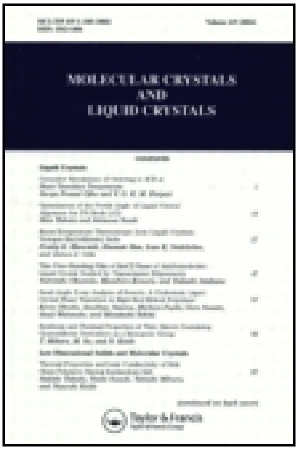

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One-Dimensional σ-Conjugated Polysilylenes—Science and Technology

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One-Dimensional σ-Conjugated Polysilylenes—Science and Technology

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Recent research on a relatively new class of polymeric materials, the polydiorganosilylenes (polysilanes), having a backbone composed entirely of Si-Si σ bonds, has demonstrated convincingly that σ-bonded materials can show many of the same consequences of electron delocalization that are normally ascribed to the more familiar π-conjugated materials like polyacetylenes, polythiophenes, and polydiacetylenes. Like the π-conjugated polymers, polysilylenes transport charge and energy efficiently in well-defined states. Unlike many π-conjugated polymers, the charge transport in polysilylenes is highly non-dispersive. Energy transport along the backbone via excitonic states is rapid relative to the rates of essentially all other photophysical and photochemical processes in polysilylenes. Thermochromic transitions are observed in both solutions and films of polysilylenes. Since these materials have no polar side chains to stabilize ordered conformations and even highly stereochemically disordered polysilylenes exhibit thermochromism, the driving force for the thermochromism is best understood as resulting from selective stabilization of an extended conformation by σ-electron delocalization. While polysilylenes share a number of properties with π-conjugated polymers, their unusual and highly adjustable photosensitivity sets them apart from carbon-based electronic materials. The particular mix of properties found in polysilylenes is unique among polymeric materials and has resulted in the rapid development of a number of interesting applications.

Long study and experience with carbon-based polymeric materials has led to the common and useful generalization that efficient charge and energy transport phenomena are the sole province of materials possessing extended π-conjugated double bond systems. While it has long been recognized from quantum chemical studies[1] that sp^3-hybridized, σ-bonded, carbon-based compounds should be capable of electron delocalization as a result of the nonzero transfer integrals between vicinal and geminal sp^3 hybrid orbitals, experiment reveals few consequences of such interactions. For example, even high molecular weight polyalkanes exhibit localized Rydberg excited states,[2] rather than any putative delocalized σ-σ* states.

Recent research[3] on a relatively new class of silicon-based materials, the polydiorganosilylenes (polysilanes), $(R_1R_2Si)_n$, having a backbone comprised entirely of Si-Si σ bonds, has demonstrated convincingly that σ-bonded materials can

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show many of the same consequences of electron delocalization that are normally ascribed to the more familiar π-conjugated materials like polyacetylenes, polythiophenes, and polydiacetylenes. In fact, in polysilylenes the effects of electron delocalization in the Si-Si backbone ripple through essentially all the properties of the materials. Although polysilylenes are the silicon analogues of polyolefins (polyalkanes) structurally, their electronic properties resemble more closely those of one-dimensional π-conjugated polymers. However, unlike many of the π-bonded carbon-based polymers, polysilylenes are almost invariably air-stable, processible by standard industrial techniques, and accessible with narrow molecular weight distributions and very high purity.

Although the study of soluble, high molecular weight polysilylenes did not begin in earnest until about 1980, a surprisingly broad group of applications has already been developed for the materials. Identified applications of polysilylenes can be grouped in three categories: those which take advantage of the unique polysilylene electronic properties, those which utilize their unusual chemistry, and those which depend upon the physical properties of the polysilylenes. Polysilylenes have been shown to be superb non-dispersive photoconductors[4] and charge transport materials for use in electrophotography.[5] As might be expected, the materials can also be doped to conductivities of about 1 S/cm.[6] Whereas the use of polysilylenes as photoconductors depends on their ability to transport charge, their application as nonlinear optical materials[7-9] takes advantage of their unusually well-developed capacity to transport ("delocalize") electronic excitations. Some polysilylenes show great promise as self-developing[10] or solvent-developed[11] positive-working photoresists for use in all manner of photopatterning operations, including VLSI microlithography. These polysilylenes have also been shown to be valuable as microlithographic contrast enhancement layers in submicron lithography,[12] and as etch barrier layers in microelectronic oxygen reactive ion etching.[10,13] Their efficient photochemistry in solution allows them to serve as photoactivated catalysts for olefin polymerization.[14] In an application already commercial in Japan, polysilylenes are useful precursors to β-SiC fibers,[15,16] which are used in advanced composites. Finally, polysilylenes are promising in applications where their high thermal stabilities and better strength may allow them to replace silicones in some cases.[10] The unique mixture of properties found in polysilylenes, unprecedented in any other single class of polymeric materials, can be substantially modified by changing the side groups, R_1 and R_2, bonded to the silicon backbone atoms, making the materials extremely flexible in their ability to meet the needs of different applications.

This paper will focus on the electronic and photochemical properties of polysilylenes, with particular emphasis on the many resemblances in the electronic properties of polysilylenes to those of the familiar π-conjugated polymers. In this context, the term "σ-conjugation" will appear in this paper, as it is almost universally prevalent in the field. However, the use of this term should only be interpreted to suggest a correspondence in the electronic properties with those of π-conjugated materials. No direct correspondence in electronic interactions at the atomic level is implied. In fact, the theoretical underpinnings of the mechanism of electron delocalization in σ-bonded systems remain incomplete, at best. The systematic name "polysilylene" will be used in place of the equivalent and widely used term "polysilane." In this context, these terms are intended to refer to poly*diorgano*silylenes, i.e. silicon backbones having substituents other than hydrogen. Moreover, since, with the exception of the commercial use of the intractable polydimethylsilylene as a precursor to β-SiC fibers, the overwhelming majority of the interest in the field is in *soluble* polysilylenes, the discussion here will be of that greatly predominant group of the materials which are fully tractable and processible.

