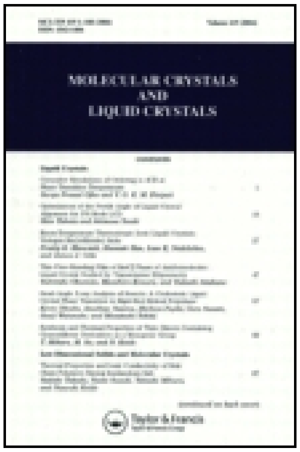

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Two-Photon Processes in Substituted Polysilanes

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TWO-PHOTON PROCESSES IN SUBSTITUTED POLYSILANES

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Abstract Chain scission induced by two-photon exposure produces a permanent birefringence in polysilane polymer films, which can be used for the formation of birefringent optical elements. Spectroscopy of the effect for poly(di-*n*-hexylsilane) reveals an unexpected sharp resonance at 579 nm. Models to explain these observations are introduced and discussed

INTRODUCTION

Polysilane polymers are polymers with a long, catenated σ-bonded silicon backbone and two sidegroups, usually carbon based, attached to each Si atom in the backbone chain [1]. In spite of the σ-bonded nature of the backbone, the polysilanes show extensive electronic delocalization, resulting in strong transitions for excitations polarized parallel to the backbone. The lowest energy transition is believed to be a σ-σ* excitation [2], with the σ* excited state even more delocalized than the ground state [3]. The oscillator strength of the σ-σ* transition in solution has been measured to be $f \approx 0.1$ (per Si-Si bond) [2], and absorption coefficients as large as 1-2x10^5 cm^{-1} in the solid state are typical. Figure 1 shows a plot of absorption vs. photon energy for 700 nm thick films of two di-alkyl substituted polysilanes. The linewidth of the UV transitions (≈350 meV) is believed to be inhomogeneously broadened by a distribution of chain segment lengths, and is comparable to the linewidth of the lowest energy excitonic transition in polydiacetylenes [4]. Unlike π-conjugated carbon compounds, such as the polydiacetylenes, polysilane absorption maxima occur in the near UV, between 300 and 400 nm, and films are completely transparent at visible wavelengths. Furthermore, polysilanes are soluble in most hydrocarbon solvents, and films of good optical quality

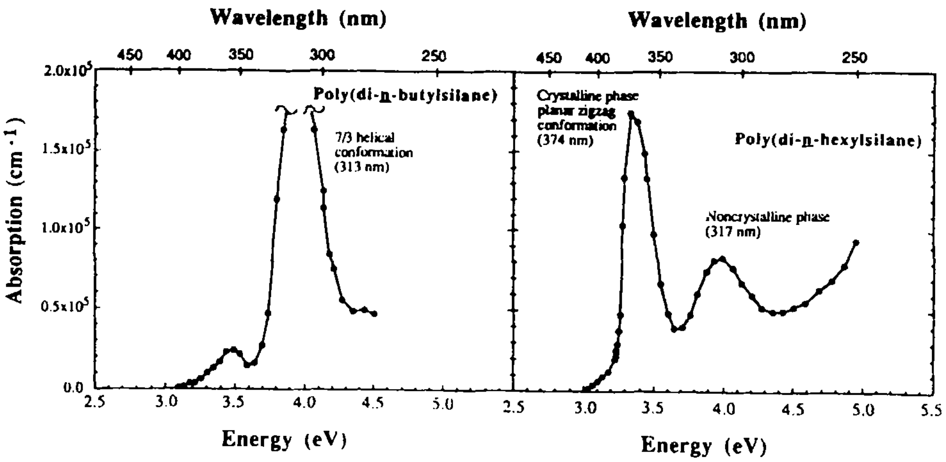

Fig. 1: Left) Absorption coefficient for a ≈700 nm thick film of poly(di-n-butylsilane), which is predominantly in the 7/3 helical conformation at room temperature. Right) Absorption coefficient for a ≈700 nm thick film of poly(di-n-hexylsilane) at room temperature. The sidechains of this polymer crystallize at room temperature, forcing the backbone into a planar zigzag conformation.

several microns thick can be fabricated with conventional spinning and coating techniques.

