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Band Gap Modifications in Functionalized Poly(methylphenylsilanes)

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ABSTRACT: For many applications of polysilanes in optoelectronic devices, it is desirable that polymer properties, such as their band gap energy levels, their (redox) stability, and their propensity to interact favorably with (semi)conducting inorganic substrates, can be tailored. It has been demonstrated that, by introduction of substituents in the aryl moiety of poly(methylphenylsilane) (**1**), i.e., poly(methyl-4-methylphenylsilane) (**2**), poly(4-methoxyphenylmethylsilane) (**3**)**,** poly[4-(dimethylamino)phenylmethylsilane] (**4**), poly(3-methoxyphenylmethylsilane) (**5**)**,** and poly[4-(2-methoxyethoxy)phenylmethylsilane] (**6**), these objectives can be achieved. For comparative purposes, poly(4,7,10,13-tetraoxatetradecylmethylsilane) (**7**) was also taken into consideration. Electrochemical measurements (cyclic voltammetry) in THF/$LiClO_4$ of **1**−**7** show that the onset of oxidation V_i of each polysilane provides a reliable estimate of its valence band edge; within series **1**−**7** V_i shifts over ca. 0.7 V. Although it is impossible to obtain a reliable estimate of the conduction band edge due to the available potential window of THF/$LiClO_4$, the position of the conduction band edge of the polysilanes is derived from their optical band gaps using fluorescence excitation and emission spectroscopy. The electrochemical and optical properties of the related polysilanes **1**−**5** correlate with the substituent Hammett constants (σ_R). The Hammett reaction constants (ρ) indicate that the optical band gap ($\rho = 0.29$) is less sensitive to electronic pertubations induced by the substituents than the valence band edge ($\rho = 0.85$). From these results the response of the conduction band edge toward substituent induced electronic pertubations was estimated to be $\rho = 0.60$. The experimental results are supported by semiempirical PM3 calculations on polysilane oligomers $n = 1{-}10$ of **1** and **4**.

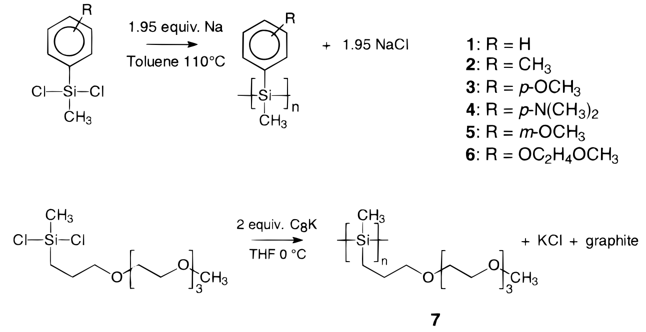
Introduction

In the past two decades the importance of polysilanes $-(SiR_1R_2)_n-$ as an exciting class of semiconducting polymers has been established.[1] The occurrence of σ-conjugation in their catenated silicon backbones results in a variety of useful electrical and optical properties. Examples are hole conduction and photoconduction, electroluminescence, microlithography, and thermo-, piezo-, solvato-, and surface-mediated chromism as well as thermoresponsive behavior.[1−3] Hence, polysilanes attract attention as materials for device applications.[4,5]

Recently, besides the common apolar polysilanes with alkyl and/or aryl side groups,[1] polar nonionic, water-soluble derivatives containing at least one oligo(oxyethylene) side chain moiety have become available.[6,7] The development of improved synthetic methods[8,9] gave access to these polar derivatives, enabling the study of their potential applications. Worthwhile is their markedly improved wettability toward inorganic (semi)conducting substrates.[10]

Although the first polysilane-based devices have been developed,[4,5] their performance still requires improvement. Topical issues are the tailoring of their band gap energy levels as well as their (redox) stability. It has been established that in the common alkyl-substituted polysilanes the valence and the conduction band are mainly localized on the silicon backbone; they both have σ-character.[1] Although it is well-known that the type of side groups affects the conformation of the catenated silicon backbone and, consequently, its optoelectric properties,[1] band gap tailoring by adjustment of the band positions in a uniform set of polymers via introduction of substituents in one of the side groups is preferred. A prerequisite is the occurrence of electronic coupling between the valence and/or conduction band of the catenated silicon backbone with energy levels of the (modified) side groups. Evidence exists that in aryl-substituted polysilanes such a coupling occurs due to an interaction between some of the aryl localized π molecular orbitals (π-MO's) with the σ-type valence and/or conduction band of the silicon backbone.[1,11] Hence, this opens the intriguing possibility to adjust the band edges by appropriate substitution of the aryl side group.

Scheme 1. Syntheses of Polysilanes 1−7



In this paper this issue is addressed by a comparison of the optoelectronic properties of a related series of polysilanes, i.e., poly(methylphenylsilane) (**1**), poly(methyl-4-methylphenylsilane) (**2**), poly(4-methoxyphenylmethylsilane) (**3**), poly[4-(dimethylamino)phenylmethylsilane] (**4**), poly(3-methoxyphenylmethylsilane) (**5**), and poly[4-(2-methoxyethoxy)phenylmethylsilane] (**6**). As a reference, the nonaryl-substituted poly(4,7,10,13-tetraoxatetradecylmethylsilane) (**7**) is taken into consideration as well (Scheme 1).

In this context it should be emphasized that evidence has been reported that during the synthesis of **1**

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structural defects can be introduced,[12] which substantially affect its photophysical properties and in particular the position of the band edges.[13] Hence, this point should be taken into careful consideration and imposes constraints on the required purity of polysilanes **1**−**7**.[14−17]

The position of the valence band edge of **1**−**7** was determined from the onset of oxidation (V_i) employing electrochemical methods, viz. solution cyclic voltammetry. The relevance of V_i and its reliability are discussed. In addition, the dependence of V_i on the substituent as well as the induced changes in the optical properties is interpreted using both a Hammett-type analysis and PM3[18] semiempirical calculations.

