Synthesis and Spectroscopic Characterization of Heteroatom Polysilylenes: Poly(dialkoxysilylene)s and Evidence for Silicon σ−Oxygen n Mixing Interaction

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ABSTRACT: A new synthetic route to polysilylenes is reported which allows access to hitherto inaccessible heteroatom-substituted poly(dialkoxysilylene)s. Perchloropolysilane, $(SiCl_2)_n$, undergoes substitution by alcohols in the presence of an amine to yield monomodal poly(dialkoxysilylene)s with molecular weights (M_w) up to 62 000, ultraviolet (UV) absorption maxima due to the lowest energy σ−σ^* transition of the silicon backbone in the range 336−347 nm (red-shifted compared to dialkyl analogues), and fluorescence emission in the range 368−398 nm. Substitution with enantiopure chiral alcohols affords optically active polymers with matching UV and circular dichroism (CD) signals, indicating preferential screw sense helicity of the main chain, which is further investigated by force field calculations. Theoretical prediction of the reduction of the optical band gap due to interaction between silicon (σ) and oxygen lone pair (n) orbitals is confirmed.

Introduction

Understanding the structure, property, and functionality of chemical compounds and the relation between them is critical in the systematic design of new materials and their uses. Polysilylene research has seen intensive activity in the past two decades as these aspects have been explored, though in some areas, experimental confirmation of theoretical considerations is lacking due to limitations in synthetic procedures.[1] For example, linear $(SiH_2)_n$, one of the most fundamental model compounds[1] for computationally modeling polysilylenes, is still unsynthesized. There are very few data, theoretical or experimental, concerning the effect of other heteroatom-connected side chains on the silicon main chain, although halogen,[2a,b] thiophene,[2c] and pyrrole[2c] substituted polysilylene systems, and oxygen substitution in polysiloxanes and siloxene,[2d] have been recently treated theoretically, the latter indicating a potential reduction of the HOMO−LUMO optical band gap of conjugated silicon chains bearing oxygen substituents as a result of σ−n mixing. One of the main reasons for this lack of experimental data is the difficulty of access to such heteratom polysilylenes. The most widely used synthetic procedure is the Wurtz-type reductive coupling of dichlorosilanes mediated by molten sodium in refluxing toluene. However, these harsh reaction conditions limit side chains to essentially alkyl (usually saturated)[1] or aryl groups.[3a] Although there have been a number of innovative approaches applied to polysilylene syntheses,[4] there have been only a very few reports of routes to heteroatom-functionalized polymers.[5] Of these, most describe incomplete functionalization and in only one of the two side chains. Interestingly, although the masked disilene approach has been applied to the synthesis of certain amino-substituted polysilylenes,[5f,g] this method was not successful in the case of alkoxy substitution.[5g] There are several reports describing partial heteroatom functionalization by replacement of aryl groups[5a−c] or H,[5d,e] though substitution usually does not exceed 50−80% of available sites. Recently, however, virtually complete chloro-dearylation of poly(aryl−alkylsilylene)s has been demonstrated using acetyl chloride/aluminum chloride, and the resulting poly(alkyl−chlorosilylene)s were successfully substituted with alcohols, amines, and mercaptans, yielding polymers with one heteroatom per Si repeat unit.[6] Concerning poly[bis(heteroatom)silylene]s, there is mention of only one example, poly(dimethoxysilylene), which was synthesized by the anionic ring-opening polymerization (ROP) of octamethoxycyclotetrasilane and reported to have a M_w of 45 000 and UV absorption at 332 nm.[7]

We now report a new synthetic route to polysilylenes which allows access to hitherto inaccessible bis-heteroatom-substituted poly(dialkoxysilylene)s, in which the alkyl chain may be saturated or unsaturated. Recently, by the ROP of octachlorocyclotetrasilane,[8,9] we obtained crystals of perchloropolysilane, $(SiCl_2)_n$, and demonstrated by single-crystal X-ray diffraction the only conclusively proved example of a polysilylene with a crystallographically all-anti backbone conformation.[10] This almost insoluble, off-white material is highly reactive, as is to be expected of a material with unprotected Si−Cl bonds, and we now describe the reaction of this material with a number of alcohols in the presence of an amine and the spectroscopic investigations of the resulting soluble dialkoxy-substituted polysilylenes **1**−**7** (molecular weights up to 62 000), which are not accessible by other routes. These experimental data are consistent with the theoretical prediction[2d] that the UV spectra of conjugated silicon should be bathochromically shifted relative to dialkyl analogues due to optical band gap reduction resulting from interaction between silicon (σ) and oxygen lone pair (n) orbitals. Force field calculations for a model perchloropolysilane, $Cl-(SiCl_2)_{30}-Cl$, indicate an all-anti structure, in agreement with our previously published single-

