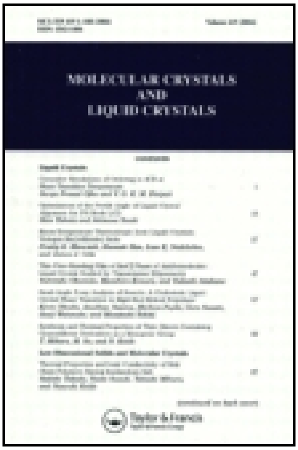

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Electronic and Vibrational Excitations in Polysilanes and Oligomers

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ELECTRONIC AND VIBRATIONAL EXCITATIONS IN POLYSILANES AND OLIGOMERS

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The polysilane polymers $[RR'Si]_n$ are the silicon analogues of the alkanes (see [1] for a review). They have a number of important applications arising largely from their photochemical activity. Of particular interest, however, are their electronic excited states which, unlike the alkanes, show evidence of delocalized sigma bonding along the polymer backbone, and lead to a host of interesting linear and non-linear optical phenomena.

We will present recent optical experiments that have been performed to investigate the consequences of sigma conjugation and the nature of excited states and excited state dynamics. These results are summarized in Table I.

1. Super Emission:

The radiative lifetime of polysilane polymers has been determined to be ~700 ps. This is ~25 times shorter than the absorption strength per Si–Si bond would predict and suggests a chromophore length of ~25 silicon atoms over which excitations are delocalized (2). The behavior is thus characteristic of a super emissive molecule. In other experiments saturation spectroscopy [15] was used to obtain an upper limit for the average excitation conjugation length. In this method the number of photons needed to bleach the absorption is measured (using fs pulses) and used to calculate the number of absorbing centers, hence the number of silicons per excitation. The experiment yielded an upper limit of 25 silicon atoms and a most probable value of 10–15 atoms for each absorbed photon, in reasonable agreement with the extent of delocalization obtained from fluorescence lifetimes [2]. The results are summarized in Table I.

The process of spatial energy transfer in the polymers has been followed by the technique of time-resolved fluorescence depolarization [2,3] which reveals relaxations occurring on several different timescales from picosecond to nanosecond and longer. We have concluded that energy migration along a twisted chain is a principal cause of the anisotropy loss that occurs prior to any possible motion of the whole polymer chain in the laboratory frame.

Table I: EXCITATIONS IN POLYSILANES

PROPERTY	RESULT	METHOD
"Size" of Excitation	20-30 Bonds	Radiative Power
	~20 Bonds	Saturation of Excitations
Motion of Excitations	100 fs-2ps	Dipole Anisotropy
Energy Transport-Spectral Diffusion	700 fs; 300 K	fs. Pump/Probe
	2-25 ps; 4K	Holeburning
Coupling to Phonons	Very small (1-2%)	Absorption
	Small (4-8%)	Resonance Emission
Localization	Localized by defects	Temperature dependence of Radiative Power
	Low energy states most localized	Resonance Emission
Dephasing	By Energy transfer below 10K (T_1 controlled) otherwise by 37 cm^{-1} phonon	Temperature dependence of holewidth
Excited State Charge separation	Exciton; Tightly bound electron-hole pair	Third order Susceptibilities
Excited State Parity	First excited state-odd parity. Second excited state-even parity	Two-photon Spectrum

2. Photochemistry and Hole burning:

The first observation of hole-burning in the optical spectra of delocalized polymer backbone states showed that narrow photochemical holes (~1cm^{-1}) could be burnt in the inhomogeneous spectrum of the glassy polymer at low temperature (4). We have studied the temperature dependence and energy dependence of the holewidth (5). There is a residual zero temperature width of ca. 0.4 cm^{-1} and an Arrhenius-like line broadening having an activation energy of 37 cm^{-1}. We find the hole width to increase with increasing separation between the excitation energy and the absorption edge. These results are shown in Figure 1.

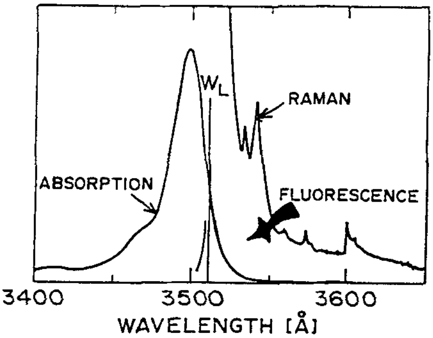

Fig. 1a Absorption (left) and emission (right) spectra of PDHS in 3MP at 1.4 K. L indicates the position of the laser. The frequencies of the vibrations observed in emission are: 175, 227/239, 390, 492, 702 cm^{-1}, the strongest lines are underlined and appear also in absorption.