Decay of the σ^* state when excited by UV photons occurs primarily through fluorescence or photochemical reactions. Decay by polymer backbone scission reduces the polymer molecular weight, changing both the solubility and optical properties. Typical scission quantum yields for polysilanes in the solid state are low (about 1%) [1]. The large UV oscillator strengths and photolability, combined with exceptional stability in an oxygen plasma environment, make these materials useful as photoresists [5], which suggests the possibility of optical waveguide fabrication through lithographic patterning. Photoconductivity [6] and high hole mobilities [7] are also observed during direct excitation in the UV.

The large UV oscillator strengths and electronic delocalization also give rise to large optical nonlinear susceptibilities. Recent publications have described measurements of $\chi^{(3)}$ for polysilanes to be on the order of 10^{-11} - 10^{-12} esu for third harmonic generation [8] and four wave mixing processes [9]. Two-photon absorption, being a $\chi^{(3)}$ phenomenon, should therefore be strong as well for this class of polymers. We have observed this to be the case, with $\chi^{(3)} \approx 3.2 \times 10^{-10}$ esu at 560 nm, and the primary excitation decay paths of energy transfer, polymer chain scission, and UV fluorescence very similar to those observed with single photon exposure [10].

We observe, however, that two-photon exposure of thick films induces a strong, permanent birefringence, with the axes of orientation determined by the exposing laser polarization. In contrast, polarized UV exposure induces an anisotropic response only in a shallow skin, due to strong polymer absorption, and the net birefringence for a film of waveguide dimensions is quite small. This high degree of polarization 'memory' produced by nonlinear photoexposure of isotropic materials is, to our knowledge, unique to the polysilanes, and has potential for many useful applications. These include the formation of birefringent gratings and variable waveplates through photoexposure [11], as well as the patterning of integrated optical devices.

EXPERIMENTAL

An optical ellipsometry measurement was used to characterize the birefringence growth and decay. Films of high molecular weight ($M_W \approx 2.3 \times 10^6$ by gel permeation chromatography) poly(di-n-hexylsilane) were prepared from solutions in isooctane (5% by weight). The solutions were passed through a 1μm filter, and spun onto quartz wafers using spin speeds of 3000 RPM. This procedure produced films that were approximately 1μm thick, although the exact thickness depended on spinning acceleration and solution viscosity. After spinning, the films were baked at 100 C for 10 minutes, and cooled to 10 C for at least a day to allow substantial sidechain crystallization. Film thickness was measured with a Tencor alpha-step 2000 stylus profilometer at the minimum force setting.

The experimental configuration is schematically represented in fig. 2. A polarized, pulsed dye laser beam (pulse width ≈8 ns; spot radius ≈275 μm) was focussed onto the polymer film to produce power densities (0.2-2.5 GW/cm^2) which were large enough to induce significant two-photon absorption. Ten different laser dyes were used to span the wavelength range 545-723 nm. A He-Ne probe at 632.8 nm (spot radius ≈25μm) with polarization oriented +45° to the dye laser polarization was overlapped with the dye laser at the polymer film. The He-Ne beam subsequently passed through an analyzer oriented at -45° to the exposing laser, and the transmitted power was measured using a calibrated

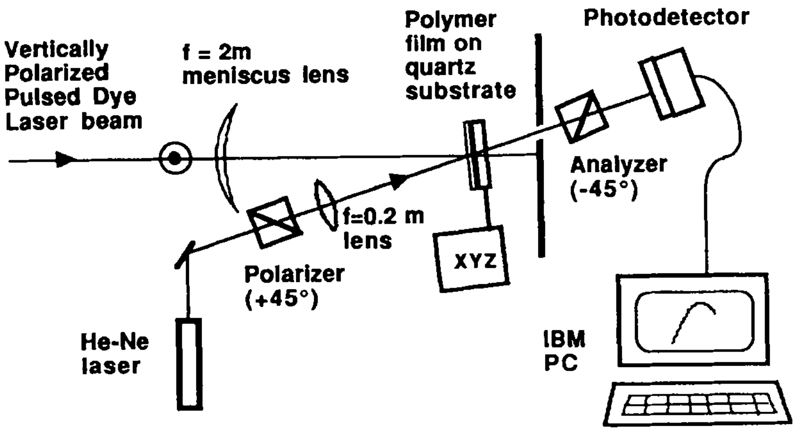

Fig. 2: Schematic Diagram of the ellipsometry setup for measuring the growth of birefringence induced by two-photon absorption.