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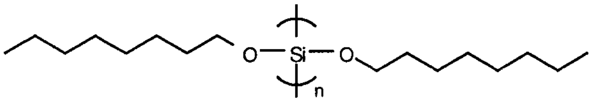
Chart 1



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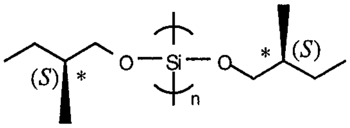

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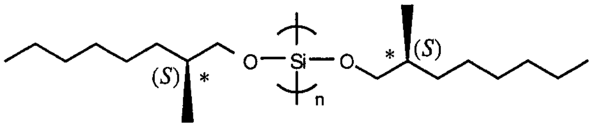

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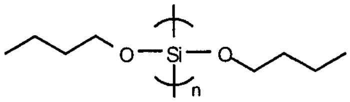

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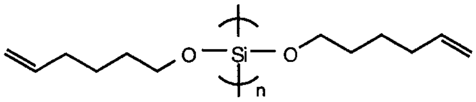

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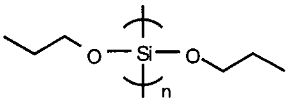

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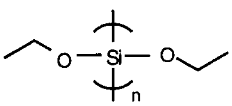

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crystal X-ray structure determination. Force field calculations for a model poly(bis-alkoxysilylene), BuO$-$[Si(OBu)$_2$]$_{30}$$-$OBu, indicate that a helical structure is preferred, in accordance with the CD studies of polymers bearing enantiopure chiral alkoxy side chains.

Experimental Section

General. Molecular weights were determined by size exclusion chromatography (SEC) on a Shodex column (eluant THF) in a Shimadzu liquid chromatograph machine equipped with a diode array detector and calibrated using polystyrene standards. UV$-$vis spectra (room temperature, 21 °C) were recorded on a JASCO V-570 spectrometer at ca. 2×10^{-4} mol dm^{-3} concentration. Variable temperature circular dichroism (CD) and simultaneous UV$-$vis spectra were recorded using a JASCO J-720 spectropolarimeter and Peltier control for temperatures from 80 to -10 °C (1 cm path length cell, sample concentration ca. 2×10^{-4} mol dm^{-3}) and with a liquid nitrogen-cooled cryostat for temperatures down to -70 °C (0.5 cm path length cell). Fluorescence spectra were recorded on a Hitachi F-850 spectropolarimeter at room temperature. NMR spectra were recorded on a Varian Unity 300 spectrometer in $CDCl_3$ or toluene-d_8. Since the elemental analyses of polysilylenes generally are very unreliable due to the high ceramic yields, these were not attempted. All of the apparatus was oven-dried, and standard techniques were employed for handling air- and moisture-sensitive compounds. Perchloropolysilane, $(SiCl_2)_n$, was synthesized as previously described.[10] Solvents and alcohols were purchased dry and stored over type 4A molecular sieves. Force field calculations were performed using Discover 3 (version 4.00, standard pcff parameters) from Molecular Simulations Inc.

Polymers. Poly(alkoxysilylene)s **1**$-$**7** (see Chart 1) were prepared by reaction of $(SiCl_2)_n$ with an excess of the appropriate alcohol in toluene at low temperature in the presence of an amine to complex liberated HCl. The synthesis of poly[bis-{(*S*)-2-methyloctoxy}silylene], **2**, is representative: to $(SiCl_2)_n$ (0.520 g, 5.253 mmol) in a Schlenk flask at -80 °C under an inert atmosphere was added toluene (30 mL) and a mixture of (*S*)-2-methyloctanol (3.026 g, 0.0210 mmol, 4 equiv; Japan Energy Corp., Tokyo) and pyridine (1.25 g, 0.0158 mmol, 3 equiv) by syringe. The vessel was shielded from light, and the mixture was allowed to warm to room temperature while stirring. After the reaction was complete, as evidenced by the precipitation of pyridinium hydrochloride and by SEC/UV analysis, the mixture was filtered through a glass frit, and volatiles were removed under high vacuum, yielding the product as a gummy, off-white material. Yield: 1.22 g (74 %). (The remainder of the yield was possibly lost by surface degradation of $(SiCl_2)_n$ either photolytically during synthesis or hydrolytically during storage or reaction.)