Results and Discussion

Polysilane Synthesis: Application of Na vs C_8K as Reducing Agent. For poly(methylphenylsilane) (**1**), viz. one of the most studied amorphous polysilanes, various synthetic procedures, which primarily differ in the employed reducing agent, temperature, and solvent, have been reported. Whereas the conventional Wurtz-type coupling (Na in toluene at reflux temperature)[14,16] gave **1** like many other alkyl/aryl-substituted polysilanes, recently, the more advantageous use of C_8K instead of Na for the preparation of **1** has been reported.[19,20] Furthermore, the promising results obtained in the C_8K-mediated polymerization of poly(4,7,10,13-tetraoxatetradecylmethylsilane) (**7**)[8] and its branched analogue poly(4,7,10,13-tetraoxatetradecylsilyne),[21] of which the latter is inaccessible by the conventional Wurtz-type procedure, prompted us to extend this method to the more polar poly[4-(dimethylamino)-phenylmethylsilane] (**4**).

The results for the polymerization of **1** and **4** with the two different reducing agents are quite distinct. Whereas for **1** synthesized via the Na route (scale 0.15 mol of monomer and 0.28 mol of Na) the yield of high molecular weight polymer was 47%, the C_8K route (scale 0.20 mol of monomer and 0.40 mol of C_8K) gave **1** in only 12% yield. In both cases the molecular weight distributions are in the range 10^4−10^5. It is noteworthy that the yield of **1** obtained using C_8K was substantially lower than expected.[19,20] In contrast to the previously reported procedures, we performed the polymerization on a considerably larger scale (up to 20-fold increase; cf. ref 19; in which a scale of 11 mmol of monomer and 23 mmol of C_8K is employed) in order to obtain sufficient amounts of polymer for further studies. Apparently, in contrast to the Na-mediated polymerization, the use of C_8K is markedly sensitive to scaling up. This is tentatively attributed to the heterogeneous character of the polymerization reaction. Whereas in small-scale polymerizations the C_8K is readily dispersed in THF by vigorous magnetic stirring, this becomes increasingly more difficult with an increase in scale. This may lead to undesired local excesses of C_8K, which results in overreduction of **1** and, consequently, reduces the polymer yield. It should be emphasized that it is documented that with excess C_8K −Si−Si− bonds are quantitatively converted into $-Si^-K^+$ species; i.e., overreduction occurs.[22] Changing from vigorous magnetic to mechanical stirring did not affect the yield of **1** significantly under the polymerization conditions.

In view of these observations the C_8K-based preparation of **4** was only attempted at a small scale (scale: 12 mmol of monomer and 24 mmol of C_8K);[19] no high molecular weight polymer was found. In contrast, the conventional Wurtz-type procedure (Na in toluene at reflux temperature) gave high molecular weight **4** in 12% yield.

Table 1. Spectroscopic Properties of 1−5

polymer	λ_{abs} (nm)	λ_{exc} (nm)[a]	λ_{em} (nm)[b]
1	340	361	364
2	342	363	367
3	349	368	373
4	353	373	384
5	332	354	361

[a] λ_{exc} for emission at λ_{em}. [b] λ_{em} for excitation at λ_{exc}.

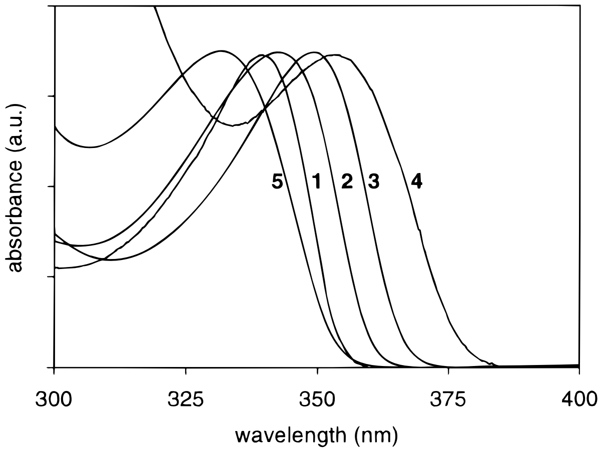

Figure 1. UV absorption spectra of polymers **1**−**5**.

On the basis of these results we have prepared the polysilanes **1**−**6** using the conventional Wurtz-type procedure; **1**−**6** were obtained in fair to good yield (12−48%). All polymers exhibit the characteristic polysilane ^1H, ^{13}C, and ^{29}Si NMR spectra, and their molecular weight distributions range from M_w of 6.4×10^3 to 3.4×10^5 with polydispersities ($D = M_w/M_n$) of ca. 2 (polystyrene standards, see Experimental Section). In agreement with previous studies of the thermal properties of **1**,[23] DSC analysis of **1**−**6** only gave featureless traces, containing neither distinct first-order nor second-order transitions. Polysilane **7** was prepared using C_8K according to a literature procedure.[8]

Optical Spectroscopy. Polymers **1**−**7** exhibit the typical optical characteristics of polysilanes. Their UV−vis absorption spectrum consists of a narrow band ($\sigma \rightarrow \sigma^*$ transition). For **1**−**5** an absorption maximum is found between 332 and 353 nm, depending on the substituent (Table 1, Figure 1). Polysilane **6** exhibits, as expected, nearly identical photophysical properties as **3**. The photophysical properties of **7** have been previously reported.[8]

With regard to the proposal that introduction of undesired structural defects, i.e., branching sites, will markedly affect the photophysical properties of **1**,[12] the fluorescence excitation and emission characteristics of polysilanes **1**−**5** warrant special attention. Polysilanes **1**−**5** exhibit the typical narrow excitation and emission spectrum in the (near) ultraviolet region (Figure 2 and Table 1). However, upon introduction of structural defects in the silicon backbone, an additional broad red-shifted band in the fluorescence emission spectrum appears already at a very low effective defect density, *D*. The relative intensity of this band is usually taken as a semiquantitative measure of *D*.[12,13] As a consequence of the sensitivity of fluorescence spectroscopy,

