Photoconductivity, Photovoltages, and Photogenerated Solitons in Polyacetylene

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The nature of photogenerated charge carriers in $(CH)_x$ is explored through the photoconductive and photovoltaic response of the polymer. Experimental results are discussed in the context of the soliton model of charge carriers. It is concluded that photogenerated charged soliton pairs may play a role in $(CH)_x$ photoconductivity but cannot produce the observed photovoltaic response of $(CH)_x$ devices.

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The existence in undoped *trans*-$(CH)_x$ of magnetic defects associated with bond-alternation kinks may be inferred from the magnetic properties[1-6] of the polymer. Such defects, originally proposed by Pople and Walmsley,[7] present in *trans*-$(CH)_x$ and absent in *cis*-$(CH)_x$, are a consequence of the symmetry of the *trans* isomer which leads to a doubly degenerate ground state. Such a magnetic, electrically neutral defect is depicted schematically at the left in Fig. 1(a). The mathematical theory of such nonlinear excitations of the polymer chain, or *solitons*, has been studied in depth.[8-11] A further consequence of the symmetry of the chain is the positioning of the energy of the electronic state associated with the defect precisely at the center of the energy gap. When ionized, by doping of the polymer with acceptors or donors, the solitons become nonmagnetic but electrically charged. The charged solitons are also depicted in Fig. 1(a). The mobility of the neutral soliton, demonstrated by the motional narrowing of its spin resonance,[5] implies that the charged soliton could be the charge carrier leading to electrical transport in the polymer. Furthermore, photoconductivity has been observed[12-14] in *trans*-$(CH)_x$ but found to be absent[13-14] in *cis*-$(CH)_x$. This fact, coupled with the theoretical prediction[15] that a photoexcited electron-hole pair should decay to a charged soliton pair in an optical-phonon period ($\sim 10^{-13}$ s), has led to the assertion[13-14] that charged solitons are the charged species involved in photoconductivity in $(CH)_x$. It should be noted that long-lived ($\gtrsim 10$ μs) photoinduced absorptions have recently been observed in $(CH)_x$.[16-18] However, the nature of these photogenerated states is still unclear.

Photogeneration of charge carriers also is inherent to the photovoltaic effect. The photovoltaic effect has been observed in $(CH)_x$ in a variety of different device configurations.[19,20] The photogeneration of charged solitons model, however, leads to certain contradictions when viewed in the context of the physics of the photovoltaic effect. The photovoltaic effect is easiest understood in terms of the uniformly illuminated p-n homojunction displayed in Fig. 1(b). (The principles to be discussed, however, apply equally well to heterojunctions and Schottky junctions.) The existence of a photovoltaic effect necessarily implies the creation in the absorbing semiconductor by the incident radiation of two populations of *mobile* charges (electrons and holes) out of thermal equilibrium with each other. This is illustrated in Fig. 1(b) by the separation of the minority-carrier chemical potentials (the so-called quasi-Fermi levels) from the majority-carrier chemical potentials. The gradients in μ_e and μ_h across the junction drive the electrons and holes in opposite directions and work is obtained from the cell when a charge is extracted from the reservoir at the higher chemical potential, passed through an external load, and reinjected in the reservoir at the lower chemical potential. The

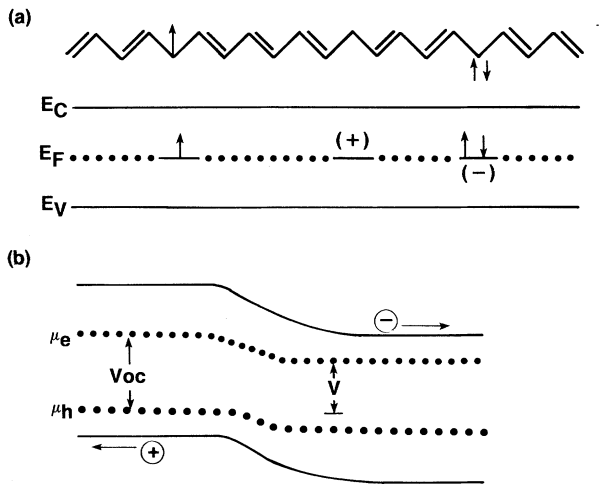

FIG. 1. (a) Chain configuration and energy-level diagram for neutral, positive, and negative solitons in *trans*-$(CH)_x$. (b) p-n homojunction under uniform illumination.

