Occurrence of Radical Cation Localization in Chemically Modified Poly(methylphenylsilane): Poly(methylphenyl-*co*-4-dimethylaminophenylmethylsilane)s and Poly(methylphenyl-*co*-4-bromophenylmethylsilane)s

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Chemical modification of poly(methylphenylsilane) **1** using triflate chemistry gave two series of random copolymers with different composition ratios, viz., poly(methylphenyl-*co*-4-dimethylaminophenylmethylsilane)s **3**–**7** and poly(methylphenyl-*co*-4-bromophenylmethylsilane)s **8**–**9**. The optical and electronic properties of the copolymers have been studied and are compared with those of the homopolymers **1** and poly(4-dimethylaminophenylmethylsilane) **2**. Electrochemical measurements in THF/LiClO$_4$ give strong evidence that, in marked contrast to the results observed for **1** and **2**, the onset of oxidation (V_i) of **3**–**7** and **8**–**9**, respectively, does not represent the silicon backbone valence band. Instead, in these copolymers, a mixture of decoupled electronic domains exists of which those possessing the lowest V_i govern the electrochemical response. As a consequence, the radical cations become confined, i.e. localization occurs. This interpretation is further supported by fluorescence emission spectroscopy; the presence of a confined exciton is indicated by the appearance of an additional broad band for the copolymers. Remarkably, copolymers with optical and electronic properties comparable to those of **3**–**7** are also accessible by (reversible) protonation of the 4-dimethylamino substituents of **2**.

Introduction

Polysilanes ($-(SiR_1R_2)_n-$) are one-dimensional semiconductive polymers consisting of a linear catenated silicon backbone with organic substituents (R_1,R_2).[1] As a result of σ-conjugation in the main chain, they have characteristic optical and electronic properties making them potential candidates for device applications.[1] These properties are strongly dependent on the choice of the substituents R_1 and R_2. Hence, in the past decade, much work has been directed toward the preparation of polysilanes with functionalized side groups.

Two distinct synthetic approaches toward functionalized polysilanes exist. The most widely used approach is the conventional Wurtz-type coupling (Na in toluene at 110 °C) of functionalized dichlorosilane monomers, giving access to various homo- and copolymers.[2] Although the severe reaction conditions limit the scope of this approach, aryl and alkyl substituents with, for example, ether and amino functionalities can be used.[3–5]

As an alternative, chemical modification after polymerization of, for example, poly(methylphenylsilane) **1** can

be employed. Although the reported procedures are generally complex and the preparation of fully functionalized polymers is troublesome, this method allows for the introduction of groups that are inaccessible using the conventional reductive coupling, such as halogens and thiols.[6–10] The most frequently applied procedure is dephenylation of **1** with trifluoromethanesulfonic acid (CF$_3$SO$_3$H), followed by substitution of the triflate groups with the desired functionality.[8,9]

Recently, we reported on the successful band gap tailoring by adjustment of the band positions in a uniform set of aryl functionalized poly(methylphenylsilane)s.[11,12] The optimization of such properties is essential for device applications of polysilanes. Hence, the question arises whether fine-tuning of the band gap energy levels can be accomplished by the preparation of copolymers with a well-defined composition.

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Here, we address this issue for the homopolymers **1** and poly(4-dimethylaminophenylmethylsilane) **2** and a series of copolymers poly(methylphenyl-*co*-4-dimethyl-aminophenylmethylsilane)s **3**–**7**. The latter were prepared by chemical modification of **1** employing triflate chemistry to ensure a fully random composition.[8] In addition, by following a similar approach, poly(methylphenyl-*co*-4-bromophenylmethylsilane) **8**–**9** were also prepared from **1**. It should be emphasized that **8**–**9** cannot be prepared by conventional Wurtz coupling of mixtures of methylphenyldichlorosilane and 4-bromo-phenylmethyldichlorosilane due to the electron-accepting properties of the 4-bromophenyl substituent.

To access the valence band edge, the copolymers are analyzed with cyclic voltammetry, which gives an estimate of the onset of oxidation (V_i). The electrochemical and spectroscopic properties of the copolymers are compared to those of the corresponding homopolymers. It is shown that in the copolymers **3**–**7** and **8**–**9** the observed V_i is determined by those electronically decoupled domains that possess the lowest onset of oxidation. Furthermore, copolymers with properties resembling those of **3**–**7** are also accessible by protonation of part of the dimethylamino groups present in **2**.

