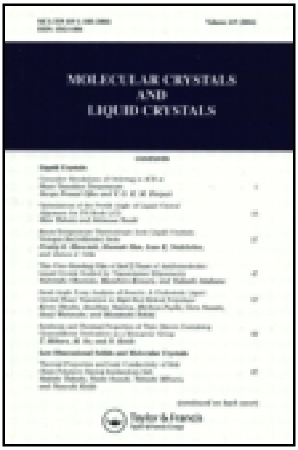

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Saturation of the Drift Velocity of Holes at High

G. Verbeek [a] , M. Van Der Auweraer [a] , F. C. Deschryver [a] , C. Geelen [a] , D. Terrell [b] & S. De Meuter [b]

[a] Lab. For Molecular Dynamics and Spectroscopy K.U. Leuven Celestijnelaan, 200-F, B-3001, Heverlee, Belgium

[b] Agfa-Gevaert N.V., Septestraat 27, B-2650, Mortsel, Belgium

Version of record first published: 04 Oct 2006.

To cite this article: G. Verbeek , M. Van Der Auweraer , F. C. Deschryver , C. Geelen , D. Terrell & S. De Meuter (1992): The Saturation of the Drift Velocity of Holes at High, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 217:1, 243-249

To link to this article: http://dx.doi.org/10.1080/10587259208046908

Mol. Cryst. Liq. Cryst. 1992, Vol. 217, pp. 243–249
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

THE SATURATION OF THE DRIFT VELOCITY OF HOLES AT HIGH ELECTRIC FIELDS IN DISPERSIONS OF ELECTRON DONORS IN A POLYMER MATRIX.

G. VERBEEK[a] M. VAN DER AUWERAER[a*], F.C. DE SCHRYVER[a*], C. GEELEN[a], D. TERRELL[b], S. DE MEUTER[b]
a Lab. for Molecular Dynamics and Spectroscopy K.U. Leuven Celestijnelaan 200-F, B-3001 Heverlee, Belgium.
b Agfa-Gevaert N.V. Septestraat 27, B-2650 Mortsel, Belgium.

Abstract The decrease of the hole mobility in polycarbonate doped with 17% of a triphenylaminobenzene derivative at electric fields exceeding 1.0 x 10^6 Vcm^{-1} is rationalized in the framework of the Marcus theory. By analysis of the mobility data in the framework of the expression, derived by Marcus and relating the free energy of electron transfer to the free activation energy of this process, the average hopping distance, the reorganisation energy and the barrierless electron transfer rate constant could be obtained. In this way physical acceptable values, amounting to 2.7nm, 0.33eV, 4.88 x 10^6 s^{-1}, were found for the respective parameters at room temperature.

INTRODUCTION

The transport of electrons or holes in disordered organic materials as e.g. dispersions of molecules with a low ionization potential in a polymer matrix is currently considered as a sequence of electron transfer processes between molecular species[1-10]. In disordered materials those molecular species are characterized by a distribution of energy levels. The increase of the charge carrier mobility as the applied electric field strength is increased has been rationalized by the induction of a better overlap[11] between the distribution of energy levels of the oxidized and reduced species[1-8] where this electron tranfer process becomes on the average more exergonic. Most of the current models[1-8] assume however a simplified relationship between the rate of the individual electron tranfer steps and the energy change associated with those electron transfer steps. Therefore they cannot explain the recent observations of the decrease of the hole mobility at high applied field strength for a molecularly doped polymer[12]. When however the rate of the individual electron transfer steps is considered[10] in the framework of the Marcus theory[11,13-18] the decrease of the hole mobility at high applied fields can be rationalized.

THEORY

The net rate constant, k_{obs}, for the transfer of a hole or an electron between two neighbouring sites can be considered as the difference of the rate constants of a forward, k_f, and a reverse, k_b, process.

$$k_{obs} = k_f - k_b \qquad (1)$$

Taking into account microreversibility equation (1) can also be written in the following way:

$$k_{obs} = k_f/[1 - \exp(\Delta G_o/kT)]=k_f/[1 - \exp(-Eer/kT)] \qquad (2)$$

Where the ΔG_o is standard free enthalpy difference between two neighbouring hopping sites, r the average distance between two neighbouring sites, e the elementary charge and E the applied electric field. As k_f describes an electron transfer process, it can be evaluated using the current theory of electron transfer processes[15-18].

$$k_f = k_o \exp(-\Delta G^{\neq}{}_f/kT) \qquad (3)$$

with

$$\Delta G^{\neq}{}_f = \frac{(\Delta G_o + \lambda)^2}{4\lambda} \qquad (4)$$

Where k_o is the rate constant of an activationless electron transfer process and λ the reorganisation free enthalpy associated with the electron transfer process. By combining and rearranging equation 3 and 4 the rate expression for electron transfer can also be written in the following way:

$$\ln(k_f) = \ln(k_o) - \left(\frac{\Delta G^2{}_o}{4kT\lambda} + \frac{\Delta G_o}{2kT} + \frac{\lambda}{4kT}\right) \qquad (5)$$

Equation (5) implies that a plot $kT \ln(k_f) + \Delta G_o/2$ versus $(\Delta G_o)^2$ should yield a straight line with slope $-1/4\lambda$ and intercept $kT \ln(k_o) - \lambda/4$. k_{obs} is related to μ, the mobility of the charge carriers through the sample with thickness d by equation 6

$$\mu = d/(Et_{tr}) = rk_{obs}/E \qquad (6).$$

Combining equation (2) and (6) k_f can be obtained from the experimentally observed values of the mobility:

$$k_f = \frac{\mu E}{r[1 - \exp(\Delta G_o/kT)]} \qquad (7)$$

Combination of equation 6 and 7 will allow to fit the experimental values of μ obtained at different field strengths to r, k_o and λ.