Polysilylene synthesis

Polysilylenes are synthesized by a Wurtz-type reaction of various dichlorosilanes, which are readily available from the silicones industry, with molten sodium metal in an inert solvent. This reaction is the same one used by Kipping[17] in the probable first synthesis of an insoluble polysilylene. It provides a complex mixture of products from which polysilylene can be isolated by addition of non-solvents. Yields are typically low, 10–30% of theoretical yield. A much more critical issue has been the breadth of the molecular weight distribution obtained by typical literature procedures.[18–20] The insolubility of the sodium in reaction solvent leads to a surface-dominated reaction[21] which typically produces very broad molecular weight distributions. Studies of the mechanism by which this reaction occurs, which include intramolecular trapping results, strongly implicate radical intermediates as the propagating species[21,23] under the usual reaction conditions, although anionic intermediates have been proposed, but not trapped, for ultrasonic-mediated versions of this reductive coupling.[22]

More important, though, is the issue of how the highly non-statistical molecular weight distributions characteristic of these reactions are generated and why they show[21,23] such extreme sensitivity to minute changes in the solvent composition. A model invoking control of monomer concentration at the reactive sodium surface by the degree of compatibility between the solvent and growing polysilylene chain has been proposed to account for the features of the molecular weight distributions[23] obtained under typical synthesis conditions. This model allows calculation of the optimum solvent composition for the manufacture of any polysilylene polymer composed of one or any number of silylene monomers, making possible routine synthesis of narrow molecular weight distribution polysilylenes ($1.1 < M_w/M_n < 1.5$).

Although the Wurtz coupling still provides the only known route to narrow polydispersity polysilylene high polymers, its limitations with respect to tolerated functionality, yield, and sensitivity to reaction parameters have inspired considerable effort to develop alternate routes to the materials. Matyjaszewski, *et al.* have shown that some functional polysilylenes can be obtained by replacement of the phenyl groups on $(PhMeSi)_n$ with triflic acid.[24] Much current work is devoted to the development of catalytic oxidative routes[25] to polysilylenes from the corresponding silanes (R_1R_2SiH). However, to date, these oxidative routes have not yielded polymeric molecular weights and suffer from their own rather severe limitations of substitution on the silicon. Perhaps the most intriguing of the new methods for the synthesis of polysilylenes has been recently developed by Sakurai, *et al.*[26] This new route utilizes the anionic polymerization of a masked disilene precursor to form reasonably high molecular weight polysilylenes with greater control over sequence distributions in copolymers and the potential for stereochemical control, as well. Neither of these aspects is usually obtainable by the Wurtz coupling which tends to given random sequence distributions[20] and atactic stereochemistries.[27] This new method has not yet achieved the low polydispersities obtainable by well-controlled Wurtz-coupling routes, however.

Physical and thermal properties

Polysilylenes can be thought of as formal derivatives of polysiloxanes (silicones) formed by removing the oxygen atoms from the silicone backbone of alternating silicon and oxygen atoms. Since the removal of these oxygen atoms implies that the polysilylenes should have less ability to rotate about backbone bonds, we expect polysilylenes to be stronger, less rubbery materials than the corresponding polysiloxanes. In fact, the glass transition temperatures are substantially higher than silicones, as shown in Table I. Consistent with the low glass transition temperatures, rotational barriers in solution have been determined to be about 1 kcal/mole by application of a RISM model fit to temperature dependent absorption spectra,[28] pointing to a kinetically mobile backbone. In nitrogen, the decomposition temperatures of polysilylenes are typically in excess of 350°C; in air, incorporation of oxygen into the silicon backbone to form siloxane linkages becomes noticeable above 200°C.

Surprisingly, atactic polysilylenes, when compared to their polyolefin counterparts, tend to be relatively highly crystalline and much more crystalline than the corresponding silicones. To the extent that their crystal structures have been studied, we can say that they tend to assume all-*trans* conformations, at least for

TABLE I

Glass transition temperatures of polysilanes and polysiloxanes.

	T_g(°K)		T_m(°K)
R, R′	$(RR'Si)_n$	$(RR'SiO)_n$	$(RR'Si)_n$
Me, Me	NONE	150	648
n-Pr, Me	249	153	316
n-HEXYL, Me	220		275, 336
n-HEXYL, n-HEXYL			315
CYCLOHEXYL, Me	384		
Ph, Me	395	245	

symmetrically alkyl-substituted materials. However, there are cases ($(n\text{-}Bu_2Si)_n$ and $(n\text{-pentyl}_2Si)_n$)[29,30] where 7/3 helical conformations have been observed. These conformational changes have major effects on the electronic properties (*vide infra*) of the polysilylene backbone, just as in polythiophenes and polydiacetylenes.

Polysilylenes prepared to date are white solids in their pure state. Most are soluble in nonpolar organic solvents, primarily due to the highly nonpolar nature of the typical substituents found on the polysilylene silicon atoms. By protection of reactive functionality, water soluble polysilylenes have also been prepared.[31] Most of the materials form coherent films—a necessity for many of the proposed applications.