Experimental Section

General. NMR spectra were recorded with a Bruker AC 300 spectrometer at 300 MHz for ^{1}H NMR, 75 MHz for ^{13}C, and 60 MHz for ^{29}Si NMR. Analytical size exclusion chromatography (SEC) was performed with a Jordi-Gel DVB mixed bed column equipped with a Thermo Separation Products series 200 pump and a UV-detector (λ 300 nm) using THF as the solvent at a flow rate of 1 mL/min. Molecular weight distributions are given relative to polystyrene standards. Fluorescence spectra were collected on a Spex Fluorolog apparatus. Electrochemical measurements were performed with a Princeton Applied Research (PAR) model 263 potentiostat [scan rate 50 mV/s; solvent THF; electrolyte LiClO$_4$ (0.2 M)]. A standard three-electrode setup was used (Pt disk and counter electrode; Ag/AgCl reference electrode). All potentials were referenced to SCE (saturated calomel electrode) employing a known standard (ferrocene/ferrocinium couple). The handling of air- and moisture-sensitive compounds as well as all syntheses was done under an Ar atmosphere using Schlenk techniques. Solvents were dried and distilled prior to use. Semiempirical calculations were performed with the MOPAC 7.0 package.[13] All calculations were performed with the RHF PM3 Hamiltonian using the Eigenvector Following routine (keyword EF) until a GNORM $\leq$ 0.1 was obtained.[13,14] For the radical cations, the UHF method was used as implemented in MOPAC.[13]

Synthesis. *Poly(methylphenylsilane).* **1** was prepared using a conventional Wurtz-type coupling according to literature procedures;[1,12] see Scheme 1.

Poly(4-dimethylaminophenylmethylsilane). **2** was prepared using a conventional Wurtz-type coupling according to literature procedures.[1,4,12]

Poly(methylphenyl-co-4-dimethylaminophenylmethylsilane)s **3**–**7**. The preparation of **6** is reported here as a representative example; see Scheme 1 and Table 1. **1** (3.00 g, 25 mmol repeating units) was dissolved in toluene (70 mL) after which the solution was cooled to 0 °C. Subsequently, freshly distilled CF$_3$SO$_3$H (0.88 mL, 9.9 mmol) was added dropwise via a syringe. The reaction was allowed to proceed at room temperature overnight. Concurrently, 4-dimethylaminophenyllithium was prepared by the addition of *n*-butyl-

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Scheme 1. Syntheses of Polysilanes 3–9

3 m=0.12, n=0.88, R=NMe$_2$
4 m=0.15, n=0.85, R=NMe$_2$
5 m=0.25, n=0.75, R=NMe$_2$
6 m=0.28, n=0.72, R=NMe$_2$
7 m=0.42, n=0.58, R=NMe$_2$
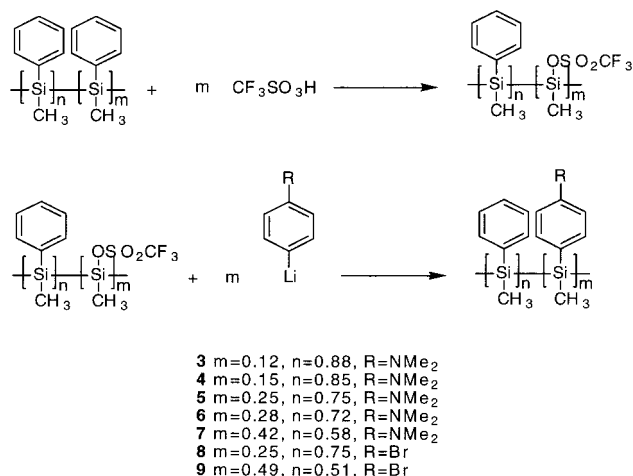**8** m=0.25, n=0.75, R=Br
9 m=0.49, n=0.51, R=Br

Table 1. Selected Polymerization Results for Copolymers 3–9

copolymer	theor. build-in ratio (%)	exp. build-in ratio (%)[a]	yield (%)[b]
3	25	12	37
4	20	15	8
5	50	25	43
6	40	28	14
7	60	42	6
8	30	25	39
9	60	49	39

[a] The copolymer build-in ratio was determined after polymerization by either ^{1}H NMR (**3**–**7**; build-in of 4-dimethylaminophenyl substituents) or inverse-gated decoupled ^{13}C NMR (**8** and **9**; build-in of 4-bromophenyl substituents). [b] Yield after three (re-)precipitations (see Experimental Section).