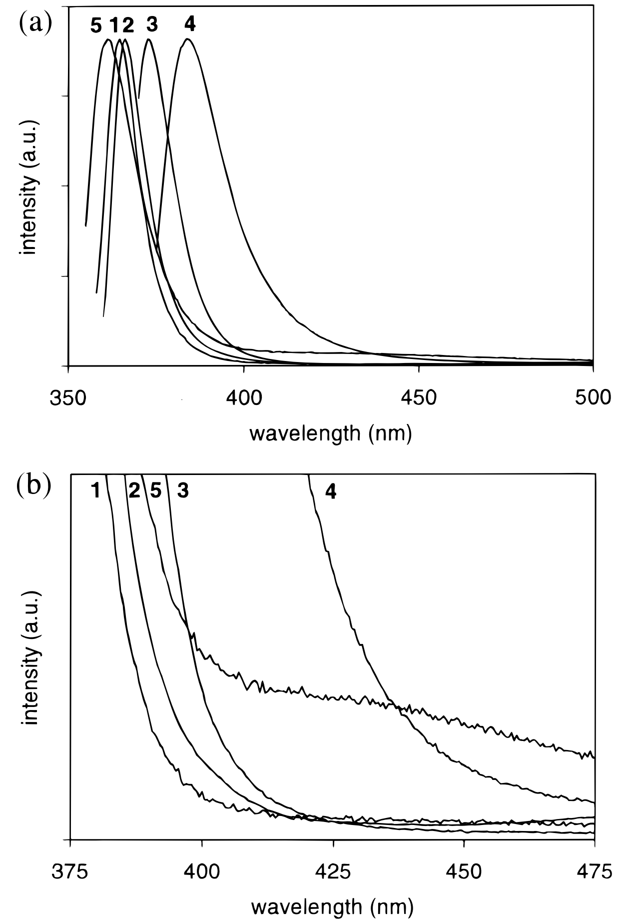

Figure 2. (a) Fluoresence emission spectra of polymers **1**−**5** (excitation at the excitation maximum). (b) An enlargement (×10) of the long wavelength band region of the spectrum.

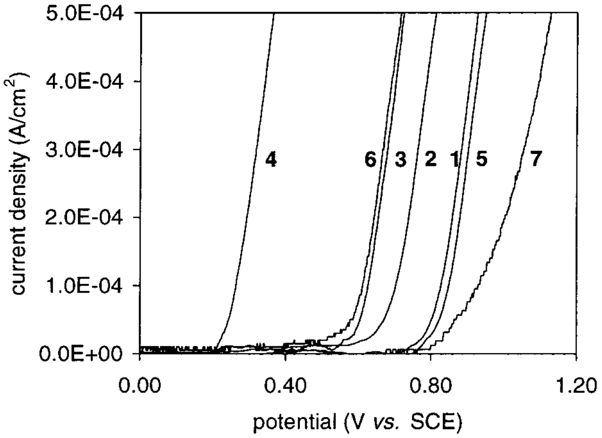

Figure 3. Onset of oxidation (V_i) of polymers **1**−**7**. For clarity the onset of the first anodic scan is shown.

Table 2. Onset of Oxidation (V_i) of 1−7

polymer	V_i (V vs SCE)	polymer	V_i (V vs SCE)
1	0.81	**5**	0.84
2	0.70	**6**	0.58
3	0.61	**7**	0.94
4	0.23		

undesired structural defects at a level of $D \ll 1\%$ are already clearly discernible.[12] In contrast, these small amounts of defect sites escape detection by either NMR spectroscopy; viz. the ^{29}Si NMR spectra of polysilanes **1**−**5** all contain only one distinct ^{29}Si resonance (see Experimental Section). In addition, they will also remain undetected by elemental analysis at these levels.[24] For **1**−**4** no additional, broad red-shifted emission is detectable in the room-temperature solution spectra, indicating that D equals 0; viz. no branching has occurred.[13] Only for **5** a low-intensity, broad emission band with a maximum positioned at ca. 440 nm was observable. The very low intensity of this band indicates that even in this case D is very small ($D \ll 1\%$). The above results indicate that the employed synthetic procedures yield high-purity polymers without any structural defects in their catenated silicon backbone.

Electrochemistry. As shown in Figure 3, polysilanes **1**−**7** are readily oxidized using cyclic volammetry in THF/LiClO$_4$ solution. Although the oxidation process is irreversible, profound differences are discernible within the series **1**−**6**. This indicates that introduction of a substituent in the aryl moiety of **1** indeed affects their electronic properties. Although previously the oxidation behavior of a limited number of polysilane thin films deposited on Pt electrodes by spin-coating was studied electrochemically in CH$_3$CN solution,[25] no structure−property relationships were derived. The thin film approach, however, is unsuitable for an electrochemical investigation of polysilanes **1**−**7** under comparable conditions due to the excellent solubility of especially **6** and **7** in CH$_3$CN. In contrast, solution cyclic voltammetry with THF/LiClO$_4$ as the electrochemical medium offers suitable conditions with sufficient solubility of both apolar and polar polysilanes. Furthermore, their electrochemical oxidation can be studied under both O$_2$ and water-free conditions.

Although the oxidation process of polysilanes in THF solution is irreversible, the onset of oxidation (V_i) gives highly reproducible results, thus enabling a semiquantitative analysis. The value of V_i can be interpreted as a direct estimate of the valence band edge position. It should be emphasized that irreversible electrochemical systems can only furnish kinetic and no thermodynamic results, such as $E°$.[26] Therefore, the measurement of peak potentials (V_{peak}) for irreversible oxidation processes, which is frequently done,[25,27] will potentially give unreliable information. This is due to the strong dependency of V_{peak} on factors such as the solvent, the electrolyte, the scan rate, and the concentration of the analyte. The importance of some of these factors has been previously established during the irreversible oxidation of cyclic silanes.[27] In contrast, the onset of the electrochemical response, viz. V_i, is virtually independent of, among others, the scan rate[28] and the concentration of the analyte.[29] Hence, only values for V_i, instead of V_{peak}, will be presented.

A marked shift in V_i of 0.58 V upon going from **1** to **4** is discernible (Figure 3 and Table 2). The presence of the strongly electron-donating *N*,*N*-dimethylamino group in **4** induces a lowering of V_i from 0.81 to 0.23 V. Polysilanes **2** and **3**, which contain less efficient electron donors, i.e., methyl and methoxy groups, respectively, exhibit intermediate values. Although the shifts V_i are not as large as those found for monomeric silicon compounds containing various electron-donating groups,[30] the influence on the conjugated polymer system is substantial.