photodetector. Data was acquired from the photodetector with an IBM PC, and the net birefringence calculated using the approximation

$$\Delta n = \frac{\lambda \sqrt{P_{sig}}}{\pi d \sqrt{P_{max}}} \qquad \{1\}$$

where d and λ are the total film thickness and wavelength in microns, and P_{max} is the maximum transmitted power with the analyzer oriented at +45°. This relation is correct within 1% as long as $\Delta n \pi d/\lambda < 0.15$

The growth of the birefringence was monitored at various wavelengths and laser powers. Because exposure induces irreversible birefringence in the polymer, a new location on the film was used used for each exposure. Care was taken so that the spot size and power, and hence the intensity, remained constant for all the exposures in each set of measurements. For comparison, an exposure using the same ellipsometry arrangement was made using an unfocussed polarized continuous wave He-Cd laser (spot radius ≈388 μm) at 325 nm in place of the dye laser beam.

Typical data from polarized two-photon exposure are shown in fig. 3. As mentioned above, the birefringence grows from a isotropic background until a saturation value is reached. For two-photon exposures at yellow wavelengths (≈579 nm), Δn is initially proportional to exposure (slope ≈1 on a log-log plot), but saturates quickly at ≈0.03 and begins to decay slowly with continued photoexposure. This corresponds to

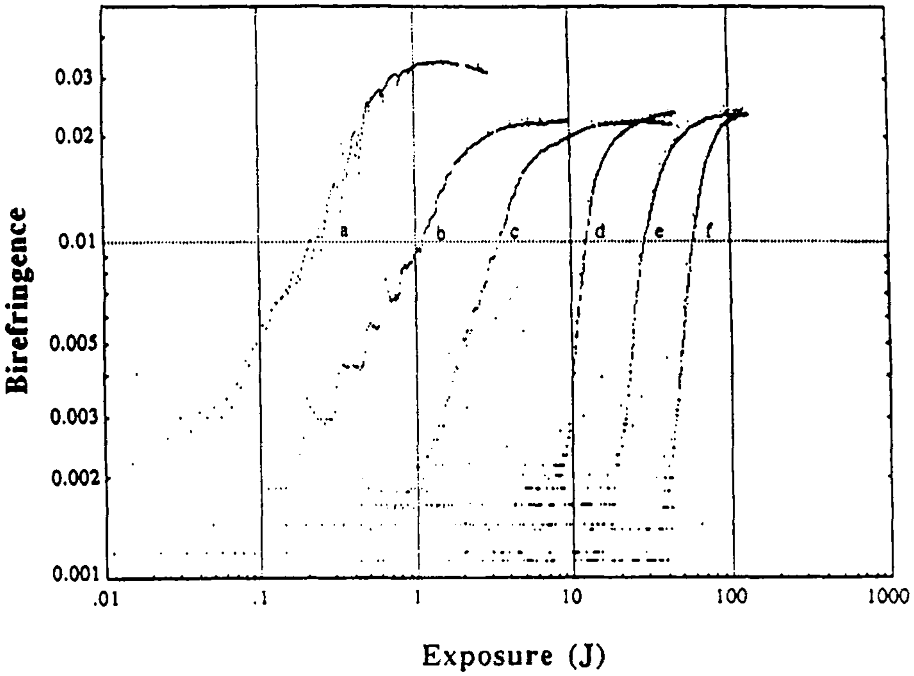

Fig. 3: Typical birefringence growth curves for poly(di-n-hexylsilane).
a) 579 nm. b) 582 nm. c) 633 nm. d) 653 nm. e) 683 nm. f)713 nm.

rapid photodegradation for chains segments aligned with the laser polarization, followed by slower degradation for chains of other orientations excited either directly or by energy transfer. At low values of birefringence, the scission of non-aligned chain segments excited by energy transfer is negligible, and Δn is proportional to the number of aligned polymer backbones segments undergoing scission p_{sc} per unit area in time t. This in turn is related to multi-photon absorption by

$$\Delta n \propto p_{sc} \propto q p_{abs} \propto q[1-e^{-\beta(\lambda) I z}] It \approx q\beta(\lambda) I z It \qquad \{2\}$$

where q is the scission quantum yield (generally ≈0.01 in the solid state), p_{abs} is the number of photons absorbed per unit area, I is the laser intensity in W/cm^2, β is the two-photon absorption coefficient in cm/W, t is the exposure time in sec, and z is the film thickness in cm.

