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Excited-State Behavior of Poly[dimethylsilylene-*co*-methyl(1-naphthyl)silylene][†]

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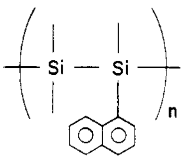
ABSTRACT: The singlet- and triplet-state properties of poly[dimethylsilylene-*co*-methyl(1-naphthyl)silylene] (PSN) in solution were characterized at room temperature and 77 K. In addition to the monomer emission, a strong excimer emission (λ_{max} 428 nm) was observed with PSN in THF solution at room temperature. However, in a MTHF matrix at 77 K, PSN exhibited intense dimer fluorescence (λ_{max} 403 nm) and a structured phosphorescence emission with a 0–0 band at 497 nm which is characteristic of dimer interaction. Transient absorption monitored upon laser-pulse (337.1 nm) excitation of PSN in the THF solution indicated the formation of two different transients. The short-lived transient (τ = 3 μs), which was assigned to the 1-naphthyl triplet state, had an absorption maximum at 460 nm, and the long-lived transient (τ = 300 μs), which was assigned to a silyl radical bearing a naphthyl group, had an absorption maximum at 380 nm. The formation of silyl radicals was confirmed by monitoring the ESR spectrum in MTHF matrix at 77 K after UV irradiation. The apparent *g* value was found to be 2.0039.

Introduction

Photolysis and excited-state properties of a number of disilane and trisilane compounds bearing a phenyl or a naphthyl group have been the subject of many recent investigations.[1-6] Such silane compounds can exhibit dual (local and charge transfer (CT)) emissions. It has been found that the intramolecular CT fluorescence appears as a broad and structureless band with a large Stokes shift, even in EPA glass matrix at 77 K. Photolysis of these silanes results in both silylenes[7,8] and rearranged intermediates,[9] whose transient absorptions have been detected by nanosecond laser spectroscopy.[10,11] Recently, a number of high molecular weight linear polysilanes containing aryl groups have been synthesized and characterized.[12-14] They all appear to be photoactive and undergo degradation upon UV irradiation. However, no attention has been given, so far, to investigate the excited-state behavior of these polymers.

Organosilane polymers possess interesting properties (e.g., sensitivity to UV irradiation and potential semiconductivity) and are used as UV photoresists,[15] as precursors to β-SiC fibers,[16] and as dopable semiconductors.[13] In view of the importance of their photoactivity, we have investigated the triplet and singlet excited-state properties of a high molecular weight organosilane polymer, poly[dimethylsilylene-*co*-methyl(1-naphthyl)silylene] (PSN) employing fluorimetry, phosphorimetry, and laser flash photolysis techniques. Direct evidence for the formation of silyl radicals in the photoinduced degradation of PSN is also presented by means of ESR measurements and nanosecond laser flash photolysis.



Experimental Section

The copolymer, poly[dimethylsilylene-*co*-methyl(1-naphthyl)silylene] (PSN) was prepared from dimethyldichlorosilane and methyl(1-naphthyl)dichlorosilane (Petrarch Systems Inc.) as described elsewhere.[17] The thus-obtained copolymer showed a Me(1-naphthyl)Si to Me_2Si ratio *m* of 1.7. Its mass spectrum showed fragments derived from $(SiMe)_2$, Si(naphthyl)MeSi$(Me)_2$ and (Si(naphthyl)Me$)_2$ moieties, with higher abundances for the latter two. This is in accordance with the observed high *m* value and furthermore suggests that PSN is a random rather than an alternating or block copolymer. Precipitation with 2-propanol from a THF solution of the copolymer gave a fraction with a $\bar{M}_w$ of 10000 (as determined by gel permeation chromatography). 1-Naphthyltrimethylsilane was synthesized according to Kerr et al.[18] Tetrahydrofuran (THF) was used as supplied by Aldrich (Gold Label, inhibitor free). Methyltetrahydrofuran (MTHF) was twice distilled over sodium hydride. Methylcyclohexane (MCHX), passed through a column containing layers of activated alumina and carbon black, was further dried with sodium and distilled twice over sodium hydride.