Additional evidence for the validity of V_i as a proper estimate of the valence band edge is furnished by polysilane **5**, which in contrast to **3** has the methoxy group at the meta position on the phenyl ring. Since this position is less strongly coupled over the aromatic

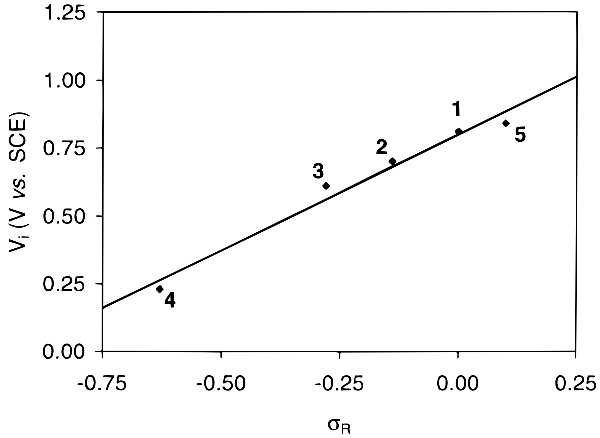

Figure 4. Onset of oxidation V_i of **1**−**5** vs the Hammett constants σ_R of the aryl substituents.[30]

ring, V_i of **5** is anticipated to approximate that of **1**. Indeed, whereas the V_i of **3** is 0.61 V, that of **5** (0.84 V) is close to that of **1** (0.81 V, Table 2).

Hammett Relationships for Polysilanes 1−**5**. The substantial effect of the substitution pattern on the optoelectronic properties of polysilanes **1**−**5** prompted us to rationalize the data in terms of a Hammett-type linear free energy relationship.[31] An excellent correlation (r^2 = 0.975) is found for **1**−**5** between V_i and the Hammett constants (σ_R) of the aromatic substituents (Figure 4). Hence, the Hammett analysis provides a valuable tool to predict the V_i of polysilanes with substituted aryl side groups. This substantiates that the coupling between the aryl moiety and the silicon backbone is considerable and that it is affected by the type and position of the substituents on the aryl moiety. In addition, the excellent correlation indicates that the amorphous polysilanes **1**−**5** must have a comparable electronic structure. Consequently, no substantial differences in conformation of their silicon backbone exist in solution.[1]

Instead of the regular Hammett equation,[31] also an extended Hammett-type linear free energy relationship (Yukawa−Tsuno equation)[32] was used. This relationship gave an excellent description of silyl cations.[33] In this approach, besides the standard substituent constant (σ_R), a resonance substituent constant (σ_R^+) is used. This analysis does not only give an improved correlation (r^2 = 0.990) but also provides an estimate for r^+, i.e. the degree of π interaction between the substituent and the positive charge, of ca. 1, indicating that this interaction is strong.[32] This value is significantly higher than that obtained for silyl cations of monomeric compounds (r^+ = 0.28).[33,34] Apparently in **1**−**5** the electronic coupling between the substituted aryl moiety and the positive charge on the silicon backbone is substantially larger.[33]

Unfortunately, as a consequence of the available potential window of THF/LiClO$_4$, it is impossible to obtain an accurate electrochemical estimate of the onset of reduction, viz the conduction band edge. Instead, the position of the conduction band edge can be assessed using optical spectroscopy, which provides an estimate of the optical band gap. In going from **1** (λ_{max} 340 nm) to **4** (λ_{max} 353 nm), only a small shift of 13 nm (0.14 eV) is discernible in the $\sigma \rightarrow \sigma^*$ transition in the UV absorption spectrum (Table 1 and Figure 1).[16,17] Hence, in contrast to the considerable change of V_i of 0.58 V, the optical band gap energy exhibits only a moderate change in going from **1** to **4**. Since V_i gives an estimate of the valence band edge of the polymer, it actually represents the oxidation energy of the lowest energy segments in the σ-conjugated main chain. In this context it should be emphasized that λ_{max} of the $\sigma \rightarrow \sigma^*$ transition is not representative for the optical band gap. The $\sigma \rightarrow \sigma^*$ band in the UV absorption spectrum represents the full distribution of chromophores, i.e., all distinct silicon backbone segments. However, the optical band gap of polysilanes is determined by the optical transition of the lowest energy all-trans silicon backbone segments only.[1] Hence, a better estimate of the optical band gap can be derived from fluorescence excitation and emission spectroscopy. In going from **1** to **4** the shift in the fluorescence excitation and emission maxima is 12−20 nm (Table 1). This is in line with a decrease of the optical band gap of ca. 0.15 eV.[35]

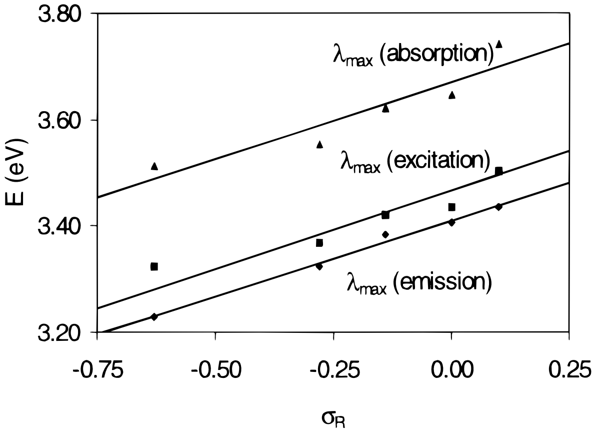

Figure 5. UV absorption maximum ($\sigma \rightarrow \sigma^*$) and the fluorescence excitation and emission maxima of **1**−**5** vs the Hammett constants σ_R of the aryl substituents.[30]

Hence, we conclude that for **1**−**5** substitution of the aryl moiety does affect not only the valence band edge considerably but also the conduction band edge, although less dramatically. The latter contention is corroborated by a Hammett analysis of the spectroscopic data (Table 1 and Figure 5). For both the excitation and emission data good to excellent correlations were found (excitation, r^2 = 0.991; emission, r^2 = 0.991). The fact that the calculated slopes are nearly identical gives further evidence that in **1**−**5** the distribution of chromophores is comparable. It is noteworthy that the Hammett correlation using λ_{max} ($\sigma \rightarrow \sigma^*$ transition) gave a considerably lower correlation coefficient (r^2 = 0.864). This is in agreement with the above-mentioned considerations that the fluorescence data provide a more accurate description of the optoelectronic characteristics of the lowest energy all-trans conformations and are consequently less sensitive for small variations in the overall polymer composition.