Electronic properties of polysilylenes

The unique character of polysilylenes among polymers lacking π-bonds was first glimpsed in early studies of the absorption spectra of oligomeric catenated silanes. These pioneering studies by Gilman[32] and later, by Allred[33] established that oligomeric silanes possess anomalously long wavelength absorptions, which shift to still longer wavelength with increasing catenation. Although the first soluble polysilylenes were reported in the patent literature by Clark in 1951–2,[34] he apparently did not study the absorption spectra over a range of molecular weights. With the essentially simultaneous work on soluble silylene high polymers by Trujillo[35] and West,[16,36] this molecular weight dependence was finally established over the full range of degree of polymerization. As in polyenes, the red shift with increasing catenation saturates asymptotically at high molecular weights.[37,38] However, in polysilylenes, the degree of catenation necessary to achieve saturation is considerably higher than in polyenes, i.e. around 50 Si-Si bonds in polysilylenes vs. about 20 C=C bonds in polyenes. It should be mentioned, however, that the effective saturation point in polysilylenes must be considered with respect to the property of interest and the method of measurement. The absorption spectrum reaches effective saturation at approximately 30 silicon atoms, while the fluorescence spectrum gives the number of about 50 quoted above. The issue of the number of silicons required to reach effective saturation has produced much disagreement in literature, primarily because different probes were utilized for measurement.

For aryl, alkyl-substituted polysilylenes with molecular weights sufficiently high to have reached the asymptote in the molecular weight dependence of the absorption position, the typical absorption is at 330–345 nm. For the corresponding alkyl polysilylenes, the asymptotic absorption is in the region 310–325 nm.[37,38,39] Recently reported diaryl polysilylenes have absorptions from 370–400 nm,[40] although it is not yet certain that the molecular weights of this last group of polysilylenes are all high enough to have reached the asymptote. For simple polysilylenes, the absorption position is not solvent dependent[38] to any significant degree, in the absence of complicating factors (*vide infra*).

Typical absorption and fluorescence spectra for an alkyl and aryl polysilylene are shown in Figure 1. As expected for a transition involving the σ-bonded backbone, the absorption spectra of polysilylenes are strongly polarized in the chain direction,[38] although several pieces of evidence suggest that the broad featureless absorption characteristic of polysilylenes is composed of more than one compo-

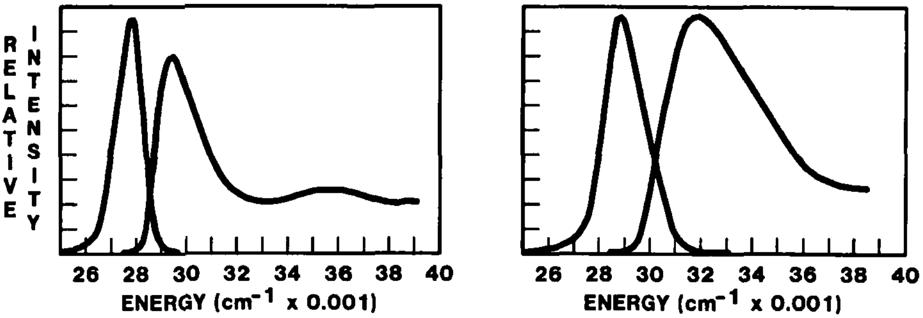

FIGURE 1 Characteristic Polysilylene Absorption and Fluorescence Spectra: (a) poly(phenylmethylsilylene); (b) poly(cyclohexylmethylsilylene).

nent.[38,42,43] The fluorescence spectra for polysilylenes are substantially narrowed relative to the width of the absorption spectra, are typically of high quantum yield (25–80%), and exhibit relatively small Stokes shifts. As in Figure 1, the fluorescent emissions of polysilylenes show no vibrational structure down to 1.4°K, although the emissions narrow somewhat at lower temperature.[28]

These findings all suggest that the low energy absorption in polysilylenes results from transitions involving the backbone electrons, despite the fact that they are in sp^3 hybrid orbitals. The narrowness of the fluorescence suggests that the width of the absorption spectrum is due to inhomogeneous broadening which is "washed out" as a result of rapid and efficient energy transfer in the excited state. By contrast, the corresponding polyolefins absorb much more weakly at much higher energy, typically about 180 nm, with a strong solvent dependence. In polyalkanes, the absorption is, in fact, of a totally different nature than that found in polysilylenes, i.e. a localized Rydberg state.[2]

While it would appear obvious to assign the low energy, molecular weight dependent absorption of polysilylenes that leads to the structureless, high quantum yield fluorescence as a σ-σ^* band-to-band transition, the actual situation is considerably more complicated. It was discovered at by Kepler, *et al.*, that the polysilylenes are exceptionally good non-dispersive photoconductors.[4] Polysilylenes were found to transport only holes with a quantum efficiency of carrier generation of about 1% and a hole mobility of 10^{-4}—numbers which compare favorably to those for polyacetylene and polydiacetylene, although these materials are considerably more dispersive in their transport than are polysilylenes. The action spectrum for carrier generation did not follow the absorption spectrum, in contrast to what would be expected for the σ-σ^* transition, but, rather, more closely followed the fluorescence spectrum. This showed very clearly that carrier generation in polysilylenes was an extrinsic process, i.e. absorption of light produced a highly mobile, but electrically neutral species which migrated to surface states and underwent charge separation to produce the hole charge carriers. This work indicated that the lowest energy transition was, in fact, a transition to a neutral exciton which creates charge carriers upon dissociation.[4] More recent work by Kepler suggests that the actual σ-σ^* band-to-band transition is almost 1 eV higher in energy that the neutral exciton state which accounts for the lowest energy transition.[41,42] Finally, recent two-photon absorption experiments by Hochstrasser, *et al.* have located yet another type of transition, which these workers have ascribed to a mobile charge-transfer exciton.[43] Thus, the characteristic featureless absorption of polysilylenes is seen to be comprised of at least three basic types of transition, all of which are inhomogeneously broadened and of which only the highest energy transition is the actual σ-σ^* so commonly referred to in the literature.