UV spectra were recorded with a Cary Model 219 spectrophotometer. Fluorescence and phosphorescence spectra were taken on a SLM 8000S single-photon-counting emission spectrophotometer, equipped with a microprocessor capable of correcting the recorded spectra for instrumental distortions. The phosphorescence lifetime was determined with the same SLM 8000S spectrophotometer setup. Singlet lifetimes were determined with a single-photon-counting fluorescence lifetime apparatus (Photochemical Research Associates Inc.) as described elsewhere.[19]

For laser flash photolysis experiments, nitrogen laser pulses (337.1 nm, 8 ns, 2–3 mJ) from a Molectron UV-400 system were used for excitation, and the rectangular quartz cells of 5-mm path lengths, with optically flat surfaces across the analyzing light, were used. Samples were renewed after $\simeq$25 laser pulses to avoid artifacts from product photolysis, and the average signal was processed with a LSI-11 microprocessor interfaced with a PDP-11/55 computer. It was necessary to attenuate the excitation intensity in order to minimize the effect of T–T annihilation. Deaeration of the solutions was performed by thorough purging with oxygen-free argon. For variable concentrations of oxygen, the solutions were saturated with O_2/N_2 mixtures of known composition (Linde).

Photolysis was performed in a Rayonet photochemical reactor equipped with 350-nm lamps. A filter solution was used to cut off light of wavelengths lower than 330 nm. The fluorescence quantum yields at room temperature were determined from the fluorescence quantum yield of quinine sulfate in 0.5 M H_2SO_4 (ϕ_{FM} = 0.56).[20] The fluorescence and phosphorescence quantum yields at 77 K in a MTHF matrix were determined from the fluorescence quantum yield of 1-naphthyltrimethylsilane in a MCHX matrix at 77 K (ϕ_{PM} = 0.32).[6]

ESR spectra were recorded with a Bruker ER 100E spectrometer, with a dual rectangular cavity, equipped with a Bruker microwave bridge ER 040 X. A 5% solution of PSN in MTHF was introduced into a Spectrosil quartz tube (o.d. of 5 mm) and sealed after degassing with oxygen-free argon. The sealed tube was placed inside a liquid N_2 Dewar flask with quartz windows and was irradiated in a Rayonet photochemical reactor, equipped with 350-nm lamps, for 10 min. A filter solution was used to cut

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Table I

Quantum Yields for Phosphorescence (ϕ_P) and for Monomer (ϕ_{FM}) and Longer Wavelength (ϕ_{FE}) Emission, λ_{max} for the Longer Wavelength Emission, and Phosphorescence Lifetimes (τ_P) for PSN and 1-Naphthylpentamethyldisilane in Different Solvents

compd	solvent	temp, K	ϕ_{FM}	ϕ_{FE}	$\lambda_{FE,max}$, nm	ϕ_P	τ_P, s
1-naphthylpentamethyldisilane[5]	MP[a]	300	0.006				
	MP	77	0.55			0.21	2.0
PSN	CHX	300	0.009	0.026	421		
	MTHF	77		0.48	403	0.39	1.2
	THF	300	0.004	0.070	428		

[a] MP is a mixture of MCHX and isopentane in a 3:1 ratio.

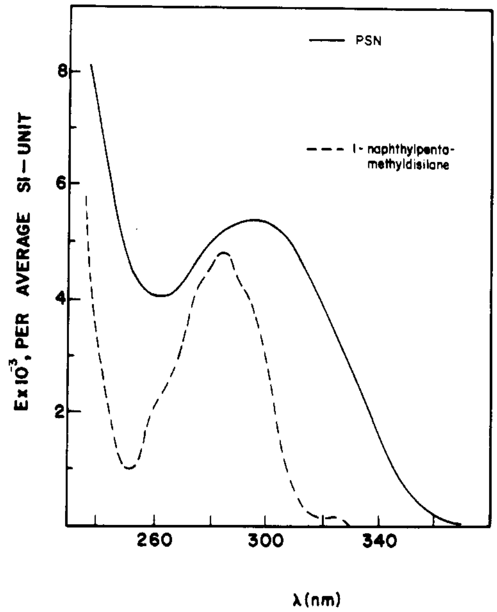


Figure 1. UV spectra of PSN (—) and 1-naphthylpentamethyldisilane (---)[5] in the THF at room temperature.