In this context the Hammett reaction constant ρ, which gives a measure of the sensitivity of the monitored process toward electrical perturbations by the substituents,[31] is of interest. The correlation of the optical characteristics, i.e., fluorescence excitation and emission and UV absorption, yields ρ = 0.29. In marked contrast, the correlation of V_i renders a substantially larger ρ (0.85). Apparently the band gap energy, which is related to the valence and conduction band edges, is less sensitive to electronic effects. As discussed above, the structures of polysilanes **1**−**5** are identical, and as a result the response of the conduction band edge toward electrical perturbations can be straightforwardly estimated (ρ = 0.60).[36]

This sensitivity of the conduction band edge is absent in polysilanes and polysilynes containing alkyl side groups, in which it remains virtually unchanged.[11,21] Therefore, the coupling has to be a result of electronic interaction of the aryl moieties with the silicon backbone, not only in the valence band but also in the conduction band. This is of considerable interest in view of the results of simple electronic structure calculations;[11] no evidence for $\sigma^*-\pi^*$ mixing was found. However, a satisfactory explanation can be found in the fact that the polysilanes **1**−**5** are amorphous materials.[23] As a result, a random conformation is expected in which no significant translational symmetry is present, thus limiting the reliability of band structure calculations, which inherently assume periodicity. It is noteworthy that electronic structure calculations on polysilane **1**, in which the phenyl groups are no longer positioned perpendicular to the backbone, already indicate slight $\sigma^*-\pi^*$ mixing.[11] In retrospect it is therefore not surprising that a disordered amorphous system also exhibits significant $\sigma^*-\pi^*$ mixing.

Effect of Si Catenation. To exclude the fact that the observed shifts in V_i are due to the onset of oxidation of an isolated substituent (chromophore), we have also compared 4-(dimethylamino)phenyltrimethylsilane with **4**. Whereas for **4** an onset of oxidation is found of 0.23 V, V_i is 0.55 V for 4-(dimethylamino)phenyltrimethylsilane. It is noteworthy that the peak potential for oxidation (V_{peak}) of 4-(dimethylamino)phenyltrimethylsilane is 0.71 V,[30] indicating that for molecular compounds only a small (0.16 V) difference exists between V_i and V_{peak}. Although, unfortunately, the onsets of oxidation of other model compounds are located outside the electrochemically available potential window in THF/$LiClO_4$, based on literature data the V_i of 4-methoxyphenylmethyltrimethylsilane can be estimated at ca. 1.6 V,[30] and consequently the V_i of phenyltrimethylsilane will be even more positive. The substantial shifts in V_i in going from monomer to polymer (ranging from 0.32 V to well above 1.00 V) further confirm that the measured V_i values of **1**−**5** reflect the valence band edge of the σ-conjugated silicon backbone. A similar effect of catenation on the oxidation potential was previously found for oligomeric permethylsilanes using both electrochemical methods[37] and photoelectron spectroscopy.[38]

Nonionic Water-Soluble Polysilanes. It is of interest to compare the results of **1**−**5** with those of the recently reported nonionic water-soluble polysilanes with one oligo(oxyethylene) substituent,[6−8] which due to the presence of their polar substituents are promising potential candidates for thin film applications. However, V_i of **7** is shifted to 0.94 V (Figure 3 and Table 2), which is significantly higher than that of the polysilanes **1**−**5**. In contrast to functionalized aryl-substituted polysilanes, adjusting the band gap in aliphatic polysilanes such as **7**, cannot be easily accomplished.

Therefore, we have combined the advantageous properties of both polysilanes, resulting in **6** as a representative example. The V_i of **6** is located at 0.58 V, showing as expected comparable electrochemical behavior to **3** (V_i = 0.61 V), combined with enhanced solubility/polarity. It is noteworthy that another advantage of polysilanes with this type of substituent is the possibility of further chemical modification after polymerization.[39]

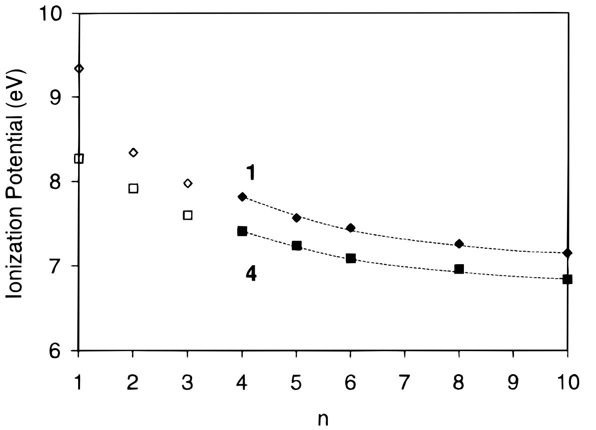

Figure 6. Dependence of the ionization potential (I_p) as a function of the oligomer length *n*. Fragments of up to 10 silicon atoms of **1** and **4** were studied with semiempirical PM3 methods.

Semiempirical PM3 Calculations. To further support the observed electronic properties, semiempirical PM3[18] calculations on oligomers of **1** and **4** of up to 10 silicon atoms were performed. Previous investigations indicated that semiempirical AM1 and PM3 methods give reasonable and quantitatively correct results in calculating various polysilane properties.[40−42] However, it should be noted that in these PM3 calculations an all-trans backbone is assumed, although, as was mentioned earlier, the polymer is amorphous and present as a random coil in solution. Because in polysilanes the backbone conformation strongly influences the polymer properties,[1,43] the PM3 calculations will only give a qualitative description. Notwithstanding, since it is our primary objective to gain insight into the pertubation induced by introduction of a substituent in the aryl moiety and especially its effect on V_i, the all-trans conformation was chosen in our calculations. Previously reported data have shown that in phenyl-substituted silanes the largest pertubation is found for this particular conformation.[11]

In contrast to the heat of formation (ΔH_f^0), the first ionization potential, I_p, of **1** and **4** does not exhibit a linear relationship with the oligomer length *n* (Figure 6).[44] As expected, with increasing conjugation length I_p converges to a constant value.[1] It should be stipulated that a survey of the PM3 highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as a function of oligomer length *n* revealed that the typical σ-conjugated character becomes discernible from $n = 4$ (HOMO; primarily Si 3p character along the catenated silicon backbone and LUMO; primarily Si 3s/3p character).

