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Fullerene-Doped Polysilane Photoconductor

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Polysilanes, $(R_1R_2Si)_n$, are a unique class of polymers with the backbone consisting entirely of tetrahedrally coordinated silicon atoms. Extensive delocalization of σ-electrons takes place along the silicon chain, giving rise to many interesting electronic properties.[1,2] For example, because of this σ-conjugation, carrier transport along the silicon backbone is very efficient. The hole mobility of polysilanes, $\sim 10^{-4}$ cm^2/V·s,[3-6] is among the highest observed for polymers. In spite of such high hole mobility, the photoinduced charge-generation efficiency of polysilanes is low.[3] Several doping experiments using organic donors and acceptors did not enhance the charge-generation efficiency significantly.[3] Here we report that fullerenes can be doped into polysilane to greatly enhance its charge-generation efficiency. The combination of high charge-generation efficiency and high carrier mobility makes fullerene-doped polysilane one of the best polymeric photoconductors.

Fullerenes are known to be good electron acceptors. In the presence of electron donors such as aromatic amines, weakly bonded charge-transfer complexes can be formed.[7] Through virtual excitation, the existence of charge-transfer interaction can enhance the second-order optical nonlinearity of fullerenes.[8] With direct excitation, excited-state electron transfer between fullerenes and various electron donors such as aromatic amines,[7,9] semiconductor colloids,[10] porphyrin,[11] and polymers[12-14] can occur. Polysilanes are usually not recognized as good electron donors, yet the present study indicates the existence of efficient excited-state electron transfer between fullerenes and polysilanes.

Fullerenes were prepared according to the standard electric arc method.[15] C_{60}/C_{70} mixtures, with a nominal ratio of 85:15, were used. Polysilanes were synthesized according to the published procedures.[16] Photoconductivity of the samples was measured by the standard photoinduced-discharge method;[17,18] the details of our experimental conditions have been described before.[19] The sample film is deposited on an electrically grounded aluminum substrate and corona-charged positively or negatively in the dark. Absorption of light generates electrons and holes which migrate to the surface and discharge the surface potential, if the sample is photoconductive. The charge-generation efficiency is determined from the initial discharge rate of the surface potential under the condition of low light intensity (typically 10^{12}–10^{13} photons/cm^2·s) and strong absorption.[20]

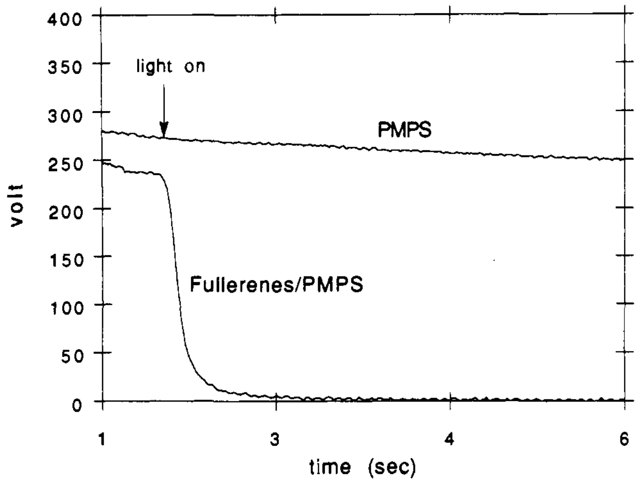

Figure 1. Comparison of photoinduced discharge curves of a 3.2 μm thick phenylmethylpolysilane (PMPS) film and a 3.0 μm thick fullerene-doped PMPS film under the same experimental conditions. A tungsten lamp (50 mW/cm^2) is used as the light source.

We first present results obtained with phenylmethylpolysilane (PMPS) where the substituents are phenyl and methyl groups. Figure 1 shows a comparison of photoinduced discharge curves between PMPS and PMPS doped with 1.6% by weight of fullerenes. PMPS does not show any detectable surface discharge upon illumination with a tungsten lamp (photon flux: 50 mW/cm^2) due to its low charge-generation efficiency. With 1.6% fullerenes as dopant, its photoinduced discharge rate is enhanced by orders of magnitude (Figure 1). The same result is obtained when the samples are irradiated with monochromatic irradiation at 340 nm. The photoinduced discharge is complete (no residual voltage left on the film), which indicates the absence of deep traps in the sample.