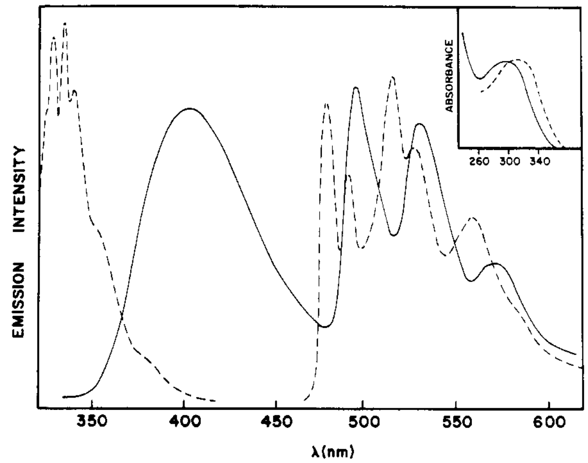


Figure 2. Corrected total emission spectra of PSN (—) and 1-naphthyltrimethylsilane (---) in MTHF at 77 K. Inserted are the absorption (—) and excitation (---) spectra of PSN at room temperature and 77 K, respectively.

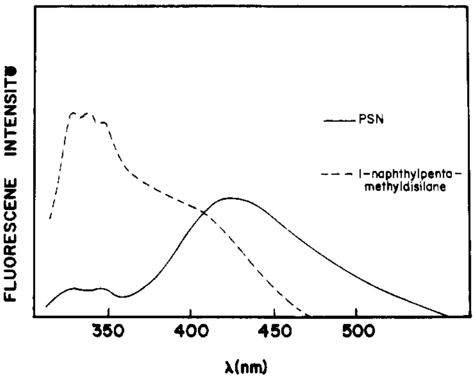


Figure 3. Corrected fluorescence spectra of PSN (—) and 1-naphthylpentadisilane (---)[5] in THF at room temperature.

off light of wavelengths lower than 330 nm. The irradiated quartz tube was then transferred quickly to a liquid N_2 Dewar flask mounted within the microwave cavity. The g factor was measured relative to galvinoxyl in THF (g = 2.00453).[21]

Electrochemical experiments were conducted in a standard three-compartment cell with a Pt disk as a working electrode and saturated sodium chloride calomel electrode (SSCE) as a reference electrode. Cyclic voltammograms were recorded with a Princeton Applied Research Model 173 potentiostat, a Model 175 Universal programmer, and a Kipp and Zonen X-Y recorder.

Results and Discussion

3.1. Absorption Characteristics. The UV spectra for PSN and the monochromophoric 1-naphthylpentamethyldisilane,[5] which is used in this study as a model compound, are shown in Figure 1. Both the wavelength and the molar absorptivity of the lowest energy band of PSN are higher compared to that of 1-naphthylpentamethyldisilane. Similar effects have been observed earlier for organosilane polymers bearing phenyl groups.[14] This hyperchromic and red shift can be explained by an increased conjugative interaction between the 2pπ orbital of the aromatic ring and the 3dπ orbital of the silicon backbone.[5,6,11,14,22]