The effect of the introduction of a functionalized aryl side chain moiety is reflected in a lowering of the ionization potential (I_p) of 0.31 eV in going from **1** to **4**, which compares favorably with the shift of V_i of 0.58 V (Table 2). Additional semiempirical PM3 calculations on polysilane radical cations indicate a noticeable stabilization of the positive charge by an electron-donating substituent. For example, in the radical cations of oligomers consisting of 10 units, upon going from **1** to **4**, the positive charge on the silicon atoms not only is spread over the full length of the silicon backbone, as expected for a delocalized system,[41] but also decreases from 0.772 to 0.703. This behavior is in agreement with the results of earlier MNDO calculations[17] and is also reflected in the changes of the Si−Si bond lengths in the neutral and the radical cationic state.[45] Effectively, in the radical cations the electron-donating substituent can partially compensate the positive charge on the polymer backbone and therefore stabilize it toward doping or (photo)oxidation. It is noteworthy that the stabilizing effect is not exceptionally large. A much larger stabilizing effect, i.e., a stronger donor, would result in more cationic charge at the substituent, ultimately leading to charge localization, which would be unfavorable for conduction. However, photophysical measurements of **4** gave a coherence length of 34 silicon units, indicating that no such substantial localization occurs.[16]

Conclusions

The nature of the substituents has a large influence on important polysilane properties. The understanding of and control over the position of the band gap energy levels is essential for applications. It has been demonstrated that electrochemical methods provide an excellent means of estimating the valence band edge “HOMO”, by measuring the onset of oxidation V_i. By a careful choice of substituents, the valence and conduction band edges can be tailored to the desired level. We have demonstrated that the valence band edge can be adjusted over 0.7 V, when going from an aliphatic polar polysilane **7** to polysilane **4**, which contains aromatic electron-donating groups. The observed shifts of V_i in **1**−**5** can be analyzed with a Hammett-type equation, indicating that V_i is a function of the σ value of the appropriate substituent, thus creating a powerful tool for the prediction and tailoring of functionalized polysilanes. Semiempirical PM3 calculations on polysilane oligomers ground state and radical cations support the experimental results. It is demonstrated that these modified polysilanes are promising candidates for application in polymer-based devices.

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. UV−vis−NIR spectra were obtained with a Varian Cary 5 UV−vis−NIR spectrophotometer. Fluorescence spectra were collected on a Spex Fluorolog apparatus. DSC measurements were performed on a Mettler DSC 12E apparatus at scan rates of 10 °C/min. The handling of air/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.

Synthesis (See Also Scheme 1). Poly(methylphenylsilane) (**1**) was prepared using either Na or C_8K as the reducing agent. However, for all electrochemical and optical experiments **1** prepared via the conventional Na-based polymerization was used (vide supra).[1,14,16] General procedure for Wurtz-type polymerizations: To a stirred suspension of molten Na (6.53 g, 0.28 mol) in toluene (250 mL) at reflux temperature was added dichloromethylphenylsilane (27.93 g, 0.15 mol) in toluene (100 mL) over a period of 15 min. The reaction was allowed to proceed at reflux temperature for 2 h, after which it was cooled with an ice bath (0 °C) and excess Na was destroyed by the careful addition of CH_3OH (80 mL). Subsequently, the heterogeneous reaction mixture was added to CH_3OH (350 mL). After standing for 2 h all polymer precipitated and was isolated by filtration. Three reprecipitations from toluene/CH_3OH mixtures yielded pure **1** (7.97 g, 47% yield). Bimodal weight distribution: $M_w = 2.3 \times 10^5$ ($D = M_w/M_n = 1.4$) and $M_w = 1.8 \times 10^4$ ($D = M_w/M_n = 1.8$). ^{1}H NMR (CD_2Cl_2): δ 7.4/6.3 (br, C−H), 0.2/-0.9 (br, Si−CH_3) ppm. ^{13}C NMR: δ 136.91, 135.39, 127.52, −5.96 ppm. ^{29}Si NMR: δ −37/−42 ppm.

For comparison **1** was also prepared using C_8K as the reducing agent following literature procedures.[6,19,20] In a typical polymerization starting from dichloromethylphenylsilane (37.52 g, 0.20 mol) and C_8K, which was prepared from K (15.38 g, 0.40 mol) and graphite (41.86 g, 3.5 mol), high molecular weight **1** was obtained (2.78 g, 12% yield). $M_w = 2.6 \times 10^4$ ($D = M_w/M_n = 2.0$) (see text).

Poly(methyl-4-methylphenylsilane) (**2**) was obtained using a conventional Wurtz-type coupling of methyl-4-methylphenyldichlorosilane. Methyl-4-methylphenyldichlorosilane was prepared by addition of 4-bromotoluene (22.50 g, 0.13 mol) in Et_2O (150 mL) to a stirred mixture of Mg [(7.13 g, 0.29 mol; activated with 1,2-dibromoethane (0.2 mL)] and Et_2O (75 mL) at such a rate to maintain the Et_2O at reflux temperature. After stirring for 2 h at room temperature, the Grignard reagent was decanted from the Mg and slowly added to a solution of CH_3SiCl_3 (44.69 g, 0.30 mol) in Et_2O (150 mL). The reaction was allowed to proceed for an additional 2 h, after which the solvents and the excess CH_3SiCl_3 were removed in vacuo. The residue was purified by Kugelrohr distillation. Pure methyl-4-methylphenyldichlorosilane (16.53 g, 61% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 7.76 (d, C−H), 7.39 (d, C−H), 2.51 (s, C−CH_3), 1.14 (s, Si−CH_3) ppm. ^{13}C NMR: δ 142.13, 133.23, 130.14, 129.30, 21.74, 5.71 ppm. ^{29}Si NMR: δ 18.90 ppm. Polysilane **2** was prepared using a conventional Wurtz-type coupling with Na in toluene[1,14,16] from methyl-4-methylphenyldichlorosilane (9.61 g, 47 mmol) and Na (2.10 g, 91 mmol) following the procedure described for **1**. After three reprecipations from toluene/CH_3OH of the crude polymer, high molecular weight **2** (1.06 g, 20% yield) was obtained. Bimodal weight distribution: $M_w = 3.4 \times 10^5$ ($D = M_w/M_n = 1.8$) and $M_w = 6.4 \times 10^3$ ($D = M_w/M_n = 1.5$). ^{1}H NMR ($CDCl_3$): δ 7.1/6.1 (br, C−H), 2.5/1.9 (br, C−CH_3), 0.3/-1.0 (br, Si−CH_3) ppm. ^{13}C NMR: δ 136.57, 135.15, 133.04, 127.77, 21.39, −6.63 ppm. ^{29}Si NMR: δ −39/−42 ppm.