Excitonic excited states are not unprecedented in π-conjugated polymers. The low energy transition in polydiacetylenes, has been assigned to an exciton.[44] Of course, excitonic states are also well-precedented in π-conjugated molecular materials such as anthracene.[45]. The surprising aspect of the excitons in polysilylenes is their high mobility,[41] despite the fact that the polysilylenes studied to date have been disordered materials, while the previous materials which were shown to support this type of excited state were all single crystals. No convincing explanation of the exceptionally high excitonic mobility in polysilylenes has been offered to date.

Although the lack of structure and the narrowing relative to the absorption width indicate that the fluorescent state(s) are highly delocalized, the number of singlet states which undergo energy transfer in their subnanosecond lifetimes, the rate of that transfer, and the ultimate fate of those states must be obtained from other experiments. Michl *et al.*, have studied the width of the fluorescent emission as a function of the position of the exciting line in the absorption band.[46] They find only a slight narrowing as the excitation is moved from the high energy part of the inhomogeneous distribution to the low energy part. From this work, we can estimate that energy is transferred to the extent of greater than 90% from the absorbing distribution to the lower energy emitting distribution. Fluorescence depolarization work by Hochstrasser and coworkers[47] indicates that, for solutions of the "relatively photostable" $(PhMeSi)_n$, the polarization decay is exponential with a lifetime of about 20 picoseconds. This result was essentially unchanged across the spectral linewidth. These workers attribute this ultrafast decay to energy transfer among randomly oriented, separately absorbing segment lengths on the polysilylene chain. Thus, this result provides a timescale for the overall energy transfer process. Quite recently, Trommsdorff and coworkers[48] have shown by hole-burning experiments carried out at 1.4°K on films of $(n\text{-hexyl}_2Si)_n$, that the actual homogeneous bandwidth in that material is only about 0.05 nm; in addition, they found that prolonged hole-burning produced a net decrease in the intensity of the absorption to the red of the exciting laser wavelength and a corresponding increase in the intensity to the blue of the laser wavelength. Thus, photochemistry must occur selectively in the lowest energy ("longest") segments of the polysilylene inhomogeneous distribution.

The mobile, vibrationally decoupled singlet excited states of polysilylenes do not look promising as immediate precursors to photochemistry, yet, photochemical backbone scission is a major distinguishing characteristic of the materials and the basis for a number of their proposed applications. The phosphorescence spectra of polysilylenes provide a possible solution to this problem. Harrah and Zeigler[10,28] observed in a number of polysilylenes at 77°K a broad emission with quantum yield of about 10^{-4}, millesecond lifetime, and a well defined vibrational progression corresponding to Si-Si and Si-C vibrations. Delayed fluorescence was very strong in these spectra, as well. These emissions were assigned to the polysilylene triplet state, which must be mobile in its lifetime to allow triplet-triplet annihilation to produce the delayed fluorescence. The assignment of the triplet state as precursor to the photochemistry was strengthened by their finding that addition of diphenyllead, an intersystem crossing catalyst, to the polysilylene film increased substantially the yield of photochemistry. Broad structureless emissions in the same spectral regime have also been observed by Michl, *et al.* and assigned to the triplet state.[49] Recently, however, Azumi and coworkers have studied emissions from polysilylenes at 1.4°K and find a narrow emission with a vibrational sideband corresponding to a Si-Si vibration and only a weak delayed fluorescence.[50] They have suggested that this emission represents the true triplet. They suggest that the broader phosphorescence observed by Harrah and Zeigler and Michl, *et al.* arises from an impurity in the polysilylene. Although this issue remains unresolved, all three groups agree that the triplet is vibrationally coupled, in contrast to the singlet.

The ultrafast one-dimensional energy transfer prevalent in polysilylenes allows a very useful simplified picture to be formulated of the otherwise exceedingly complex photophysics of these materials. As Figure 2 depicts diagrammatically, to a good first approximation, essentially all photophysical processes (fluorescence, phosphorescence, internal conversion, photoconductivity), as well as photochemistry can be viewed as occurring from the lowest energy portion of the inhomogeneous distribution. These are often referred to as the lowest energy chain "segments." Thus, a high molecular weight polysilylene chain can be approximated as having many segments of different lengths which absorb over a broad range of energies, but emit from only the lowest energy part of the segment length distribution. Both calculations[51] and experimental studies (*vide infra*) show that these segments are runs of all-*trans* conformational sequences separated by rotational defects.

Electronic-conformational coupling (thermochromism)

In addition to the effects of polymer structure and molecular weight, the absorption position in polysilylenes is dramatically affected by changes in temperature. This phenomenon is seen both in solution and in the solid-state. As shown in Figure 3

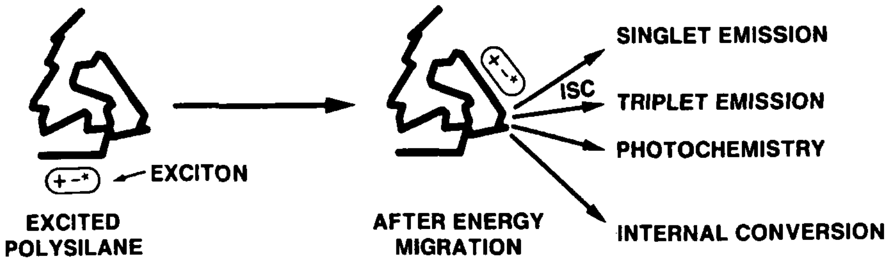

FIGURE 2 Schematic Depiction of Exciton Migration in Polysilylenes.

