19** with triflic acid. These reactions are summarized in Scheme 8.

The prepared polymers show strong absorption bands in the UV region in THF solution. The absorption maxima appear between 328 and 346 nm (see Tables 1–3), and are significantly red-shifted relative to those of dithiophene (304 nm), indicating the presence of σ–π conjugation. However, the influence of the substitution pattern of the silicon atoms on the UV maximum is relatively low. The UV spectrum of polymer **17** is shown in Fig. 2 as an example.

From the literature it is known that branched polymers show a higher thermal stability than purely linear derivatives. The stability can be also increased by the presence of Si–H functionality, which cross-links the polymer at lower temperatures than those required for depolymerization. Therefore, we studied the thermal behavior of selected polymers by TGA measurements. For the purely linear polymer **1** a monotonic weight loss (20%) was observed up to 400 °C. Between 400 and 600 °C major degradation occurs, leaving the final char content above 700 °C at around 35%. The cross-linked polymer **15** shows a similar behavior, but the final char content was found to be higher (51%). The vinyl-substituted derivative **17** gave a residue of 58% and the highest ceramic yield was found for polymer **16**, containing Si–H bonds (Fig. 3). About 20% mass loss was observed up to 300 °C. At higher temperatures, almost no weight change was detected until small hydrocarbon elimination started at 500 °C. Total weight loss was found to be 35% up to 800 °C.

In general, polymers composed of alternating silylene units and π-electron systems are insulators. However, when the polymers are treated with an oxidizing agent, they become conducting. Preliminary doping studies showed, when cast films of selected polymers were exposed to iodine vapor under reduced pressure, that the conductivity of the

Table 1 Physical and spectroscopic data of the polymers [—MeSiR—Th—]$_r$ (**1–9**)

Polymer	R	Yield (%)	M.P. (°C)	PD: M_w/M_R	UV, λ_{max} (nm)	δ^{29}(Si) (ppm)	δ (^{3}C) (ppm) in $CDCl_3$	δ (^{1}H) (ppm) in $CDCl_3$
1	Phenyl	93	177–188	24 500, 2.6	333	−17.0	−2.6 (MeSi), 127.0, 129.7, 134.0, 134.6 (Ph), 125.6, 135.1, 139.0, 141.8 (Th)[a]	0.85 (MeSi), 6.88–7.71 (Ph, Th)
2	*p*-Anisyl	89	133–142	19 600, 2.5	328	−20.5	−1.5 (MeSi), 52.8 (OMe), 114.9, 120.5, 137.6, 161.0 (Ph), 126.1, 134.5, 138.2, 142.4 (Th)	0.79 (MeSi), 3.52 (OMe), 6.92–8.03 (Ph, Th)
3	Allyl	79	Viscous oil	—	337	−15.6	−2.0 (MeSi), 25.5 ($SiCH_2$), 116.6 (=CH_2), 133.0 (CH), 124.8, 135.1, 138.2 141.5 (Th)	0.61 (MeSi), 1.77 ($SiCH_2$), 4.79 (= CH_2), 5.81 (CH), 7.03, 7.27 (Th)
4	Me_2N	84	Viscous oil	—	—	−12.8	−0.9 (MeSi), 31.7 (NMe_2), 126.7, 136.2, 138.6, 142.7 (Th)	0.69 (MeSi), 2.39 (NMe_2), 7.08, 7.23 (Th)
5	TfO	97	Viscous oil	—	—	+33.0	6.3 (MeSiOTf), 118.5 (CF_3), 125.7, 135.0, 137.9, 142.9 (Th)	0.89 (MeSi), 7.11, 7.33 (Th)
6	H	76	67–80	10 800, 2.6	338	−31.8[b]	−3.1 (MeSi), 124.9, 133.9, 138.6, 141.7 (Th)	0.82 (MeSi),[c]), 5.17 (SiH), 7.04, 7.22 (Th)
7	$PhSiMe_2$	81	214–225	28 800, 3.0	342	−29.9 −19.6	−3.2 (MeSi), −0.9 (Me_2Si), 126.7, 130.3, 133.8, 135.5 (Ph), 126.9, 134.5, 138.9, 141.7 (Th)	0.44 (Me_2Si), 0.59 (MeSi), 7.02–7.75 (Ph, Th)
8	Vinyl	84	99–113	17 200, 3.1	—	−20.6	−2.9 (MeSi), 135.0, 135.9 (CH_2 = CH), 125.8, 134.7, 137.9, 142.4 (Th)	0.64 (MeSi), 5.71–6.44 (vinyl), 7.08, 7.21 (Th)
9	C≡ CH	87	88–105	16 600, 3.5	—	−30.1	−2.1 (MeSi), 81.0 (SiC≡), 94.8 (≡ CH), 127.0, 135.3, 138.7, 142.5 (Th)	0.59 (MeSi), 2.66 (≡ CH), 7.08, 7.23 (Th)

[a] Th = -dithienyl.
[b] ^1J(SiH) = 211 Hz.
[c] ^3J(*H*SiC*H*$_3$) = 3.7 Hz.

