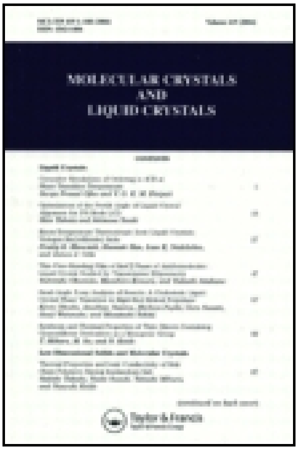

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R. G. Kepler [a] & J. M. Zeigler [a]

[a] Sandia National Laboratories, Albuquerque, NM, 87185

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Mutual Annihilation of Singlet Excitons in σ-Conjugated Polysilanes†

R. G. KEPLER and J. M. ZEIGLER
Sandia National Laboratories, Albuquerque, NM 87185

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In previous papers, we have reported that the exciton-exciton annihilation rate constant is very high for singlet excitons in poly(*n*-propyl methyl silane) and that it is insensitive to temperature. In this paper, we report further that this rate constant is roughly the same magnitude as that found earlier in both poly(phenyl methyl silane) and poly(di-*n*-hexyl silane), and that it is not affected by the molecular weight of the polymer, at least in poly (di-*n*-hexyl silane). However, solid films of poly(di-*n*-hexyl silane) undergo an order-disorder transition near 42°C, and it appears that this transition causes an order of magnitude decrease in the annihilation rate constant.

INTRODUCTION

During the past thirty years, there have been extensive studies of the electronic properties of organic materials,[1] essentially all of them on the role of π electrons. The contribution of σ electrons to the interesting electronic properties of these materials could be neglected. Recently it has been found that polysilanes exhibit many of the same electronic properties as those thought to arise exclusively from the conjugated π electrons. Polysilanes are polymers with a backbone composed of σ-bonded silicon atoms with two organic side groups attached to each silicon atom. Poly(di-*n*-hexyl silane) is, for example, a silicon chain with two *n*-hexyl groups, six carbon atoms in a linear chain with appropriate hydrogen atoms attached to each carbon atom. Solid films of polysilanes have been shown to be excellent photoconductors.[2] Both in solution and the solid state polysilanes exhibit high quantum efficiencies for fluorescence and absorption spectra which depend strongly on molecular weight[3] and conformation. [4] We have also shown that singlet excitons are highly mobile in solid films.[5,6]

It has been clearly shown that these interesting properties result from the delocalized σ electrons on the silicon backbone and from σ-σ* electronic transitions.[3,7]

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The theoretical model that appears, at the present time, to describe best the experimental observations, considers the polysilane chain to be composed of a large number of shorter ordered segments (on the order of 10 to 30 silicon atoms) which are separated by conformational chain defects. Within the shorter segments, the electronic states are believed to be well defined with energies which depend strongly on the variable length of the segments.[3,7]

In earlier papers,[5,6] we have reported that the exciton-exciton annihilation rate constant for singlet excitons in poly(*n*-propyl methyl silane), is very high,[5] on the order of 1×10^{-7} cm^3 s^{-1}, and quite insensitive to temperature. We found that the rate constant changed by less than a factor of three between room temperature and 20 K, if it changes at all.[6]

In this paper, we report that the exciton-exciton annihilation rate constants in poly(di-*n*-hexyl silane) and poly(phenyl methyl silane) are essentially the same as that in poly(*n*-propyl methyl silane). We could find no molecular weight dependence for the rate constant in poly(di-*n*-hexyl silane), and we present evidence that it may decrease by an order of magnitude when poly (di-*n*-hexyl silane) undergoes an order-disorder transition which occurs in solid films in the vicinity of 42°C.[8]

EXPERIMENTS

Films of varying thickness, up to 10's of microns, were prepared by solvent (toluene) casting on UV quartz substrates. Spin casting was used to prepare films less than 1μm thick. The samples were mounted on a temperature controlled finger in a vacuum chamber. Polysilanes were synthesized by adding sodium dispersion to a solution of the appropriate dichlorosilane in refluxing dry solvent by the method of Zeigler.[9] All samples had narrow molecular weight distributions ($M_w/M_n < 1.5$) and typical molecular weights of about 7×10^5. In order to look for a molecular weight dependence, we also conducted experiments on a specially prepared poly(di-*n*-hexyl silane) sample with a weight average molecular weight of 28×10^3. These weights correspond to chain lengths of approximately 10,000 Si atoms and 400 Si atoms, respectively.