output voltage of the device [V in Fig. 1(b)] is the free-energy change per particle. The maximum output voltage obtainable occurs under open-circuit conditions (V_{oc}) where the cell self-biases so that μ_e and μ_h are constant across the cell and no current flows. V_{oc}, therefore, is a measure of the chemical potential difference between the electron and hole populations produced by the radiation field. V_{oc} of 0.8 V under one sun-equivalent illumination has been reported[21] in $(CH)_x$ devices implying a quasi-Fermi level separation in $(CH)_x$ at least that large. However, the photogeneration of charged soliton pairs produces soliton "holes" and soliton "electrons" at the same energy [Fig. 1(a)]. Transfer of an electron from one through the external circuit to the other produces two neutral solitons but results in no net free-energy change and consequently can produce no output voltage. The energy stored in the system will only be released when the two neutral solitons so formed annihilate each other. Electron-electron correlation in the doubly occupied soliton (and symmetrically hole-hole correlation in the unoccupied soliton) would displace the levels oppositely from gap center. However, the spatial extent of the soliton wave function[5,8] (~ 15 lattice constants) argues against a correlation splitting as large as 1.0 V.

A far more complicated process must be invoked if photogenerated charged-soliton pairs are to lead to a photovoltage. *Isolated* solitons are topogically constrained from leaving or being injected onto a $(CH)_x$ chain. Consequently a photovoltaic process must involve the annihilation of soliton pairs and the simultaneous transfer of all the energy stored in the kinks to the ejected charge. Such a process seems unlikely to occur with quantum efficiency of order unity which is the observed value in $(CH)_x$ devices for large photon energies (Fig. 2). Furthermore, the quantity of energy stored in a charged soliton pair, $(2/\pi)E_{gap}$ (= 0.89 eV for E_{gap} = 1.4 eV),[8] is inconsistent with an available *free* energy per pair (the measured V_{oc}) as large as 0.8 eV. For comparison, the *best* crystalline Si solar cells under one sun illumination produce a V_{oc} of $E_g - 0.5$ eV.[22] It must be concluded, therefore, that photogeneration of charged soliton pairs is incapable of producing the observed photovoltaic response of $(CH)_x$ devices.

A comparison of the photovoltaic and photoconductive response of $(CH)_x$ is instructive. Room-temperature spectra are plotted in Fig. 2. The photovoltaic device employed the Al:$(CH)_x$ Schottky configuration described in detail elsewhere.[19,20] The photoconductive gain spectrum was obtained by use of a two-probe surface-cell arrangement on a 75-μm-thick fully isomerized *trans*-$(CH)_x$ film with an applied voltage of 200 V across a 0.3 cm gap. Both the photovoltaic and photoconductive spectra were obtained with monochromatic light chopped at 14 Hz using lock-in detection. Etemad *et al.*,[13] whose measurements were performed on thin (~ 1 μm thick) films, argued that the measured photoconductive response was due to a direct photogeneration of charge carriers rather than an indirect effect due to heating of the film. The spectrum presented here of the response of a thick film supports this assertion. Although the photoconductive gain of $(CH)_x$ is small and the activation energy of the dark conductivity is large (0.3 eV), implying that an overall film temperature rise of a few millikelvins would produce an equivalent bolometric effect,

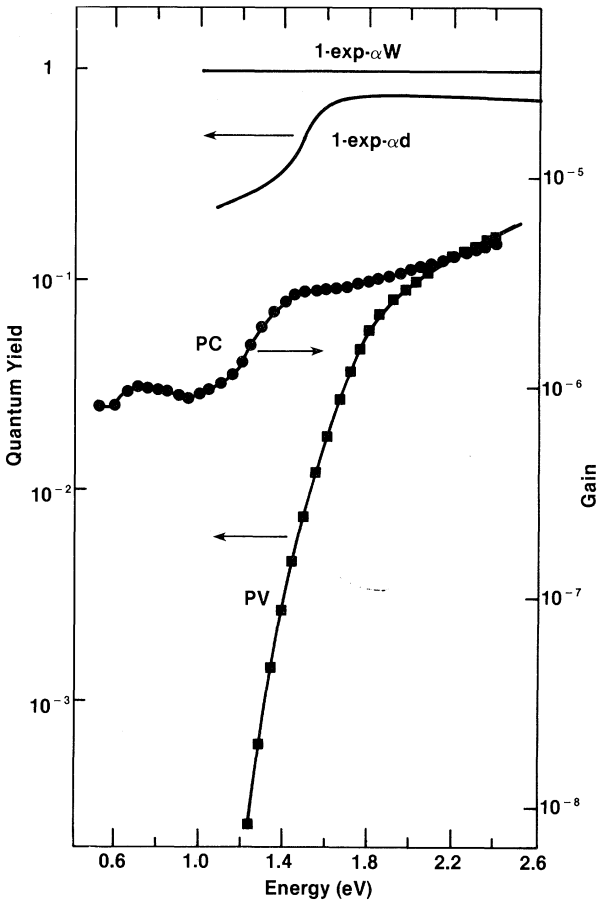

FIG. 2. Photoconductive (PC) and photovoltaic (PV) response spectra. (Quantum yield = short-circuit current/photon.)

the sharp spectral feature which appears at 1.2 eV in the response of the thick film is inconsistent with heating. Plotted also in Fig. 2 is $1-\exp(-\alpha W)$ (α is the absorption constant; $W = 75$ μm), the fraction of photons as a function of energy that are absorbed in the thick film. A purely bolometric effect would not produce the spectral feature observed in the photoconductivity. Furthermore, the existence of a photovoltaic effect conclusively proves that photogeneration of charge carriers occurs in $(CH)_x$, as heating does not produce the quasi-Fermi level separation necessary for photovoltaic response.

