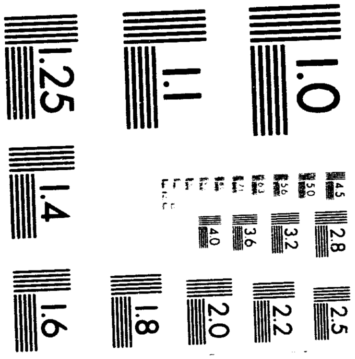
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TEMPERATURE DEPENDENCE OF THE EXCITON-EXCITON ANNIHILATION RATE CONSTANT IN POLY(DI-N-HEXYLSILANE)

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ABSTRACT

Fluorescence depolarization studies of polysilane chains in solution have shown that energy transfer along the polymer chains occurs for only a very short time relative to the excited state lifetime and only over short distances before the excited states become trapped in long, low-energy segments. However, in solid films we have shown in previous work that excitons are highly mobile throughout their 600 ps lifetime at room temperature, presumably because energy transfer among neighboring, parallel chain segments becomes possible. In this paper we report that the exciton-exciton annihilation rate constant decreases by only a factor of five between room temperature and 12 K, showing that the excitons do not become trapped even at low temperatures.

INTRODUCTION

With the advent of organic light emitting diodes, interest in those phenomena which might limit the quantum efficiency for fluorescence in organic solid films has increased markedly. Exciton-exciton annihilation, in which two singlet excitons interact to create one highly excited state which nonradiatively decays to a single exciton, is one of those phenomena. In previous work we have shown that this process is very efficient in polysilanes, σ-conjugated polymers with an all silicon backbone.

The absorption spectra of polysilanes consist of broad, featureless bands which, it is generally assumed, result from absorption by random length, ordered, all-trans segments on the order of 20 silicon atoms long, which are separated by undefined, conformational chain defects[1, 2]. The fluorescence spectra are narrower and on the low energy side of the absorption band. These observations have led to the conclusion that energy is transferred from shorter, higher energy segments to longer, lower energy segments before fluorescence occurs[2]. Fluorescence depolarization experiments on molecules in solution[3] have shown that this energy transfer occurs only on a very short time scale, <30 ps, even though the excited state liftime in solution is about 150 ps, and that fluorescence depolarization is far from complete, indicating that the distance over which the energy is transferred along the chain is very short.

In solid films, on the other hand, even though the absorption and fluorescence spectra are essentially the same as those in solution, we have found that the excitons are highly mobile[4, 5]. The exciton-exciton annihilation rate constant is about 10^{-7} cm^3 s^{-1}, ten times larger than the same rate constant in an anthracene crystal[4], and the excitons remain mobile throughout their 600 ps lifetime[5]. The annihilation rate constant was determined by measuring the fluorescence intensity versus the excitation intensity and fitting the results with the following rate equation for the exciton concentration, n

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$$\frac{dn}{dt} = \alpha I_0 e^{-\alpha x} - \beta n - \gamma n^2 \qquad (1)$$

where a is the absorption coefficient, Io is the intensity of the incident light in photons cm-2 s-1, x is the distance into the sample, β is the reciprocal of the exciton lifetime and γ is the exciton-exciton annihilation rate constant. The fluorescence intensity was assumed to be proportional to the exciton concentration n. In the more recent work[5], we found that about 0.1% of the annihilation events in poly(di-n-hexylsilane) create a free charge carrier and that observation allowed us to show that the excitons remain mobile throughout their 600 ps lifetime. By using two 30 ps laser pulses separated by a variable amount of time, we were able to show that the number of active excitons was equal to the sum of the number left from the first pulse and those created by the second pulse. The concentration of excitons in this experiment was kept low so that loss of excitons by exciton-exciton annilation could be neglected.

The results reported in this paper show that γ is only weakly dependent on temperature, decreasing only by a factor of five between room temperature and 12 K, and thus that excitons are not trapped in long, low-energy segments in poly(di-n-hexylsilane), even at low temperature. The clear evidence that excitons are trapped in long segments in polysilane molecules in solution has led some to conclude that the same thing is happening in the solid state and these results clearly show that is not the case. Presumably the fact that energy transfer can occur to neighboring, parallel chain segments through dipole-dipole interactions is responsible for the very different behavior.

EXPERIMENTAL RESULTS

We have measured the fluorescence intensity as a function of the incident light intensity and we conducted the measurements at two temperatures, ambient and 12 K. The sample used was spun from a toluene solution onto a UV quartz substrate and was about 100 nm thick. For all experimental measurements it was mounted on a cold finger in a vacuum. The light used for excitation was a 5 ns pulse at 297 nm from a Nd:YAG pumped dye laser and the fluorescence intensity was measured at the peak of the fluorescence intensity, 378 nm at ambient temperature and 370 nm at 12 K, with a photomultipler-monochromator combination and the signal from the photomultiplier was integrated over the fluorescent light pulse with a gated boxcar averager. The absorption coefficient at 297 nm was measured to be 2 x 10^4 cm^{-1} at ambient temperature so that for a 100 nm thick sample the light intensity decreases by less than 20% in traversing the sample. We assumed that the light intensity was constant throughout the sample and used Eq. 1 to compare theory and experiment.