EXPERIMENTAL

The charge transport compound, 5′-[4-[bis(4-ethylphenyl)amino]phenyl]-N,N,N′,N′,-tetrakis(4-ethylphenyl)-[1,1′:3′,1"-terphenyl]-4,4"diamine (p-pEFTP), was prepared and purified as described elsewhere[19]. The transit times were determined by the time of flight technique[20,21]. All experiments are performed in a small-signal time of flight mode[21,22] ($Q = 2$ à 20×10^{-3} Jm^{-2}) and the entrance impedance of the transient digitizer is adapted to avoid distortion of the transient photocurrents by the RC-time of the set-up.

RESULTS AND DISCUSSION

While at fields below 1.0 x 10^6 Vcm^{-1} the transient photocurrent consists typically of an initial spike and a plateau region followed by a tail; at fields exceeding 1.0 x 10^6 Vcm^{-1} only an initial spike and a tail were observed. The plateau region and tail can be analysed in the framework of equations (8a and 8b) yielding t_{tr}, α, β.

$$i(t) \sim t^{-1+\alpha} \qquad t<t_{tr} \tag{8.a}$$

$$i(t) \sim t^{-1+\beta} \qquad t>t_{tr} \tag{8.b}$$

α and β amount to 0.95±0.10 and -1.06±0.19 respectively and do not depend upon the applied field strength. The values obtained for α and β indicate that charge transport is non-dispersive. The initial spike is in this case probably due to the relaxation phenomena, as described by Bässler[8,23], preceeding the onset of non-dispersive transport. Although at fields exceeding 1.0 x 10^6 Vcm^{-1} the distorsion of the plateau region by the initial spike (figure 1) no longer allows to analyse the transient photocurrents in the framework of equation 8a and b the transit time can still be obtained from the inflection point of a log-i versus log-t plot. The hole mobility in polycarbonate film doped with 17% p-pEFTP decreases as the electric field is increased above 1.0 x 10^6 Vcm^{-1} (Fig. 2).

Combination of equation (5) and equation (7) yields equation (9). It was possible to analyse the experimental data in the framework of equation (9) using r, λ and k_o as adjustable parameters. It this way 2.7nm, 0.33eV and

4.88×10^6 s^{-1} were obtained for r, λ and k_o respectively.

$$kT\ln\left[\frac{\mu E}{r[1-\exp(\Delta G_o/kT)]}\right]+\Delta G_o/2=kT\ \ln(k_o)-\lambda/4-\Delta G_o{}^2/4\lambda \tag{9}$$

The average distance between two neighbouring molecules, r_m, calculated from the macroscopic properties of the dispersion according to equation 10 amounts to 2.5 nm for a sample containing 17 % p-EFTP.

$$r_m = 2(3M/(4\pi Ad))^{1/3} \tag{10}$$

Where M is molecular weight (976.4) of the hole transporting molecule, d is the density (1.12) of the dispersion and A Avogadro's number.

Acknowledgments:

M.V.d.A. is a "Onderzoeksleider" of the "Fonds voor Kollectief Fundamenteel Onderzoek". The authors thank Agfa-Gevaert for financial support and a scholarship to GV. The continuing support of Scientific Programming to the K.U.Leuven research group is gratefully acknowledged.

REFERENCES

(1) L.B. Schein, Electrophotography and Development Physics (Springer, New York, 1988)
(2)J.O. Williams, Adv. Phys. Org. Chem. 16 26 (1978)
(3) M. Stolka, J.F. Yanus and D.M. Pai, J. Phys. Chem. 88 (1984) 4707.
(4) G. Pfister, Phys. Rev. B 16 3676 (1977).
(5) W.G. Gill, Mol. Cryst. Liq. Cryst. 87 1 (1987)
(6) L.B. Schein, A. Rosenberg and L.S. Rice, J. Appl. Phys. 60 4287 (1986).
(7) J.S. Santos Lemus and J. Hirsh, Philos. Mag. B 53 25 (1986).
(8) H. Bässler, Philos. Mag. 50 347 (1984).
(9) M.R.V. Sahuyn, Photogr. Sci. Eng. 28 185 (1984).
(10) J.S. Facci and M. Stolka, Phil. Mag. B 54 1 (1986).
(11) H. Gerischer, Z. Phys. Chem. N.F. 26 223 and 325 (1960).
(12) Huoy-Jen Yuh and D.M. Pai, Mol. Cryst. Liq. Cryst. 183 217 (1990).
(13) J.J. Hopfield, Proc. Nat. Acad. Sci. 71 3640 (1974).
(14) T. Kakitani and N. Mataga, J. Phys. Chem. 92 5059 (1988).
(15) R.A. Marcus, Ann. Rev. Phys. Chem. 13 155 (1964).