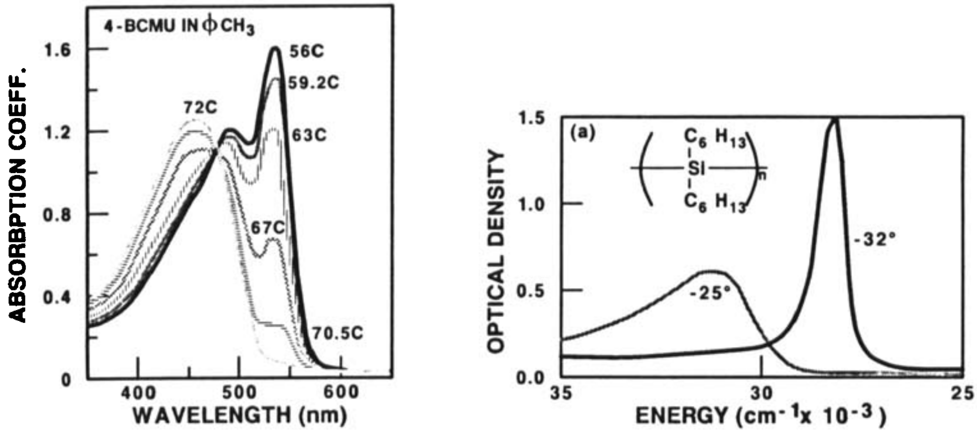

FIGURE 3 Solution Thermochromism of a Representative Polydiacetylene and Polysilylene: (a) 4-BCMU in toluene; (b) PDHS in hexanes.

for solutions of a representative symmetrically-substituted polysilylene[52] and polydiacetylene,[53] these thermochromic, first-order phase-like transitions result in abrupt shifts of the absorption position to lower energy with a concomitant narrowing of the bandwidth, strongly indicative of a narrowing of the inhomogeneous distribution and, by implication, a change in the global conformation to a more ordered one. Although the solution transition temperatures are at lower temperatures in polysilylenes, these same phenomena are observed in polydiacetylenes[53,54] and, more recently, in polythiophenes, as well.[55] Because polysilylenes typically possess nonpolar substituents, polar interactions of the sort that have been proposed to dominate the transition in polydiacetylenes[54] can be ruled out. In fact, somewhat more recent work has shown that polydiacetylenes with nonpolar substituents also exhibit thermochromic transitions,[56] so polar interactions are clearly not a necessary precondition for first-order phase transition-like thermochromic behavior in either class of materials.

Solution thermochromism in polysilylenes is not limited to symmetrically-substituted materials. Atactic, asymmetrically-substituted homopolysilylenes, and even atactic, asymmetrically-substituted copolysilylenes are thermochromic, although the transition regimes become increasingly broad and the transition temperatures progressively lower as the amount of disorder in the polymer structure increases. These observations suggest that the thermochromism is not driven predominately by side chain microcrystallization in solution, as has been suggested by some workers.[57,60] A particularly interesting set of solvent effect studies[28,58] show that the thermochromic transition temperature is not related to solvent polarity or compatibility in any obvious way. Thus, $(n\text{-hexyl}_2\text{Si})_n$ undergoes a thermochromic transition at −31°C in hexanes and tetrahydrofuran, but at −23°C in dichloromethane and −17°C in 1,2,3,4-tetrohydronaphthalene. Similarly, $(n\text{-hexylMeSi})_n$ gives only a gradual, continuous shift when its solutions in hexanes are cooled, but shows well-defined abrupt thermochromism at −60°C in toluene solvent.

Schweizer has proposed a theory which accounts for the observed changes in transition temperature as the solvent or polymer structure is changed.[58,59] In his model, the driving force for the formation of the extended ("rod") conformation is provided by favorable dispersion interactions (van der Waals forces) between the solvent and the highly polarizable polysilylene backbone. Since the optical polarizability of a material is characterized by its refractive index, the degree of interaction between the polarizable solvent and the polarizable polysilylene backbone should increase (causing an increase in the transition temperature) with increasing solvent refractive index. In fact, the observed transition temperatures correlate quantitatively with this model, providing strong support for the idea that the delocalization of the backbone σ-electrons is the ultimate source of the solution thermochromism.