Poly[bis-(*S*)-2-methylbutylsilylene] (**15**) was synthesized from dichlorobis[(*S*)-2-methylbutyl]silane (**18**) for the purpose of comparison of symmetrical dialkoxy and dialkyl polysilylenes according to the conventional Wurtz-type procedure. Monomer **18** was synthesized according to the literature.[11a] **15** was prepared by addition of the monomer to a flask containing 7 equiv of sodium and 0.01 equiv of 15-crown-5 in toluene with stirring at 110 °C (toluene reflux). After 8 h, the purple mixture was diluted with toluene and filtered through a 10 μm Teflon filter. **15** ($M_w = 2000$, yield 6.5%) was isolated by centrifugation after fractional precipitation in a mixed 2-propanol$-$toluene solution and vacuum-dried at 80 °C for 24 h. (See Supporting Information for spectroscopic data for **15**.)

Results and Discussion

Suspension of $(SiCl_2)_n$ (synthesized from octachlorocyclotetrasilane) in toluene at -80 °C, injection of an alcohol$-$pyridine mixture, and allowing the solution to warm to room temperature with gentle stirring afforded solutions of essentially monomodal poly(alkoxysilylene)s, as indicated in Scheme 1. Removal of precipitated chloride salts by filtration, and of volatiles under reduced pressure, afforded the poly(alkoxysilylene)s **1**$-$**7** as off-white gums.

Characteristics of Poly(dialkoxysilylene)s. Data for the polymers are reported in Table 1. As exemplified

Scheme 1

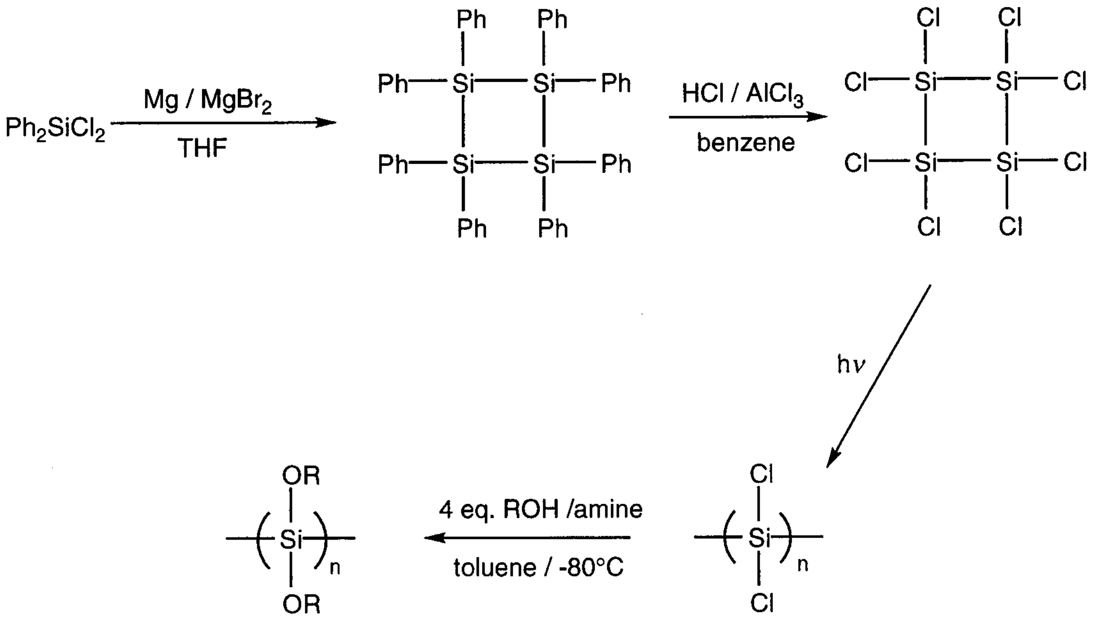

Table 1. Data for Poly(alkoxysilylene)s[a]

compd	substituent	UV[b] ϵ /λ_{max}/fwhm	FL λ_{max} /nm	^{29}Si NMR δ/ppm	M_w[c]	PDI[d]	yield[e] (%)
1	*n*-OctO	9300/344/22	370	−9.1	16 000	1.8	44
2[f]	(*S*)-2-MeOctO	3400/347/23	368, 497	−7.8, −58, −67	33 000	2.2	74
3	1-HexenO	2600/345/23	378	−9.0	27 000	2.3	71
4[f]	(*S*)-2-MeBuO	4500/340/30	377	−8.2	62 000	1.7	68
5	*n*-BuO	3800/340/29	375	−9.1	18 000	1.6	63
6	*n*-PrO	4000/336/31	386	−9.3	13 000	1.7	60
7	EtO	3100/337/38	347, 398	−10.4	3 000	1.5	41