The exposure time (t) needed to induce a fixed birefringence (i.e. fixed p_{abs}) for a given $\beta(\lambda)$ is inversely proportional to the square of the exposure intensity for a two photon process. This is the case for our measurements, as can be seen from the plot of t vs I for a fixed wavelength shown in Fig. 4. The data is well fit on a log-log scale by a straight line of slope -2, agreeing well with the proportionality expected from a two-photon process, until saturation occurs for intensities I >1.5 GW/cm^2. Similarly, for fixed p_{abs} and intensity, the exposure dose is inversely proportional to $\beta(\lambda)$, the nonlinear absorption coefficient. Relative values of β calculated from the exposure needed to induce a fixed birefringence can therefore be normalized by comparing the absolute change in UV absorption (also proportional to the number of bonds broken) for both UV and two-photon exposure to infer the number of excitations. This treatment assumes similar scission quantum yields for both two-photon and UV excitation.

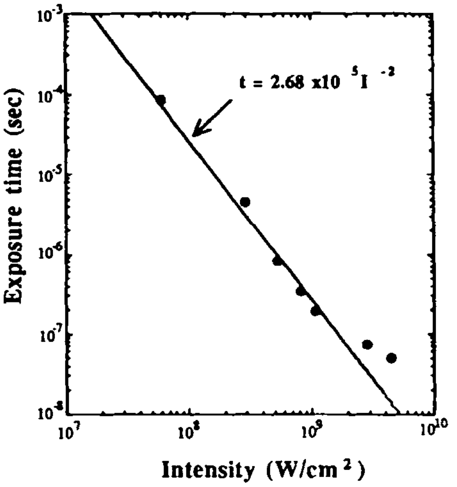

Fig 4: Exposure time t needed to produce a fixed birefringence of Δn=0.01 vs. intensity. For intensities below 1 GW/cm2, the solid line of slope -2 fits the data well, confirming the two-photon nature of the transition.

A spectrum of β for poly(di-n-hexylsilane) calculated by the method outlined above is shown on a logarithmic scale as a function of two-photon excitation energy in fig. 5. The squares are data, normalized to the previously measured value of $\chi^{(3)}=3.2\times10^{-10}$ esu. (corresponding to β=0.45 cm/MW) at 560 nm [10]. The spectrum shows a sharp peak at 579 nm (corresponding to a two-photon energy of 4.3 eV), on top of a broad background centered at 570 nm. The solid line is a least-squares fit of the sum of two gaussians to the data, with the linewidths of 33 meV and 410 meV for the sharp and broad features, respectively. The width of the broad band is comparable to that observed for single photon absorption, shown as the dotted line in the figure. The sharp spike, however, seems to bear little resemblance to any feature observed in the single photon absorption case. Although it is not unusual for two-photon absorption spectra to show transitions normally forbidden for linear absorptions, the narrow linewidth of the multi-photon transition inducing the birefringence suggests a more localized or site-selective excitation, without inhomogeneous broadening by the distribution of chain segment lengths.

