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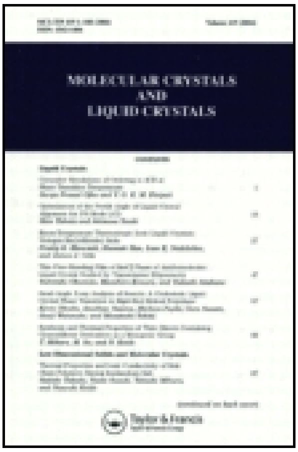

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Photocarrier Generation and Transport in Polyene Crystals

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PHOTOCARRIER GENERATION AND TRANSPORT IN POLYENE CRYSTALS

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Abstract Photoconductive properties of polyenes have been studied. The results suggest that a single descrete trapping level is involved in carrier generation. SCLC theory has been used to evaluate various transport parameters. Polyenes behave as a non-extrinsic material for dark conduction but for photoconduction these become extrinsic. The light intensity dependence suggests that carrier generation is one-photon process and is trap limited. The photoconduction action spectrum suggests two distinct mechanisms of photocarrier generation, one through photoinjection from the illuminated electrode and the other through direct electron-hole pair production.

INTRODUCTION

Photoconductive properties of biologically important polyene compounds have been and continue to be of much interest. Highly conjugated π-electronic structure of these molecules results in their semi- and photoconductive properties in the solid state[1]. All-trans β -carotene, its various isomers and β -apo-8'-carotenal have been studied extensively and this has led to photoconductive theory of visual receptor process[2,3]. Investigation on the photoconductive properties of other polyenes is, however, rare. We have, therefore, undertaken a programme to study the photoconductivity of some crystalline polyenes as a function of applied field, temperature, light intensity and excitation wavelength. In this paper we report the results of our investigation.

EXPERIMENTAL

Highly pure polyenes were obtained as a gift from Hoffman La-Roche Co., Switzerland and were used without further purification after checking the purity of the sample spectroscopically. Details of the experimental procedure has been reported elsewhere[4].

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RESULTS AND DISCUSSION

1. Current-Voltage Characteristics

We have measured dark- and photocurrent in methylbixin, astacin, crocetin, crocetinaldehyde and lycopene as a function of applied voltage and temperature. In Fig. 1 we show the representative I-V plots in dark and in illuminated condition at room temperature ($\simeq$ 30°C) for lycopene. The I-V characteristic is almost identical in all the other polyenes. At high field the square law behaviour is observed whereas at low field it is ohmic. The cross over fields (V_t) from ohmic to space charge limited current (SCLC) region of different polyenes are given in Table 1 for both dark and illuminated condition. The dark I-V characteristic for crocetinaldehyde is found linear in the experimental range (upto $1x10^4$ Volt/cm).

The square law behaviour may be interpreted in terms of either a single discrete trapping level or of exponential trap distribution[5,6]. For a single discrete trap level, the slope for Arrhenius plot is independent of applied voltage, whereas, for exponential trap distribution the slope is voltage dependent. A representative Arrhenius plot at different applied voltages for lycopene is shown in Fig. 2. A constant slope of plots show that a single discrete dominant trapping level is involved in dark- and photoconduction. Similar results have been observed in other polyenes also. For single discrete trapping level the SCL current is given by

$$I_{SCL} = (9/8)\ \varepsilon_o \varepsilon \mu\ [N_c/N_t(s)]A\ \exp\ (-E_s/kT)(V^2/d^3) \qquad (1)$$

where the notations have their usual meanings[4]. The quantity $[N_c/N(s)]\text{Exp}(-E_s/kT)$ is usually denoted by θ which is the ratio of free to trapped charges. The ohmic current (I_Ω) is given by

$$I_\Omega = n_o q \mu\ (A/d)V \qquad (2)$$

where n_o is the free carrier density. Combining eq. 1 and eq. 2 the onset of the SCLC injection takes place at cross-over voltage which can be expressed as

$$V_t = (8/9)(qd^2 n_o/\varepsilon\ \varepsilon_o \theta\ ) \qquad (3)$$

$$= (8/9)(d^2/\mu_e \tau \varepsilon_o) = (8/9)\ (d^2 e/\ \mu_e \varepsilon\ \varepsilon_o) \qquad (4)$$

