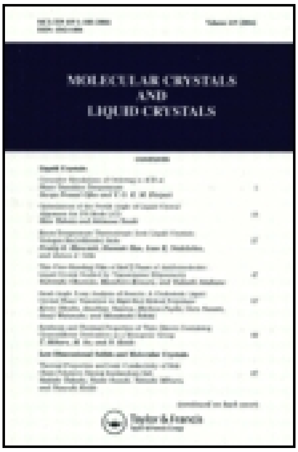

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Photophysical Dynamics of the [sgrave]-Delocalized Network Alkylpolysilynes: $(R\text{-}Si)_n$

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Version of record first published: 04 Oct 2006.

To cite this article: William L. Wilson & T. W. Weidman (1991): Photophysical Dynamics of the [sgrave]-Delocalized Network Alkylpolysilynes: $(R\text{-}Si)_n$, Molecular Crystals and Liquid Crystals, 194:1, 85-91

To link to this article: http://dx.doi.org/10.1080/00268949108041153

Mol. Cryst. Liq. Cryst., 1991, vol. 194, pp. 85–91
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Printed in the United States of America

Photophysical Dynamics of the σ-Delocalized Network Alkylpolysilynes: $(R\text{-}Si)_n$

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Abstract We review the first transient photophysical data on the "***polysilynes***", a new class of extensively crosslinked silicon skeletal polymeric materials. Using steady-state and picosecond spectroscopic techniques we develop a consistent structural picture which illustrates the evolution of the polymer spectral characteristics. The data suggests that in polysilynes photoexcitation results in the generation of localized electron-hole pairs. The recombination dynamics of these carriers may be successfully predicted by a recombination model similar to those used to explain luminescence in amorphous semiconductors.

Keywords: Polymer, silicon, photoluminescence time resolved

The novel spectral and photophysical properties of linear silicon backbone polymers, the polysilylenes (often called polysilanes) have currently been the focus of intense research. While electronically analogous to saturated hydrocarbons, these polymers exhibit intense near UV absorption bands similar to those normally associated with materials exhibiting π-conjugation[1]. This phenomenon is now generally attributed to transitions between σ-delocalized silicon bonding and antibonding molecular orbitals[2].

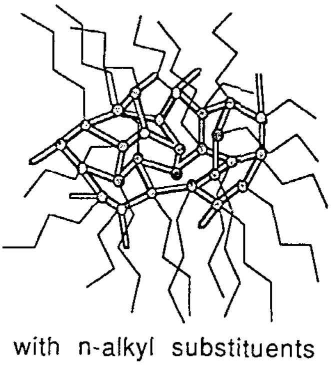


Figure 1 Postulated polymer structure.

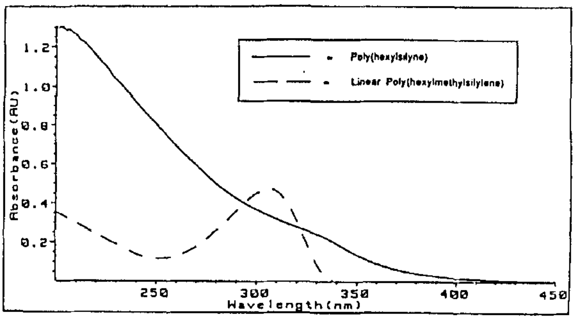


Figure 2 Absorption spectra comparison of the polysilanes and the polysilynes.

Recently, we reported the synthesis of the first soluble "*polysilynes*", a new class of amorphous silicon skeletical network materials[3]. The postulated structure of the material with n-akyl side chains is illustrated in figure 1 . All spectroscopic data collected indicate that the polysilynes are constructed primarily of *sp^3*-hybridized alkyl silicon units assembled via Si-Si bonds into irregular amorphous networks. One can infer from steric considerations that these materials exist as semirigid "quasi" two-dimensional sheet-like structures. This conclusion is supported by solution and solid state Si NMR data which indicate that ~80% of the silicons are bonded to three other Si atoms with one akyl group attached with the geometry dominated by six member rings. ESR data indicates that all atoms are fully coordinated, i.e., there are essentially no dangling bonds present.