Of course, the inherently single chain nature of the solution thermochromism is still considered controversial in some quarters. Other workers have proposed that the solution thermochromism is due merely to aggregation of the polysilylene chains as the temperature is lowered.[57] Since aggregation is evident in the solutions of polysilylenes which have undergone the thermochromic transition, the real question is whether conformational change occurs to give an extended, "rod-like" chain, which then aggregates, or whether aggregation occurs which only then drives the conformational change via interaction of side chains. Light scattering experiments have been reported on solutions of $(n\text{-hexyl}_2\text{Si})_n$ some two orders of magnitude higher in concentration than that at which the absorption spectroscopy is normally carried out which indicate that aggregation occurs prior to the thermochromic transition.[60] This is the primary piece of evidence adduced in favor of an aggregation model. Evidence in favor of a single chain model includes: the observed lack of concentration dependence of the transition temperature[28,52]; the observation of thermochromism in atactic, asymmetrically-substituted polysilylenes, in which side chain crystallization is very unfavorable[52,58]; the success of the inherently single-chain theoretical model above in quantitatively correlating and predicting transition temperatures[58,59]; the observation of red-shift thermochromism in solution, but blue-shift thermochromism in the solid-state for both $(n\text{-pentyl}_2\text{Si})_n$ and $(n\text{-butyl}_2\text{Si})_n$[30]; a report that $(n\text{-hexyl}_2\text{Si})_n$ which has undergone the thermochromic transition in a dilute frozen glass has a fluorescence lifetime characteristic of isolated chains in solution,[61] the finding that $(n\text{-butyl}_2\text{Si})_n$ precipitated from very dilute solution after undergoing the thermochromic transition has an predominately *trans* structure, but no crystallographic order[62]; and a report from a simultaneous light scattering/fluorescence experiment performed at low concentration that the increase in light scattering due to precipitation is the same 10° above and below the known transition temperature, but the fluorescence intensity attributable to the extended form increases dramatically below the transition temperature.[63] Thus, the bulk of the evidence favors a single chain interpretation in which the polysilylene adopts an extended rod-like conformation rich in all-*trans* segments as it passes through the thermochromic transition (schematically depicted in Figure 4).

Electronic-conformational coupling in the solid state of polysilylenes has been particularly well-studied. The material which has received most attention is $(n\text{-hexyl}_2\text{Si})_n$ (PDHS). The position of absorption of this particular polysilylene shifts

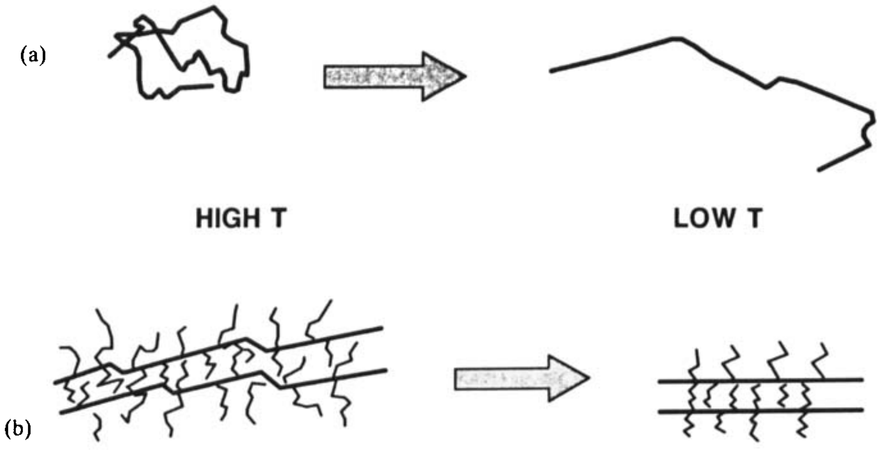

FIGURE 4 Global Conformational Changes in Polysilylene Thermochromism: (a) solution; (b) solid state.

by over 50 nm on heating through a well-defined transition temperature of 42°C.[64,65] Its solid state structure has been extensively studied by X-ray[64,65,66] and electron diffraction,[66] solid state NMR,[67] and Raman.[64,65] At temperatures below 40°C, the polysilylene silicon atoms all lie in the same plane in the all-*trans* conformation; as one passes through the thermochromic transition temperature, "kinks" are introduced into the silicon backbone which have the effect of reducing the effective chain length, thus shifting the absorption to higher energy. The thermochromic transition results in a disordering of the side chains[64,65,66,67] with a concomitant relatively slight "kinking" of the silicon backbone, accounting for the rather substantial change in the absorption position. The disordering of the backbone must be relatively minor, because the overall hexagonal packing of the chains is maintained after passing through the melting-like transition temperature.[66] Work done on this material leads to a consistent picture of a transition in which it is mainly the side chains which disorder, thus the well-defined melting-like transition is really associated with side chain disordering. Studies of other di-*n*-alkylsilylene polymers with side chains up to C_{12} in length show a similar pattern of all-*trans* solid state structures in which it is predominately the side chains which disorder upon passing through the transition temperature (Figure 4).

The importance of side chain interactions in the thermochromic disordering led to the proposal that all such thermochromic transitions for polysilylenes in both solutions and solid state were dominated by side chain melting. Recently, however, it has been found that both $(n\text{-pentyl}_2\text{Si})_n$[29,30] and $(n\text{-butyl}_2\text{Si})_n$[30,62] adopt *7/3 helical structures* in the solid state. The disordering temperatures of these materials are at substantially higher temperatures (about 90°C vs. 42°C) than those for the higher homologues. Moreover, these materials exhibit a relatively high energy absorption at about 313 nm which undergoes a gradual slight red-shift and broadening as the temperature is increased which is uncorrelated with the DSC-determined "melting" transitions. Since both these polysilylenes exhibit classic abrupt red-shift thermochromism in solution,[30] it is clear that the solid state and solution structures and the factors which influence them are decoupled in these materials. Since side chain packing is clearly unimportant for such solid state structures, it has been proposed on the basis of calculations[68] that polysilylenes should adopt preferred helical structures in the absence of overruling side chain interactions. Such a result is at odds with the finding that these materials exhibit red-shift thermochromism in solution characteristic of preferred all-*trans* conformations, but new evidence allows the hypothesis of preferred helical conformations for polysilylenes to be discarded for the solid state, as well. Workers at AT&T Bell Laboratories and Sandia National Laboratories have now shown that all of the lower homologues through $(Me_2Si)_n$ adopt all-*trans* structures in the solid state.[69] Since packing interactions among side chains are minimal in these materials, it can now be said with authority that the preferred conformation of polysilylenes in both solution and solid state must be all-*trans*. It seems highly likely that this preference is established as a result of lowering of the ground state energy due to more efficient σ-delocalization in such planar structures.[51] The real driving force for the formation of helical structures in two members of the homologous series remains unknown.

