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POLYACETYLENE, (CH)_x, AS AN EMERGING MATERIAL FOR SOLAR CELL APPLICATIONS

Final Technical Report, March 19, 1979—March 18, 1980

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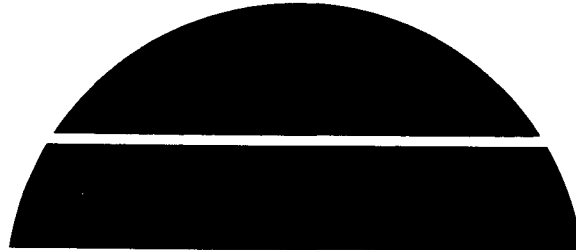
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FINAL TECHNICAL REPORT

POLYACETYLENE, $(CH)_x$, AS AN EMERGING MATERIAL
FOR SOLAR CELL APPLICATIONS

March 19, 1979 - March 18, 1980

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Despite great theoretical and technological interest in polyacetylene, $(\text{CH})_x$, the basic features of its band structure have not been unambiguously resolved. Since photoconductivity and optical absorption data have frequently been used to infer information on the band structure of semiconductors, we have carried out such measurements on $(\text{CH})_x$. This work was initiated under DOE funding (contract No. DE-AC04-79ET-23002) and supported by DARPA (N00014-75-C-0962) on a grant monitored by the Office of Naval Research.

We report the main results of an extensive study of the photoconductivity ($\Delta\sigma_{\text{ph}}$) and absorption coefficient (α) in $(\text{CH})_x$. The absence of photoconductivity in cis- $(\text{CH})_x$, despite the similarity in optical properties indicates that $\Delta\sigma_{\text{ph}}$ in trans- $(\text{CH})_x$ is induced by isomerization. We find that isomerization generates states deep inside the gap that act as "safe traps" for minority carriers and thereby enhance the photoconductivity. Compensation of trans- $(\text{CH})_x$ with ammonia appears to decrease the number of safe traps, whereas acceptor doping increases their number. Thus, chemical doping can be used to control the photoconductive response. The energy of the safe traps inside the gap is independent of the process used to generate them; indicative of an intrinsic localized defect level in trans- $(\text{CH})_x$. A coherent picture based on the soliton model can explain these results, including the safe trapping.

The photoconductivity studies were carried out at room temperature

on thin film samples (thickness of a few microns) polymerized¹ directly on glass substrates. A surface cell configuration was employed using ohmic contacts made with silverpaste or Electrodag conducting paints. The measurements were carried out in the range 0.6 - 3.0 eV using phase sensitive detection of the voltage change across a resistor in series with the sample. Due to excellent thermal anchoring of the sample to the massive glass substrate, sample heating was found to be unimportant.² Where necessary, corrections were made for transmitted light. The absorption coefficient studies were carried out on freshly grown semi-transparent thin films on glass substrates. All films were kept under vacuum or in an inert atmosphere.

In Fig. 1 the logarithm of the photocurrent (I_{ph}) in trans-(CH)_x is shown as a function of incident photon energy. The results were corrected for transmission (less than 15% over the whole spectrum for this sample). The inset in Fig. 1 shows a comparison of the same data (curve A) with results from three other samples of varying quality (see below) in order to point out the sample dependence of the photocurrent spectrum. Despite the large variation in the four sets of results, a distinct common feature is the rather sharp rise above 1.1 eV. The peak below 1.5 eV, which may be related to the 1.35 eV peak reported earlier,³ is not seen in all samples.

Measurements of I_{ph} in cis-(CH)_x were attempted under similar conditions without success; no photocurrent has been detected in samples