lithium (1.6 M solution in *n*-hexane; 96 mL, 0.15 mol) via a syringe to a solution of 4-bromo-*N,N*-dimethylaniline (21.31 g, 0.11 mol) in *n*-hexane (150 mL). The reaction mixture was stirred overnight, after which a pale yellow precipitate was formed. After filtration, the residue was washed with *n*-hexane (3 × 40 mL) and, subsequently, dried in vacuo. Solid 4-dimethylaminophenyllithium was dissolved in THF (100 mL), and the solution was added to the solution of triflated **1** in small portions over a period of 3 h until a sample quenched with water gave a pH > 7. The reaction mixture was stirred for another 2 h, after which water (50 mL) was added. The layers were separated, and the water layer was extracted with toluene (3 × 25 mL). The combined toluene fractions were concentrated under reduced pressure, and the remaining yellow/gray crude polymer was purified by repeated (3×) precipitation from toluene/MeOH; 0.49 g (14%) of pure **6** was obtained; $M_w = 7.5 \times 10^3$ ($D = M_w/M_n = 1.3$). Polysilane **3** was obtained in 37% yield; $M_w = 1.3 \times 10^4$ ($D = M_w/M_n = 1.6$). Polysilane **4** was obtained in 8% yield; $M_w = 8.6 \times 10^3$ ($D = M_w/M_n = 1.3$). Polysilane **5** was obtained in 43% yield; $M_w = 9.7 \times 10^3$ ($D = M_w/M_n = 1.4$). Polysilane **7** was obtained in 6% yield; $M_w = 5.6 \times 10^3$ ($D = M_w/M_n = 1.2$). The actual copolymer composition ratio was estimated using ^{1}H NMR spectroscopy (Table 1). Copolymers **3**–**7** exhibit similar ^{1}H, ^{13}C, and ^{29}Si NMR spectra; ^{1}H NMR (CD$_2$Cl$_2$): δ 7.8/6.2 (C–*H*), 3.1/2.5 (N–C*H*$_3$), 0.8/-0.9 (Si–C*H*$_3$) ppm. ^{13}C NMR δ 150.96, 136.26, 135.24, 127.81, 120.91 (br), 112.19, 40.29, −6.39 (br) ppm. ^{29}Si NMR δ −28/−43 (br) ppm.

Poly(methylphenyl-co-4-bromophenylmethylsilane)s **8**–**9**. The preparation of **8** is reported here as a representative example; see Scheme 1 and Table 1. **1** (2.01 g, 17 mmol repeating units) was dissolved in toluene (70 mL), after which the solution was cooled to 0 °C. Subsequently, freshly distilled CF$_3$SO$_3$H (0.44 mL, 5.0 mmol) was added dropwise via a syringe. The reaction was allowed to proceed at room temperature overnight. Concurrently, 4-bromophenyllithium was prepared by the

addition of *n*-butyllithium (1.6 M solution in *n*-hexane; 63 mL, 0.10 mol) via a syringe to a solution of 1,4-dibromobenzene (15.20 g, 64 mmol) in a mixture of *n*-hexane (95 mL) and toluene (20 mL). The reaction mixture was stirred overnight, after which a pale yellow precipitate was formed. The solvent was decanted, and the remaining precipitate was washed with *n*-hexane (3 × 40 mL). After decanting the *n*-hexane, the 4-bromophenyllithium solid was immediately dissolved in Et$_2$O (125 mL) without further drying. *Caution: Upon drying of solid 4-bromophenyllithium in vacuo, an explosion occurred.* This solution was added to the solution of triflated **1** in small portions over 3 h until a sample quenched with water gave a pH > 7. The reaction mixture was stirred for another 2 h, after which MeOH (100 mL) was added. After being cooled (−20 °C), yellow crude **8** precipitated. After the solvents were decanted, the remaining solid was purified by repeated (3×) precipitation from toluene/MeOH; 0.92 g (39%) of pure **8** was obtained; $M_w = 1.2 \times 10^4$ ($D = M_w/M_n = 1.6$). Polysilane **9** was also obtained in 39% yield; $M_w = 1.0 \times 10^4$ ($D = M_w/M_n = 1.6$). The actual copolymer composition ratio was estimated using ^{13}C NMR spectroscopy (inverse-gated decoupled). Copolymers **8**−**9** exhibit similar ^{1}H, ^{13}C, and ^{29}Si NMR spectra; ^{1}H NMR (CDCl$_3$): δ 7.7/6.5 (C−*H*), 0.8/-0.9 (Si−C*H*$_3$) ppm. ^{13}C NMR: δ 137.4, 135.9, 133.8, 132.1, 129.9, 128.8, 126.8, 123.4 (br), −5.0 (br) ppm. ^{29}Si NMR: δ −37/−43 (br) ppm.