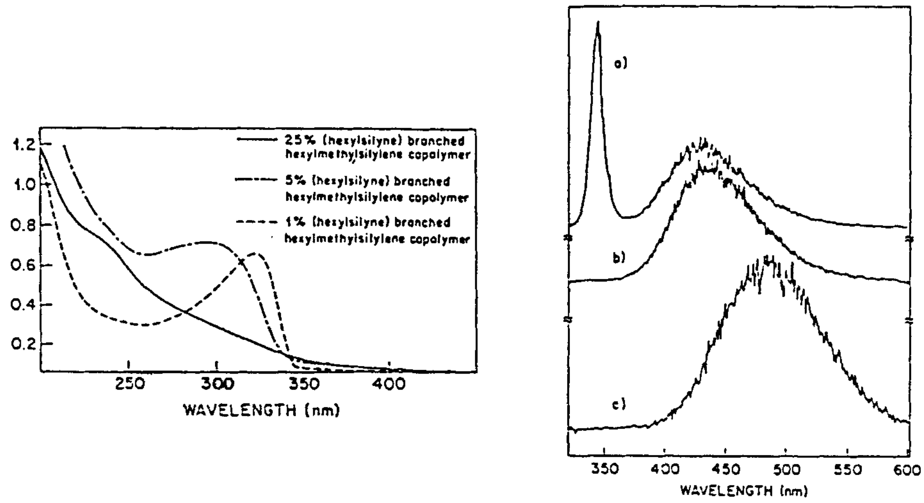
Spectroscopically the polysilynes exhibit intense near UV absorptions indicative of Si-Si σ-conjugation analogous to the polysilanes. The absorption spectrum comparison shown in figure 2 illustrates both the similarities and differences between this network polymer and the linear material. Although there is clear near UV to visible absorption present, there is no distinct well resolved σ-σ^* transition observed. In addition, the absorption tails far into the visible region of the spectrum. In emission the differences are also apparent. In linear polysilanes there is strong emission, slightly stokes shifted,(i.e. $<1000\text{cm}^{-1}$), with a bandwidth of the order of 1-10nm. In polysilynes, the intense emission is highly stokes shifted, (>2000 cm^{-1}), with bandwidths typically 100nm or greater.

In this paper we review the steady-state and time resolved spectral properties of the network polysilynes. We establish a correlation between the structure of the material and it's observed spectral properties. We show that all spectral evidence suggests that these novel materials have properties which may be interpreted using the same models successfully applied to amorphous semiconductors.

All thin film samples used in this work were prepared using the sonochemical techniques described in detail in references 3 and 4. Photoluminescence decays and time resolved spectroscopic data were obtained using a time correlated single photon counting apparatus which is described in detail elsewhere[4]. Decay data were analyzed using an iterative convolution analysis. The typical impulse response through the entire time resolved spectrometer varied from 55-65ps. All luminescence data were taken in a front face reflection configuration. The emission behavior at 20K was independent of excitation wavelength in the range studied (280-320nm).

One can develop a structural picture which illustrates how both the absorption and emission spectra evolve by probing a series of alkyl silicon copolymers where different levels of branch-points are incorporated into a linear polysilane backbone. The effects of branching on the electronic spectrum are illustrated by the comparison in Figure 3. While the 1-2% branched copolymer absorption spectrum is similar to linear polysilane data, at 5-10% branching, a noticeable blue shift and broadening of the Si-Si σ-σ^* transition is clearly observed. Further increase in branching results in the redistribution of oscillator strength along the absorption edge with loss of the well resolved Si-Si σ-σ^* absorption feature. While the greatest increase is noted towards higher energy, there is also a distinct tailing of the absorption edge into the visible region of the spectrum. The effect of low levels of branching is far more evident in the comparison of the emission spectra illustrated in Figure 4(a-c). The ratio of the band edge, (σ-σ^* 340nm), to red "***impurity***" emission (430nm) is greater than 50 : 1 in linear polysilanes. (It should be noted the that assignment of this red emission is still in question.) This ratio dramatically decreases to nearly 2 : 1 in the 1% branched sample,(trace (a)), and to more than 1 : 50 in the 5% branched polymer, (trace (b)). Further increases in branching result in the slow shift of the entire visible emission band to lower energy with the complete loss of σ-σ^* excitonic emission, (trace (c)).