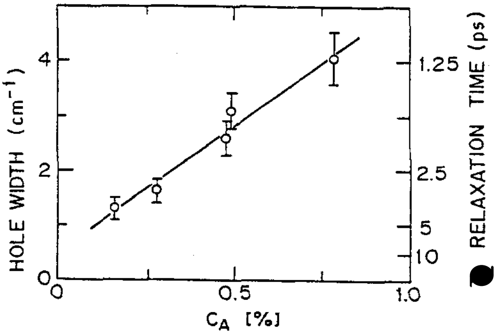

Fig. 1b Variation of the observed holewidth of PDHS in 3MP at 1.4 K as a function of the concentration of states at energies lower than the burning laser. The measurements correspond, for increasing values of C_A, to laser wavelengths of 351.5, 351.0, 350.5, and 350.0 nm.

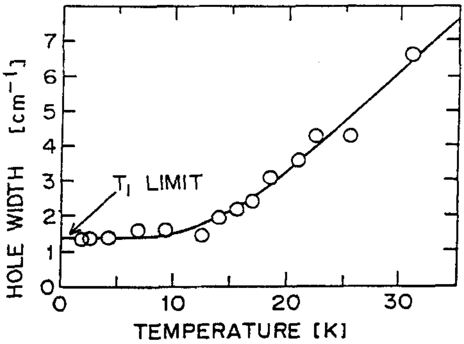

Fig. 1c Temperature dependence of holewidth

Narrow-band laser excitation of low-temperature solid films of poly(di-n-hexylsilane) showed photochemically induced absorption changes that indicated that extensive energy transfer occurred after light absorption [6].

The low temperature glassy spectrum of the polymer can be modelled by introducing a small random Gaussian energy disorder at silicon sites in a linear chain, analogous to the continuous disorder caused by curvature of the skeleton, proposed for polydiacetylene [7] leading to the conclusion that the lowest energy states of the chain have extents of about 10 silicon atoms as a result of Anderson type localization. In this model, energy transfer prior to photochemistry (5,8-10), determines the holeburning spectrum.

Evidence from these hole-burning studies and the very small (<10 cm^{-1}) shift of the fluorescence and absorption peaks found in low-temperature glasses shows that an individual chromophore upon excitation does not strongly relax due to coupling to the lattice. Negligible phonon structure is seen in absorption and emission spectra, and the excitations in polysilanes do not have the character of small polarons. By careful sample manipulation we have obtained spectra that directly display weak phonon coupling. Fluorescence emission is found to be highly sensitive to sample preparation, particularly the effects of dissolved molecular oxygen (9,10). Of particular interest is the increased Franck-Condon factor for resonance emission compared with absorption, consistent with localization occurring in the relaxation process.

We have observed transient absorptions at 450 nm and 370 nm in room temperature solutions of polyphenylmethylsilane (11) using picosecond laser pulses. We attribute a persistent transient absorption at 450 nm to photogenerated phenylmethylsilylene. The precursor state is likely to be a relaxed triplet state. Photochemical selection from the length distribution occurs from the solution-phase polymer at ambient temperature (the first example of *room temperature* hole-burning in solution) (11).

3. Multiphoton spectroscopy and excited state spectroscopy:

Two-photon excitation studies have identified a dipole forbidden even parity excited state ~1eV above the first excited odd parity state [12]. The 2-photon cross-section is large, indicative of high non-linear polarizability: i.e. $\delta = 10^{-48}$ cm^{4}sec^{-1}. This work has stimulated a theoretical reexamination of the problem of the energetic ordering of covalent/ionic states of 'alternated' linear chain polymers and the effects of electron correlation (13).

We have shown that the excitations in these polymers are best regarded as delocalized excitons and are similar to those found in the π-conjugated polydiacetylenes. Observation of 1,2 and 3 photon resonances (the latter by third harmonic generation [14]) has clarified this picture of excited states.

Excited states of poly(di-n-hexylsilane) appear in femtosecond transient absorption [13,15]. The state in the near infrared (~1eV) correlates well with that seen in two-photon spectroscopic measurements and is attributed to an exciton having charge transfer character. The even parity state in the ultra-violet (~3.5eV) is possibly a biexciton. Ab initio calculations present an alternative view of these g-states (16).

Femtosecond pump/probe experiments on linear-chain poly (di-n-hexylsilane) (15) allow energy transfer to be followed by the technique of time-resolved excited state absorption depolarization (15) which reveals highly dispersive kinetics characteristic of relaxations occurring on many different timescales from subpicosecond to nanosecond and longer. Fast energy transfer in the linear chain polymer is observed to occur on a time scale of 700 fs after excitation at short wavelength. This process populates a distribution of lower energy states through phonon assisted relaxations.

4. <u>Absorption spectra in the deep UV (2-30eV)</u>:

Polysilane properties depend on sidechains. To evaluate sidechain-backbone coupling spectra at high energies are needed: We have accomplished this with a plasma source reflectance spectrometer. Si-Si backbone excitonic transitions are seen from 3 to 5 eV and their energy is conformation dependent. At intermediate energies, from 5 to 8 eV, a transition ascribed to Si-C bond excitation, is invariant at 7.2 eV. At high energy, 8 to 20 eV, C-C excitations, comparable to those measured in polyethylene, are observed. Five such spectra are shown in Figure 2 [17].

