

## Photocarrier generation and transport in $\sigma$ -bonded polysilanes

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Polysilanes, even those containing no  $\pi$  electrons, are found to be excellent photoconductors. In the materials studied to date, only holes are mobile but they have a well-defined mobility of about  $10^{-4}$  cm<sup>2</sup>/Vs at room temperature. In poly(phenylmethylsilane), the material we have studied most intensely, the hole-generation quantum efficiency is about 1% at high electric fields and the experimental results indicate that the holes are generated when excitons, formed when a photon is absorbed, diffuse to the surface of the film. The exciton diffusion length is found to be 500 Å. These results help confirm the existence of extensive conjugation among  $\sigma$  bonds in polysilanes.

### INTRODUCTION

Studies of the electronic properties of polymers have been conducted almost exclusively on polymers containing  $\pi$  bonds in the backbone,  $\pi$ -bonded side groups, or  $\pi$ -bonded molecules dispersed in the polymer matrix.<sup>1</sup> It is found that charge-carrier transport in these materials involves the  $\pi$  electrons and that the transport is dispersive, i.e., the carriers do not exhibit a well-defined mobility. The polymers exhibiting the most interesting electronic properties are those in which the polymer backbone contains conjugated  $\pi$  electrons, and this class of polymers has been under intensive investigation in recent years.<sup>2</sup> In polymers not having conjugated  $\pi$  bonds in the backbone, on side groups, or on added molecules, charge carriers usually are quickly trapped in very deep traps making it difficult to perform definitive experiments.<sup>3</sup>

In this paper we report photoconductivity studies on a variety of  $\sigma$ -bonded polysilane polymers in which it has recently been shown that the effects of  $\sigma$ -electron delocalization are strong. We have found these materials to be excellent photoconductors and believe that the carrier transport involves these delocalized  $\sigma$  electrons. It is well known that  $\sigma$  electrons are delocalized but in  $\sigma$ -bonded, carbon-backbone polymers the effects are so small that they can usually be neglected. It has been recognized for some time that  $\sigma$ -electron delocalization plays an important role in the electronic states of short-chain silanes,<sup>4</sup> but until recently very little work was done in the area. It has now been shown<sup>5</sup> that the first electronic transition in  $\sigma$ -bonded alkyl polysilanes is a  $\sigma$ - $\sigma^*$  transition. The energy of this transition is strongly conformation dependent<sup>6</sup> and depends strongly on the length of the molecule up to a chain length of about 30 silicon atoms.<sup>5</sup> Coil-to-rod transitions have been observed in solution,<sup>6</sup> and the experimental results have been explained in terms of conformation-dependent polymer-solvent dispersion interactions resulting from the strong coupling between the  $\sigma$  electrons and the backbone configuration.<sup>7</sup> Some doping experiments have been done which show that it is possible to make polysilanes highly conductive.<sup>8</sup> In other work it has been shown that some polysilanes are extremely photosensitive in the solid state and are useful as self-developing photoresists.<sup>9</sup>

In this paper we discuss the results of photoconductivity studies that we have conducted on a variety of polysilanes. Our efforts have concentrated on poly(phenylmethylsilane), but no major differences among phenyl- and alkyl-substituted materials studied have yet been observed. For poly(phenylmethylsilane) our results indicate that only holes are mobile and they have a well-defined mobility of  $10^{-4}$  cm<sup>2</sup>/Vs at room temperature. The drift mobility is thermally activated with an activation energy of 0.24 eV. We also present results which indicate that the holes are not created by band-to-band transitions, but that they are created when excitons, generated when photons are absorbed, diffuse to the surface of the film.