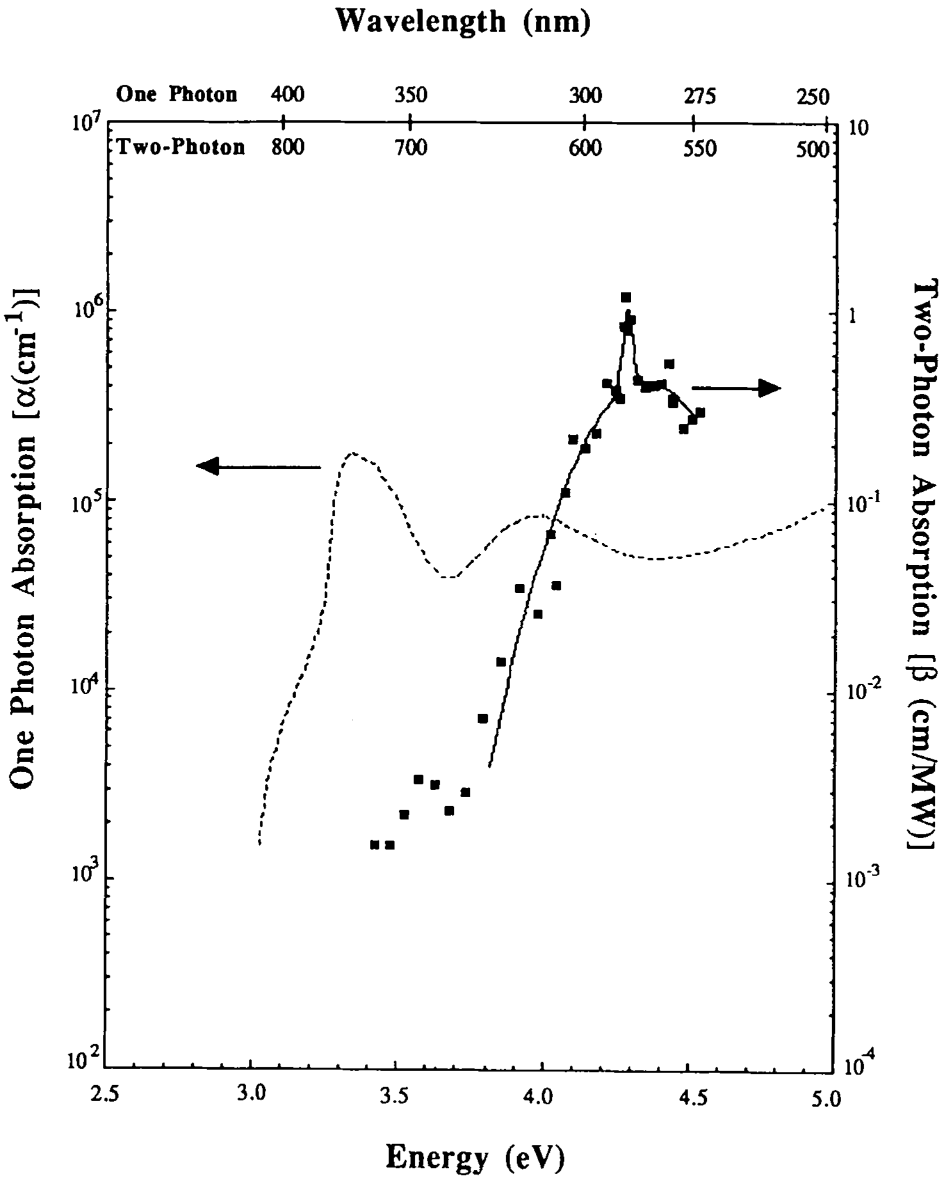

Fig. 5: Spectrum of the two photon absorption coefficient β in cm/MW for poly(di-n-hexylsilane), calculated from birefringence growth curves, as a function of two-photon energy (•), compared with the single photon absorption spectrum (- - -). Solid line is a least squares fit to β using the sum of two gaussians, one broad (≈412 meV), the other narrow (≈33 meV)

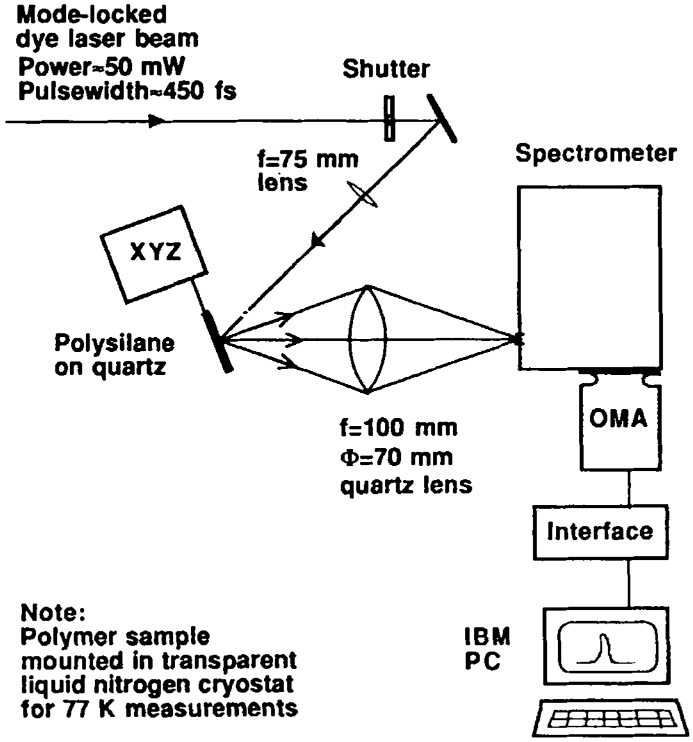

Fig. 6: Schematic diagram of the equipment setup used for two-photon fluorescence measurements.