Excitons were created in the films by single-photon transitions using strongly absorbed light. The strongly absorbed light, 320 nm, was obtained by pumping a dye laser with the 532 nm frequency doubled light from a neodymium doped YAG laser with a pulse width at half maximum of about 4.5 nsec.

An experiment consisted of measuring an approximation of the peak fluorescent light intensity during a pulse as a function of the intensity of the incident light. The incident light intensity was measured using a pellicle to reflect a fraction of the beam into a light meter (Laser Precision Corporation Energy Ratiometer, Model Rj-7200). This measurement provides only a measure of the total energy in the beam. We have neglected the temporal variations in the incident light pulse and assumed that the pulse shape was triangular with a full width of 9 nsec. The intensity was varied using a series of filters. The fluorescence intensity was measured using a Hamamatsu R2024V gated microchannel plate photomultiplier and a Tektronix 7912 AD Programmable Digitizer with a 7A29 plug-in. As discussed below, the lifetimes of the excitons ranged from near 70 ps to 600 ps. Therefore, evidence for the rapid temporal fluctuations in the incident light could be seen, but only the peak intensity of the fluorescence observed was recorded. It was assumed that this peak intensity was a measure of an equilibrium concentration of excitons. The light intensity incident on the photomultiplier was maintained in the linear range of the photomultiplier by using a series of calibrated neutral density filters and the intensity of the light incident on the sample was limited to those intensities which caused negligible damage to the sample as evidenced by the repeatability of the experimental results.

The experimental data were analyzed using the following phenomenological equation

$$\frac{dn}{dt} = \alpha I_o e^{-\alpha x} - \beta n - \gamma n^2$$

where n is the exciton concentration, α the absorption coefficient for the incident light at 320 nm, I_o the incident light intensity, x the distance from the illuminated surface, β the reciprocal of the exciton lifetime, and γ the exciton-exciton annihilation rate constant. In writing this equation, we are assuming that singlet excitons annihilate one another, presumably by creating one very highly excited state from the two excitons. We have assumed that the highly excited state is quickly converted to a thermalized singlet exciton by radiationless transitions. If we were to assume that both excitons disappeared in each event, it would only change the annihilation rate constant, γ, by a factor of two.

The absorption coefficient α at 320 nm was determined by measuring the optical density and thickness of several spin cast films. The values obtained were 2.4×10^5 cm^{-1} for poly(*n*-propyl methyl silane) and 1.3×10^5 cm^{-1} for poly(phenyl methyl silane). As mentioned above, poly(di n-hexyl silane) films undergo an order disorder transition at about 42°C, and this transition has a significant effect on the electronic states.[8] Below the transition α is 3.7×10^4 cm^{-1} and above the transition, it is 8.4×10^4 cm^{-1}. The exciton lifetime, β^{-1}, in poly(phenyl methyl silane) is reported to be 73 ps,[10] and in poly(di-*n*-hexyl silane), about 600 ps[11] and about 200 ps[11] below and above, respectively, the order-disorder transition.

Typical experimental results obtained when we measured the fluorescence intensity as a function of the incident laser light intensity for a 16 μm thick sample of poly(di-*n*-hexyl silane) are shown in Figure 1. The ordinate and abscissa in these figures are the total number of excitons in the sample and the total number of photons arriving per unit time, respectively. The approximate area of the laser beam was 0.1 cm^2.