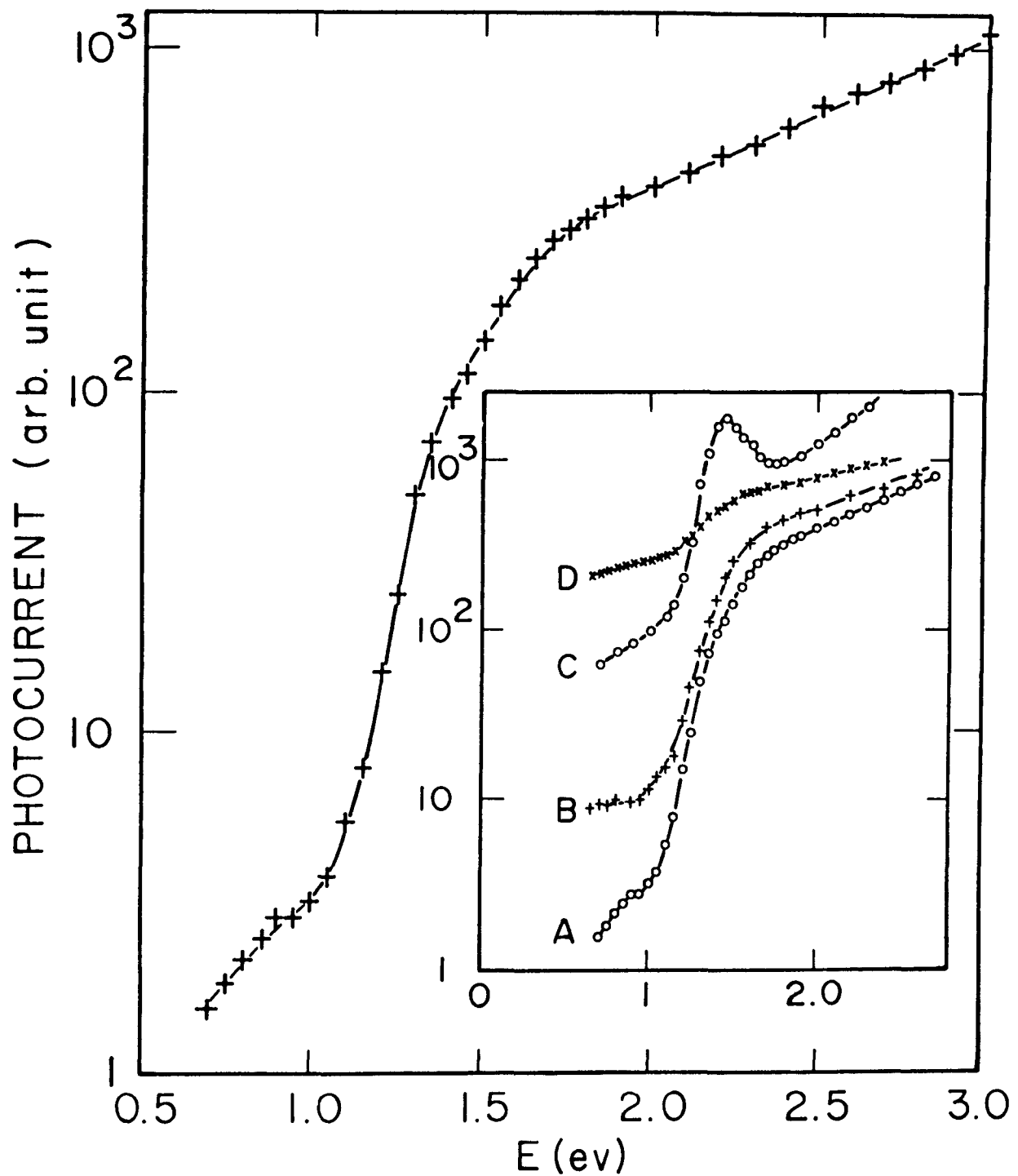


Fig. 1: Photocurrent of order of 10^{-22} amperes per photon per second at 2.0 eV has been generated through application of a 10^4 volt/cm electric field.

of 80% cis-rich $(CH)_x$. In situ isomerization of the same film resulted in the sizeable I_{ph} shown in Fig. 1. The upper limit on I_{ph} in cis- $(CH)_x$ is three orders of magnitude smaller than in trans- $(CH)_x$.

Since the dark conductivity can be varied by more than twelve orders of magnitude through doping and compensation, we have investigated the corresponding effects on $\Delta\sigma_{ph}$. The data, after compensation with ammonia (NH_3) and after light doping with AsF_5 are also shown in Fig. 2. The curve labeled "compensated" is from the same sample as that labeled "initial result"; the "compensated" data were obtained after exposure to ammonia sufficient to increase the dark resistance by several orders of magnitude. The curve labeled "acceptor doped" in Fig. 2 was obtained subsequently from the same sample after light doping with AsF_5 .