We have also measured fluorescence produced by two-photon excitation for thick films of polysilane. The experimental arrangement is shown in fig 6. For this experiment, the laser was a Spectra-Physics sub-picosecond dye laser system, focussed onto the polymer films to produce intensities of ≈440 MW/cm^2. Emission was focussed into a 0.5 m spectrometer with an OMA detector. Spectra from the OMA were collected and analyzed using an IBM PC. For poly(di-n-hexylsilane), the two-photon induced emission is broadband ($\Delta\lambda_{FWHM} \approx 10$ nm at room temperature), with line center at ≈380 nm. The emission spectrum is identical to that observed for this compound by UV excitation, and the average degree of fluorescence anisotropy (≈0.2) produced at the two-photon resonance (579 nm) is quite similar to that observed for on-resonance UV excitations in polysilanes [12]. Fig. 7 shows the quadratic dependence of the emission intensity on power, confirming the two-photon dependence.

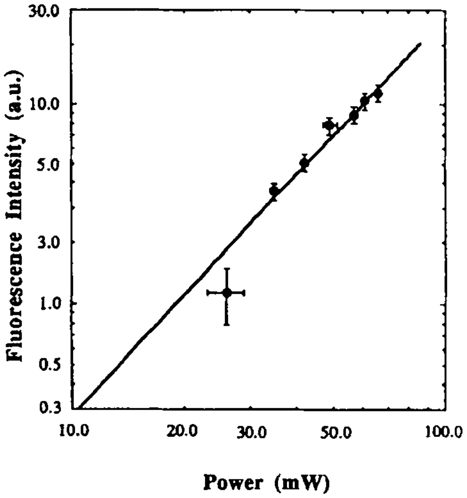

Fig. 7: Dependence of the fluorescence intensity on exposing power for poly(di-n-hexylsilane). The data are fit well by $y=(2.77\times10^{-3})\ P^2$, where P is in mW, confirming the two-photon dependence.

The spectrum of $\beta(\lambda)$ is complemented by the low temperature excitation spectra of the integrated fluorescence, as is shown in fig 8. At 77 K, the fluorescence excitation spectrum mimics identically the sharp peak and broad background seen in induced birefringence at room temperature, with the respective linewidths of ≈25 meV and ≈235 meV. At room temperature, seen on a logarithmic scale for comparison in fig 9, only a broad spectrum of width ≈295 meV is observed, and the integrated emission intensity when exciting at 579 nm is reduced by a factor of ≈15 from the spectrum at 77 K. Furthermore, while no decay in fluorescence intensity was observed for exposures at 77 K, fluorescence was observed to decay within seconds for exposures at room temperature. This decrease in fluorescence correlates well with the birefringence growth curves, and is therefore probably caused by a reduction of the population of the fluorescing species through photochemical reactions. The temperature dependence also suggests thermal assistance for the two-photon chain scission process.

Also shown in fig 9 is fluorescence for poly(di-n-hexylsilane) elevated above the sidechain crystallization temperature of 42° C. At these temperatures, the backbone conformation is not believed to be planar zigzag, and $\chi^{(3)}$ should be significantly reduced, as has been observed for third harmonic generation [8]. This is indeed the case, with the emission reduced by a factor of ≈100 from the room temperature value. Furthermore, the excitation spectrum is quite similar to that observed from poly(di-n-pentylsilane) at room temperature, which is known to form a 7/3 helical conformation at room temperature [16].

