Time Resolution of Carrier Photogeneration Controlled by Geminate Recombination

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With use of a delayed-field technique, the unusual observation has been made that the quantum efficiency in poly(N-vinyl carbazole), for a given field, is the same whether the pulse photoexcitation occurs with the field applied or delayed up to many seconds. A possible explanation is that the geminate recombination rate is sufficiently slow that it allows the photogeneration process to be time resolved.

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Onsager's treatment of classical diffusion in a Coulomb potential with an applied field, and its widespread application to describe the photogeneration process in low-mobility materials, is well established.[1-4] Conceptually, some fraction of the electron-hole pairs which thermalize around a distance r_0 (where r_0 is less than or comparable to the Coulomb radius) diffuse together to give geminate recombination without even having undergone thermal dissociation into free electron-hole pairs. The remainder of the electron-hole pairs of course dissociate and give rise to the observed photogeneration efficiency. Normally, for most materials and experimental conditions, it is a good assumption that the geminate recombination process is sufficiently fast that its only manifestation is in determining the subsequent photogeneration efficiency at the given applied field. However, for appropriate materials and experimental conditions this may not be the case, and in this Letter we report results on photogeneration in poly(N-vinyl carbazole) (PVK) which are consistent with the time resolution of the initial geminate recombination process.

We use two different kinds of measurement. First, the xerographic discharge technique can be used under appropriate conditions to measure directly the photogeneration efficiency in a solid. Second, we can integrate the number of charge carriers which cross the sample in a time-of-flight experiment. This in turn is done in two ways: In the first, the light pulse is incident on the sample and carrier transit occurs with a fixed applied bias; in the second, the light pulse excites the sample in zero field and a collection field is applied after a variable time delay Δt. This delayed-collection-field technique has been used to measure the field dependence of photogeneration, in particular the zero-field quantum efficiency, in a-Se,[2] a-Si:H,[3] and a-As_2Se_3.[5]

Our samples of PVK films were fabricated by solution coating, as described elsewhere. Experimental details for the determination of the quantum efficiency by both experimental techniques are also well described in the literature.[6,7]

Figure 1 shows the results of the measurement of the photogeneration efficiency η for PVK (up-

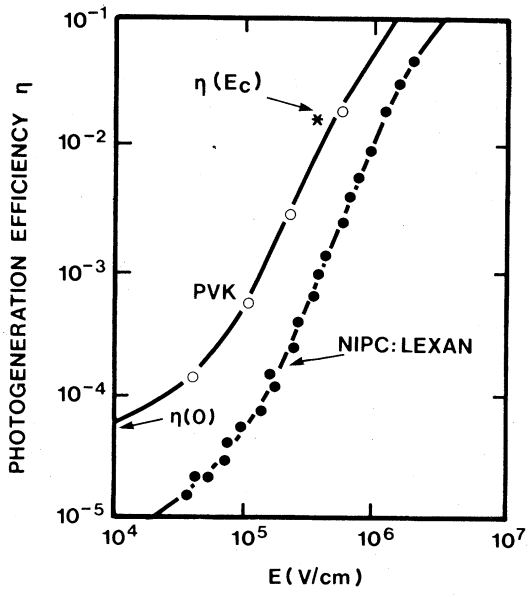

FIG. 1. Comparison of photogeneration efficiencies: (i) Xerographic discharge determinations of η vs electric field strength for PVK (open circles) and for NIPC-doped polycarbonate (solid circles) according to Ref. 4; (ii) η measured in PVK by a delayed collection field $E_c = 5\times10^5$ V/cm applied 1 sec after zero-field photogeneration (asterisk).

per curve). For comparison, data for N-isopropyl carbazole (NIPC) -doped polycarbonate, obtained by Borsenberger and Ateya,[4] are shown (lower curve). With respect to PVK, the open circles refer to data points determined from the xerographic discharge technique, or by integration of a transit signal in which no delay exists between photoexcitation and the application of the electric field. Although our data are less extensive than that for NIPC-doped polycarbonate, the close similarity is consistent with an Onsager description for PVK (in analogy with the interpretation of Borsenberger and Ateya[4] for the NIPC-doped polymer), with somewhat larger values for the thermalization distance r_0 and the efficiency of production of initial thermalized pairs η_0. The solid line through the PVK data points in Fig. 1 represents the theoretical calculation based on the Onsager dissociation model with an initial δ-function distribution centered at $r_0 = 25$ Å and $\eta_0 = 0.1$.

On the other hand, the point indicated by the asterisk in Fig. 1 was measured by the delayed-collection-field technique. In this case, the pulse excitation occurred in zero applied field and only after a time delay Δt was a field E_c applied. The purpose of the field E_c was to collect those carriers created under zero-field conditions which had not undergone geminate recombination up to time Δt. Surprisingly, it was found that the photogeneration efficiency measured under these conditions (indicated by the asterisk in Fig. 1) was two orders of magnitude larger than the zero-field value, indicated as $\eta(0)$ in Fig. 1. As a result, unlike the cases of a-Se, a-Si:H, and a-As_2Se_3, it has not proved possible to measure the zero-field photogeneration efficiency for PVK by means of the delayed-collection-field experiment. In marked contrast to these materials, it has been found in PVK that the magnitude of the collection field E_c applied *after* a delay Δt *itself* determines the efficiency with which free carriers are created following a light pulse excitation. This is the case even though the photoexcitation is over at a time Δt before the application of the field. Experimentally, we found this effect for time delays as long as $\sim 10 - 100$ sec at room temperature.