Poly(4-methoxyphenylmethylsilane) (**3**) was obtained using a conventional Wurtz-type coupling of 4-methoxyphenylmethyldichlorosilane. 4-Methoxyphenylmethyldichlorosilane was prepared by the addition of 4-bromoanisole (19.21 g, 0.10 mol) in THF (125 mL) to a stirred mixture of Mg [(4.22 g, 0.17 mol; activated with 1,2-dibromoethane (0.2 mL)] and THF (125 mL) at such a rate to maintain THF at reflux temperature. After stirring overnight at room temperature, the Grignard reagent was decanted from excess Mg and slowly added to a solution of CH_3SiCl_3 (36.06 g, 0.24 mol) in THF (100 mL). The reaction was allowed to proceed for an additional 48 h, after which the solvents and the excess CH_3SiCl_3 were removed in vacuo. The residue was purified by Kugelrohr distillation. Pure 4-methoxyphenylmethyldichlorosilane (10.48 g, 46% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 7.73 (d, C−H), 7.03 (d, C−H), 3.86 (s, O−CH_3), 1.08 (s, Si−CH_3) ppm. ^{13}C NMR: δ 162.27, 134.74, 124.24, 113.99, 54.96, 5.52 ppm. ^{29}Si NMR: δ 18.78 ppm. Polysilane **3** was prepared using a conventional Wurtz-type coupling with Na in toluene[1,14,16] from 4-methoxyphenylmethyldichlorosilane (4.98 g, 23 mmol) and Na (1.02 g, 44 mmol) following the procedure described for **1**. After three reprecipations from toluene/CH_3OH of the crude polymer, high molecular weight **3** (1.19 g, 35% yield) was obtained. Bimodal weight distribution: $M_w = 1.4 \times 10^5$ ($D = M_w/M_n = 1.4$) and $M_w = 1.8 \times 10^4$ ($D = M_w/M_n = 1.7$). ^{1}H NMR (CD_2Cl_2): δ 7.0/5.9 (br, C−H), 3.9/3.3 (br, O−CH_3), 0.3/−1.0 (br, Si−CH_3) ppm. ^{13}C NMR: δ 159.57, 135.74, 127.34, 112.91, 54.80, −5.96 ppm. ^{29}Si NMR: δ −39/−42 ppm.

Poly[4-(dimethylamino)phenylmethylsilane] (**4**) was obtained using a conventional Wurtz-type coupling of 4-(dimethylamino)phenylmethyldichlorosilane. 4-(Dimethylamino)phenylmethyldichlorosilane was prepared by the addition via a syringe of *n*-butyllithium (1.6 M solution in *n*-hexane; 96 mL, 0.15 mol) to a solution of 4-bromo-*N*,*N*-dimethylaniline (21.31 g, 0.11 mol) in *n*-hexane (150 mL). The mixture was stirred overnight, after which a pale yellow precipitate was formed. The reaction mixture was filtered, and the residue was washed with *n*-hexane (3 × 40 mL) and, subsequently, dried in vacuo. The 4-(dimethylamino)phenyllithium solid was dissolved in THF (100 mL) and added dropwise to a solution of CH_3SiCl_3 (41.93 g, 0.28 mol) in THF (100 mL) for 3 h. The mixture was stirred at room temperature for 48 h, after which the precipitated salts were removed from the reaction mixture by filtration. The solvents and the excess CH_3SiCl_3 were removed in vacuo, and the crude 4-(dimethylamino)phenylmethyldichlorosilane was purified by Kugelrohr distillation, yielding the pure monomer (9.70 g, 39% yield). ^{1}H NMR ($CDCl_3$): δ 7.62 (d, C−*H*), 6.79 (d, C−*H*), 3.04 (s, N−C*H*$_3$), 1.05 (s, Si−C*H*$_3$) ppm. ^{13}C NMR: δ 152.48, 134.43, 117.98, 111.58, 39.98, 5.84 ppm. ^{29}Si NMR: δ 18.86 ppm. Polysilane **4** was prepared using a conventional Wurtz-type coupling with Na in toluene[1,14,16] from 4-(dimethylamino)phenylmethyldichlorosilane (9.70 g, 41 mmol) and Na (1.85 g, 80 mmol) following the procedure described for **1**. After three reprecipations from toluene/CH_3OH of the crude polymer, high molecular weight **4** (0.79 g, 12% yield) was obtained. $M_w = 9.5 \times 10^3$ ($D = M_w/M_n = 2.4$). ^{1}H NMR ($CDCl_3$): δ 7.5/6.2 (br, C−*H*), 3.2/2.8 (br, N−C*H*$_3$), 0.5/−0.5 (br, Si−C*H*$_3$) ppm. ^{13}C NMR: δ 149.00, 136.17, 130/120 (very broad), 112.54, 40.17, −6.18 ppm. ^{29}Si NMR: δ −38/−43 ppm.