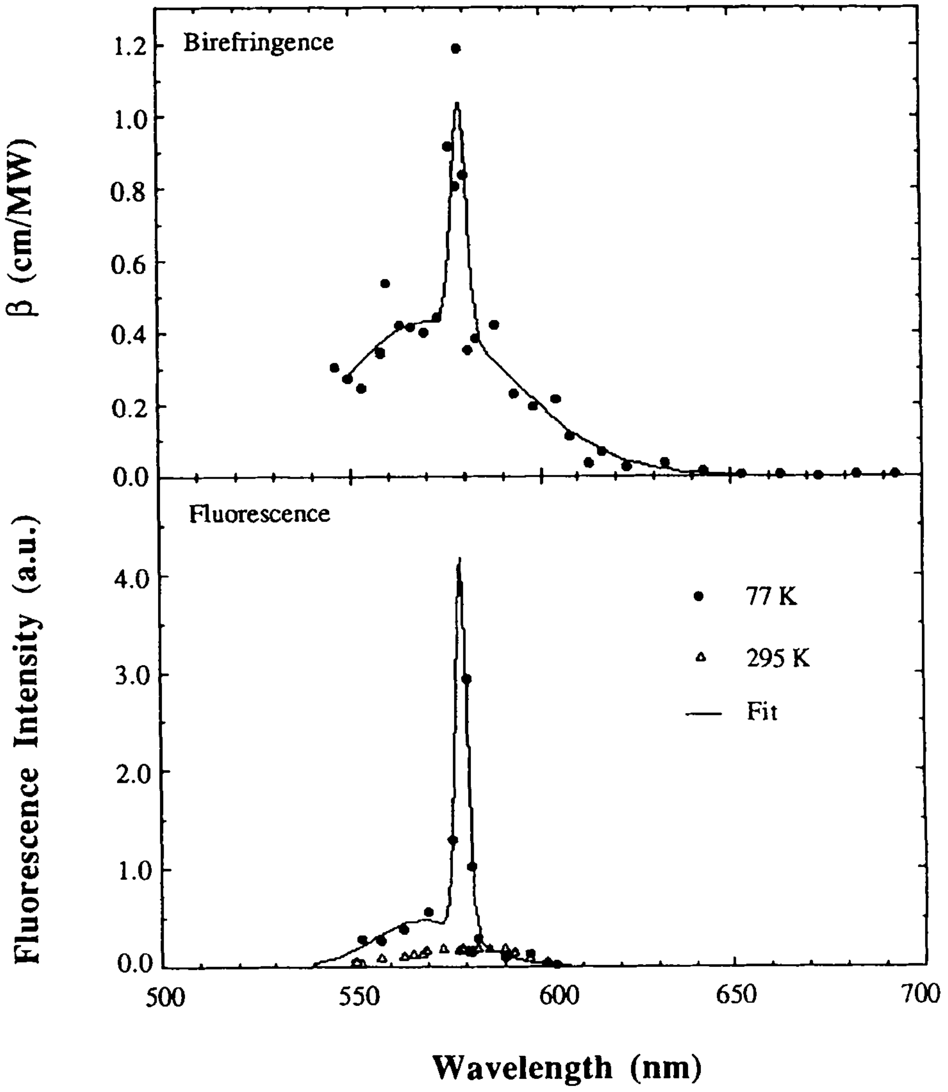

Fig. 8:Upper) Plot of β for poly(di-n-hexylsilane) calculated from birefringence growth curves (•) on a linear scale as a function of exposing wavelength. The solid line is the double gaussian of fig. 5.
Lower) Linear plot of fluorescence for poly(di-n-hexylsilane) vs. exposing wavelength for both 77 K (•) and room temperature (Δ). The solid line is a least-squares fit of the sum of two gaussians to the low temperature data, adding one broad feature (≈234 meV) and one narrow (≈25 meV).