Figure 2 shows the plots of the integrated charge signal as a function of the delay times Δt for three different temperatures. As the temperature increases the integrated signal decreases at shorter delay times. This effect is not associated with transport losses in the bulk of the

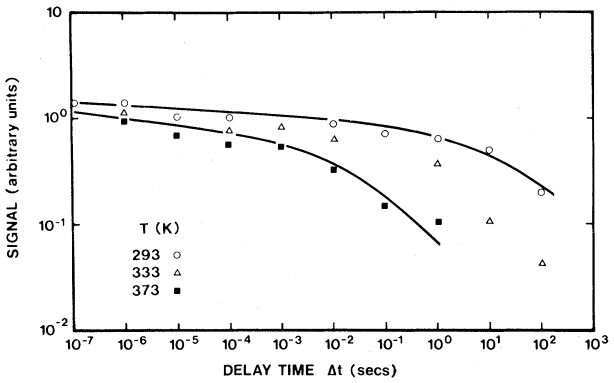

FIG. 2. Integrated charge signal (arbitrary units) as a function of time delay for three different temperatures. The solid lines correspond to the theoretical calculations described in the text.

film, since the transit time decreases as the temperature increases [mobility $\propto \exp(-\Delta/kT)$] and therefore transport losses due to bulk trapping should decrease at higher temperatures.

These results are in general agreement with the theoretical predictions of the time-dependent Onsager model,[8] which was recently solved analytically. The physical basis of this model is that if an electric field can be applied on a time scale comparable to the geminate recombination time, then time-dependent photogeneration would be observable. Thus, for an applied field E with no time delay, a quantum efficiency $\eta(E)$ will be observed. For finite time delays Δt less than the geminate recombination lifetime, quantum efficiencies lying between $\eta(E)$ and $\eta(0)$ would be observed. It is only for delays ~100 times the geminate recombination lifetime that the zero-field quantum efficiency $\eta(0)$ would be measured in the delayed-collection-field experiment.

The theoretical model has been described in considerable detail elsewhere.[8] Here we review only some basic features of interest to us. For a step-function electric field E applied at time Δt after the initial creation of charge carriers, the quantum efficiency is given by

$$\eta(E, \Delta t, r_0) = \eta_0 \int d^3r\ \Omega(E, r, \theta)\rho(r, \Delta t | r_0), \quad (1)$$

where $\Omega(E, r, \theta)$ is the usual Onsager escape probability, and $\rho(n, \Delta t\,|r_0)$ is the electron-hole pair distribution function at $t = \Delta t$. The initial thermalized distribution is assumed to be a (normalized) δ function centered at r_0, i.e.,

$$\rho(r, t = 0\,|r_0) = (4\pi\eta_0^2)^{-1}\delta(r - r_0). \quad (2)$$

The time evolution of the distribution function in

zero field from $t=0$ to $t=\Delta t$ is obtained analytically from the classical Smoluchowski equation. For a given time delay, the quantum efficiency is then obtained by quadrature from Eq. (1). Typical curves for the quantum efficiency at various field strengths and thermalization distances r_0 are shown in Ref. 8, where the evolution from $\eta(E)$ to $\eta(0)$ is shown as a function of the time delay.

Fitting the PVK data by this theoretical model gives the solid lines shown in Fig. 2, with $D \sim 10^{-16}$ cm^2/sec for $T=293$ K and $D \sim 10^{-14}$ cm^2/sec for $T=373$ K. These small values of the diffusion constants mean that in zero applied field the charge carriers are essentially immobile, and we are close to the "Anderson limit,"[9] where the disorder in the system precludes any diffusion at all. The small values of the mobilities we deduce from this experiment are perhaps not inconsistent with the known fact that hole drift mobilities in PVK are strongly field dependent, ranging from 10^{-7} cm^2/V sec at 10^5 V/cm to 10^{-9} cm^2/V sec at 10^4 V/cm,[10] although the actual value at zero field is not known. Nevertheless, it is difficult to understand why the carriers do not have a larger diffusion constant in the presence of their mutual Coulomb field. A possible answer is that the number of paths available for geminate recombination to take place at rather small values of r_0 (25 Å) is severely reduced by the local disorder, whereas the number of paths available for dissociation by the external electric field is not affected to the same extent.

In conclusion, we believe that it is an exciting development to be able to resolve the photogeneration process in some systems by a relatively simple experimental technique, and that these preliminary results should stimulate further experimental and theoretical work in this area.

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Instability of the Electron-Hole Plasma in Silicon

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It is shown that the electron-phonon interaction in covalent semiconductors drives an instability in the electron-hole plasma at high temperature. The instability might be the reason for melting of tetrahedrally bound semiconductors. If this is true, the intrinsic carrier concentration of silicon at the melting temperature would be of the order of 10^{21} cm^{-3} instead of the commonly accepted value of 2×10^{19} cm^{-3}.

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In the last few years, there has been a large amount of work[1-9] induced by the discovery of laser annealing for ion-implanted semiconductors, which is a promising technique in microelectronics. However, the actual mechanism responsible for annealing is still rather controversial.[6-8] The problem is to know if the laser pulse is essentially heating the sample which simply melts or if the electron-hole (e-h) pairs created by the laser generate a new fluidlike state.[6]

Previous work[9,10] on the electron-phonon interaction has shown that if a certain fraction α of the