Table 2 Physical and spectroscopic data of the polymers [—MeSiX—Th—Me_2Si—Th—]$_n$ (**11–15**)

Polymer	X	Yield (%)	M.P. (°C)	M_w, PD	UV λ_{max} (nm)	δ (^{29}Si) (ppm)	δ (^{13}C) (ppm) in $CDCl_3$	δ (^{1}H) (ppm) in $CDCl_3$
11	NMe_2	85	Viscous oil	—	—	−10.6 −15.1[a]	−2.5–(−0.1) (MeSi, Me_2Si), 30.9 (NMe_2), 123.9–143.0 (8 signals, Th)	0.64 (Me_2Si), 0.70 (MeSi), 2.44 (NMe_2), 7.03–7.31 (Th)
12	OTf	97	Viscous oil	—	—	+35.9 −12.8[a]	−1.4 (Me_2Si), 5.6 (MeSiOTf), 117.1 (CF_3), 122.9–144.1 (8 signals, Th)	0.67 (Me_2Si), 0.88 (MeSi), 6.99–7.34 (Th)
13	CH_2 = CH	86	127–136	18 700, 2.3	342	−21.9 −15.0[a]	−2.9–(−0.6) (MeSi, Me_2Si), 134.4, 136.1 (CH_2 = CH), 123.5–141.7 (8 signals, Th)	0.64–0.73 (MeSi, Me_2Si), 5.68–6.52 (vinyl), 7.01–7.30 (Th)
14	H	73	45–52	15 000, 2.4	338	−33.7[b] −14.7[a]	−3.1–(+0.5) (MeSi, Me_2Si), 124.5–142.0 (8 signals, Th)	0.63 (Me_2Si), 0.79 (MeSi),[c]) 5.11 (SiH), 7.06–7.32 (Th)
15	CH_2CH_2	88	>250 (de.)	44 000, 5.0	346	−14.0 (br)	−2.8–(−0.1) (MeSi, Me_2Si), 9.3 ($SiCH_2$), 122.6–142.3 (8 signals, Th)	0.57–0.66 (MeSi, Me_2Si), 0.77 ($SiCH_2$), 7.00–7.35 (Th)

[a] δ(^{29}Si) (Me_2Si).
[b] ^1J(SiH) = 207 Hz.
[c] ^3J(*H*SiC*H*$_3$) = 3.2 Hz.

Table 3 Physical and spectroscopic data of the polymers [—Me_2Si—MeSiX—Me_2Si—Th—]$_n$ (**16–20**)

Polymer	X	Yield (%)	M.P. (°C)	M_w, PD	UV λ_{max} (nm)	δ (^{29}Si) (ppm)	δ (^{13}C) (ppm) in $CDCl_3$	δ (^{1}H) (ppm) in $CDCl_3$
16	H	88	125–131	27 000, 2.2	341	−56.6[b] −22.0[a]	−4.1–(−1.3) (MeSi, Me_2Si), 125.5, 134.9, 138.0, 142.8 (Th)	0.11 (*Me*SiH),[c]) 0.26 (Me_2Si), 4.87 (SiH), 7.02, 7.24 (Th)
17	CH_2 = CH	83	140–146	29 500, 2.5	339	−46.0 −21.1[a]	−3.4–(−1.1) (MeSi, Me_2Si), 135.0, 136.8 (CH_2 = CH), 124.8, 134.6, 138.5, 142.1 (Th)	−0.12–0.25 (MeSi, Me_2Si), 5.83–6.48 (Vi), 7.09, 7.22 (Th)
18	Cl	94	Viscous oil	—	—	+2.5 −23.8[a]	−1.9–2.6 (Me_2Si, MeSi), 125.3, 134.7, 138.2, 142.4 (Th)	0.14–0.49 (Me_2Si, MeSi), 7.06, 7.26 (Th)
19	NMe_2	88	Viscous oil	—	—	−35.5 −20.9[a]	−3.8–(−0.4) (MeSi, Me_2Si), 32.6 (NMe_2), 124.0, 135.1, 137.9, 141.3 (Th)	0.06–0.34 (Me_2Si, MeSi), 2.39 (NMe_2), 7.04, 7.28 (Th)
20	OTf	92	Viscous oil	—	—	+28.9 −19.9[a]	−1.9 (Me_2Si), 4.4 (MeSiOTf), 118.0 (CF_3), 124.8, 134.0, 138.9, 143.5 (Th)	0.19–0.57 (Me_2Si, MeSi), 7.12, 7.32 (Th)

[a] δ (^{29}Si) (Me_2Si).
[b] ^1J(SiH = 201 Hz.
[c] ^3J(*H*SiC*C*$_3$) = 2.9 Hz.