The short discussion here cannot do justice to what has been one of the most active parts of polysilylene research. A more complete discussion can be found in a recent review.[70]

Optical and transport properties

Electronic-conformational coupling in polysilylenes is more than an esoteric scientific issue, since the electronic structure changes brought about by the conformational changes manifest themselves directly in the ability of the polysilylene to transport charge and energy. The mobility of the electrons in the polysilylene backbone leads to high electron polarizability, a requirement for large nonlinear optical effects to be present. The second microscopic hyperpolarizability, $\chi^{(3)}$, for a polysilylene (PDHS)[8] is 11×10^{-12} esu—within a factor of forty of the *p*-TS-PDA value, despite the fact that *p*-TS-PDA is a highly optimized single crystal, while the polysilylene is a relatively crude polycrystalline material. Above the thermochromic transition temperature, $\chi^{(3)}$ decreases by about a factor of two. Even though the polysilylene shows a lesser value of $\chi^{(3)}$ than PDA, it is generally thought to be one of the leading nonlinear optical candidate materials for several reasons: (1) it is amenable to large-scale synthesis; (2) it is transparent to visible light; (3) the response time is no more than a few picoseconds[9]; and (4) polysilylenes exhibit wavelength dependent photochemistry (*vide infra*) which allows the same polysilylene to be photopatternable at short wavelengths, yet have reasonable photostability for nonlinear optical applications at longer wavelengths.

Just as the incorporation of conformational defects into the backbone has a significant effect on the nonlinear optical properties of polysilylenes, it has recently been shown by Kepler to be one of the most important elements in determining the exciton mobility.[41] Exciton mobility in polysilylenes is relatively insensitive to changes in structure, e.g. $(PhMeSi)_n$ and $(n\text{-hexyl}_2Si)_n$ below its thermochromic disordering temperature exhibit about the same exciton mobility—a surprising result when the fact that $(PhMeSi)_n$ is glassy whereas $(n\text{-hexyl}_2Si)_n$ is highly crystalline, is taken into account. At 60°C (above the transition temperature), however, the exciton mobility in $(n\text{-hexyl}_2Si)_n$ decreases by a factor of ten.

Polysilylenes, like polyenes, change from an insulating state to a conductive one (0.5 S/cm) when they are "doped."[36] This is expected, given the ability of the electrons in the polysilylene backbone to move rapidly up and down the polymer chain. They suffer from instability when doped, however. The molecular weight rapidly decreases after doping presumably due to nucleophilic attack by dopant counterions on the silicon. There is reason for hope that polysilylenes more stable to doping can be synthesized, but the more promising application in electrophotography (xerography) has overshadowed this use to date.

The highly efficient nondispersive photoconductivity of polysilylenes[4] made them attractive candidate materials for photoreceptors. Since the excitons formed on photoexcitation in the UV generate carriers only upon dissociation at surface states,[4] polysilylenes have been examined mainly in conjunction with various generator layers (a-Se, organics) which produce carriers more efficiently in visible light. A full discussion of this work is outside the scope of this paper, but an excellent recent review exists.[71] Only a brief summary will be given here.

Holes traverse almost all polysilylenes studied to date with a room temperature mobility of 10^{-4} cm^2/Vsec. Activation energies for transport in $(PhMeSi)_n$ and $(n\text{-PrMeSi})_n$ are 0.25 and 0.1 eV, respectively. Trapping experiments suggest that the holes move in well-defined states at around 7 eV below the vacuum level.[4,71] Transport is thought to involve trap-modulated hopping via states associated with the silicon backbone, since side groups have only a small effect on the mobility.[4,71]

Photochemistry of polysilylenes

Although not a major focus of this paper, no discussion of polysilylenes would be complete without some mention of their photochemistry, because photochemical processes directly affect so many of the proposed applications for the materials. The photochemistry of polysilylenes sets them apart both from π-conjugated polymers and from polyalkanes. These carbon-based materials exhibit only very inefficient photochemistry which is usually associated with structural defects. In polysilylenes, on the other hand, the Si-Si bond is the "photochemical unit." Thus, every backbone bone is a potential site of photochemistry. In spite of this, the photosensitivity of polysilylenes is an exquisitely sensitive function of structure, exposure wavelength, phase (solution vs. solid state), and morphology, among others. The discussion which follows is intended to introduce the reader to an area which, like most of polysilylene research, is becoming better understood and more complex at a rapid rate. The reader is encouraged to consult the original literature referenced here and the cited reviews.[3,72]

Pioneering studies of the solution photochemistry of dimethylsilylene oligomers were carried out by Ishikawa and Kumada.[73] By trapping reactive intermediates, they showed that the predominant mode of photochemistry involved Si-Si bond scission with the creation of silyl radicals and silylenes (the silicon analogue of a carbene). Since carbenes are not usually created by photolysis of polyalkanes, these results serve to illustrate the increased stability and, hence, greater importance of silylenes in polysilylene photochemistry relative to their carbene analogues. Later studies by Trefonas, *et al.* revealed a similar set of intermediates in the photochemistry of high molecular weight polysilylenes in solution.[74] As in the work of Ishikawa and Kumada, Trefonas, *et al.* found that the disilanes formed by prolonged photolysis of the polysilylene chain were relatively resistant to further photolysis. To account for this observation, it was postulated that silylene expulsion and radical formation must occur together in the same photochemical bond breaking process, if not in a rigidly concerted fashion. Although trapping experiments confirm the formation of chain end silyl radicals, these species have not yet been observed directly. ESR studies found persistent radicals, but the structure of these was found to be highly hindered at silicon; i.e. these are secondary photoproducts. A radical disproportionation process proceeding through silene species has been proposed to account for the formation of these persistent radicals.[72]

