Photodielectric Effect in Thin Films of Ethyl 2,5-Dianilinoterephthalate

Stanislav Nešpůrek [a] & Hynek Valerián [a]

[a] Institute of Macromolecular Chemistry, Czechoslovak Academy of
Sciences, 162 06, Prague 6, Czechoslovakia
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PHOTODIELECTRIC EFFECT IN THIN FILMS
OF ETHYL 2,5-DIANILINOTEREPHTHALATE

STANISLAV NEŠPŮREK and HYNEK VALERIÁN
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6, Czechoslovakia

Abstract   The photodielectric effect in ethyl 2,5-dianilinoterephthalate has
been studied. The experimental data could be explained using a conductivity
hypothesis in which charge carrier trapping is included.

INTRODUCTION

Dielectric changes caused by illumination of a photoconductive capacitor is termed
as a photodielectric effect (PDE). This effect has been investigated in many
inorganic photoconductors (see, e. g. refs[1,2]) but for organics only little information
is available.[3] Most of the authors derived expressions for analyzing the PDE based
on the following hypotheses:

(i) The PDE arises due to the increase of the free carrier gradient
concentration during sample illumination.[4]

(ii) Space charge generally causes PDE, which can be interpreted by a linear
theory of space charge polarization.[5]

(iii) The polarization of traps containing loosely bound charge carriers can
increase the PD response.[6]

(iv) Samples with photoconductive domains in a heterogeneous dielectric can
be treated as insulators interspread with "conducting" regions.[7]

(v) A great change of the molecular dipole moment in the excited state
and formation of polar inter- and intramolecular charge transfer states can induce
a strong photodielectric response.

EXPERIMENTAL

The preparation of ethyl 2,5-dianilinoterephthalate (DTA)

$$COOC_2H_5$$

⟨⟩—NH—⟨⟩—NH—⟨⟩

$$COOC_2H_5$$
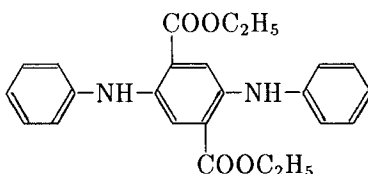
was described elsewhere.[8] Photoconductive properties of DTA were summarized in previous papers.[9,10] Amorphous sandwich samples were prepared from the melt between two Uviol NESA – coated glasses. The General Radio 1621 assembly was used for the dielectric measurements.