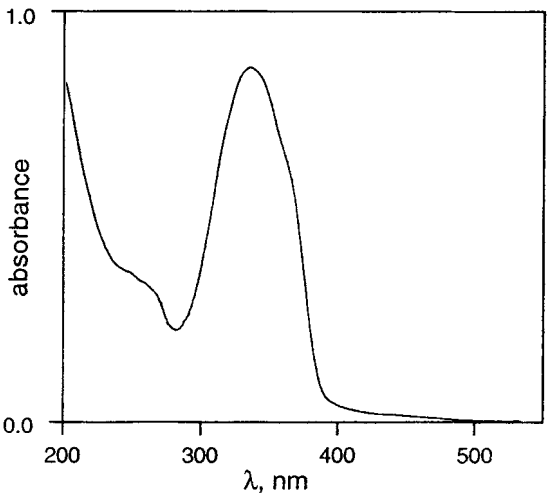


Figure 2 UV spectrum of polymer **17**.

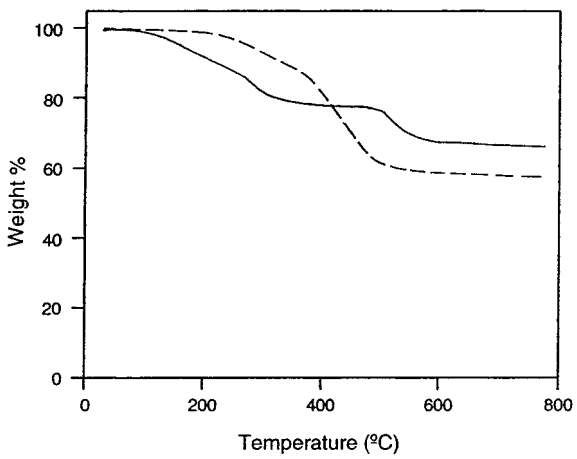


Figure 3 TGA data of polymers **16** (——) and **17** (– – –).

films increased and reached almost constant values after 10 h of doping. The conductivity at this point was found to be 2.5×10^{-5} (**6**), 3.1×10^{-5} (**7**), 5.9×10^{-5} (**15**), 8.6×10^{-5} (**16**), and 6.5×10^{-5} S cm^{1} (**17**). On the basis on these data, the number of silicon atoms which are present between two dithienylene units exerts no significant influence on conductivities.

CONCLUSION

Novel poly[5,5′-(silylene)-2,2′-dithienylene]s have been prepared by polycondensation of 5,5′-dilithio-2,2′-dithiophene with silyl bis(triflates) followed by subsequent protodesilylation reaction with triflic acid. The silicon–element bond cleavage could be better controlled using amino substituents as leaving groups. In this way the regular alternating arrangement of silicon atoms and dithienylene units in the polymer main chain has been maintained during the substitution. Intermolecular hydrosilylation reactions led to novel organosilicon network polymers. The polymer syntheses described here are too expensive for technical applications. However, the essential advantage of the method consists of the possibility of synthesizing, with relatively little effort, small amounts of numerous differently structured organosilicon polymers for investigations in material and surface science.

EXPERIMENTAL

All reactions were carried out under nitrogen or argon using Schlenk tubes. Solvents were dried and distilled before use. **The strongly hygroscopic triflic acid must be distilled before use and should be kept under nitrogen. Traces of moisture in CF_3SO_3H always led to undesired formation of siloxanes during the protodesilylation reaction.** Detailed information about the purification is included in Ref. 47, Section 7. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker AC-250 spectrometer; the chemical shifts are relative to tetramethylsilane. The ^{29}Si NMR spectra were measured for solutions containing 0.1 mol% of the relaxation reagent $Cr(acac)_3$. The molecular weights of hydrolytically stable polymers were determined by GPC (Shodex 806, THF, 1 ml min^{-1}, 25 °C, relative to polystyrene standards). Solutions of silyl triflates in THF are not stable for longer times, because they can initiate the cationic ring-opening polymerization of cyclic ethers.[51] Reactions of silyl triflates with organolithium compounds in THF solution can be carried out, because these reactions proceed very quickly. Lithium derivatives of 2,2′-dithiophenes were obtained by published methods.[24,52]