### EXPERIMENTS

Polysilanes are polymers composed of an all-silicon-atom backbone with two organic side groups attached to each Si atom. Poly(phenylmethylsilane) is, for example, a silicon chain with a phenyl and a methyl group attached to each silicon atom in a stereochemically random fashion. For our experiments crude poly(phenylmethylsilane) was obtained by adding sodium dispersion to a solution of purified phenylmethylchlorosilane in refluxing dry toluene or in dry toluene mixed with heptane under well-controlled conditions.<sup>10</sup> Two precipitations of the crude material from toluene with hexane and two from tetrahydrofuran with methanol afforded a pure white fluffy solid in 12% overall yield. The modal molecular weight of this material was found to be  $4.5 \times 10^5$  dalton by gel permeation chromatography which corresponds to a polymer containing 3750 Si atoms in the backbone chain. The other polymers discussed were obtained by similar procedures.

Samples a few micrometers thick were cast from toluene solution on indium tin oxide-coated quartz plates and aluminum electrodes about 10 mm in diameter were evaporated on top of the polymer films. The light source used in pulsed photoconductivity experiments was a nitrogen laser,  $\lambda = 337$  nm; the laser light was filtered and diffused so that the light-intensity incident on the sample

was about  $0.5 \mu\text{J}$  per pulse.

Charge transport was observed using one version of the time-of-flight technique.<sup>1</sup> Charge carriers were generated near the tin oxide electrode by a strongly absorbed, short light pulse from the laser, and their motion through the sample was observed by measuring the change in voltage across the sample induced by the carrier motion. A typical result is shown in Fig. 1. In the vicinity of room temperature, the transit time was sufficiently short that a field-effect-transistor probe with input impedance of  $10^7 \Omega$  could be used, giving an  $RC$  time constant of about 3 ms. The sample capacitance was typically 300 pF. At low temperatures, the transit time increased and an electrometer with a higher input impedance had to be used for some measurements. Carrier lifetime in poly(phenylmethylsilane) was found to be in excess of several milliseconds.

Most of the experimental results described in this work have been obtained with poly(phenylmethylsilane). When the experimental results being discussed were obtained on other silane polymers, that fact has been carefully pointed out.

Only hole transport could be seen in poly(phenylmethylsilane), i.e., a signal could be observed only when the illuminated electrode was positive relative to the other electrode. No evidence for electron transport could be observed with the polarity reversed and the experimental sensitivity was such that a signal as large as 1% of the hole-transport signal would probably have been detected. The extinction coefficient at 337 nm in the polymer films is estimated to be  $4.8 \times 10^5 \text{ cm}^{-1}$  from solution measurements and measurements of film density. Therefore, signals from the motion of holes toward the illuminated electrode when the illuminated electrode is negative should be less than 1% of the signal produced by holes when the illuminated electrode is positive.

The hole mobility is electric field and temperature dependent. At room temperature and approximately  $2 \times 10^5 \text{ V cm}^{-1}$  the hole mobility was found to be  $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The electric field dependence of the mobili-

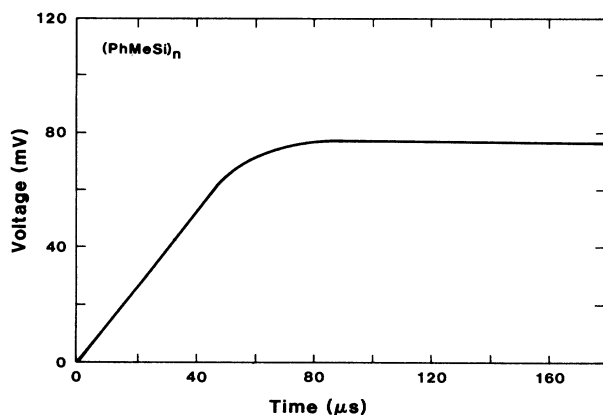


FIG. 1. The voltage induced on an electrode by the motion of holes through a cast film of poly(phenylmethylsilane). The laser pulse lasted approximately 10 ns. The voltage risetime corresponds to the charge-carrier transit time.