[a] UV and fluorescence data at 21 °C. [b] ϵ units: (Si repeat unit)$^{-1}$ dm^3 cm^{-1}; λ_{max} units: nm; fwhm = full width (nm) at half-maximum of λ_{max}. [c] Molecular weights determined by size exclusion chromatography (SEC) and relative to polystyrene standards; eluant: THF. [d] PDI = polydispersity index (M_w/M_n). [e] Yields from $(SiCl_2)_n$. [f] CD data for **2**: (−10 °C): $\Delta\epsilon$ /λ_{max} = 0.37/339.4; $g_{abs} = 1.37 \times 10^{-4}$; for **4**: (−10 °C): $\Delta\epsilon$ /λ_{max} = −0.12/334; $g_{abs} = -0.25 \times 10^{-4}$; a small positive effect is also evident: $\Delta\epsilon$ /λ_{max} = −0.05/352; minor ^{29}Si NMR resonances at −58 and −67 ppm.

by poly[bis{(*S*)-2-methyloctoxy}silylene], **2**, the ^{29}Si NMR spectrum of poly(dialkoxysilylene)s obtained from primary alcohols typically exhibits a single resonance at ca. −8 to −9 ppm, assigned to catenating $Si(OR)_2$ units. In some cases, as in that of **2**, a resonance at ca. −67 ppm is apparent, which we tentatively assign to chain end $Si(OR)_3$ groups. The ^{1}H and ^{13}C NMR spectra of the polymers show broad resonances at chemical shifts close to those of the free alcohols (see Supporting Information), though not unexpectedly, the α-carbons adjacent to oxygen in the polymers resonate about 3 ppm to low field of the signal in the free alcohols. The room-temperature UV spectrum exhibits an absorption due to the polymer Si backbone σ−σ* transition at 336−347 nm, depending on substituent, with a half-height line width of about 20−30 nm. Fluorescence emission occurs at about 375 nm (see Figure 1), giving a Stokes shift of about 30 nm. (The fluorescence quantum yields were not quantitatively determined but are a factor of 2−4 smaller than those of typical poly(dialkylsilylene)s.[1]) The polymers are formed essentially monomodally (see Figure 2), indicating that within a particular sample of perchloropolysilane reasonable conformity of chain length is obtained and that, upon substitution, scission and cross-linking are not major processes. This is in contrast to the Wurtz-type synthesis, by which polymer products are often obtained polymodally (although under appropriate conditions, such as using C_8K at low temperature, monomodal product distributions have been reported[3] from the Wurtz reaction). Molecular weights are in the range 3000−60 000, lower values generally being observed for the shorter alkyl chain cases, though differences are observed from one synthesis to the next (presumably as a result of variation in perchloropolysilane crystal sizes) and hence degree of polymerization (DP). The indicated molecular weight for **4** of 62 000 corresponds to a DP of ca. 300, which may thus also be taken as a guide to the DP of perchloropolysilane. These data indicate essentially bis-substituted polymers and are consistent with the literature data for poly[di-

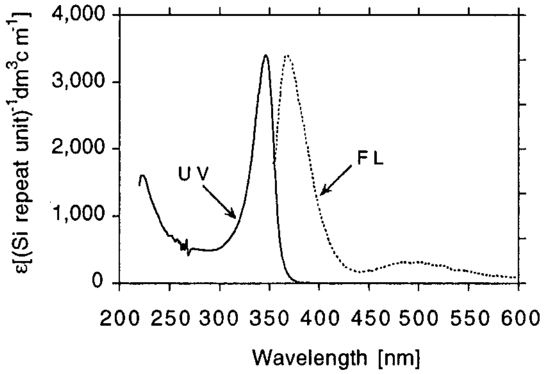

Figure 1. UV and fluorescence (FL) spectra for **2** at 21 °C in isooctane.

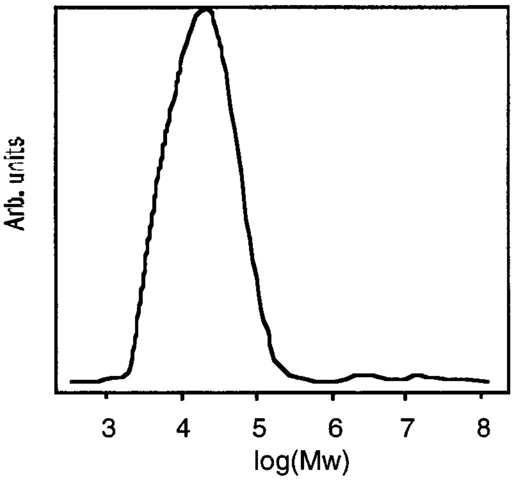

Figure 2. Molecular mass distribution of **2** (size exclusion chromatogram).