The field dependence of the charge-generation efficiency was measured at 340 nm (Figure 2). The charge-generation yield is $\sim 10^{-2}$ at a field strength of 10^5 V/cm, which increases to 0.6 at 10^6 V/cm. The low-field charge-generation efficiency is about 1 order of magnitude greater than in the previously reported fullerene-doped poly(vinylcarbazole)[12] (Figure 2). The observed field dependence can be fitted by the Onsager model of charge recombination,[21,22] which assumes that the absorption of a photon creates a bound electron–hole pair with a thermalized separation distance of r_0. This thermalized, bound electron–hole pair can either recombine or separate into a free electron and free hole. The fraction of absorbed photons that result in bound electron–

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[20] The charge-generation efficiency, ϕ, can be obtained from the initial discharge rate of the surface potential, $(\mathrm{d}V/\mathrm{d}t)_{t=0}$,[17-19] that is,

$$\phi = -\frac{\epsilon}{4\pi e L I}\left(\frac{\mathrm{d}V}{\mathrm{d}t}\right)_{t=0}$$

where ϵ is the dielectric constant, e the electronic charge, L the film thickness, and I the absorbed photon flux. The incident light intensity was measured with a calibrated radiometer (International Light IL700A). The photon flux at 340 nm was determined to be 1.47×10^{12} photons/(cm^2·s), which was essentially all absorbed by the sample at this wavelength. The dielectric constant of the film is determined to be 3.2 from capacitance measurement using a HP Model 4194A impedance/gain-phase analyzer.

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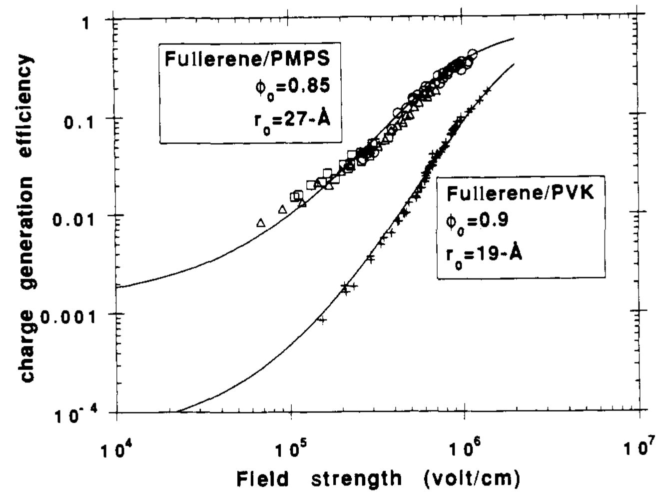

Figure 2. The field dependence of the charge-generation efficiency of a 2.0 μm thick (○), a 1.1 μm thick (□), and a 1.8 μm thick (△) fullerene/PMPS film obtained with positive charging and 340-nm irradiation. The solid lines are calculated from the Onsager model. The best-fit curve is obtained with r_0 = 27 Å and ϕ_0 = 0.85. Also plotted for comparison purposes is the field-dependence data of fullerene-doped PVK (+) taken from ref 12.

hole pairs is the primary quantum yield ϕ_0, which is assumed to be field-independent. By fitting the experimental data to the Onsager model,[21,22] one obtains values of r_0 and ϕ_0.