In order to compare the low temperature data to the ambient temperature data and thus determine the change in γ, we had to measure the absorption coefficient and the exciton lifetime at ambient temperature and at 12 K. The absorption coefficient was measured by illuminating the sample with monochromatic light from a xenon arc-monochromator combination and measuring the intensity of light transmitted with a photomultiplier. The experimental results are shown in Fig. 1. The exciton lifetime was measured with a fast photodiode and fast-gated boxcar integrator. The rise and fall time of the photodiode was less than 100 ps and the gate width of the fast sampler was

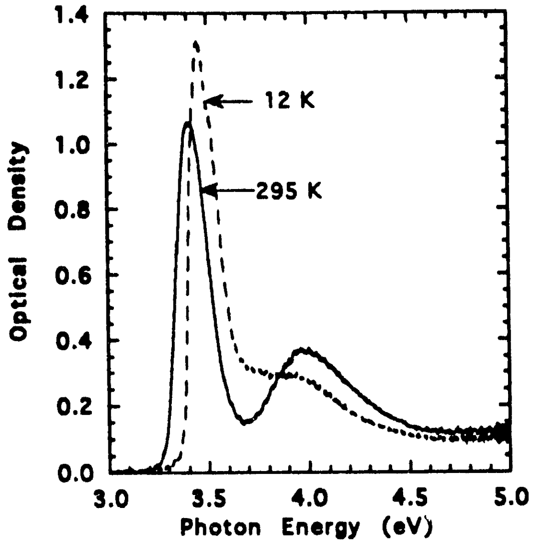

Fig. 1. Absorption spectrum of poly(di-n-hexylsilane) at 295 K and 12 K.

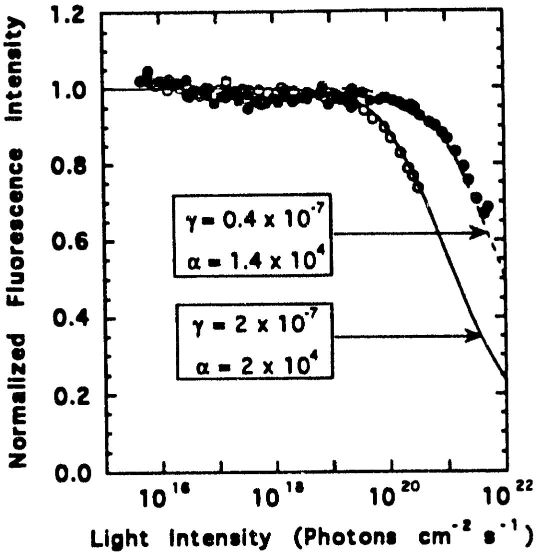

Fig. 2. The ratio of the fluorescence intensity to the incident light intensity normalized to one at low intensity, at 295 K open circles and at 12 K solid circles. The solid and dashed lines were calculated from Eq. 1 using the constants in square boxes.

100 ps. Within the accuracy of our measurements, which we estimate to be on the order of 100 ps, the fluorescence lifetime of the sample, which was about 600 ps, did not change between room temperature and 12 K.

The fluorescence intensity data as a function of exciting light intensity are plotted in Fig. 2. The ratio of the fluorescence intensity to the exciting light intensity, normalized to one at low exciting light intensity, is plotted versus the exciting light intensity. The prediction of Eq. 1 with $\gamma = 2 \times 10^{-7}$ cm^3 s^{-1}, $\alpha = 2 \times 10^4$ cm^{-1} and $\beta = 1.67 \times 10^9$ is shown as the solid line which agrees well with the room temperature data, open circles. The value of γ at room temperature was taken from our recent paper on exciton kinetics in poly(di-n-hexylsilane)[5]. The dashed line was calculated using the value of α determined from the data in Fig. 1, keeping β constant and using γ as an adjustable constant. The line shown was calculated using $\alpha = 1.4 \times 10^4$ cm^{-1} and $\gamma = 0.4 \times 10^{-7}$ cm^3 s^{-1}.

DISCUSSION

These results indicate that γ does become somewhat smaller at 14 K but only by a factor of about 5. Previous measurements on poly(n-propylmethylsilane)[6] also indicated that γ decreased in that material upon lowering the temperature from room temperature to approximately the same low temperature but again by at most a factor of three.

These results, coupled with the results which demonstrated that the excitons remain mobile throughout their lifetime[5], show quite conclusively that excitons are not trapped in long low-energy segments, even at low temperatures in solid polysilane films. This conclusion contrasts sharply with that reached based on studies of isolated molecules in dilute solutions as described in the introduction. In isolated molecules, energy is transferred only during a small fraction of the excited state lifetime and only for a short distance, presumably along the chain. The difference seems to be that in the solid state energy transfer to neighboring parallel segments is possible and that transfer in that direction is very fast. If we assume that $\gamma = 8\pi DR$ [7] and R = 3 nm, we conclude that the exciton diffusion coefficient D is 0.03 $cm^2\ s^{-1}$. By contrast, the exciton diffusion coefficient in anthracene crystals is generally believed to be[8] about 0.001 $cm^2\ s^{-1}$.

In spite of the fact that we have found that γ can be quite large, it is highly unlikely that exciton-exciton annihilation will be a factor in organic light emitting diodes. Even though γ is unusually large in polysilanes, an LED would have to be operating at a brightness considerably above 10^6 candela m^{-2} before a significant fraction of the excitons are lost by exciton-exciton annihilation.

ACKNOWLEDGEMENTS

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