RESULTS AND DISCUSSION

Dependences of photocapacitance, ΔC (curve 1), dielectric losses under photoexcitation, ε_λ'' (curve 2), and dark ac-conductivity, σ_{ac} (curve 3) on frequency are plotted in Figure 1(a). Frequency dependence of $\sigma_{ac} \sim \omega^{0.3}$ suggests that from low frequencies up to 3×10^4 Hz, a dispersion region occurs. Photocapacitance decreases with frequency and significantly diminishes at the edge of the dispersion region. Dielectric losses ε_λ'' under illumination follow the same dependence. For lower frequencies, a saturation in the curve $\Delta C = \Delta C(f)$ has been observed. As follows from Figure 2(a), the photocapacitance ΔC (curve 1) and ac-photoconductivity $\Delta\sigma_{ac}^\lambda$ (curve 2) increase with photoexcitation intensity I as $I^{0.4}$. The coincidence of photocapacitance, and ac and dc-photoconductivity indicates that photoelectric and photodielectric phenomena are closely related and free charges are responsible for these effects. The low time constants of the kinetic curves of these photoprocesses after switching on/off light (ca. 0.01 s) as well as the ΔC and $\Delta\sigma_{ac}^\lambda$ vs. I^q ($q < 1$) dependences suggest that trapping phenomena are important. These results could be interpreted as a consequence of activated hopping of charge carriers between shallow localized states accompanied by an intensive deep trapping. The σ_{ac} frequency dependence does not exclude the possibility of the adiabatic hopping.[12]
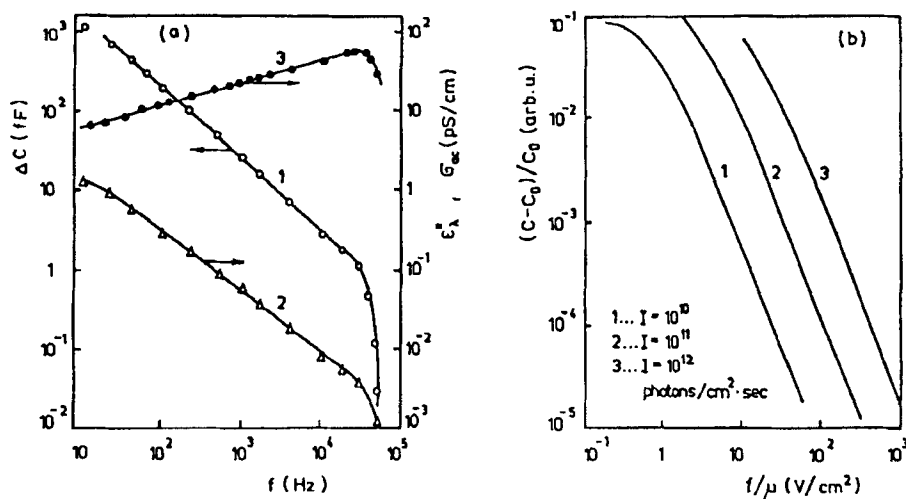
FIGURE 1 (a) Experimental dependences of photocapacitance, $\Delta C = C - C_o$ (curve 1), dielectric losses at photoexcitation, ε_λ'' (curve 2), and dark ac-conductivity, σ_{ac} (curve 3) on frequency. (b) Theoretical dependences of relative photocapacitance $(C - C_o)/C_o$ on the ratio frequency/charge carrier mobility for different light intensities.
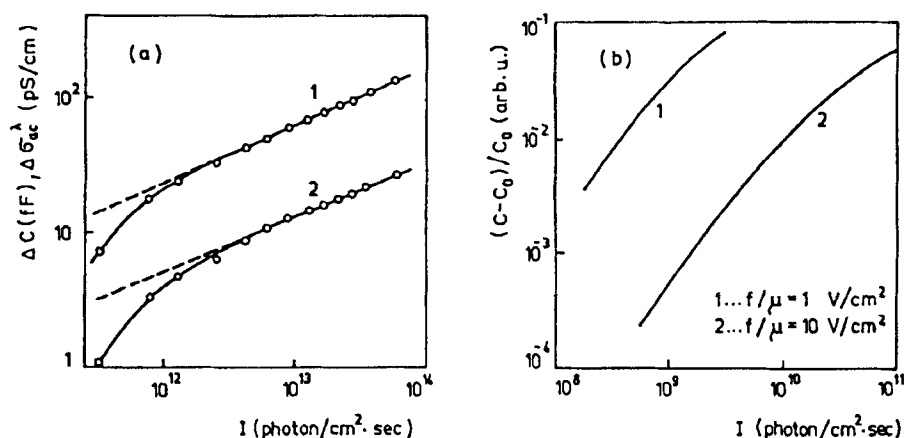

FIGURE 2 (a) Experimental dependences of photocapacitance, $\Delta C = C - C_o$ (curve 1) and ac-photoconductivity, $\Delta\sigma_{ac}^\lambda = \sigma_{ac}^\lambda - \sigma_{ac}$ (curve 2) on light intensity. (b) Theoretical dependences of relative photocapacitance $(C - C_o)/C_o$ on light intensity for different ratios of frequency/charge carrier mobility.