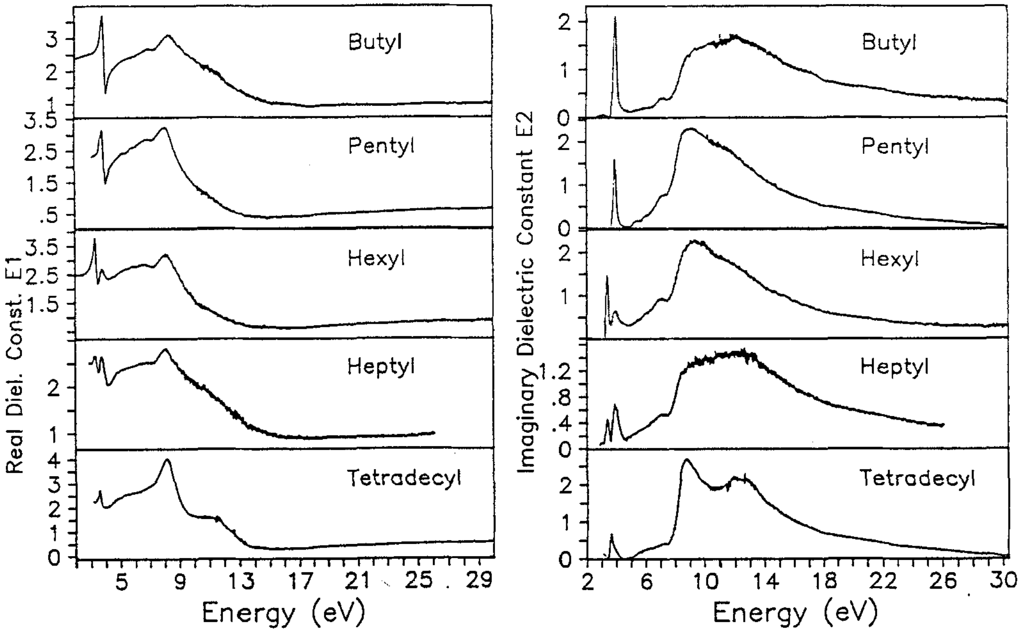

Fig. 2: Real and imaginary Parts of the dielectric constant for a series of poly(dialkylsilanes)

5. <u>Confinement of Excitations in Silicon Oligomers</u>:

Recently the absorption and fluorescence spectra of silanes, $Cl(SiMe_2)_2(SiPh_2)_5(SiMe_2)_2Cl$ and $Cl(SiMe_2)_2(SiPh_2)_5(SiMe_2)_2(SiPh_2)_5(SiMe_2)_2(SiPh_2)_5(SiMe_2)_2Cl$ with chain lengths, n = 9 and 23, silicon atoms were reported. As the silicon chain length decreases, the quantum yield of fluorescence drops, the emission becomes broad, structured and red shifted and the radiative lifetime increases. We have suggested that this demonstrates the change in character of the excitation from large super-emissive exciton-polaron to small exciton-polaron vibronically coupled molecular transition [18].

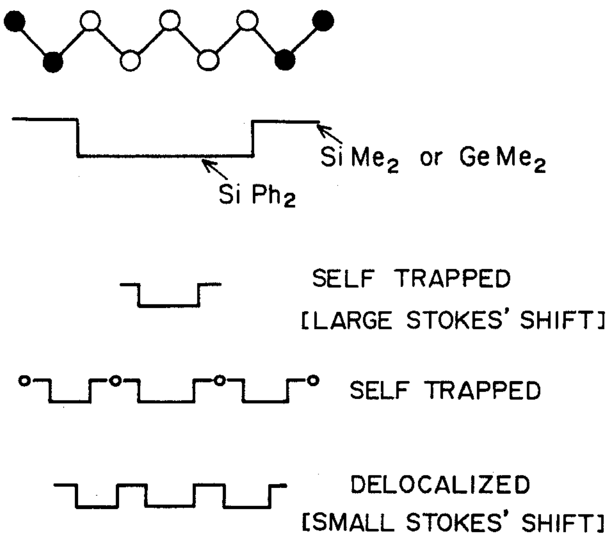

Fig. 3: Confinement of Excitations on Silicon Segments

The molecules studied are shown in cartoon form in Figure 3. The unit exciton "well" system cannot apparently support a delocalized state. The additional electronic vibrational interaction may be influeneced by the presence of another $(\sigma\pi^*)$ state caused to be nearby in the shorter chain . The oxygen bridges do not permit delocalization of the excitation but both $SiMe_2$ and $GeMe_2$ allow for efficient superexchange.

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