Results and Discussion

Chemical Modification of 1. 1, which can be prepared in excellent yield using the conventional Wurtz-type coupling (Na in toluene at 110 °C),[1,12] is a suitable starting material for further chemical modification. In this work, we prepared a series of copolymers by side-group modification of **1** using triflate chemistry. Treatment of **1** with freshly distilled CF$_3$SO$_3$H leads to the replacement of phenyl groups by triflate groups.[8,9] These triflates can subsequently be substituted by other functionalities, such as 4-dimethylaminophenyl or 4-bromophenyl (Scheme 1). Although only partial substitution can be achieved and the copolymer composition can only be controlled to some extent,[8,9] the use of this method is preferred over the direct copolymerization of two different monomers. Especially, the fact that random copolymers are obtained is of relevance for the evaluation of the electronic properties.[8,9,15,16] It should be emphasized that block copolymers, which possibly can be formed when two monomers of different reactivity are copolymerized, are expected to have markedly different properties. Furthermore, this method allows a facile introduction of a new substituent, such as 4-bromophenyl, which cannot be introduced via conventional Wurtz-type coupling due to its reactivity toward the employed Na.

All copolymers **3**−**9** are amorphous solids and exhibit the characteristic polysilane ^{1}H, ^{13}C, and ^{29}Si NMR spectra. The composition of polysilanes **3**−**7** was established by ^{1}H NMR. Unfortunately, this was not possible for **8**−**9**. Hence, for the latter, inverse-gated decoupled ^{13}C NMR was used instead.[17] From the results presented in Table 1, it is inferred that the theoretical build-in ratios deviate from those determined by NMR
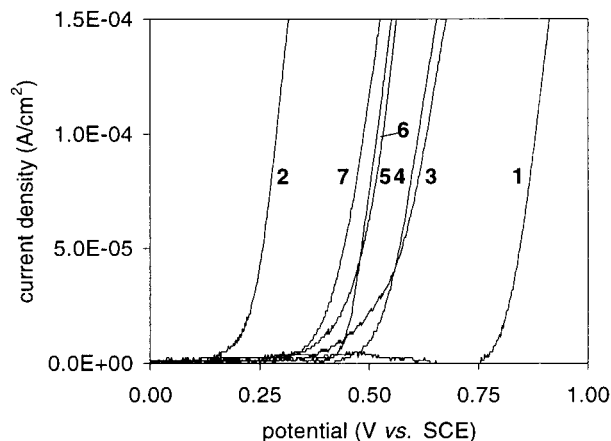
(15) For **3**−**9**, analytical SEC measurements using dual-wavelength detection (λ 320 and 350 nm) indicate that no preferential incorporation of any of the monomers occurs throughout the molecular weight distribution.

(16) Wolff, A. R.; Nozue, I.; Maxka, J.; West, R. *J. Polym. Sci., Polym. Chem.* **1988**, *26*, 701.

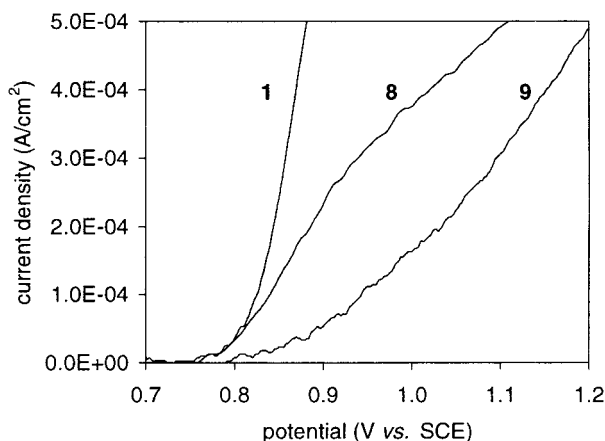(17) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: Weinheim, Germany, 1993; p 34.