TEST OF THE CONDUCTIVITY HYPOTHESIS

The applicability of the conductivity hypothesis to our experimental results was tested by solving the system of differential equations bounding together the current density, the electric field strength F and the concentrations of charge carriers in the sample of the thickness L when illuminated by light. The equations were published previously by Kneppo et al.[4] and Pillai et al.[11] Assuming steady-state, immovable electrons (electron mobility $\mu_n = 0$) and open-circuit conditions (external circuit current $j = 0$) the fundamental system of differential equations reduces to

$$\frac{\mathrm{d}F}{\mathrm{d}x} = \frac{e}{\varepsilon}\left[\Delta p + \Delta p_t - \frac{1}{\gamma(p_o + \Delta p)}(\eta\alpha I \exp(-\alpha x) - \gamma n_o \Delta p)\right] \tag{1}$$

$$\frac{\mathrm{d}\Delta p}{\mathrm{d}x} = \frac{e}{kT}(p_o + \Delta p)F \tag{2}$$

where e is elementary charge, ε electric permittivity, γ recombination coefficient, η photogeneration quantum efficiency, α absorption coefficient, I light intensity, k Boltzmann constant, T temperature, $p_o(n_o)$ concentration of free holes (electrons) in thermal equilibrium, and Δp and Δp_t are changes in concentrations of free and trapped holes, respectively under the illumination. The relation between free and trapped charge carriers is taken for a single level approximation as

$$\Delta p_t + p_{to} = \frac{(p_o + \Delta p)P_t}{p_1 + p_o + \Delta p} \tag{3}$$

where P_t is the concentration of traps, $p_1 = N_v \exp(-E_t/kT)$ N_v being the effective concentration of states and E_t the trap depth, and p_{to} is the concentration of trapped holes in thermal equilibrium.

To solve this system of equations boundary conditions must be taken into account. Thus we assume that

(i) the sample is electrically neutral as a whole, from which follows $F(0) = F(L)$

(ii) no external field is applied to the sample and consequently, if no surface states are present, $F(0) = 0$.

These boundary conditions differ from those published by Kneppo et al.[4] and Pillai et al.[11], who used the following ones:

— Δp and Δp_t are assumed to be zero in $x = \infty$,

— changes of electron and hole concentrations are equal for $x = 0$ (generally, this means that the sample under the steady – state condition could not fulfill the neutrality condition for one carrier case).

The authors[4,11] assumed small changes in charge carrier concentrations, and therefore linearized the Equations (1) and (2). Their approach seems to be oversimplified. Generally, in the framework of the conductivity hypothesis, for the observable PDE, changes in charge carrier concentrations cannot be assumed to be too low; hence, Eqs. (1) and (2) cannot be linearized. Solving Equations (1) and (2) under the above mentioned boundary conditions one can calculate the conductivity $\sigma(x)$

$$\sigma(x) = e\mu_p(p_o + \Delta p(x)) \tag{4}$$

where μ_p is the hole mobility. The admittance Y of the sample can be then expressed as

$$Y = \frac{1}{R} + i\omega C = \left[\int_o^L \frac{dx}{\sigma(x) + i\omega\varepsilon}\right]^{-1} \tag{5}$$

where R is the sample resistance and ω is the frequency of the applied voltage.

The results of model calculations are given in Figures 1(b) and 2(b). The parameters taken into account were: $L = 10^{-2}$ cm, relative permittivity $\varepsilon_r = 3$, $T = 300$ K, $N_v = 4 \times 10^{21}$ cm^{-3}, $P_t = 10^{14}$ cm^{-3}, $E_t = 0.6$ eV, $\gamma = 10^{-11}$ cm^3 s^{-1}, $p_o = 10^6$ cm^{-3}, $p_{to} = 3.03 \times 10^8$ cm^{-3}, $n_o = 3.04 \times 10^8$ cm^{-3}, $\alpha = 10^5$ cm^{-1}, $\eta = 10^{-6}$ charges per photon.

It could be pointed out that materials with small free charge carrier concentrations, low carrier mobility and weak photoconductivity could not show a large PDE within the conductivity hypothesis. Unfortunately, organic materials are generally of low mobility. Thus, the important contribution to PDE of many other organics should be anticipated as resulting from changes in the dipole moment and polarizability in the excited states, and polarization of Coulombic traps.

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