(methoxy)silylene] (λ_{max} = 332 nm, M_w = 45 000) synthesized by the ROP of octamethylcyclotetrasilane.[7] However, for **2**, some additional features are observed: a resonance at ca. −58 ppm in the ^{29}Si NMR spectrum of **2** and in the fluorescence spectrum a low intensity, long wavelength, broad emission at 496 nm (these features are not evident, though, in the spectra of **1**). Takeda et al. calculated[2d] the electronic band structures of several forms of siloxene, one of which was based on a linear chain model which effectively comprises polysilane chains with Si−O−Si cross-links. The band structure calculated renders possible both direct-gap and indirect-gap optical transitions and thus dual emission (though very weak from the indirect gap). The broad long wavelength emission observed for **2** could possibly, therefore, indicate Si−O−Si cross-links, presumably arising due to slight hydrolysis of Si−OR groups (or any remaining Si−Cl) and cross-linking at silicons bearing hydroxy groups. This would also account for the small, very high M_w fraction (4×10^7) peak in the size exclusion chromatogram (SEC) of **2** which shows the same UV absorption maximum (350 nm) as the main band (M_w = 33 000). An alternative possible origin for the broad weak emission would be from a Si−Si−Si branching defect caused by photdecomposition of the polymer and insertion of the resulting silylene radical into the backbone. While polymers with longer alkoxy chains are stable for months under inert atmosphere and react only slowly with water, as evidenced by the controlled addition of water to a sample and monitoring by UV spectroscopy, such cross-linking is greater in polymers with alkoxy groups of shorter length, such as **4**−**7**, presumably due to the lesser steric protection of the Si−OR bond afforded by the shorter alkyl chains.

The formation of soluble polymers with side chain alkenyl groups is often unsuccessful via the Wurtz synthesis; e.g., the polymerization of (6-hexenyl)methyldichlorosilane with a terminal alkene function[1] yields mainly insoluble, cross-linked material, though better results were obtained with the cyclic alkene-containing monomer,[11b] {2-(3-cyclohexenylmethyl)ethyl}methyldichlorosilane). The preparation from $(SiCl_2)_n$ of soluble **3** bearing two 6-hexenyloxy substituents, however, demonstrates that this method can provide access to polysilylenes with side chain double bond functionalities.

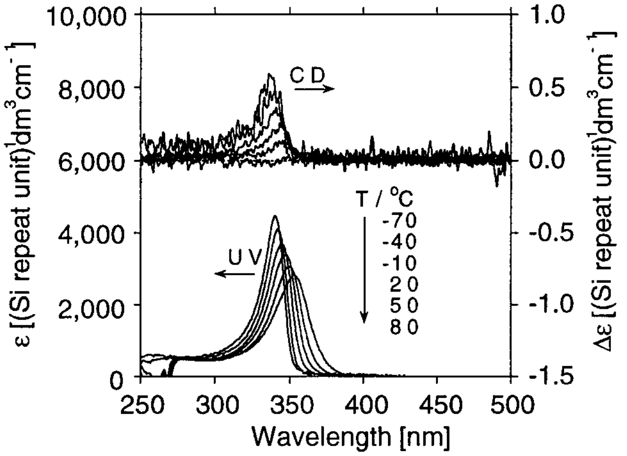

Figure 3. Variable temperature CD and UV spectra for **2** in isooctane.

Table 2. UV Spectroscopic Data for Symmetrical Poly(dialkylsilylene)s

compd	substituents R in $(SiR_2)_n$	λ_{max}/nm	ϵ^a	temp/°C	solvent	ref
8	*n*-Pr	310		RT	hexane	18a
9	*n*-Bu	314	4 600	RT	hexane	18a
10	*n*-Pent	315		RT	hexane	18a
11	*n*-Hex	316	8 600	RT	hexane	18a
12	*n*-Hep	318	10 700	RT	hexane	18b
13	*n*-Oct	321	11 200	RT	hexane	18b
14	*n*-Dec	322	10 900	RT	hexane	18b
15	*(S)*-2-MeBu	324	15 600	25	isooctane	this work
16	4-MePe	316	10 000	25	isooctane	18c
17	*(S)*-4-MeHex	316	8 800	20	isooctane	18c

[a] ε units: (Si repeat unit)$^{-1}$ dm^3 cm^{-1}.

Reaction of $(SiCl_2)_n$ with bulky or secondary alcohols afforded highly moisture-sensitive, soluble, gummy polymers, of lower molecular weight (<8000) with the UV absorption (maximum ca. 320 nm) blue-shifted and broadened relative to the products with primary alcohols described above. This is indicative of incomplete substitution, which is presumably due to the greater steric bulk of these alkoxy moieties: those already substituted onto the silicon chain preclude the nucleophilic attack of free alcohol molecules at the same and possibly adjacent silicon atoms.