Analysis of the systems photophysical dynamics can give us a greater insight of the nature of the polymer excited states. The time resolved luminescence decays associated with the emission maxima of the polysilyne and the polysilane copolymers are illustrated in Figure 5. The strong 340nm"***excitonic***" emission of the linear polymer decays as a single exponential with a 300 ps lifetime, (Fig. 5a). This lifetime is consistent with what has been measured for the σ-σ^* transition in other silicon chain polymers[5]. The temporal characteristics of the "***impurity/relaxed***" emission in Figure 5b is substantially different. The decay dynamics are highly nonexponential with decay times distributed over at least 3 orders of magnitude, (100ps-100ns). The polysilyne emission, which consists of a single strong band centered at approximately 480nm, is also highly non-exponential, resembling temporially the weak emission of the linear polymer.



Figures 3 and 4: Absorption and emission spectra of polymers studied. Data shows the correlation of the spectral features to changes in the polymer structure.

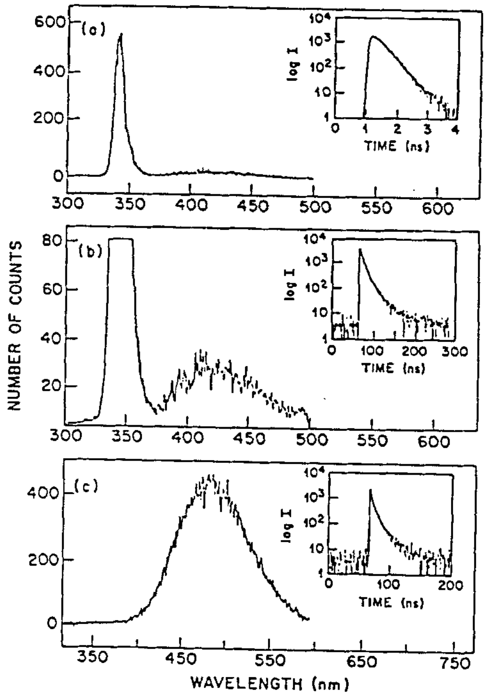


Figure 5(a-c): Timeresolved emission data. a) Linear polysilane. b) Linear polymer relaxed emission. c) Polysilyne enission.

It should be noted that both these cases the luminescence quantum efficiency is greater than 10%. One important observation, (which is shown in figure 6), is that there is a large variance in decay time distribution as one tunes across the emission band with the blue edge lifetimes substantially faster than those on the red edge.

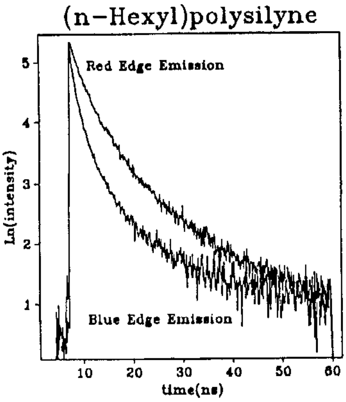


Figure 6: Frequency dependence of polysilyne decay dynamics

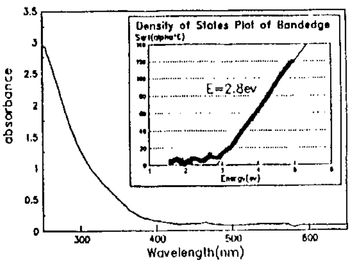


Figure 7: Plot of absorption edge of (n-hexyl)polysilyne. The insert shows a density of states plot of the edge which is used to extract a approximate bandgap.