In interpreting these experiments, we assume that the exciton concentration is in equilibrium, $dn/dx = 0$, so that the solution to the phenomenological equation is

$$n = \frac{\beta}{2\gamma}\left(-1 + \sqrt{1 + Ae^{-\alpha x}}\right)$$

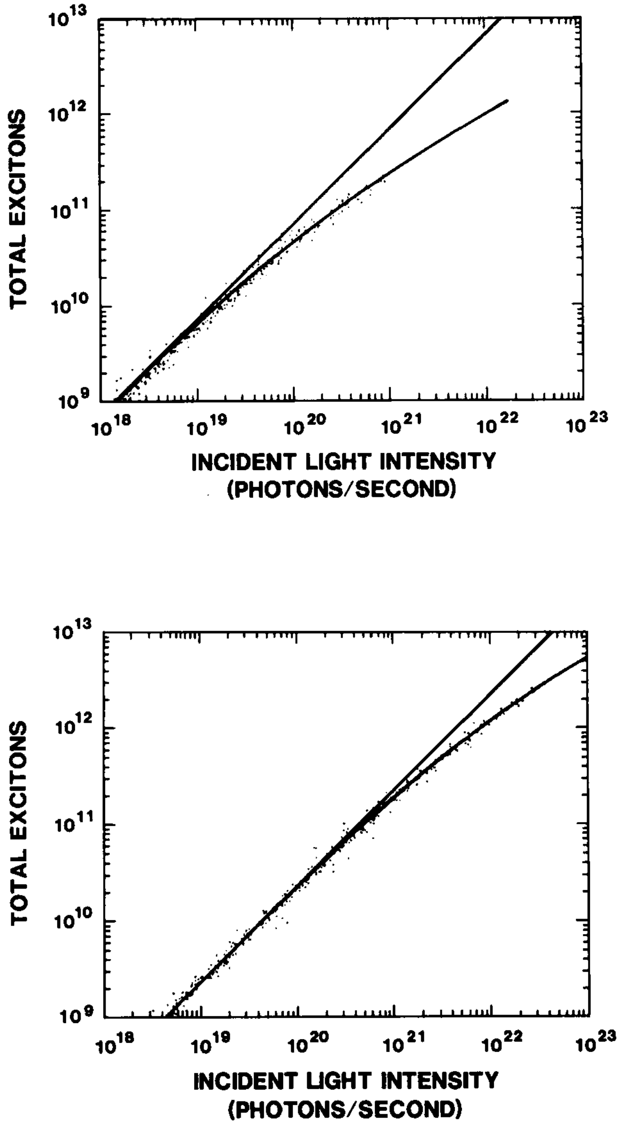

FIGURE 1 The total number of excitons present at equilibrium as a function of strongly absorbed laser light intensity in poly(di-*n*-hexyl silane). The wavelength of the exciting light was 320 nm. The data in Figure 1(A) were taken at room temperature, those in Figure 1(B) at 60°C. The approximate area of the laser beam was 0.2 cm^2.

where

$$A = \frac{4\alpha \gamma I_o}{\beta^2}$$

Experimentally we measured the total number of excitons created and thus our signal ϕ is

$$\phi = \int_o^\infty n dx = \frac{\beta}{2\gamma}\left[\sqrt{1 + A} - 1 - \ln\left(\frac{\sqrt{1 + A} + 1}{2}\right)\right]$$

Since the beam intensity was not uniform spatially, we calculated the expected signal by dividing the beam into 900 equal area regions and measured the incident light intensity in each region. We then calculated the expected number of excitons in each region and summed over all 900 regions. The curved lines in Figure 1 were determined in this fashion, and the experimental data were fit by using the exciton-exciton annihilation rate constant as the only adjustable parameter.

Using this procedure, the γ obtained for a 2 μm thick sample of poly(*n*-propyl methyl silane) was 6×10^{-8} cm^3/sec and for a 26 μm thick sample of poly(phenyl methyl silane), γ was found to be 8×10^{-8} cm^3/sec. For poly(di-*n*-hexyl silane), we made measurements on two samples (one 5 μm thick and one 16 μm thick) at two temperatures (23°C and 60°C). At 23°C, the γ's obtained for the 5 μm samples were 12×10^{-8} cm^3/sec and 7×10^{-8} cm^3/sec, respectively, and at 60°C, they were both 1×10^{-8} cm^3/sec. These data indicate that in poly(di-*n*-hexyl silane) the exciton-exciton annihilation rate constant is about an order-or-magnitude smaller above an order-disorder-transition than it is below the transition.