The nature of the photogenerated carriers in $(CH)_x$ must still be resolved, and in fact the species may be different in the photoconductive and photovoltaic effects. While photogenerated solitons cannot produce a photovoltaic current, they can contribute to a photoconductive response as the driving potential is provided by the external battery. The shift in the photoconductive edge from the photovoltaic edge may be evidence of this. As pointed out by Etemad *et al.*,[13] the position of the photoconductive edge corresponds well to the energy predicted by theory, $(2/\pi)E_{gap}$,[8-11] for the direct photogeneration of a charged soliton pair. A further interesting feature appears in the photoconductivity spectrum at low temperature shown in Fig. 3, a peak at 0.9 eV which has also been observed in the absorption spectra[23] of lightly doped films and has been associated with excitations involving the soliton mid-gap state and the peaks in the band-edge density of states. One may speculate that the photoconductive peak represents the creation of a single charged soliton plus an electron (or hole) from a neutral soliton.

The photovoltaic edge corresponds to the threshold for producing a mobile electron-hole pair, and agrees well with the position of the edge in $1-\exp(-\alpha d)$ (d is the Schottky diode depletion width,[19] 1000 Å), also shown in Fig. 2. However, the discrepancy in magnitude and the increase in quantum yield of the photovoltaic effect at high photon energy bears comment. What is suggested is geminate recombination,[24] which is excacerbated by the one-dimensional structure of the polymer. An intriguing effect which may be occurring concurrently is the geminate decay of photogenerated electron-hole pairs into charged soliton pairs which removes them from contributing to the photovoltaic current. Such a process implies an energy dependence to the soliton formation time. The concept of an electron-hole

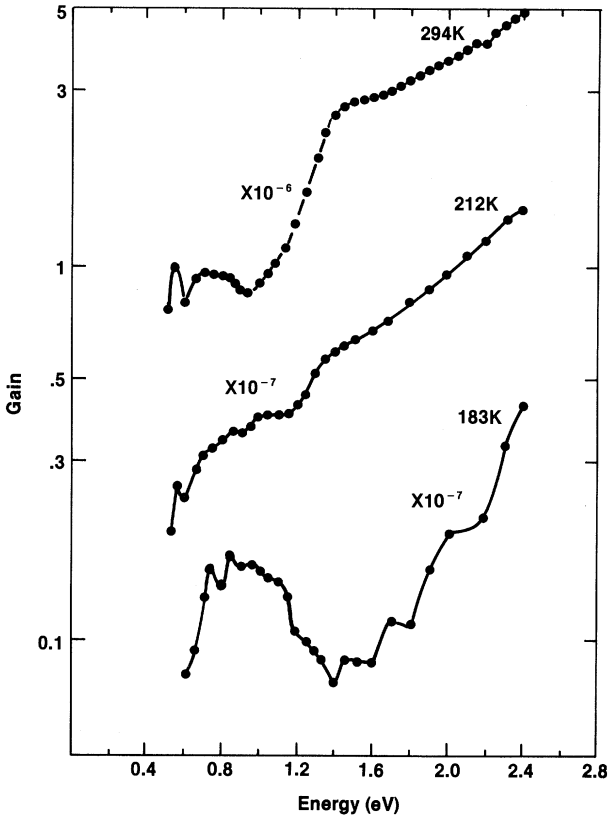

FIG. 3. Photoconductive response spectra at three different temperatures.

thermalization length,[24] which has been applied to geminate recombination, may be useful here; the electron-hole pair excited with photon energy substantially greater than E_{gap} thermalize to a separation of many lattice constants inhibiting the formation of the topological kinks.[9]

To summarize, an inspection of the photovoltaic and the photoconductive behavior of *trans*-$(CH)_x$ in the context of the soliton model leads to the conclusion that photogeneration of charged soliton pairs cannot be responsible for the observed photovoltaic effect. However, the shift of the photoconductive edge to lower energies and the appearance of the mid-gap peak at low temperature suggests that photogenerated solitons could play an important role in the photoconductivity of $(CH)_x$.

Discussions (and arguments) with several people helped to coalesce the ideas presented here. Among them were: S. Etemad, H. Deckman, A. Rose, A. Heeger, C. Fincher, T. Moustakas, and E. Yablonovitch.

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