Preparation of the polymers 1–4, 11, 16 and 17 (general procedure)

A solution of 20 mmol 5,5′-dilithio-2,2′-dithiophene in THF/tetramethylethylenediamine was prepared according to the literature, and a solution of 20

mmol $RMeSi(OTf)_2$ (R = C_6H_5,[35] *p*-CH_3O-C_6H_4,[35] CH_2=CH—CH_2,[49] NMe_2[41]) or (TfO)$SiMe_2$—MeRSi—$Me_2Si(OTf)$ (R = H, CH_2 = CH)[35,40] respectively in 50 ml of toluene was added slowly for 20 min at −20 °C. The reaction mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure and replaced by 150 ml of toluene. Lithium triflate was precipitated as a white solid and was filtered off. Toluene was removed under vacuum to give yellow-brown viscous oils (**3, 4, 11**) or yellow solids (**1, 2, 16, 17**). The hydrolytically sensitive polymers **4** and **11** were used without purification for the following reactions. The solids can be purified by dissolution in $CHCl_3$ and reprecipitation with ethanol. The data are summarized in Tables 1–3.

Synthesis of the triflate-substituted polymers 5, 12 and 20 (general procedure)

A solution of triflic acid (3.0 g, 20 mmol) in 100 ml of diethyl ether was added to the corresponding amino-substituted poly[5,5′-(silylene)-2,2′-dithienylene] **4, 11** or **19** (10 mmol) dissolved in 200 ml of toluene at 0 °C. The mixture was stirred at room temperature for 2 h. Dimethylammonium triflate was precipitated as a white solid and was filtered off. The solvent was removed under reduced pressure to give **5, 12** or **20** as a highly viscous oil in 92–97% yield. The hydrolytically sensitive polymers were used without purification for the following reactions. The data are summarized in Tables 1–3.

Reaction of triflate-substituted polymers 5 or 12 with organomagnesium and organolithium compounds (general procedure)

A solution of the triflate-substituted polymer **5** or **12** (20 mmol) in 200 ml of a diethyl ether/toluene mixture (1:1) was added to the corresponding organomagnesium or organolithium reagent dissolved in 100 ml of diethyl ether or THF at 0 °C. The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and replaced by 200 ml of toluene. Magnesium or lithium triflate was precipitated as a white solid and was filtered off. Toluene was removed under vacuum to give **7–9** or **13** as a yellow-brown solid. The solids can be purified by dissolution in $CHCl_3$ and reprecipitation with ethanol. The data are summarized in Tables 1 and 2.

Reduction of triflate-substituted polymers 5 or 12 with lithium tetrahydridoaluminate (general procedure)

The triflate-substituted polymer **5** or **12** (20 mmol) was dissolved in 200 ml of a diethyl ether/toluene mixture (1:1). $LiAlH_4$ (0.2 g) was added at 0 °C and the mixture was stirred for 2 h. Then 20 ml of 1 M NH_4Cl solution in water was added dropwise and the resultant solution was stirred for another hour. The organic layer was separated and dried with anhydrous Na_2SO_4 over 1 h. The solvent was removed under reduced pressure to give a yellow-brown powder **6** or **12**. The data are summarized in Tables 1 and 2.

Hydrosilylation reaction of the polymers 13 and 14 (general procedure)

A mixture of 10 mmol of **13** and 10 mmol of **14** was dissolved in 100 ml of chlorobenzene. The mixture was stirred and a solution of 0.1 mmol of H_2PtCl_6 diluted in 10 ml of chlorobenzene was added dropwise. After an initial highly exothermic period, the mixture returned to room temperature. The stirring was maintained for 24 h at 40 °C. Then the chlorobenzene was removed under reduced pressure and replaced by 250 ml of toluene. The catalyst was filtered off and half of the toluene was removed under vacuum. The polymer **15** was precipitated by slow addition of 2-propanol and was dried in vacuum at 50 °C. The data are summarized in Table 2.

Synthesis of the chloro-substituted polymer 18

A mixture of 3.6 g (10 mmol) **16** and about 5 mg of palladium dichloride in 100 ml of CCl_4 was heated to reflux for 4 h. Then tetrachloromethane was removed under reduced pressure and replaced by 250 ml of toluene. The catalyst was filtered off and toluene was removed under vacuum to give **18** as a yellow-brown, viscous, hydrolytically sensitive oil. The data are summarized in Table 3.

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