3.2. Emission Characteristics. The total emission spectrum of PSN in MTHF at room temperature and at 77 K is shown in Figures 2 and 3. Emission quantum yields, longer wavelength fluorescence emission maximum, and phosphoresence lifetimes are summarized in Table I. The spectral shape of the phosphorescence spectrum is very similar to that of a 1-(trialkylsilyl)-substituted naphthalene chromophore.[6] However, the 0–0 band is located at 495 nm, showing a red shift of about 10 nm when compared with that of 1-naphthyltrimethylsilane or 1-naphthylpentamethyldisilane,[6] and there is a clear decrease of the vibronic fine structure. Furthermore, the phosphorescence lifetime of PSN was found to be 1.2 s while that of 1-naphthylpentamethyldisilane was 2.0 s.[6] Similar features have been noted for the phosphorescence properties at 77 K of poly(2-vinylnaphthalene),[23] of the cleaved endo cyclomer of 1,3-di(1-naphthyl)propane,[24] and of the cis dimer of acenaphthalene[25] and were ascribed to weak electronic interaction between two naphthyl groups. This suggests that no triplet excimer for PSN is observed under these conditions, although some dimer-like interactions are present. The phosphorescence excitation spectrum, which is slightly shifted to longer wavelengths as compared to the absorption spectrum (Figure 2), suggests this to be the case.

The fluorescence spectrum at 77 K in MTHF consists of a broad, structureless band with a maximum at 403 nm, whereas at room temperature this broad emission is red shifted to 428 nm and fluorescence from the locally excited state shows up (Figure 3). Shizuka et al.[6] observed a broad

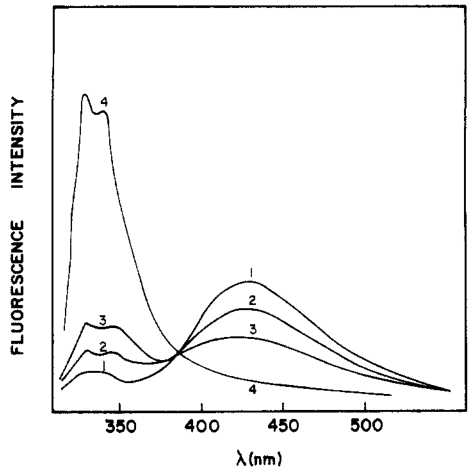


Figure 4. Fluorescence spectra of PSN as a function of irradiation time at 350 nm in THF: (1) 0 min; (2) 5 min; (3) 10 min; (4) 4 h.

structureless emission in addition to monomer fluorescence for a number of monoaryldisilanes. They ascribed it to the emission from an intramolecular $^1(2p\pi, 3d\pi)$ CT state and showed that the formation of this CT state requires a planar aryl-Si-Si configuration. For 1-naphthylpentamethyldisilane, the emission maximum of the CT state was found to be 402 nm in THF solution at room temperature. However, no such emission was observed for the same compound in nonpolar solvents like cyclohexane and 2-methylpentane. As the longer wavelength emission of PSN is still present in MCHX (both at 77 K and at room temperature), we concluded[17] that it originates from an intramolecular excimer between two adjacent naphthalene groups, rather than from an intramolecular CT state. Furthermore, it is clear from a molecular model of PSN that a planar 1-naphthyl-Si-Si configuration is highly improbable due to severe steric hindrance in the polymer chain. That we probably deal with the intramolecular excimer formation was further substantiated by the fact that upon UV-induced photodegradation of PSN, which resulted in a decrease in the polymer chain length, a marked decrease in the ratio $I_{\mathrm{EXC}}/I_{\mathrm{MON}}$ (Figure 4) was observed.[17] This is in accordance with the already well-established finding that in aromatic polyvinyl compounds, there is a large dependence of the ratio of the excimer to monomer fluorescence on the polymer weight ($I_{\mathrm{EXC}}/I_{\mathrm{MON}}$ increases with increasing $\bar{M}_w$).[26-29]

The difference in the wavelength maximum of the excimer emission at 77 K (403 nm) and room temperature (428 nm) can be explained as follows. At 77 K in MTHF matrix, emission probably results from a dimer state, with nearly an excimer configuration as imposed by the rigid matrix. On the other hand, at room temperature in liquid solution, fluorescence most probably occurs from the stable excimer conformation. Similar shifts in the wavelength maxima of the excimer at 77 K at room temperature have been observed in the fluorescence spectra of solid poly(methyl methacrylate) solutions of poly(1-vinylnaphthalene).[30] Furthermore, the slightly red-shifted excitation spectrum at (Figure 2) also indicates a dimer-like interaction.

