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EXCITED STATE DYNAMICS OF POLY-DI-N-HEXYL-SILANE+

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The soluble, disubstituted polysilanes, (SiXY)$_n$, present a class of novel materials with interesting electronic, optical, and conformational properties. The lowest energy electronic transitions correspond to $\sigma\sigma^*$ excitations, delocalized over many (ca. 20-30) silicon atoms, and give rise to a strong absorption in the near UV. The excited state dynamics is governed by fast competing processes of radiative decay, energy transfer along and between polymer chains, and photochemistry leading to chain scission.[1]

These compounds also exhibit a remarkable polymorphism in both liquid solutions and solid films. Solutions of symmetrically disubstituted compounds such as poly-di-n-hexyl-silane (PDHS), for example, undergo on cooling a first order like phase transition, accompanied by an abrupt large bathochromic shift from 320 to 350 nm and a dramatic narrowing of the very intense UV absorption spectrum. The nature of this phase transition as well as the precise description of the electronic excitations are still a matter of active research. In this work we summarize recent spectral measurement on PDHS in liquid solutions at room temperature and glasses at liquid helium temperatures and relate the observations ,within a linear chain exciton model, to the properties of the polymer chain.

In room temperature solutions the processes of spatial energy transfer have been folllowed by time-resolved fluorescence depolarization on a picosecond timescale.[2] Transient absorption measurements show that the initial decay of the excited state occurs on a 700 fs timescale.[3]

The excitation dynamics of PDHS in low temperature glassy solutions has been followed by monitoring the spectral distribution of the photodamage subsequent to frequency selective laser excitation.[4,5] The width of the narrow hole at the exciting laser wavelength measures the lifetime of the initially excited state and is predominantly determined by excitation transfer to lower energy states. This transfer is traced by the photolysis of material absorbing at longer wavelengths.

The excitations of the polymer chain have been described by a model which regards the polymer as a weakly disordered chain, in which the excitation is treated as a Frenkel exciton.[5,6] The model does not specify the nature of the elementary excitation which may be described as a mixture of bond as well as charge transfer excited configurations.[7] This model was successfully used to numerically simulate the absorption spectra both in room temperature

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solutions above the phase transition and in the low temperature glasses, to explain the observed holeburning spectra as a function of excitation wavelength, and to predict the position of the maximum and the width of the emission spectra. All observations can be understood in terms of excitation transfer to lower energy states. No additional energy relaxation such as polaron formation is needed. Altogether it appears that the energy disorder model gives a very satisfactory description of the spectral properties of PDHS in solutions above as well as below the phase transition.

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