Figure 1. Onset of oxidation (V_i) of **1**−**7**. For clarity, the onset of the first anodic scan is shown.

in the respective copolymers. This is attributed to the repeated precipitations essential for polymer purification; i.e., the final precipitate is enriched in copolymers with a high methylphenyl content (lowest build-in ratio). Polymers with a maximum degree of substitution of 42% (**7**) and 49% (**9**) are reached. This is in line with previous reports that the triflate-mediated dephenylation reaction allows for a maximum degree of substitution of ca. 50%.[8]

It should be emphasized that even though all reactions are performed under an Ar atmosphere, in contrast to earlier reports,[8] a comparison of the molecular weight distribution of starting polysilane **1** [bimodal weight distribution: $M_w = 2.3 \times 10^5$ ($D = M_w/M_n = 1.4$) and $M_w = 1.8 \times 10^4$ ($D = M_w/M_n = 1.8$)][12] and those of copolymers **3**−**9** isolated after (re-)precipitation [M_w ranging from 5.6×10^3 to 1.3×10^4 ($D = M_w/M_n = 1.2$−1.6)] indicates that during the substitution reaction backbone scission can occur. As a result, a monomodal weight distribution is obtained for all copolymers with a comparatively low polydispersity (D). The molecular weight decrease becomes larger at higher substitution ratios. However, even in those cases, the molecular weight distributions show that high molecular weight polymers consisting of at least 50 monomer units are obtained.

The yields of the chemically modified polysilanes **3**−**9** are low to moderate (**3**−**7**, 6−43%; **8**−**9**, 39%; see Table 1). In this context, it is noteworthy that purification of **3**−**7** by (re-)precipitation is hindered by the occurrence of undesired protonation of the acid-sensitive dimethylamino moieties. Upon extensive protonation, aggregation and, subsequently, precipitation of the protonated polymer chains occur (vide infra). In addition, **3**−**7** as well as **8**−**9** were reprecipitated, which will also reduce the final yields, but it is imperative to obtain polymers of sufficient purity for optical spectroscopy and electrochemistry.

Electrochemistry. Polysilanes **1**−**9** are readily oxidized using cyclic voltammetry in THF/LiClO$_4$ solution (Figures 1 and 2). This oxidation process is irreversible, as in many other electrochemically studied silicon-based polymers.[11,12,18,19] Notwithstanding, we have previously demonstrated that in the case of polysilane homopolymers the onset of oxidation (V_i) is highly reproducible, thus enabling a semiquantitative analysis of their

Figure 2. Onset of oxidation (V_i) of **1**, **8**, and **9**. For clarity, the onset of the first anodic scan is shown.

Table 2. Onset of Oxidation (V_i) of (Co)Polymers 1−9

(co)polymer	V_i (V vs SCE)
1	0.81
2	0.23
3	0.55
4	0.53
5	0.47
6	0.45
7	0.41
8	*ca.* 0.8
9	*ca.* 0.8

valence band edge.[11,12] The results show that marked differences are discernible between the various polysilane homo- and copolymers. In the series **1−7**, a distinct V_i is observed for all (co)polymers. At first sight, upon introduction of the 4-dimethylaminophenyl group, V_i shifts gradually from the initial position of **1** (0.81 V vs SCE) to that of **2** (0.23 V vs SCE; see Table 2). In view of the positive Hammett substituent constant (σ_R) of the 4-bromophenyl substituent,[20,21] the V_i of **8** and **9** is expected to be shifted to substantially higher potential. However, whereas for **8** and **9** in comparison to **1** the current density with increasing potential differs, no shift in the position of V_i is discernible (Figure 2).

Close scrutiny of the V_i values in the series **1−7** revealed that the V_i deviates from a linear relationship with the degree of substitution (Figure 3). Instead, already at a low degree of substitution, V_i exhibits a large shift, followed by only a small and nearly linear shift concomitant with a further increase in the degree of substitution.

Hence, the question arises if substitution of phenyl groups in **1** by either 4-dimethylaminophenyl (copolymers **3−7**) or 4-bromophenyl groups (copolymers **8−9**) will lead to a reduction or even breakdown of σ-conjugation in the catenated silicon backbone of **1**. If no breakdown of σ-conjugation occurs, V_i has to be the weighted average of the V_i values of the respective

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(19) Diaz, A.; Miller, R. D. *J. Electrochem. Soc* **1985**, *132*, 834.