(16) R.A. Marcus, J. Chem. Phys. 81 4494 (1984).
(17) J. Jortner, J. Chem. Phys. 64 4680 (1976).
(18) J. Jortner and M. Bixon, J. Chem. Phys. 88 167 (1988)
(19) M. Van Der Auweraer, F.C. De Schryver, G. Verbeek, C. Geelen, D. Terrell and S. De Meuter, Eur. Pat. EP 349034
(20) F.J. Dolezak, Photoconductivity and related Phenomena, Mort J. & Pai D.M., editors (Elsevier Sci. Publ. Co., New York), p27 (1976)
(21) W.E. Spear, J. Non-Cryst. Solids 1 197 (1969)
(22) F.C. Bos and D.M. Burland, Phys. Rev. Lett. 58 152 (1987)
(23) H. Bässler, Phys. Stat. Sol. b 107 9 (1981)

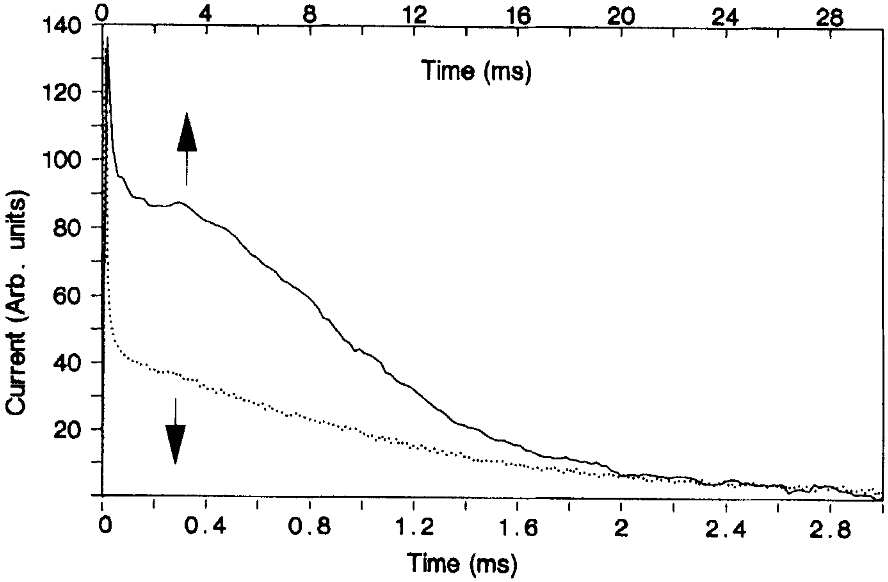

FIGURE 1 A typical current pulse of a 11.5-μm sample measured at an electric field of 2.1 x 10^5 Vcm^{-1} (———) and 1.2 x 10^6 Vcm^{-1} (·······)

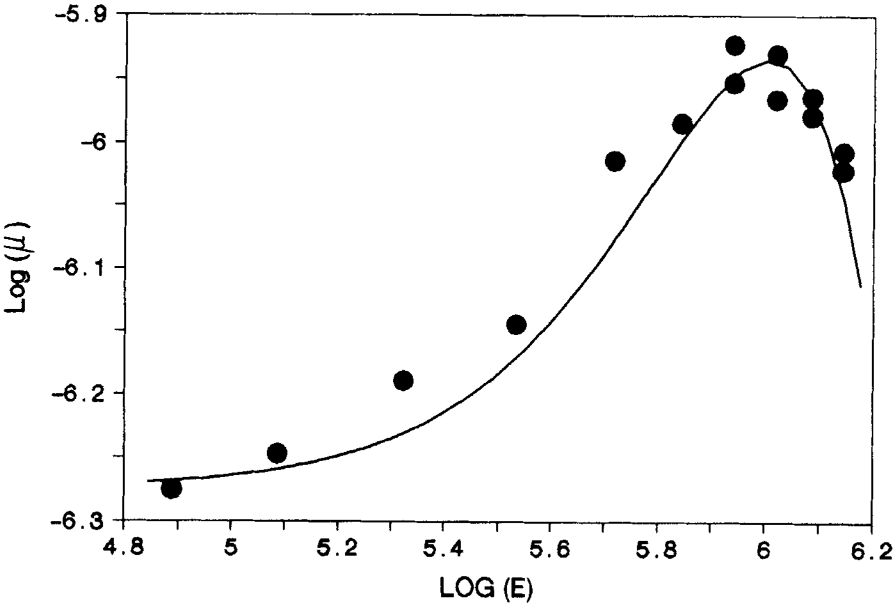

FIGURE 2 Drift mobility as a function of electric field for 17% doping of p-pEFTP in polycarbonate.