Optical Activity of Poly(dialkoxysilylene)s Bearing Enantiopure Chiral Side Chains. In the case of **2**, containing two enantiopure chiral (*S*)-2-methyloctoxy groups per Si atom, optical activity is evidenced by the observation of a positive Cotton effect in the circular dichroism (CD) spectrum. This CD band is coincident with the UV absorption due to the silicon backbone σ−σ^* transition (see Figure 3) and indicates preferential screw sense helical order, arising from cooperative chiral side chain interactions, as has been observed in a number of dialkyl-,[12] alkyl−aryl-,[13] and diaryl-substituted polysilylene[14] systems. This is supported by the narrower UV absorption bandwidth and slightly longer wavelength, indicating a very regular backbone structure (optically active **15**, bearing two *(S)*-2-methylbutyl side chains, also absorbs at a longer wavelength compared to the other poly(dialkylsilylene)s in Table 2). The dissymmetric ratio, g_{abs} (defined[15] as the ratio of CD to UV molar absorptivities, $\Delta\epsilon/\epsilon$), for **2** at −70 °C is 1.61×10^{-4}. It has been suggested that in the case of poly[{*(S)*-2-methylbutyl}(6,9,12-trioxatetradecyl)silylene] a g_{abs} value of 2.8×10^{-4} (at −60 °C) may correspond to

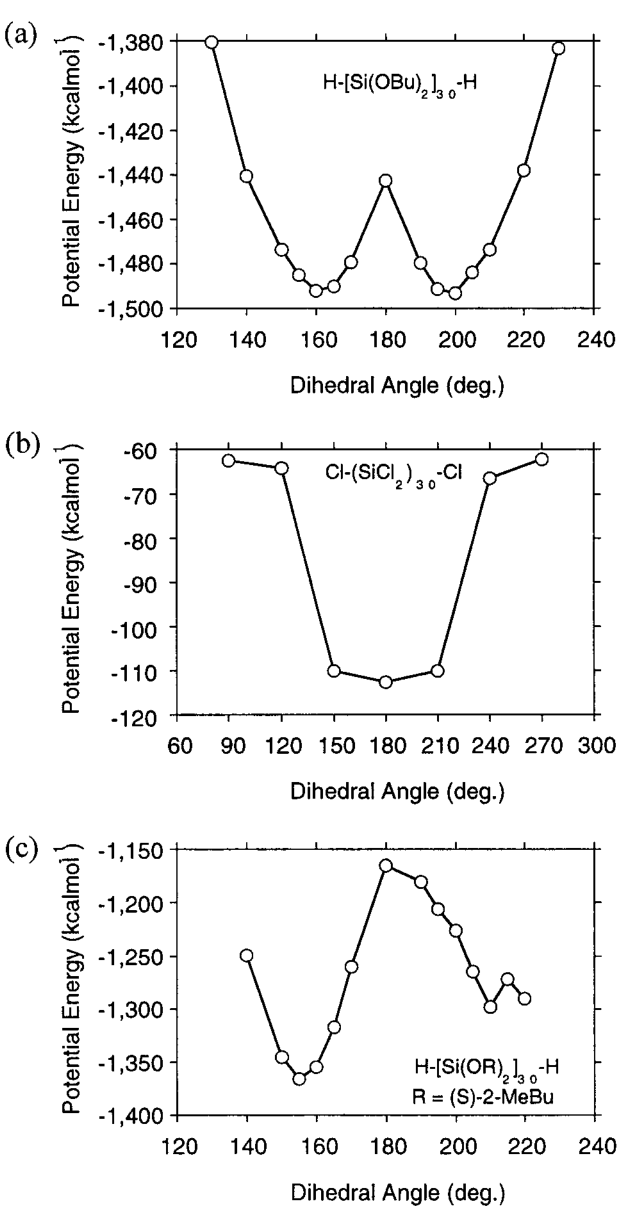

Figure 4. Results of force field calculations plotted as potential energy vs dihedral angle for the model polymers (a) $H-[Si(OBu)_2]_{30}-H$, (b) $Cl-(SiCl_2)_{30}-Cl$ and $H-[Si(OR)_2]_{30}-H$, where R = *(S)*-2-methylbutyl.