(20) Exner, O. *Correlation Analysis of Chemical Data*; Plenum Press: New York, 1988; p 61.

(21) The Hammett substituent constant (σ_R) of the 4-bromophenyl group is 0.22. This increases the scope of the Hammett analysis, as thus far only a variety of functionalized poly(methylphenylsilane)s with negative σ_R values were studied.[12,20]
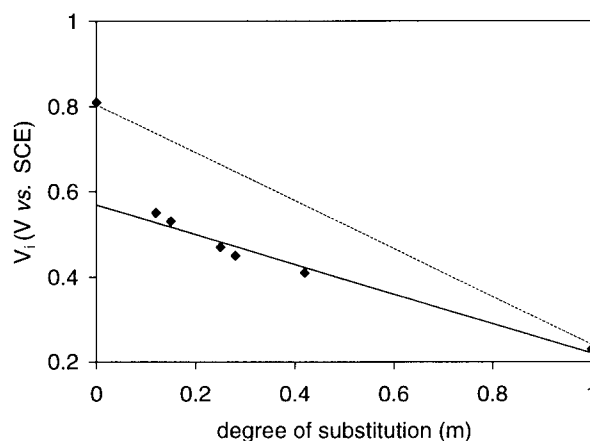

Figure 3. Dependence of V_i on the copolymer composition of **3−7** (solid line). Note the extrapolated value of ca. 0.55 V vs SCE for the intersection with the *y*-axis. The broken line represents the expected V_i if no localization occurs and full electronic mixing takes place; i.e. V_i is the weighted average of the V_i values of the respective homopolymers taking into account the copolymer composition ratio (see Text).

homopolymers expected on the basis of the copolymer composition ratio. It should be emphasized that cyclic voltammetry has shown that the homopolymers **1** (V_i 0.81 V vs SCE) and **2** (V_i 0.23 V vs SCE) indeed possess a σ-conjugated catenated silicon backbone.[11,12] However in the copolymers **3−7**, the V_i values are clearly not weighted averages as expected on the basis of their copolymer composition ratio (Tables 1 and 2 and Figure 3). This suggests that substitution of phenyl by 4-dimethylaminophenyl even at very low levels leads to the formation of electronically decoupled domains, which may even consist of only one repeating unit. If this is the case, the electrochemical response of the copolymer will be governed by those decoupled domains that possess the lowest V_i. Whereas for **1** V_i equals 0.81 V vs SCE, the V_i of a suitable reference compound for one repeating unit of **2**, i.e., 4-dimethylaminophenyltrimethylsilane,[22] is 0.55 V vs SCE,[12] which is considerably lower than that of **1**. Hence, in line with the experimental results for **3−7** at a low degree of substitution, V_i should be approximately 0.55 V (cf. V_i of **3** and **4**, Table 2). Upon further substitution, the average 4-dimethylaminophenyl-substituted domain length will increase, which accounts for the observed gradual shift of the V_i of **3−7** to the V_i of **2** [(0.23 V vs SCE), Table 2 and Figure 3]. This effect of catenation on the oxidation potential is also documented for oligomeric permethylsilanes.[23,24]

Unfortunately, V_i of 4-bromophenyltrimethylsilane[22] is located outside the available potential window of the employed electrochemical medium (THF/LiClO$_4$). Notwithstanding, V_i has to be positioned well above 1.00 V vs SCE. Therefore, because V_i of the copolymers **8** and **9** resembles that of **1**, it is presumably dictated by the remaining methylphenylsilane sequences of appropriate conjugation length, which are electronically decoupled

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(23) Boberski, W. G.; Allred, A. L. *J. Organomet. Chem.* **1975**, *88*, 65.

(24) Bock, H.; Ensslin, W.; Fehér, F.; Freund, R. *J. Am. Chem. Soc.* **1976**, *98*, 668 and references cited therein.

from the introduced 4-bromophenylmethylsilane sequences (Table 2 and Figure 3).[25] Hence, the initial drop in V_i at a low degree of substitution in the series **1**–**7**, as well as the absence of a shift in V_i for **8** and **9**, gives strong evidence for the occurrence of a breakdown of σ-conjugation, viz., the occurrence of radical cation localization.