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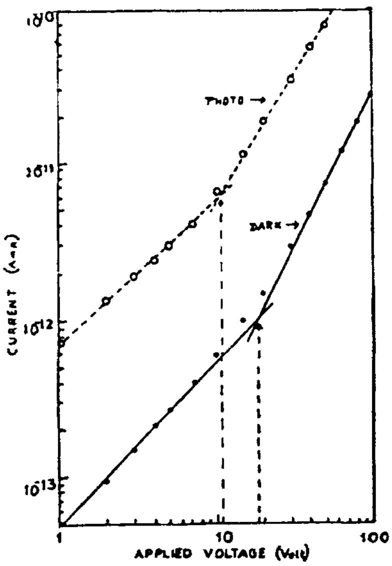

FIGURE 1 I-V Characteristics of lycopene

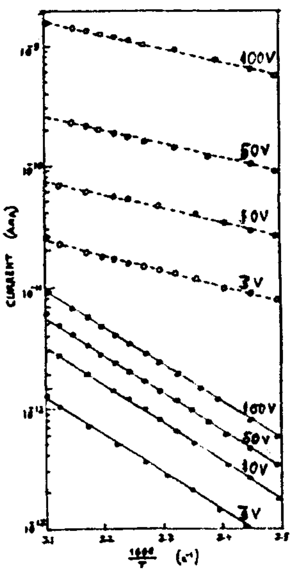

FIGURE 2 Arrhenius plots of lycopene at different voltages

Here $\tau = \varepsilon / \sigma$ is the ohmic relaxation time and $\mu_e = \mu \cdot \theta$. The dielectric constant of β -carotene is 2.5[7]. Using this value for the dielectric constant of other polyenes, effective drift mobility may be calculated from eq. 4. The value of n_o / θ can be obtained from eq.3. The values of these parameters are summarised in Table 1. It can be seen that the values of μ_e are very small. The low value of μ_e's observed may suggest that the conduction mechanism through these polyene samples is hopping[8]. Decrease in cross-over voltage due to illumination suggests additional carrier injection which may be due to photoinjection from the electrodes.

2. Temperature Dependence of Dark- and Photoconduction

The temperature dependence of steady state dark current (I_d) and photocurrent (I_{ph}) of organic materials generally follow the expressions

$$I_d = I_{od} \exp(-E_d/2kT) \quad (5)$$

$$I_{ph} = I_{op} \exp(-E_{ph}/kT) \quad (6)$$

where E_d and E_{ph} are the dark and photoactivation energy respectively. In eq. 5 we have used a half energy as was originally done by

TABLE 1 Values of different transport parameters, dark and photoactivation energies of polyenes.

Polyenes	Type of conductivity	V_t (Volt/cm)	μ_s using eq.4($cm^2 V^{-1} sec^{-1}$)	n_o/θ at 303K (cm^{-3})	E_d and E_{ph} (eV)
Methyl-bixin	Dark	$2.68x10^3$	$7.69x10^{-8}$	$3.1x10^{-11}$	1.98
	Photo	$2.08x10^3$	$2.14x10^{-7}$	$2.42x10^{11}$	0.20
Astacin	Dark	$7.8x10^3$	$1.3x10^{-9}$	$2.44x10^{12}$	1.32
	Photo	$6.35x10^3$	$2.2x10^{-8}$	$1.97x10^{12}$	0.43
Crocetin	Dark	$9.1x10^3$	$2.64x10^{-9}$	$2.84x10^{12}$	1.66
	Photo	$3.7x10^3$	$6.2x10^{-7}$	$1.16x10^{12}$	0.175
Crocetinal-dehide	Dark	----	----	----	1.52
	Photo	$3.3x10^3$	$6.6x10^{-5}$	$1.05x10^{12}$	0.15
Lycopene	Dark	$3.8x10^3$	$3.08x10^{-8}$	$1.33x10^{12}$	1.22
	Photo	$2.2x10^3$	$5.18x10^{-7}$	$7.73x10^{11}$	0.225