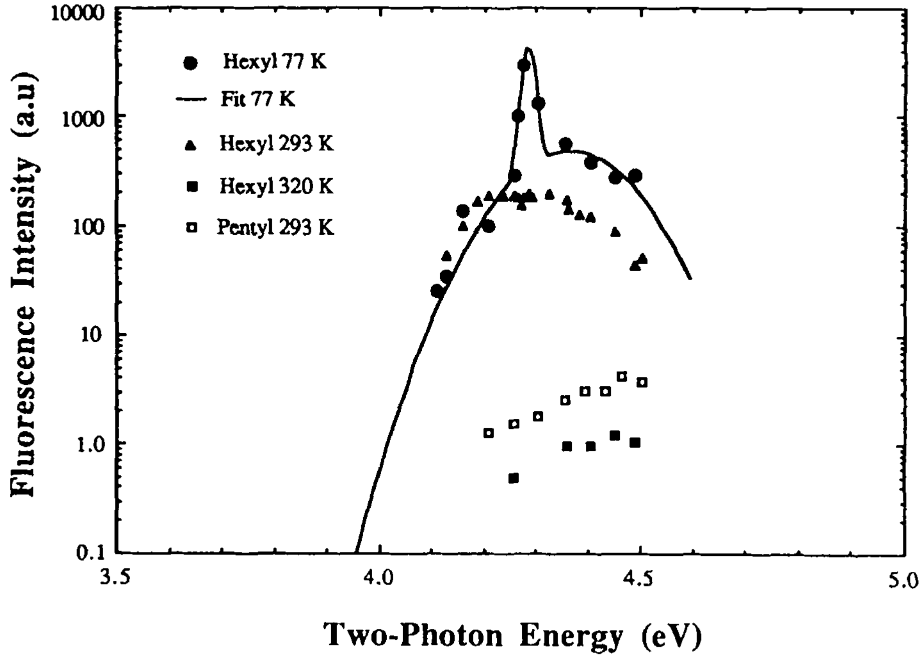

Fig. 9: Semi-log plot of fluorescence for poly(di-n-hexylsilane), at 77 K (•), room temperature (▲), and elevated temperature (■). Also shown is two-photon fluorescence from poly(di-n-pentylsilane) at room temperature (□).

DISCUSSION

Although the highest occupied molecular orbital of polysilane polymers has been conclusively determined to involve the delocalized σ-bonded conjugated backbone [1,2], there is some debate in the literature on the nature and energy levels of the excited states. Mintmire [13] and others [14] have extensively modeled these polymers as one-dimensional semiconductors. In this model, the lowest energy σ–σ* optical absorption at ≈3-4 eV corresponds to the direct band gap of these materials. These band structure calculations also predict the existence of a delocalized π* band approximately 1 eV above the σ–σ* transition, coincident with the energy difference we observe in two-photon absorption. Although a direct σ–π* transition is normally symmetry forbidden, it might be allowed for two-photon absorption and could be a possible explanation for spectrum we observe. Even though these *ab initio* calculations underestimate the energy of the lowest transition by about 40% [13], the calculated energy shifts for various regular backbone conformations correlate well with those actually measured for a number of polysilanes of known structure, giving some credibility to the model and the methods used.

Photoconductivity studies of various polysilanes have suggested, however, that the lowest energy absorption is due to the formation of a highly mobile 'exciton-like system' [6]. If true, the electronic structure would be similar to that observed in the polydiacetylenes, for which the lowest energy absorption has been unambiguously assigned to exciton formation [15]. Resonant two-photon absorption with a linewidth comparable to the single-photon exciton linewidth has also been observed for the polydiacetylenes, and has been attributed to the formation of a exciton. If an exciton model is assumed for the UV transition in polysilanes, it is possible that the two-photon absorption we observe is also due to the formation of an exciton. However, no conclusive spectroscopic evidence of a high energy conduction band has yet been observed for di-alkyl polysilanes, and a satisfactory explanation of the large binding energies needed for such an exciton (1-2 eV) has not yet been put forth.

At this time, there are insufficient data to conclude which model is the most probable explanation of the unusual two-photon absorption we observe. Each model has elements which agree with our data, but each raises questions that, as yet, are unanswerable. Only more thorough characterization of photoconductivity and spectroscopic properties of a variety of di-alkyl substituted polysilanes will allow the determination of whether the band-to-band model or the exciton model is more appropriate for the polysilane polymers.

CONCLUSIONS

In conclusion, we have observed that the chain scission produced by two-photon exposure produces a remarkable permanent birefringence in polysilane films. Spectroscopic studies of this effect for poly(di-n-hexylsilane) reveal an unexpected, sharp resonance at 579 nm on top of a broad background. Two-photon excitation induces localized scission, causing birefringence, or decays into conventional excitations, which subsequently decay by processes identical to that found in UV excitation. Both band-to-band and exciton models have some features which agree with the spectra we observe, while each leave some questions unanswered. Further detailed spectroscopic studies of the polymers are needed before an unambiguous assignment can be made.

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