a single screw sense helical polysilylene main chain.[12d] It is likely, therefore, that the catenating Si backbone of **2**, while helical, contains segments of both plus (*P*) and minus (*M*) screw senses, one of which predominates. Similarly for **4**, bearing the enantiopure chiral (*S*)-2-methylbutyl side chain, a Cotton effect, negative at −10 °C, in contrast to the positive Cotton effect for **2**, is evident, indicating that this polymer also adopts a preferential, though opposite, screw sense. The suggestion that poly(dialkoxysilylene)s adopt helical backbone conformations is supported by force field calculations for the model polymer, $H-[Si(OBu)_2]_{30}-H$, which indicate equivalent minimum-energy conformations for dihedral angles of 160° and 200° (see Figure 4a); i.e., these polymers adopt helical backbone structures, of between approximately 7_3 and 15_7 screw pitch (ca. 47_{21}), but are optically inactive due to the presence of equal *P* and *M* turns. This is in contrast to the perchloropolysilane precursor, which we previously showed by a single-crystal X-ray diffraction study to adopt an all-anti conformation.[10] Although we surmised that crystal packing forces might be responsible for the observed all-anti alignment, force field calculations for $Cl-(SiCl_2)_{30}-Cl$ (see Figure 4b) also produce a minimum-energy conformation with dihedral angles of 180° (0 K, simple minimization). Force field calculations for the model polymer containing enantiopure chiral alkoxy side chains, $H-[Si(OR)_2]_{30}-H$, where R = *(S)*-2-methylbutyl, afford a markedly asymmetric potential energy vs dihedral angle plot (Figure 4c), indicating a preference for one screw sense over the other (dihedral angle 155°), consistent with the experimentally observed optical activity. For comparison with the butoxy-substituted model polymer, force field calculations were similarly carried out for $H-(SiPent_2)_{30}-H$, also containing a five-atom side chain. Minima are evident at 170° and 190° (see Supporting Information), indicating a helical conformation, consistent with the X-ray determination for poly(dipentylsilylene), though the experimentally determined[16] dihedral angles are ca. 154° and 206° (room temperature, solid state).

Comparison with Poly(dialkylsilylene)s. As can be seen by comparing the data for the poly(dialkoxysilylene)s in Table 1 with those for some closely related poly(dialkylsilylene)s in Table 2, the UV absorption wavelength maxima for the former are generally red-shifted about 20 nm compared to their symmetrical poly(dialkylsilylene) structural analogues. Such bathochromic shifts upon substitution of C with O on a silicon backbone have been reported in an interesting study on the free radical hydrosilylation of poly(phenylsilylene),[5e] in which substituted poly(phenylsilylene)s containing alkoxy side chains, $(PhSiOR)_n$, or their aliphatic structural analogues, $(PhSiR)_n$, were synthesized such as to allow the comparison of UV data between structurally comparable polymers. The UV absorption maxima of the alkoxy-substituted polymers were found to be red-shifted about 26 nm relative to the aliphatic-substituted polymers. The reason for this was discussed in terms of the interaction between the lone pair of electrons on the oxygen substituent and the polymer backbone electronic structure, resulting in a destabilization of the HOMO and concomitant decrease of the transition energy.[2d,5e] Our experimental results for poly(dialkoxysilylene)s are consistent with these observations and conclusions (though the UV absorption maxima occur at slightly shorter wavelengths than those in ref 5e, since the latter contain also one phenyl ring per Si repeat unit, which is acknowledged to cause a bathochromic shift[17] due to Si σ−phenyl π interaction). From these and our force field calculations, which indicate similar helical structures for alkoxy- and alkyl-substituted polymers, we conclude that the origin of the bathochromically shifted UV absorption in poly(dialkoxysilylene)s compared to poly(dialkysilylene)s is indeed electronic, through silicon σ−oxygen *n* orbital interaction, and not steric.

Thermochromism. Some of the poly(dialkylsilylene)s in Table 2 (e.g., **9**−**11**) exhibit abrupt thermochromism at lower temperatures with the appearance of a sharper, longer wavelength absorption (ca. 354 nm),[18a] the driving force of which has been attributed to both a single chain mechanism and conformation-dependent polymer−solvent dispersion interactions.[19] According to Schweizer's thermochromism theory, these polymers are strongly coupled, with $V_D/\epsilon > (V_D/\epsilon)_c$ (V_D is the backbone delocalized-electron contribution to the attractive polymer−

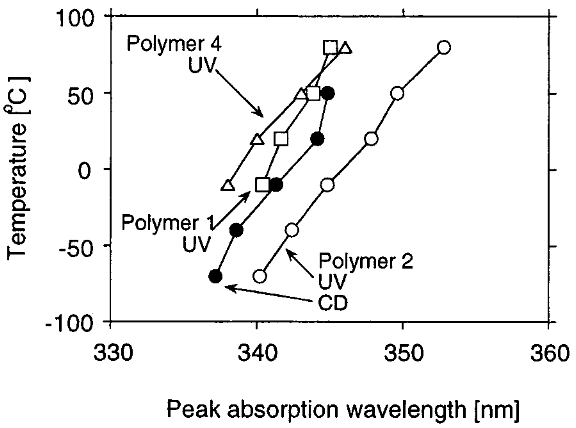

Figure 5. Thermochromism of **1** (toluene), **2** (isooctane), and **4** (toluene).