3.3. Emission Lifetimes. The lifetime of the 403-nm fluorescence at 77 K in MTHF is found to be 6 ns. From this value, combined with the quantum yield of 0.48, a rate constant of 8×10^7 s^{-1} for the decay of fluorescence was calculated. This is at least an order of magnitude larger than the value usually obtained for the inter- and intramolecular naphthyl excimers in solution.[31-35] This further supports our assignment of this emission to a dimer, with a configuration differing from the strongly overlapping sandwich structure in the excimer, and hence a larger rate constant for radiative decay is expected.[36,37]

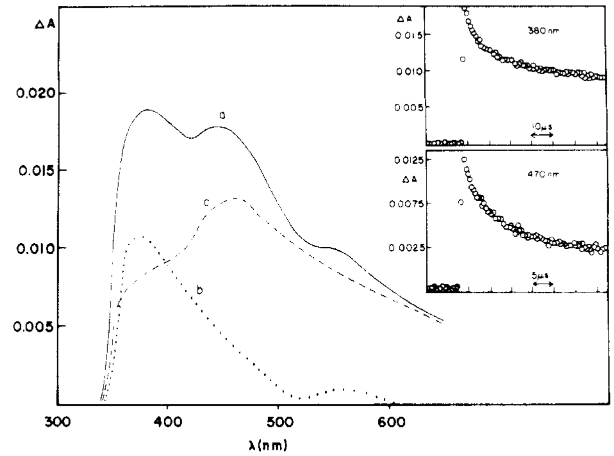


Figure 5. Absorption spectra of the transients generated upon laser-pulse excitation (337.1 nm) of PSN in THF. The spectra were recorded (a) (—) immediately after the flash, and (b) (···) 50 μs after the flash. Spectrum (c) (---) is a differential spectrum of (a) and (b) and corresponds to the spectrum of the short-lived transient. Inserts are the absorption profiles recorded at 380 nm and 470 nm, representing the decay of two transients.

The fluorescence decay curve, recorded at 450 nm, in the region of excimer fluorescence, in THF solution at room temperature, may be adequately represented by a dual-exponential decay function of the form

$$i_D(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

where A_1 and A_2 are the preexponential terms and τ_1 and τ_2 are the singlet lifetimes.[17] From this analysis values of 0.035 and 0.050 for A_1 and A_2, respectively, and 1.0 and 10.5 ns for τ_1 and τ_2, respectively, were obtained. Attempts to fit $i_D(t)$ to a triexponential function[38] were unsuccessful. It is worthwhile noting that no excimer rise time is observed. This may be a consequence of the short lifetime of the model compound 1-naphthylpentamethyldisilane (3.7 and 8.0 ns in diethyl ether and cyclohexane, respectively, at room temperature).[6] If an excimer/monomer interaction exists in PSN, the monomer lifetime should be subject to considerable quenching relative to that of the unassociated chromophore (model compound).[39,40] For instance, Phillips et al.[38] reported the monomer fluorescence lifetime to be 1.6 ns in poly(1-naphthyl methacrylate), which was shorter by a factor of about 30 relative to that of 1-methylnaphthalene. This means that in PSN the monomer lifetime and hence the excimer rise time would lie in the subnanosecond time scale, which is beyond the capability of the SPC apparatus used in this work. Whether the two components in the excimer decay originate from two different excimers (like in the case of poly(2-vinylnaphthalene)[41]) or from an excimer and a CT state is not clear yet.