We have measured γ in samples of poly(di-*n*-hexyl silane) with vastly different chain lengths, two with chain lengths of approximately 10,000 Si atoms (reported above) and another with chain lengths of approximately 400 Si atoms. We were unable to detect a significant difference. The rate constant determined for the low molecular weight sample was 8×10^{-8} cm^3/sec.

DISCUSSION

As we have pointed out previously,[5] it is important to examine the possibility that our observations result from some process other than exciton-exciton annihilation. The most obvious experiment to conduct to establish exciton-exciton annihilation as the process would be to look for a decrease in the exciton lifetime at high concentrations. We have been unable to carry out this experiment so far. The most obvious possible alternate process which might explain the experimental results is exciton photo-ionization. We believe that it is unlikely that our results can be explained by this process because the exciton photo-ionization coefficient at 320 nm would have to be unrealistically high to account for the observations. If σ is the exciton photo-ionization cross-section, then σI would equal β at the intensity at which the rate of exciton loss by the intensity dependent process equals the rate of loss at low intensities. Since the intensity at which this occurs is about 10^{22} photons cm^{-2} sec^{-1}, σ would have to be about 10^{-13} cm^2, an unreasonably large value.

We believe that these results are strong evidence that excitons in polysilanes are highly mobile. The exciton concentration at which the rate of loss by exciton-exciton annihilation equals the rate of loss by other non-annihilation processes, can be determined by setting $\beta n = \gamma n^2$, giving $n = \beta/\gamma \sim 10^{16}$ cm^{-3}. At this concentration, the excitons are, on the average, several hundred angstroms apart.

If we assume that the excitons are particles, diffusing with a diffusion coefficient D, which annihilate one another if they come within the distance R of each other, the rate constant for exciton-exciton annihilation is given[12] by $\gamma = 8\pi DR$. If we further assume that $R = 20A$, a typical value for rapid energy transfer by dipole-dipole interactions, D is found to be about 0.01 cm^2/s^{-1}.

Further evidence for the fact that the values of γ observed in polysilanes are surprisingly large can be obtained by comparing them with the values observed in molecular crystals.[1] In anthracene single crystals, the reported values[13] for γ range from 2×10^{-9} to 4×10^{-8} cm^3 s^{-1}, and the largest value ever reported is 1×10^{-7} cm^3 s^{-1} in tetracene single crystals.[14] One possible explanation for the very large value of the interaction rate constant is that the excitons are moving very rapidly along the chains, thus sweeping out an unusually large volume or creating a very large interaction cross-section compared to excitons in molecular crystals. We know of no attempts to develop a theory for the effect of such a phenomena. In an attempt to test this hypothesis, we measured γ in samples made up of molecules approximately 10,000 silicon atoms long and in one sample made up of molecules approximately 400 silicon atoms long. Since we observed no significant difference in γ between those samples, as reported above, it appears unlikely that this can be an important effect.

We find it surprising that the exciton-exciton annihilation rate constant is so insensitive to its environment. In a previous publication,[6] we reported that we could observe no change in the magnitude of γ in poly(*n*-propyl methyl silane) when we lowered the temperature from room temperature to 20 K and in this paper we report that γ is comparable in poly(*n*-propyl methyl silane), poly(phenyl methyl silane) and poly(di-*n*-hexyl silane). Therefore, it is gratifying to find that γ in poly(di-*n*-hexyl silane) changes by an order of magnitude when the polymer undergoes an order-disorder transition. If these results stand up under our planned further scrutiny, it will be interesting to consider the theoretical implications. The evidence to date seems to suggest that excitons in polysilane films are very similar to excitons in molecular crystals with short segments (10 to 20 Si atoms) of the long polysilane molecules playing the role of the molecules in molecular crystals.

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