Rosenberg[9]. This assumes that dominant electron and dominant whole levels contribute equally to the conduction in these wide gap materials. These type materials are known as "non extrinsic" semiconductors[10]. However, for photoconduction it is more realistic to write down the activation energy according to the convention of extrinsic semiconductors. E_{ph} is now equal to E_s (photo) in eq. 1. These values, as shown in Fig. 2 are independent of applied field. E_d and E_{ph} values evaluated from Arrhenius plots of different polyenes are summarised in Table 1. The photoconduction activation energy is the thermal energy required for carrier generation after photoexcitation. This may be either the energy difference between the transport band edge and the highest exciton level or just depth of shallow exciton traps.

3. Excitation light intensity dependence of photocurrent

The dependence of photocurrent, I_{ph}, on light intensity, I_B, is given by

$$I_{ph} \propto I_B^{\nu} \qquad (7)$$

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where the slope, ν, is the characteristic of the photoconductive system. For a given range of light intensity one recombination channel predominates and this particular channel determines the value of ν. In general, for polyenes, ν lies between $0.5 > \nu > 1$. This type of dependence of photocurrent on light intensity generally indicates the presence of several defect states in the crystal[11]. The result also suggests that the photo generation process is one photon process. At a particular temperature with the increase of applied voltages the value of exponent, ν, increases slightly. This suggests that there is at least one kinetically important process which is weakly field dependent; this may be a rate of detrapping which increases or a rate of recombination which decreases with increasing electric field[12].

4. Photoconduction action spectra

In Fig. 3 we represent the wavelength dependence of photocurrent in crocetinaldehyde and also its optical absorption spectrum in thin solid film. Two photoconduction bands, one in the 300-400 nm region and the other in 550-750 nm region, do not show any correlation with the absorption band. The short wavelength photoconduction band can be attributed to photoinjection of charge carriers from the electrode[13]. The Fowler relationship[14] should be valid in that case and the photocurrent quantum yield Q should satisfy the relation

$$Q \propto (\phi - \phi_1)^2 \tag{8}$$

where ϕ is the photon energy and ϕ_1 is the electron or hole

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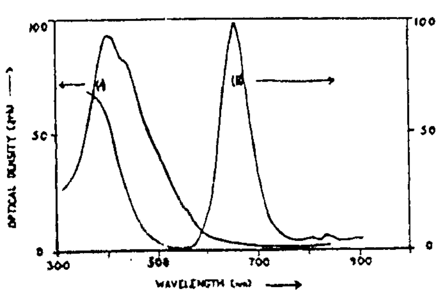

FIGURE 3 Absorption spectrum(A) and photoconduction action spectrum(B) of Crocetinaldehyde

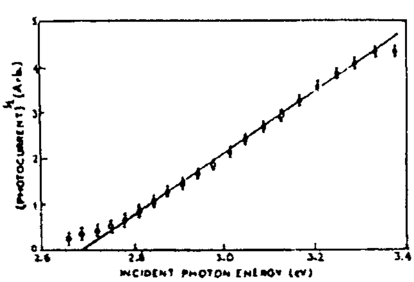

FIGURE 4 Flower plot for SnO_2 electrode injection current into crocetinaldehyde

photoinjection threshold energy. A plot of the square root of photocurrent versus photon energy should be linear and from the intercept, photoinjection threshold energy should be obtainable. In Fig. 4 such a plot is shown and a value of 2.68eV is obtained for ϕ_1, a reasonable value[13].

The long wavelength peak has also been reported in some other polyenes[13,15]. If we extrapolate the long wavelength tail of this band, it intersects the abscissa at 1.6eV. This is the photon energy at which the compound displays photoconductivity. This value is in excellent agreement with the thermal activation energy for dark conduction obtained from eq. 5. These results suggest that intrinsic mechanism of carrier generation is operative both in dark and photoconduction.

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