While a number of studies of the solution photochemistry of polysilylenes have been carried out, there is relatively little reported data on the solid state photochemistry of polysilylenes. The work that has been carried out suggests that the intermediates formed in solid state photolysis of polysilylenes are similar to those formed in solution, although the solid state reactions are more complicated.[10,13] However, due to the interest in polysilylenes as resist materials, a considerable number of measurements of scission and crosslinking quantum yields, or more correctly stated, G values have been determined as a function of a variety of parameters. These measurements provide a great deal of insight into the parameters which increase or decrease the photosensitivity of a polysilylene.

Reproduced in Table II are a few of the quantum yields that have been reported for photolysis of various polysilylenes (films, except where noted) under various exposure conditions. Since polysilylenes bleach when photolyzed as a result of the dependence of the absorption position on molecular weight, the position of the exciting wavelength in the absorption band plays an important role in determining

TABLE II

Scission and crosslinking quantum yields for polysilanes.

POLYSILANE	EXPOSURE (nm)	λ_{max}(nm)	ϕ_s	ϕ_x	REF.
$(PhMeSi)_n$ (soln.)	313	342	0.97	0.12	37
$(PhMeSi)_n$	313	342	0.017	0.0036	37
(*n*-dodecyl MeSi)$_n$ (*s*oln.)	313	309	0.20	0.00	37
(*i*-PrMe Si/*n*-PrMeSi)$_n$	Mid UV	331	0.034	0.008	13
(*c*-hexyl MeSi/Me_2Si)$_n$	Mid UV	307	0.034	0.007	13
	248.4	307	0.24	0.027	13
(PhMeSi/*i*-PrMeSi)$_n$	Mid UV	333	0.014	0.003	13

the extent of photolysis achieved with a given polysilylene in a given experiment. Thus, $(n\text{-dodecylMeSi})_n$ with an absorption λ_{max} at 309 nm will be photolyzed to a much lesser degree with 313 nm light than will $(PhMeSi)_n$ at the same wavelength, due to the much longer wavelength absorption of the aryl polysilylene. Thus, some caution must be used in interpreting quantum yields in which the relative position of the exciting wavelength in the absorption band differs significantly.

A significant wavelength dependence is evident from the data in Table II. When the 1:1 copolymer of cyclohexylMeSi with Me_2Si is photolyzed with mid-UV (a band of wavelengths from about 300 nm to 380 nm), a scission quantum yield of 0.034 and crosslinking quantum yield of 0.007 is measured.[13] Thus, this material is on net, a scissioning one, although a crosslinking component is also present. However, the same material exposed at 248.4 nm to the same degree of photochemical conversion, shows a greatly increased scission yield of 0.24 and a lesser increase in the crosslinking component to 0.027. It appears that this change in photochemical efficiency reflects a change in the photochemical mechanism, since it has been shown that the primary reactive intermediates formed by photolysis of this material at 253.7 nm are silylenes,[10] while silylenes are relatively minor products, if present at all, in the mid-UV photolysis.[13] Since the ratio of these two numbers is directly related to the lithographic contrast achievable, this polysilylene is a more useful photoresist at 248.4 nm (deep-UV) than in the mid-UV. This observation also suggest the possibility of designing polysilylenes for nonlinear optical applications which can be both photostable at the lower energy operating wavelength and photopatternable at short wavelengths.

Other features in Table II are also noteworthy. Solution photolysis of $(PhMeSi)_n$ occurs with much higher quantum yield than solid state photolysis.[37] This phenomenon is general for polysilylenes and is due, at least partially, to a cage effect, since the solution/film quantum yield ratio is smaller for materials above their glass transition temperatures. Conversely, highly crystalline polysilylenes often exhibit near zero quantum yields for scission in the solid state, presumably because radical chain ends are locked in place in the crystal, allowing ready reclosure of the broken bond. The scission and crosslinking quantum yields for the phenyl-containing copolymer film in Table II are essentially the same as that of the phenyl homopolymer film. Under like exposure conditions, all phenyl-containing polysilylenes examined to date are more photostable in the solid-state than peralkyl polysilylenes. Thus, the limited data available suggest that the presence of phenyl groups in a polysilylene acts to stabilize the materials to light. This effect is not due entirely to the high glass transitions typical of the phenyl polysilylenes, since the 1:1 copolymer of cyclohexylMeSi with Me_2Si has a similar glass transition temperature to that of $(PhMeSi)_n$, yet, is substantially more photosensitive in the solid state.

Summary and conclusions

Although polysilylenes have only been under intensive study for a few years, it is clear that they possess a mix of properties unique among polymeric materials. Applications interest in the polysilylenes has grown rapidly to encompass a wide range of potential uses. In spite of their uniqueness, polysilylenes possess electronic properties which parallel many of those of π-conjugated polymers. Only very limited work has been carried out on the corresponding polygermylenes,[75] but the limited data available show that these σ-bonded polymers are σ-conjugated in the same way as polysilylenes, at least at a qualitative level. Thus, polysilylenes represent only the first well-explored group of materials which may well include a much wider range σ-bonded polymers having interesting and useful electronic properties.

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