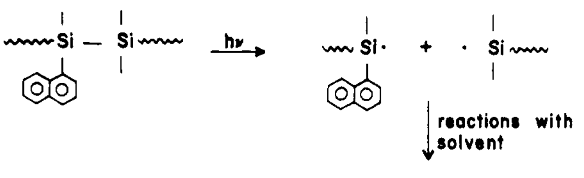
3.4. Transient Absorptions. Laser-pulse excitation at 337.1 nm of PSN in deoxygenated THF led to the generation of two transients, as indicated by absorption signals in Figure 5. The shorter lived transient (τ = 3 μs) had an absorption maximum at 460 nm, while the longer lived transient (τ = 300 μs), whose absorption manifold overlapped with that of the shorter lived species, displayed a $\lambda_{\max}$ at 380 nm (Figure 5). The 380-nm transient was no longer observed in the aerated solutions.

The spectral shape of the absorption at 460 nm is similar to that of the T–T absorption of poly(2-vinyl-

Table II
Transient Absorption Characteristics of PSN in THF at Room Temperature

transient	λ_{max}, nm	lifetime, μs	ϵ_{520nm}	ϕ_{TM}	$k_q(O_2)$, 10^8 s^{-1}
triplet	460	3	3296	0.0037	3.8
radical	380	300			

Scheme I



naphthalene)[42,43] but is red shifted and exhibits a significant tail at the longer wavelengths. This red shift of the main band probably reflects the altered triplet electronic state caused by Si substitution of the naphthalene chromophore. The long-wavelength feature, ascribed to the triplet excimer absorption by Lim et al.[44] from their study of di(1-naphthyl)alkanes, has also been observed by Pratte et al.[42] in the T–T absorption spectrum of poly(2-vinylnaphthalene). The absorption at longer wavelengths, which is more pronounced in PSN, decays essentially with the same rate as that of the triplet naphthalene absorption (in PSN) at 460 nm. We therefore ascribe the broadening of the triplet naphthalene absorption (PSN) to the polymer environment. The transient absorption characteristics of PSN in THF are summarized in Table II. The quantum yield for the triplet formation was measured by using the anthracene triplet as a reference.[45]

The next step is to identify the long-lived transient that has an absorption maximum at 380 nm. This can be assigned to a silylene,[10] a disilene,[8,10,47] a rearranged intermediate,[11] or a silyl radical.[46] The precursor of this transient could be assigned to the triplet state of the polymer, as the formation of the long-lived transient was not observed when the triplet state was quenched with O_2. In a previous paper[17] we showed that photodegradation of PSN in toluene at room temperature when irradiated with 330-nm light probably proceeds as depicted in Scheme I. However, photodegradation caused by elimination of the silylenes $(CH_3)_2Si$: or (CH_3)(1-naphthyl)Si: could not be excluded completely.[46]

It is known that silylenes, especially arylsilylenes, have absorptions in the visible region.[8] Furthermore rigid solutions of silylenes show no ESR signal, in accordance with the fact that they are ground-state singlets.[47] In order to see if silylenes were formed in the photolysis of PSN, the photolytic method described by West et al.[47,48] to detect silylenes in rigid matrices at 77 K was used. Samples of PSN in MCHX and MTHF at 77 K were subjected to extensive irradiation with 300- and 350-nm light. The visible absorption spectrum of the irradiated samples at 77 K gave no indication of any formation of Me_2Si: or Me(1-naphthyl)Si: silylenes. Furthermore no changes occurred in the fluorescence and phosphorescence spectra taken at 77 K. These results clearly indicate that no silylenes are formed, and hence the formation of disilenes is improbable.[8,47]

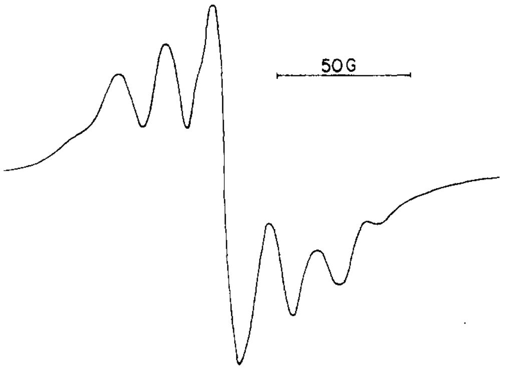


Figure 6. Electron spin resonance spectrum of PSN in MTHF, irradiated and monitored at 77 K.