solvent dispersion interactions when the polymer main chain is in the fully ordered all-anti conformation; ϵ is the mean free energy of "defect" formation; subscript c refers to the critical value of the coupling constant, V_D/ϵ). For weakly coupled systems the theory predicts a smooth increase of conjugation length, and hence UV absorption maximum, on cooling (nonabrupt thermochromism). Such behavior is observed for polymer **8** in Table 2 and also poly(*n*-propylmethylsilylene) and poly(*n*-hexylmethylsilylene), which all show smooth bathochromic shifts (and no abrupt transition), attributed to a continuously increasing relative population of extended backbone sections with cooling.[18a] The theory has also been used[19] to explain the lack of, or only very weak, thermochromism in polymers such as poly(cyclohexylmethylsilylene),[20,21] poly(phenylmethylsilylene),[20,21] and poly(diarylsilylene)s,[22] which are considered to be conformationally locked, since the steric effects of the bulky groups imply a large value of ϵ and thus small coupling constant, V_D/ϵ. Indeed, the poly(diarylsilylene)s actually show small, smooth hypsochromic shifts on lowering the temperature.[14,22] Poly(dialkylsilylene)s bearing β-branched side chains are also considered to be sterically conformationally locked and exhibit small hypsochromic shifts.[12d]

For the poly(dialkoxysilylene)s, "coupled" thermochromic behavior as for **8**−**11**, where reduction in temperature results in bathochromic spectral shifts, has not been observed. Instead, as can be seen for **2** in Figure 3, and is replotted in Figure 5 for **2** and also for **1** and **4** (UV only), with wavelength as a function of temperature, both UV and CD spectral profiles undergo small monotonic *hypsochromic* shifts as the temperature is reduced from 80 to −70 °C for **2** and −10 °C for **1** and **4**, without any abrupt changes. This behavior is similar to that observed for the poly(diarylsilylene)s and β-branched poly(dialkylsilylene)s, though it is not clear whether conformational locking is responsible for the small V_D/ϵ value. If this were the case, it may reflect electronic locking in a helical conformation, since an all-anti backbone conformation would lead to a presumably unfavorable alignment of oxy-substituent dipoles on silicon atoms 1,3 to one another.[24] The fact that the observed shifts are hypsochromic in the poly(dialkoxysilylene)s may indicate that a decrease in temperature results only in slight bond contraction[12d,23] and little conformational change. Another factor in the unusual thermochromism of the alkoxy polymers may be greater side chain mobility: where the substituent is divalent oxygen, as opposed to tetravalent carbon, side chain packing effects may be significantly inhibited.

In conclusion, we have demonstrated a new synthetic approach to polysilylene synthseis which allows the preparation of hitherto inaccessible poly(dialkoxysilylene)s with saturated and unsaturated alkyl chains. The spectroscopic properties of these materials and effect of oxygen directly bound to the polysilylene backbone on the $\sigma-\sigma^*$ transition energy of the HOMO−LUMO optical band gap have been demonstrated and are consistent with experimental predictions. Data from experiment and calculation indicate these polymers adopt helical backbone conformations. The thermochromic characteristics are generally similar for all the poly(dialkoxysilylene)s studied and indicate that these polymers are conformationally robust. These thermochromic trends are different from those of related poly(dialkylsilylene)s. Further work on these and other heteroatom polysilylenes and the investigation of other reactions of perchloropolysilane are in progress.

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Supporting Information Available: NMR data (^{1}H, ^{13}C, and ^{29}Si) for poly(dialkoxysilylene)s (**1**−**7**) and poly[bis{(*S*)-2-methylbutyl}silylene] (**15**), circular dichroism (CD) and ultraviolet (UV) spectra for **15** (isooctane, 25 °C, 5×10^{-5} mol dm^{-3}), and plot of force field calculated potential energy vs dihedral angle for H−(SiPent$_2$)$_{30}$−H. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Although the ^{29}Si NMR resonances for **2** and **4** are broad ($\Delta\nu_{1/2}$ ca. 25 Hz), consistent with restricted backbone segmental motion and thus conformational locking, that for **1** ($\Delta\nu_{1/2}$ ca. 2 Hz) is sharp, although from the thermochromic characteristics are the same as **2** and **4** (see Figure 5).

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