Compensation with ammonia appears to have two distinct effects. First, at energies near and below the threshold, I_{ph} is decreased considerably relative to the photocurrent at higher energies. Second, the overall photoconductive response, including the energy region above the edge, decreases after compensation. Subsequent light doping with AsF_5 causes a uniform increase in the photoresponse. Note that the doping and compensation experiments cause I_{ph} to vary by more than two orders of magnitude with essentially no shift of the photoconductive threshold. After compensation, the results for samples (C) and (D) (inset to Fig. 1) change to resemble that shown by curve (A). The effect of compensation is shown in more detail for sample (C) in the inset to Fig. 2.

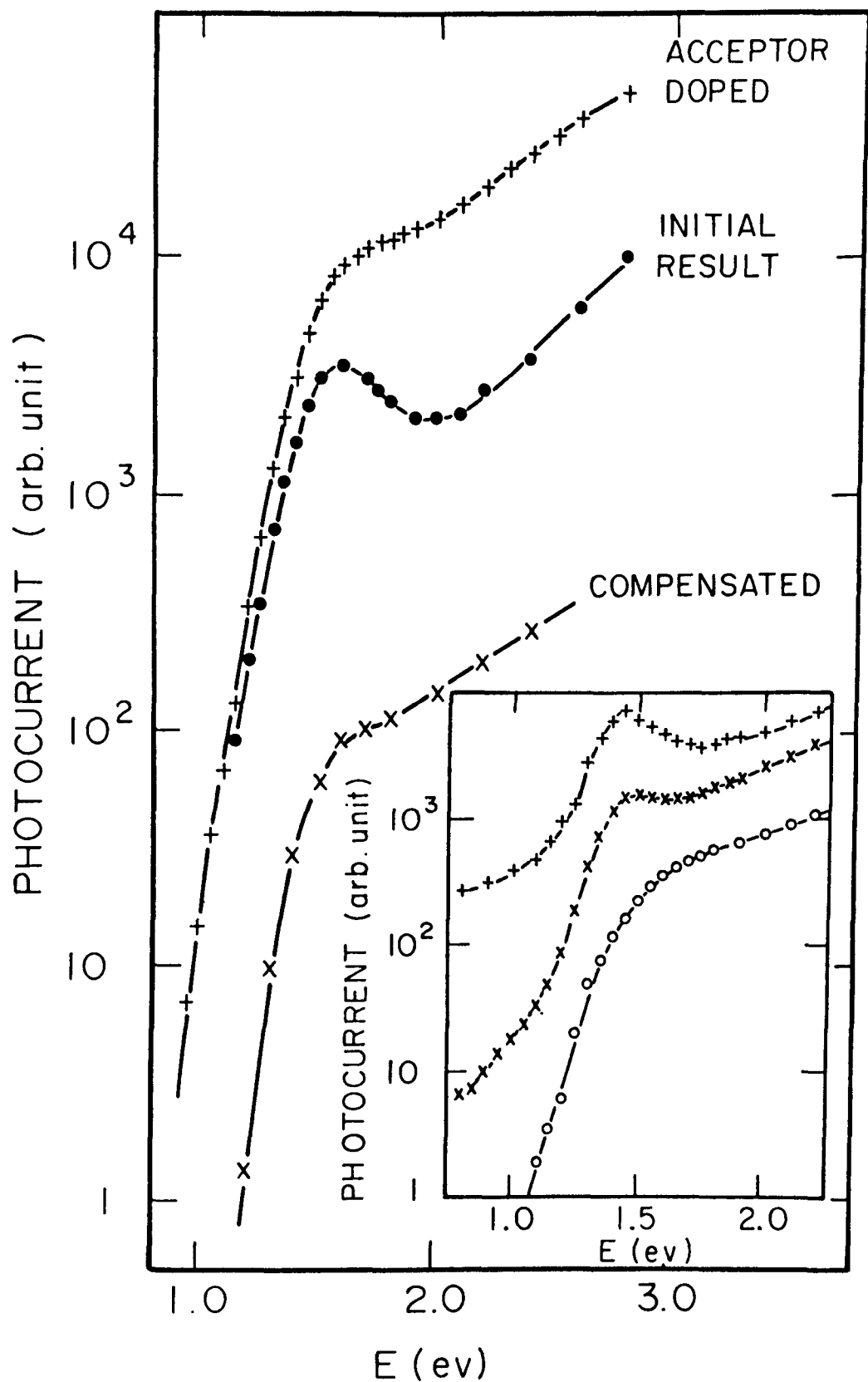


Fig. 2: Photocurrent spectrum for $\text{trans}-(\text{CH})_x$. (o) as-grown $\text{trans}-(\text{CH})_x$; (x) after compensation with NH_3 ; (+) after doping with AsF_5 ; all on the same sample. The inset shows the effect of compensation on sample (C) of Fig. 1.