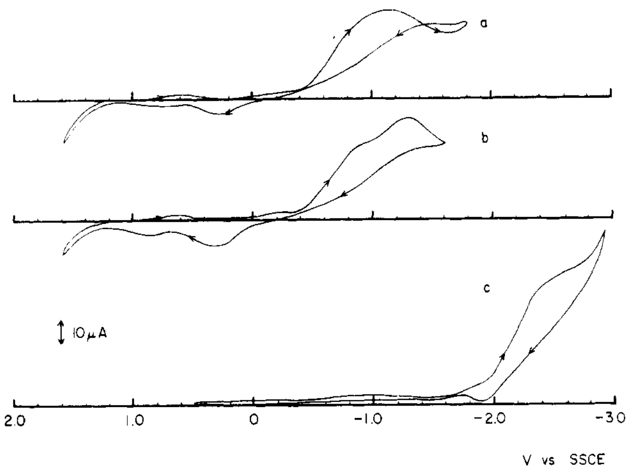


Figure 7. Cyclic voltammograms of PSN in THF solution containing 0.1 M TBAP recorded at a scan rate of 100 mV/s: (a) first scan, (b) second scan, and (c) after irradiation with UV light.

On the other hand, an ESR spectrum of a UV-irradiated MTHF glass of PSN at 77 K clearly showed the occurrence of silyl radicals (Figure 6). The asymmetric shape is indicative of the formation of at least two different kinds of radicals in accordance with Scheme I. For these radicals an apparent *g* value of 2.0039 was obtained, which is in accordance with the *g* values found earlier for silyl radicals with a β-silicon atom.[49,50] Thus from the above results it is reasonable to conclude that the 380-nm species can be associated with a 1-naphthylsilyl radical. Furthermore its transient spectrum resembles that of 1-ethylnaphthalen-α-yl[51] and the acenaphthene radical[52] in position, though in shape it is broadened, which could be a consequence of interactions with adjacent naphthyl chromophores.

Electrochemical Characteristics. PSN was electrochemically characterized with the aid of the cyclic voltammetry, and the cyclic voltammograms are recorded in Figure 7. During the first scan a broad absorption peak was seen around −1.2 V vs. SSCE. During second and subsequent scans two peaks were observed at −0.95 and −1.3 V vs. SSCE. Similar behavior was also noted earlier by Boberski et al.[53] for chloropermethylpolysilanes in acetonitrile. The emission spectrum recorded after the continuous electrolysis at −1.2 V vs. SSCE showed a decrease in the emission intensity ratio I_{EXC}/I_{MON}, indicative of the degradation of the polymer. The cyclic voltammogram of the UV-irradiated sample of the PSN (Figure 7c) indicated a reduction peak around −2.5 V, which is very similar to the reduction peak observed for naphthalene in THF. Electrochemistry corresponding to PSN was not observed in the photolyzed sample. These observations are in accordance with the fact that UV photolysis of PSN results in extensive degradation of the silane polymer, probably yielding mono- and disilane compounds containing the naphthyl group.

Conclusion

PSN is a photoactive polysilane polymer, characterized by a strong excimer fluorescence in dilute solution at room temperature and by dimer emission at 77 K in a MTHF matrix. This excimer emission can be used to monitor the UV-induced photodegradation of PSN.

ESR spectra and nanosecond laser flash photolysis experiments, combined with the photolytic method of West et al.[47,48] to detect silylenes, strongly suggest that the photoscission of Si–Si bonds, yielding silyl radicals, is the main reaction pathway for the photodegradation of PSN with 330-nm light.

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