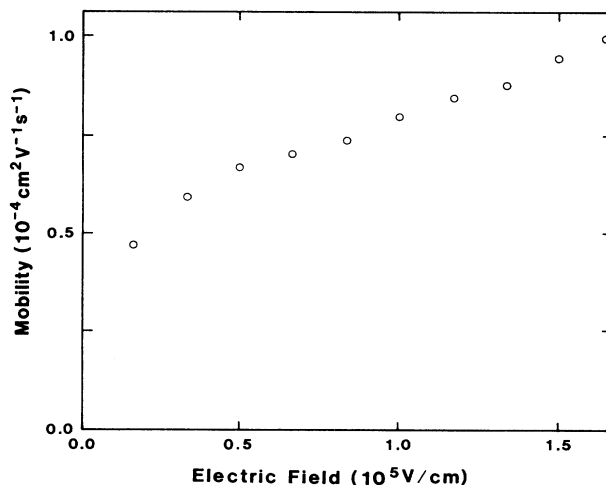


FIG. 2. Electric field dependence of the mobility of holes in poly(phenylmethylsilane).

ty varied somewhat from sample to sample but a typical result is shown in Fig. 2.

The drift mobility of holes in poly(phenylmethylsilane) is thermally activated with an activation energy of 0.24 eV. At low temperature (below about  $-50^\circ\text{C}$ ) the mobility is strongly dispersive as has been observed in most photoconductive polymer systems. The temperature dependence of the mobility is shown in Fig. 3.

In order to determine whether or not hole transport in poly(phenylmethylsilane) involved the phenyl side groups,

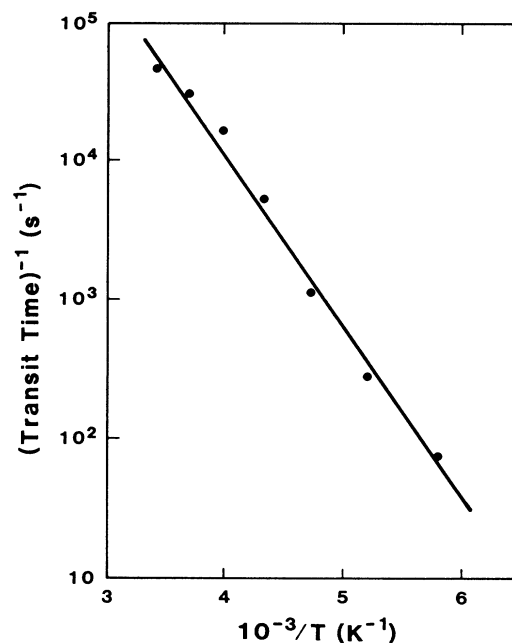


FIG. 3. Temperature dependence of the mobility of holes in poly(phenylmethylsilane). The straight line corresponds to an activation energy of 0.24 eV.

we have also measured the mobility of holes in poly(*n*-dodecylmethylsilane) and poly(*n*-propylmethylsilane). We have found that the mobility of holes in all these materials is about  $10^{-4}$  cm<sup>2</sup>/Vs at room temperature, essentially the same as that observed in poly(phenylmethylsilane). Transport in these systems is a little more dispersive than in poly(phenylmethylsilane) but these materials are much more susceptible to photodegradation and we speculate that they contain more low-molecular-weight fragments created by photolysis, which exhibit somewhat different energy levels. The temperature dependence of hole mobility in poly(*n*-propylmethylsilane) was measured and found to be thermally activated with an activation energy of 0.1 eV.

We have also investigated the effect of a variety of impurity molecules on transport in poly(phenylmethylsilane). The donors triphenylamine (TPA) and *N,N,N',N'*-tetramethylphenylenediamine (TMPD) and the acceptors 2,4,7-trinitrofluorenone and tetracyanoquinodimethane (TCNQ) were studied. These molecules were chosen because it was anticipated that for the donors the highest occupied molecular orbital might lie, in energy, above the top of the highest occupied molecular orbitals in the silicon backbone, thus acting as a hole trap; and that for the acceptors, the lowest unoccupied molecular orbital might lie below the lowest unoccupied molecular orbital of the silicon backbone, thus acting as an electron trap. As expected, since only the holes are mobile, the acceptors had no effect on the carrier-transport experiment. Of the donors, only TMPD had an effect and it acted like a deep

trap. A concentration of  $10^{17}$  molecules/cm<sup>3</sup> reduced the carrier lifetime to 6  $\mu$ s. There was some evidence in carrier-generation experiments, discussed below, that the acceptors might assist in ionization of excitons to create holes, but the experiments were inconclusive.