To further investigate the occurrence of charge localization, semiempirical PM3[14] calculations were performed on oligomeric silicon compounds ($n = 6, 10$). Calculations on methylphenyl-substituted oligomers with only one 4-dimethylaminophenyl group support the proposed perturbing effect of the 4-dimethylaminophenyl substituents. Although in the radical cations of such oligomers, no full-charge localization occurs, more positive charge (ca. 5%) is present on the silicon atom and the attached 4-dimethylaminophenyl group as compared to oligomers with methylphenyl substituents only.

Fluorescence Spectroscopy. It is noteworthy that steady-state and time-resolved fluorescence measurements of a series of poly(methylphenyl-*co*-methyl-4-dimethylaminophenylsilane)s related to **3**–**7** but prepared differently, i.e. by copolymerization of a mixture of two different monomers using conventional Wurtz-type coupling, have provided evidence for the perturbing effect of 4-dimethylaminophenyl substituents on the optical and electronic properties.[4] Support for our conclusions concerning radical cation localization may be found in the observed dependence of the coherence length for neutral excitations on copolymer composition. To establish whether a similar process occurs for the copolymers **3**–**9** prepared via the triflate route, their photophysical properties were also evaluated.

Whereas in the fluorescence emission spectra ($\sigma \leftarrow \sigma^*$ transition) for the homopolymers **1** and **2** a typical narrow band in the (near) ultraviolet region is found with a maximum at λ 364 and 384 nm, respectively,[4,12] for **3**–**9** an additional broad emission was found with a maximum around λ 425 nm (Figure 4).[26] It is noteworthy that it has been previously suggested that upon introduction of structural defects in the silicon backbone of **1**, an additional broad redshifted band in the fluorescence emission spectrum appears already at a markedly low effective defect density.[27,28] Evidence has been put forward that this band is caused by the presence of branching points in the initially linear polysilane backbone.[27,29] Although these branching points can act as scattering points, they can also act as trapping sites, in which excitons become localized.[4,29] The appearance of the broad emission band is directly related to these trapping phenomena.

The additional emission band of **3**–**9** resembles a related "defect" emission. Apparently, in these cases, the
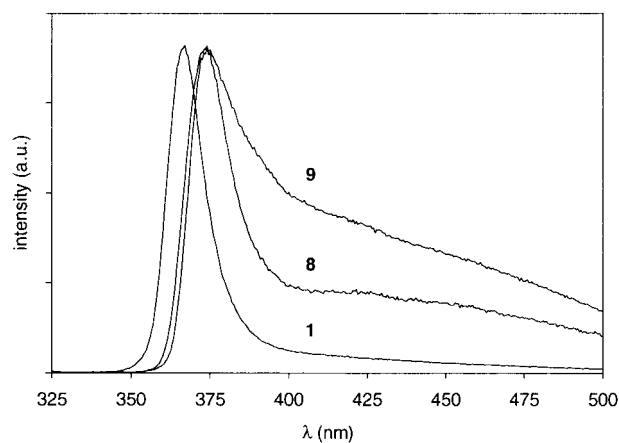

Figure 4. Fluorescence emission spectra of **1**, **8**, and **9** (excitation at 320 nm).[26]
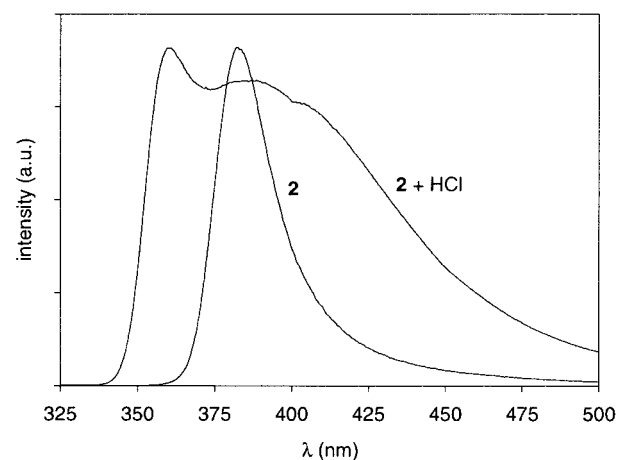

Figure 5. Fluorescence emission spectra of **2**, before and after the addition of HCl (excitation at 300 nm).