The optical density of a carefully prepared uniform thin film is shown on Fig. 3 as a function of photon energy. The data were obtained with the film cooled to 77 K and have been normalized to show the absorption coefficient. Note that the absorption increases by more than two orders of magnitude at the sharp edge above 1.4 eV. As in the case below threshold in I_{ph} , the absorption below 1.4 eV is somewhat sample dependent. The basic differences between this result and those reported earlier^{1,5} are the somewhat sharper edge and wider range in α due to the high quality $(CH)_x$ film. The photocurrent results from Fig. 1 are also shown as $\log_{10} I_{ph}$ for comparison. We note that the photoconductivity edge is about 0.3 eV lower in energy than that of the absorption coefficient.

In addition to the main absorption, a weak absorption peak at about 0.9 eV is also evident in the data of Fig. 3. A second weak absorption at about 1.45 eV, reported previously,³ is detectable when the data are expanded to a proper scale. The oscillator strengths of these two weak absorptions are comparable and about three orders of magnitude smaller than that of the main absorption.

Summarizing; isomerization gives rise to photoconductivity in trans- $(CH)_x$ with a threshold near 1.1 eV, about 0.3 eV below the absorption edge. Compensation and acceptor doping decrease and increase the photoconductivity, respectively, without changing the threshold energy.

The sharp rise in α together with the monotonic decrease above 2 eV has been attributed^{5,6} to the direct interband transition in a one-dimensional