The wavelength dependence of the number of carriers produced by a pulse of light is shown in Fig. 4. The light source for this experiment was a high-pressure mercury arc, the light from which passed through a monochromator before impinging on the sample. A camera shutter was used to expose the sample to the light for one second and the current flowing through the sample was integrated with an electrometer. For comparison, the wavelength dependence of the absorption coefficient is also shown in Fig. 4. It is important to note that over most of the wavelength range of interest in the photoconductivity studies, the light is all absorbed very near the illuminated surface of the films. The films were typically a few micrometers thick.

The number of carriers generated by a pulse of light is electric field dependent, qualitatively as expected based on geminate recombination processes. At fields on the order of  $2 \times 10^5$  V/cm, the quantum efficiency for carrier generation is close to saturation at a value of about 1%. The field dependence varied somewhat from sample to sample for reasons unknown. Typical results are shown in Fig. 5. Detailed attempts to compare the experimental results to the geminate recombination model have not been made.

## DISCUSSION

Our early observations of excellent hole transport in poly(phenylmethylsilane) lead us to speculate that the holes were hopping through the phenyl groups.<sup>11</sup> It is well established that holes and electrons can be made mobile in a variety of polymers simply by adding aromatic molecules, i.e., molecules containing  $\pi$  electrons.<sup>1</sup> The concentration of phenyl groups in poly(phenylmethylsilane) is quite high, and a mobility of  $10^{-4}$  cm<sup>2</sup>/V sec was consistent with an extrapolation of data

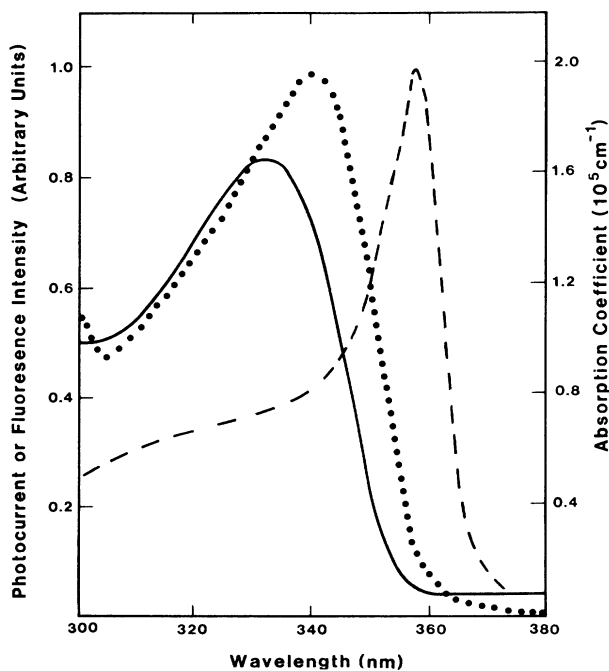


FIG. 4. Wavelength dependence of the absorption coefficient (solid line), fluorescence-intensity dependence on the excitation wavelength (dashed line), and wavelength dependence of charge-carrier generation (dotted line).