Poly(3-methoxyphenylmethylsilane) (**5**) was obtained using a conventional Wurtz-type coupling of 3-methoxyphenylmethyldichlorosilane. 3-Methoxyphenylmethyldichlorosilane was prepared following the procedure described for **3** from the Grignard reagent of 3-bromoanisole (8.25 g, 44 mmol) and 1,2-dibromoethane (0.2 mL) activated Mg (3.20 g, 0.13 mol). Starting from this Grignard reagent and CH_3SiCl_3 (18.83 g, 0.13 mol) pure 3-methoxyphenylmethyldichlorosilane (5.10 g, 46% yield) was obtained after Kugelrohr distillation. ^{1}H NMR ($CDCl_3$): δ 7.34−7.23 (m, C−*H*), 6.99 (m, C−*H*), 3.75 (s, O−C*H*$_3$), 0.97 (s, Si−C*H*$_3$) ppm. ^{13}C NMR: δ 159.48, 134.80, 129.80, 125.21, 118.43, 117.33, 55.16, 5.54 ppm. ^{29}Si NMR: δ 18.61 ppm. Polysilane **5** was prepared using a conventional Wurtz-type coupling with Na in toluene[1,14,16] from 3-methoxyphenylmethyldichlorosilane (3.86 g, 17 mmol) and Na (0.79 g, 34 mmol), following the procedure described for **1**. After three reprecipations from toluene/CH_3OH of the crude polymer, high molecular weight **5** (1.26 g, 48% yield) was obtained. Bimodal weight distribution: $M_w = 1.6 \times 10^5$ ($D = M_w/M_n = 1.5$) and $M_w = 1.1 \times 10^4$ ($D = M_w/M_n = 1.8$). ^{1}H NMR (CD_2Cl_2): δ 7.4/5.9 (br, C−*H*), 3.8/3.0 (br, O−C*H*$_3$), 0.5/−0.8 (br, Si−C*H*$_3$) ppm. ^{13}C NMR: δ 158.73, 137.85, 128.23, 127.40, 119.56, 114.50, 54.85, −5.93 ppm. ^{29}Si NMR: δ −38/−42 ppm.

Poly[4-(2-methoxyethoxy)phenylmethylsilane] (**6**) was synthesized in a three-step reaction sequence. First, 1-bromo-4-(2-methoxyethoxy)benzene was made according to a literature procedure.[46] Subsequently, a Grignard reagent was prepared by adding 1-bromo-4-(2-methoxyethoxy)benzene (10.0 g, 43 mmol) in THF (25 mL) to I_2 (50 mg) activated Mg (1.58 g, 65 mmol) and THF (75 mL) over a period of 1 h. CH_3SiCl_3 (12.9 g, 86 mmol) was added to the Grignard reagent, at −78 °C over a period of 1.5 h. The reaction mixture was allowed to warm to room temperature and stirred overnight. Subsequently, the excess CH_3SiCl_3 and the solvent were removed in vacuo, and the monomer was purified by two consecutive Kugelrohr distillations. Pure 4-(2-methoxyethoxy)phenylmethyldichlorosilane was obtained (2.0 g, 18% yield). ^{1}H NMR ($CDCl_3$): δ 7.67 (d, C−*H*), 7.00 (d, C−*H*), 4.15 (t, O−C*H*$_2$), 3.78 (t, O−C*H*$_2$), 3.44 (s, O−C*H*$_3$), 1.00 (s, Si−C*H*$_3$) ppm. ^{13}C NMR: δ 161.57, 134,85, 120.90, 114.66, 70.86, 67.19, 59.22, 5.69 ppm. ^{29}Si NMR: δ 18.80 ppm. Polysilane **6** was prepared in a conventional Wurtz-type coupling with Na in toluene,[1,14,16] from 4-(2-methoxyethoxy)phenylmethyldichlorosilane (1.71 g, 6.5 mmol) and Na (0.29 g, 13 mmol), following the procedure described for **1**. As a result of the enhanced solubility of **6**, as compared to **1**−**5**, preparative SEC (biobeads SX-1 gel, eluent THF) was employed to isolate the high molecular weight fraction; 0.55 g of high molecular weight **6** (44% yield) was obtained. $M_w = 3.7 \times 10^4$ (polydispersity = 1.8). ^{1}H NMR (CD_2Cl_2): δ 7.51 (br, C−*H*), 6.90 (br, C−*H*), 4.11 (t, O−C*H*$_2$), 3.73 (t, O−C*H*$_2$), 3.42 (s, O−C*H*$_3$), 0.32 (br, Si−C*H*$_3$) ppm. ^{13}C NMR: δ 159.23, 136,89, 128.00 (br), 114.23, 71.38, 67.47, 59.13, −0.01 ppm. ^{29}Si NMR: δ −39/−43 ppm.

Poly(4,7,10,13-tetraoxatetradecylmethylsilane) (**7**) was prepared according to a literature procedure.[8] All polymer properties were in agreement with those previously reported.[8]

Electrochemistry. Electrochemical measurements were performed with a Princeton Applied Research (PAR) model 263 potentiostat. The scan rate employed was 50 mV/s. All measurements were conducted in THF solution, which was directly distilled before use from Na/benzophenon. All measurements were performed under an inert (N_2) atmosphere. Anhydrous $LiClO_4$ was used as the electrolyte in 0.2 M concentration. A three-electrode setup was used, with a Pt disk electrode (with an area of 0.78 mm^2) and a Pt counter electrode. The reference system (Ag/AgCl reference electrode) was obtained according to a literature procedure.[47] This electrode appeared to be substantially more stable than the Ag/$AgClO_4$ reference system, which is frequently employed in THF.[48] All potentials were referenced to SCE employing a known standard (ferrocene/ferrocinium couple) and are given in volts (V) versus SCE. All polymer solutions were prepared in a concentration of ca. 2 mg/mL. The onset of oxidation was determined by extrapolating the semilinear part of the initial current−potential curve, viz. between about 50 and 300 μA/cm^2, to a current density of 0 μA/cm^2.

Semiempirical PM3 Calculations. Semiempirical calculations were performed with the MOPAC 7.0 package,[49] which was compiled under IRIX6.2 for up to 250 heavy atoms. All calculations were performed with the RHF PM3 Hamiltonian; for radical cations both the UHF and the half electron approach RHF PM3 method were used as implemented in MOPAC.[18,49] All structures were optimized using the Eigenvector Following Routine (keyword EF) until a GNORM ≤ 0.05.

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