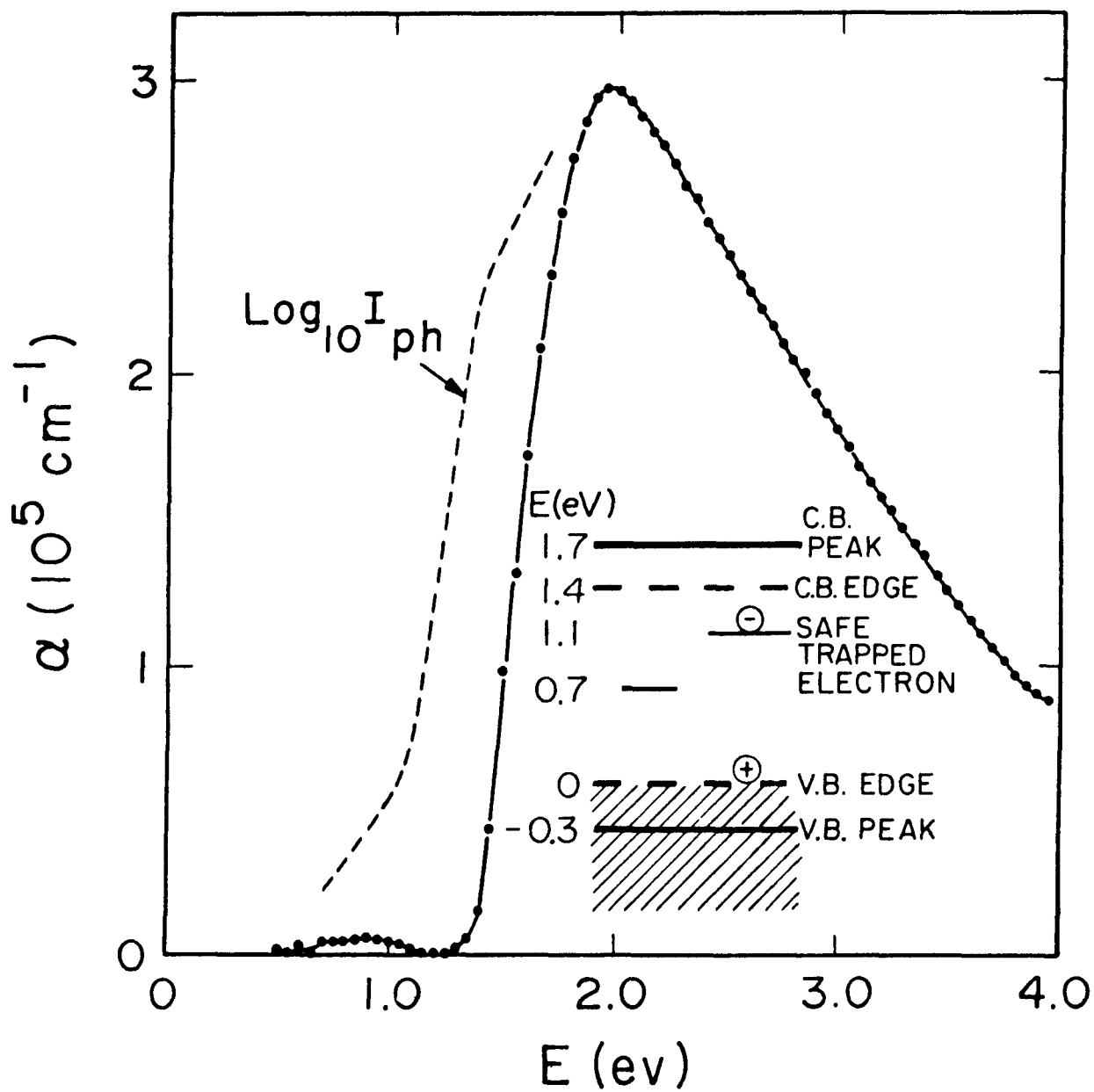


Fig. 3: Absorption coefficient (α) and photocurrent (I_{ph}) vs. photon energy. The inset is a band diagram outlining the relevant energies (uncertainty of about 0.1 eV).

(1-d) band structure. The square root divergence of the joint density of states is presumably rounded by disorder and three-dimensional (3-d) interchain coupling.⁷ The results of Fig. 3 would then imply a 1-d direct band gap of about 1.6 eV with 3-d coupling and disorder decreasing the minimum gap to about 1.4 eV.

The peak in α near 2 eV is related to the transition from the peak in the density of states in the valence band (VB) to that of the conduction band (CB). The rounding appears to shift the position of the peaks in the VB and CB densities of states by about 0.2 eV. The weak absorption near 0.9 eV would then correspond to a transition between the peak in VB density of states and a level inside the gap. Relative to the VB edge, the gap state occurs at about 0.7 eV. Similarly the second weak absorption peaking near 1.45 eV described above locates a second level near 1.1 - 1.2 eV above the VB edge. Independent evidence of this second level is found in the structure observed in $\Delta\sigma_{ph}$ starting at about 1.1 eV with a maximum near 1.4 eV (see Figs. 1 and 2). The magnitude of the peak is sample dependent, and it is removed by compensation. We note that in this analysis we have ignored any shifts resulting from energy dependent matrix elements associated with the optical transitions. The relevant energies are sketched on a band diagram in the inset of Fig. 3, referring all values to the edge of the valence band.

Photoconductivity arises when photon absorption results in generation of electron-hole (e-h) pairs which can be separated in an electric field. Often, the photogenerated e-h pairs cannot be separated due to exciton formation or geminate recombination. In such a case one has absorption without photoconduction. Since the onset of $\Delta\sigma_{ph}$ is about 0.3 eV lower in energy than the onset of α , it is clear that the photoconduction process in trans-(CH)_x is intimately associated with the presence of states deep inside the gap. The fact that we have not been able to detect photoconductivity in cis-(CH)_x indicates that such states have been created in the isomerization process.

It is well-known that photoconductivity can be enhanced by the presence of states in the gap, so-called "safe-traps"; i. e. localized states that can capture electrons (minority carriers) and prevent recombination with mobile holes. As a result, the recombination time is lengthened considerably, thereby enhancing the photoconductivity. In the absence of trapping, and under steady state conditions

$$\Delta\sigma_{ph} = e\tau_R r (1 + b) \mu_e \quad (1)$$

where r is the carrier photogeneration rate, τ_R is the recombination lifetime, μ_e is the electron mobility and $b\mu_e$ is the hole mobility. In the case of safe trapped minority carriers (electrons), the additional photogenerated holes will increase with the number of trapped electrons. They will continue to produce a photocurrent until the trapped electrons eventually

recombine either directly or by primary excitation back into the conduction band. If the average time a minority carrier spends in a safe trap is τ_2 , and τ_1 ($\tau_1 < \tau_R$) is the average time before it is trapped, equation (2) then becomes:

$$\Delta\sigma_{ph}^* = e r \tau_R \left[1 + b + b \frac{\tau_2}{\tau_1} \right] \mu_e \quad (2)$$

For $\tau_2 \gg \tau_1$, I_{ph} is enhanced by $\tau_2/\tau_1 \gg 1$ and the photoconductive decay is determined by τ_2 . In such a case $\Delta\sigma_{ph}^*$ would turn on at an energy corresponding to the transition from the VB to the safe trap state inside the gap, explaining the unusual result of Fig. 3. Transient measurements indicate a long decay time of order a few milliseconds, consistent with these ideas. The sample dependent peak in the photocurrent spectrum (Figs. 1 and 2) corresponds to direct excitation of an electron from the VB peak into a safe trap. For such a direct excitation one obtains essentially 100% trapping, or $\tau_1 \rightarrow 0$ resulting in a maximum in I_{ph} .