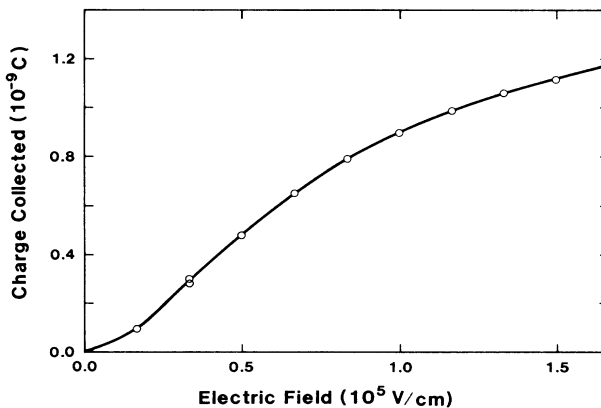


FIG. 5. Electric field dependence of the number of holes generated in poly(phenylmethylsilane). The quantum efficiency at 337 nm and  $1.5 \times 10^5$  V cm<sup>-1</sup> was about 1%.

obtained on other polymer systems. However, the observation of essentially the same mobility in all alkyl polysilanes, polymers containing no  $\pi$  electrons, proves quite conclusively that the transport is through the conjugated  $\sigma$  electron states of the silicon backbone. The fact that the transport is not dispersive in these amorphous systems implies that transport is occurring through quite well-defined energy states. There have been extensive discussions of the mechanisms that might account for these experimental observations. One type of model invokes trap-modulated mobility<sup>12</sup> and another involves small polaron hopping.<sup>13</sup> We do not have sufficient experimental data to distinguish between these possible models. It is very surprising that the room-temperature mobilities are all approximately equal to  $10^{-4}$  cm<sup>2</sup>/V s, even though the temperature dependences of the mobilities are consistent with activation energies for transport ranging from 0.25 eV to 0.1 eV.

Additional evidence that hole transport results from hopping between well-defined energy states is provided by the trapping studies with TMPD and TPA. The ionization potentials for TMPD and TPA in the gas phase are about 6.6 eV (Ref. 14) and 6.9 eV (Ref. 15), respectively, but only TMPD acts as a trap for holes. Photoemission studies indicate that the valence band is about 7.5 eV below the vacuum level,<sup>16</sup> a result which is consistent with these trapping results if polarization of the polymer matrix increases the ionization potential of TMPD and TPA by about 0.5 eV as might be expected. Using the trapping lifetime  $\tau$  of 6  $\mu$ s for a TMPD trap concentration of  $10^{17}$  cm<sup>-3</sup>, we can calculate a trapping cross section or radius. For diffusion-limited trapping,<sup>17,18</sup> the trapping rate constant  $\gamma$  is given by

$$\gamma = 4\pi DRN_T = 1/\tau,$$

where  $D$  is the diffusion coefficient of the carriers,  $R$  is the radius of the trap, and  $N_T$  is the trap concentration. From the Einstein relation  $D = (kT/e)\mu$ , where  $\mu$  is the carrier mobility,

$$R = \frac{e}{4\pi kT\mu N_T\tau}.$$

The experimental results give  $R = 5 \text{ \AA}$ , essentially a geometrical cross section of the dopant molecule.

The wavelength dependence of the number of holes created by a pulse of light in poly(phenylmethylsilane) is initially surprising. From 300 to about 350 nm the light is all absorbed near one electrode and, if holes are generated by a band-to-band transition, to a first approximation the number of holes generated and the photocurrent observed should be independent of wavelength over this range. The experimental observations clearly eliminate this process unless there is some competing transition which fortuitously results in the wavelength dependence of the hole-generation efficiency being similar to the wavelength dependence of the absorption coefficient.

A mechanism that explains this observation is that holes are generated when singlet excitons, created when the photons are absorbed, diffuse to the surface of the film. This is the process which has been used successfully to explain the wavelength dependence of hole generation

in anthracene single crystals.<sup>18</sup> The fluorescence quantum efficiency of poly(phenylmethylsilane) is quite high [approximately 0.15 at 320 nm (Ref. 5)] strongly indicating that singlet excitons are the states which result from the absorption of a photon.