(This variance is observed to a lesser extent for the polysilane impurity emission). These unusual spectral observations are quite consistent with the behavior seen for carrier recombination processes in semiconductors. The similarity of the lifetime distributions observed in the polysilyne emission data to those reported for amorphous silicon suggests its recombination processes may be described by models assuming a "***bandtail-like***" distributions of localized electronic states. Physically the network structure, (branch points in the linear polymer), results in bond angle and length distortions which induce the formation of localized states giving the "***bandtail***" like absorption. MO calculations for linear polysilanes indicate that distortions of this nature could easily result in a .5-1ev shift in the material bandgap[6a]. These sights which tend to localize the electronic states possibly serve as centers for radiative and nonradiative recombination. Figure 7 illustrates the absorption edge of (n-hexyl)polysilyne. The amorphous semiconductor nature of the edge is evident. The "***pseudo***" band gap obtained from the Tauc plot, (insert), (2.8cm^{-1}), is consistent with recent band structure calculations for an idealized 2D polysilane[6b]. A more accurate description of our material incorporating the random ring structure of our polymer needs to be developed and will be the subject of future work.

The observed recombination behavior can be described as shown in figure 8. Upon excitation, the excited entity, (an correlated electron-hole pair), either ionizes with the electron and hole localizing to different spatial positions on the polymer structure, or possibly forms a polaron-like self trapped entity. These processes are mediated by the electron-phonon interaction, (EPC), and allows the polymer to minimize the energy of the excited configuration. In either case the spatial extent of the carriers is greatly reduced. The lifetime therefore is determined by the effective overlap of the electron and hole wavefunctions with the larger electron radius mainly responsible for the decay dynamics. The luminescence energy of the emitting state is modified due to coulomb interaction of the electron-hole pair, (due to the effective binding energy), and carrier thermalization via EPC.

In summary, the polysilyne photoluminescence data suggests that the species generated following photoexcitation in this system behave as trapped electron-hole pairs rather than small radius excitons. This result is consistent with the observations of both a distribution of decay times and the change in the emission lifetime as a function of wavelength. The luminescence dynamics in this electron-hole recombination picture can be fit using trapping parameters, (effective wavefunction localization

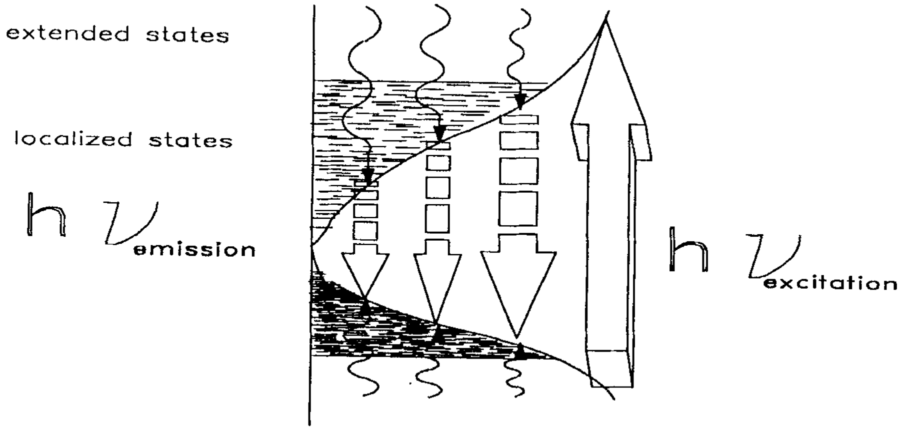


Figure 8 Bandtail diagram.

information), from *a*-Si data[4] using the finite size of the polymer molecule to limit the maximum lifetime. Additionally the branched copolymer data suggests that the linear polymer "***impurity***" emission may in fact result from a small concentration of branch points in the Si-Si backbone. These sites tend to localize the σ-σ^* exciton by serving as defect centers in the material. Detailed study of the thermalization and recombination dynamics are underway.

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