Compensation of trans-(CH)_x would chemically fill the safe traps making them unavailable for photoexcited electrons. Acceptor doping would tend to generate new safe traps and/or empty the filled ones making them available for photoexcited electrons. The fact that (Fig. 2) acceptor doping can increase $\Delta\sigma_{ph}^*$ well beyond the undoped result while leaving the photoconductivity edge at the same energy is, therefore, particularly important.

The observation that isomerization induces safe trap states inside the gap is suggestive of the applicability of the soliton model. The acceptor doping experiments further indicate that positively charged solitons (S^+), present even in the undoped material, are of principle importance. Although other mechanisms for generating safe trapping states in the gap must be considered, the fact that the threshold for $\Delta\sigma_{ph}$ does not shift, either after compensation or after subsequent doping, points to an intrinsic defect which is not specific to a particular dopant. Detailed assignments must await a more thorough understanding of the role of the electron-electron Coulomb interaction and the binding of charged solitons to the negative dopant ions.

The long photoconductive decay time is of special interest since one would anticipate rapid minority carrier recombination in a disordered system with a high density of majority carriers. The identification of the important role played by solitons suggests a more detailed understanding of the long lifetime. The transition rate of safe trapped electrons to the VB ($S^0 + h \rightarrow S^+$) would be dependent on finding a mobile hole nearby. Since within the soliton picture the dark carriers are all charged solitons the number of VB holes would be restricted to the small number of photogenerated carriers. As a result, τ_2 would be long even though the dopant level is in excess of 10^{18} cm^{-3} . Thus although considerable detailed theoretical work is required, it may be possible to understand the safe trapping as a direct result of soliton formation in trans-(CH)_x.

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Stability of Polyacetylene

To check the effect of the air exposure on the undoped $(CH)_x$, an on-line experiment was set up to monitor conductivity vs. time. Samples were mounted in a glove bag under argon atmosphere. In the first three hours of air exposure, the conductivity of cis- $(CH)_x$ increased by one order of magnitude while that of trans- $(CH)_x$ increased by only about a factor of three. Upon pumping out the air, the conductivity returned to its initial value. Such reversibility was also observed earlier in electron spin resonance experiments.¹⁰ Air exposure of heavily doped metallic samples for 2 hours resulted in a 40% and 20% decrease, respectively, for $[CH(AsF_6)_y]_x$ and $[CH(I_3)_y]_x$. Studies of the effect of oxygen on metallic $[CH(I_3)_y]_x$ samples showed a decrease in conductivity of about 10% in the first four hours.

In an initial attempt to stabilize the samples after doping, paraffin wax coatings were applied. Conductivity measurements of uncoated and wax coated metallic $[CH(I_3)_y]_x$ were carried out on samples doped at the same time and under identical conditions. The conductivity of the wax coated sample decreased only 10% after 12 hours, whereas the conductivity of the uncoated sample fell by a factor of five during the same period.

Similar tests were carried out in connection with the temperature dependence measurements. The temperature dependence exhibited by doped samples obtained from the bottom of the reactor was not significantly different from that obtained from samples extracted from the side walls.

Using cis samples of either origin, metallic AsF_6 -doped $(\text{CH})_x$ showed a slight increase in conductivity (a few per cent) below room temperature as noted previously. Samples mounted after doping, or samples re-painted with solvent containing Electrodag, showed a monotonic decrease in conductivity with decreasing temperature. Exposure to air had similar effects; the weak maximum reduced in magnitude and shifted toward higher temperature before disappearing after ~ 30 minutes exposure. The wax coated samples showed similar temperature dependences to those of the uncoated ones.

Stabilization studies are continuing at the University of Pennsylvania and at Rohm and Haas Company. Through coatings and anti-oxidants, Rohm and Haas have achieved major improvements in long term stability. For information on their work contact the following:

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