The appropriate differential equation for the exciton density in a steady state as a function of distance  $x$  from the illuminated surface is

$$0 = \alpha I_0 e^{-\alpha x} - n(x)/\tau_e + D \left[ \frac{d^2 n}{dx^2} \right],$$

where  $\alpha$  is the wavelength-dependent absorption coefficient,  $\tau_e$  is the exciton lifetime, and  $D$  is the exciton diffusion coefficient. With the boundary conditions  $n(0) = n(\infty) = 0$ , the exciton flux to the surface is  $D(dn/dx)_{x=0} = I_0(1 + 1/\alpha l)^{-1}$ , where  $l = (D\tau_e)^{1/2}$ . If we assume that the number of carriers generated per unit time is proportional to the flux of excitons to the surface, then a plot of the reciprocal of the photocurrent or of the number of carriers produced by a pulse of light  $N$  versus the reciprocal of the absorption coefficient should yield a straight line, and the ratio of the intercept to the slope of the line gives the exciton diffusion length  $l$ .

In order to compare our experimental results to this model, we have to take into account the fact that we have found that the fluorescence quantum yield is wavelength dependent over the wavelength range of interest, as shown in Fig. 4, suggesting that at least two different electronic transitions may be involved.<sup>5</sup> In order to take this observation into account, we assume that the number of excitons created by a pulse of light is proportional to the fluorescence quantum efficiency,  $I_{fl}(\lambda)$ , and that to compare our experimental results with the model described

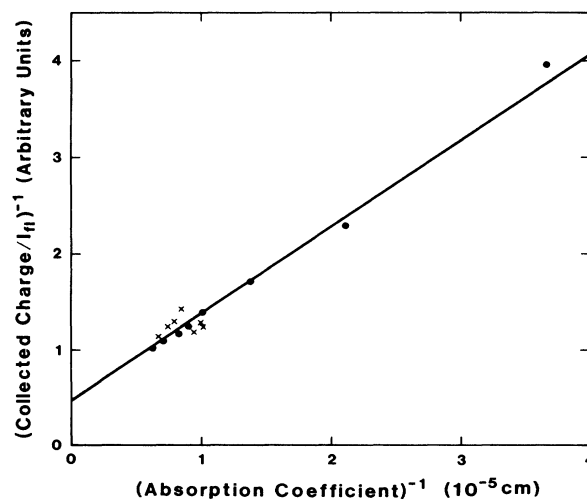


FIG. 6. A plot of the reciprocal of the collected charge normalized by the fluorescence quantum-yield wavelength dependence versus the reciprocal of the absorption coefficient. The ordinate is in arbitrary units. The circles were obtained from data collected with  $\lambda > 335$  nm and the  $\times$ 's from data with  $\lambda < 335$  nm.

above, we therefore have to normalize the number of carriers created by a pulse of light by  $I_{\eta}(\lambda)$ . Figure 6 is a plot of  $I_{\eta}(\lambda)/N$  versus  $1/\alpha$  obtained from the data of Fig. 4, and it is seen that the data are consistent with a straight line indicating that the fraction of excitons leading to free holes is a single-valued function of the absorption coefficient as required by this hypothesis. Assuming 100% conversion of singlet excitons to charge carriers at the surface, the slope and intercept obtained in Fig. 6 predicts an exciton diffusion length of approximately 500 Å.

An important difficulty with this model, in the case of poly(phenylmethylsilane), is that we have to assume that the excitons are quenched radiatively when they interact with the surface. In anthracene single crystals, the excitons are quenched nonradiatively.<sup>18</sup>

### SUMMARY

We have shown that  $\sigma$ -bonded polysilanes, even those containing no  $\pi$  electrons, are excellent photoconductors.

In the materials studied to date, it appears that only the holes are mobile with a mobility of about  $10^{-4}$  cm<sup>2</sup> V s at room temperature. The mobility is thermally activated and typically nondispersive at room temperature but becomes dispersive as the sample temperature is lowered. Carrier generation appears to be an extrinsic process, that is, at 337 nm the photons appear to create excitons rather than electron-hole pairs and free charge carriers are not created until the excitons interact with the film surface. The experimental results indicate that the exciton diffusion length is 500 Å.

### ACKNOWLEDGMENTS

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