The two parameters, r_0 and ϕ_0, characterize quantitatively the field dependence of the charge-generation efficiency of the photoconductor. A large r_0 value indicates that the photoconductor has a large low-field charge-generation efficiency while the ϕ_0 value represents the ultimate charge-generation efficiency achievable in high field. In the present case the data can be fitted with ϕ_0 = 0.85 and r_0 = 27 Å (Figure 2). The value of ϕ_0 is comparable to that of fullerene-doped polyvinylcarbazole while the value of r_0 is larger, which accounts for the observed enhancement in low-field charge-generation efficiency. It is also useful to compare these numbers with those of thiapyrylium dye aggregate doped amine/polycarbonate photoconductor,[23] generally regarded as the best commercial polymeric photoconductor, which has ϕ_0 = 0.58 and r_0 = 44 Å.[23] At lower field, thiapyrylium dye aggregate photoconductor has higher charge-generation efficiency due to its larger r_0 value, while at higher field the charge-generation efficiency of fullerene-doped polysilane is greater due to the larger ϕ_0 value. In phenylmethylpolysilane a 1.6 wt % fullerene doping produces high photoconductivity, while thiapyrylium dye aggregate doped amine/polycarbonate is a two-phase system where the dye phase (~5%) exists as a fibrous structure segregated from the polymer phase.[23]

The wavelength dependence of the charge-generation efficiency (the gain spectrum) is shown in Figure 3. In the longer than ~400 nm spectral region, the gain spectrum follows the absorption spectrum of fullerene, indicating that fullerenes are the light absorber and function as the sensitizers for photoconductivity. However, in the shorter wavelength region (<350 nm), the absorption coefficient of PMPS dominates over that of fullerene (~1000:1 at 340 nm). In this region, PMPS is the light absorber and charge is generated by electron transfer from an excited state of the polysilane to the fullerene.

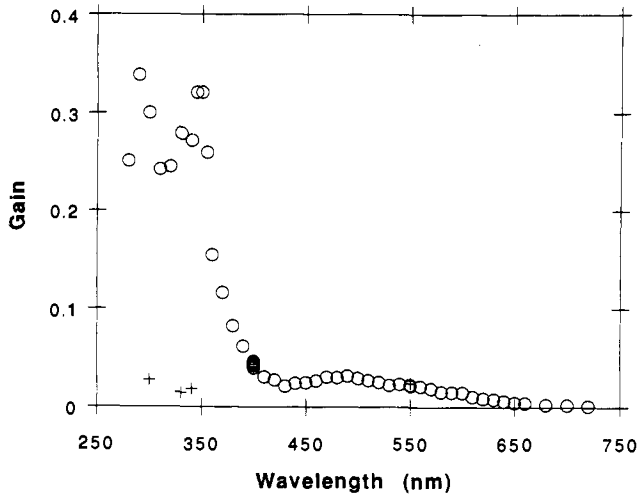

Figure 3. The wavelength dependence of the gain spectrum of a 2.0 μm thick fullerene/PMPS film, obtained with either positive charging (○) or negative charging (+). The field strength is 7 × 10^5 V/cm. Note that incident photon flux was used in calculating the gain which was not totally absorbed by the sample in the longer wavelength region.

When the film is irradiated with shorter wavelength light (<350 nm), where the absorption is confined near the surface and the carriers have to migrate through the whole thickness of the film, discharge occurs only when the film is positively charged (Figure 3). This indicates that only holes can migrate through the whole thickness of the film and fullerene-doped polysilane is mainly a hole photoconductor. This provides an interesting comparison with pure solid fullerene film, which was found to be an electron photoconductor.[24]

We attempted to extend this approach to other polysilanes such as cyclohexylmethylpolysilane and dimethylpolysilane. No significant photoinduced discharge can be observed from these polysilanes even when doped with fullerenes. This is a very surprising result since it is known from previous studies that photoinduced holes move along the silicon backbone and the photoconductivity is reported to be insensitive to the nature of the substituents.[3-6] These results suggest that a specific interaction exists between fullerene and the phenyl group in PMPS which leads to the formation of a weakly bonded complex between them and enhances the transfer of an electron from PMPS to fullerene. For nonaromatic polysilanes, such specific interaction is absent. Fullerene may exist mostly as aggregates or small crystallites, which can inhibit the electron-transfer processes. Fundamental electron-transfer processes of fullerenes and the effects of electric field and magnetic field are being studied at present to increase understanding of the photoconductive mechanism.

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