defects represent polymer sites where a substantial electronic perturbation of the backbone states, viz., decoupling or breakdown of σ-conjugation, occurs, which can ultimately lead to trapping of the exciton. Whether this occurs as a result of branching[27,28,29] or is caused by the copolymer substitution pattern (polysilanes **3**–**9**)[4] does not substantially influence the observed optical and electronic characteristics. Hence, the additional emission band of **3**–**9** can be tentatively attributed to a localized exciton! Therefore, the 4-dimethylaminophenyl and 4-bromophenyl substituents cause the introduction of initially small, isolated electronic domains, in which apparently some excitons become confined. Consequently, in the copolymers **3**–**9**, a distribution of polymer segments is present with markedly reduced coherence lengths, as compared to the homopolymers **1** and **2**. This reduction in σ-conjugation is similar to that observed in other polysilane copolymers.[4]

Reversible Protonation of 2. Copolymers comparable to **3**–**7** can also be prepared from homopolymer **2** by protonation of part of its dimethylamino functionalities. The acid sensitivity of these groups was already observed during the synthesis (vide supra) and prompted us to study the effect of protonation on the electronic

(25) Although it is tempting to interpret the observed differences in current density and the initial slopes around V_i to reflect changes in the concentration of methylphenylsilane sequences and the distribution of their conjugation lengths, respectively, it should be stipulated that the observed oxidation processes are irreversible.[12]

(26) The fluorescence emission spectra of **3**–**7** are essentially identical to those reported previously for copolymers possessing a related composition.[4] The latter copolymers were obtained by a conventional Wurtz-type (Na in toluene at 110 °C) copolymerization of mixtures of methylphenyldichlorosilane and 4-dimethylaminophenylmethyldichlorosilane.

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properties. Upon introduction of HCl/2-propanol (5 M) in the electrochemical cell, V_i instantaneously shifts by ca. 0.4 V from 0.23 to 0.65 V vs SCE. This can be attributed to the fact that the protonated dimethylamino groups are no longer electron-donating,[30] and as a result, a copolymer is formed. This copolymer consists of different electronic domains, i.e. unaffected segments and protonated segments. Unfortunately, full protonation cannot be accomplished in THF solution, as aggregation and subsequent precipitation of the polymer occur at higher HCl concentrations.

The formation of a copolymer with both unprotonated and protonated dimethylamino groups is confirmed by fluorescence emission spectroscopy. Whereas for **2** a single emission band is found with a wavelength maximum at λ 384 nm, for protonated **2** a more complex emission spectrum is found of two superimposed bands (Figure 5). The narrow $\sigma \leftarrow \sigma^*$ emission maximum is shifted to λ 361 nm, which is in excellent agreement with that of **1** (λ 364 nm). In addition, a broad redshifted band is visible (λ 375 nm to λ 500 nm) that is comparable to the band found for the copolymers **3**−**9** and, hence, can be attributed to a confined exciton, viz. a defect emission similar to that discussed in the Fluorescence Spectroscopy subsection. It should be emphasized that protonation is reversible; upon introduction of base [MeOH saturated with $NH_3(g)$] to the solution

of protonated **2**, only the narrow $\sigma \leftarrow \sigma^*$ emission is observed with a maximum at λ 384 nm, viz., the emission maximum of **2**.

Conclusions

Chemical modification of poly(methylphenylsilane) using triflate chemistry is a useful method to obtain aryl-substituted random polysilane copolymers. By employing this method, a series of poly(methylphenyl-*co*-4-dimethylaminophenylmethylsilane)s and poly(methylphenyl-*co*-4-bromophenylmethylsilane)s were prepared with different composition ratios. We have provided evidence that in **3**−**9** the substituents perturb the optical and electronic properties in such a way that isolated electronic domains are formed in which the excitations, viz., the radical cations, become confined. As a result, the observed onset of oxidation V_i no longer represents the silicon backbone valence band, although it does represent the valence band edge for polysilane homopolymers.[11,12] Instead, the electronic domains with the lowest V_i will dictate the electrochemical response. Additional evidence comes from fluorescence spectroscopy, in which the presence of a confined exciton is reflected in the appearance of an additional broad redshifted band. Similar results are obtained upon (reversible) protonation of **2**. The results indicate that the aryl-substituted polysilane copolymers **3**−**9** are unsuitable for applications in which a long coherence length is desired, such as charge migration or photoconductivity.

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(30) Although to the best of our knowledge no σ_R substituent constant is available for the protonated dimethylamino group, the resulting substituent is expected to have a positive σ_R value [cf.: Exner[20]; the σ_R value of $N^+(CH_3)_3$ in H_2O is 0.96].