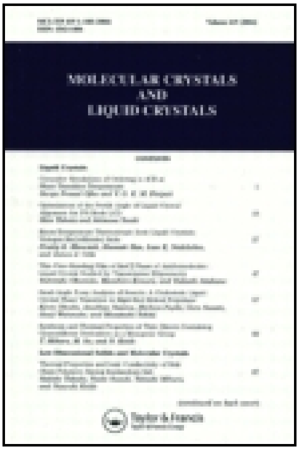


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Nonlinear Electrophysical Properties of Thin Films of Dibenzotetraazaannulenelapplication of Percolation Model

Boris A. Snopok [a] & Yaroslaw D. Lampeka [a]

[a] Institute of Physical Chemistry, Academy of Sciences of Ukraine, Prospekt Nauki 31, Klev-39, 252039, Ukraine

Version of record first published: 24 Sep 2006.

To cite this article: Boris A. Snopok & Yaroslaw D. Lampeka (1994): Nonlinear Electrophysical Properties of Thin Films of Dibenzotetraazaannulenelapplication of Percolation Model, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 242:1, 171-177

To link to this article: http://dx.doi.org/10.1080/10587259408037749

Mol. Cryst. Liq. Cryst. 1994, Vol. 242, pp. 171–177
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

NONLINEAR ELECTROPHYSICAL PROPERTIES OF THIN FILMS OF DIBENZOTETRAAZAANNULENE:APPLICATION OF PERCOLATION MODEL

BORIS A. SNOPOK , YAROSLAW D. LAMPEKA
Institute of Physical Chemistry, Academy of Sciences of Ukraine, Prospekt Nauki 31, Kiev-39, 252039, Ukraine.

Abstract The results obtained demonstrate the applicability of nonlinear percolation theory for the description of charge-transfer processes in thin films of organic semiconductors, with the model object being a polycrystal with a system of intercrystalline barriers with large dispersion in heights. It was shown that the appearance of non-linear phenomena in electrophysical properties of such samples (long-time current relaxations, nonlinear VAC) is caused by changing of barrier heights distribution under the influence of external electric field on the filling of structural (defects) or impurity (adsorbed O_2) states.

INTRODUCTION

The widespread application of polycrystalline films of organic molecular semiconductors (OMS) as elements of microelectronic devices, energy converters, gas analysers *etc*.[1] is restrained largely for the lack of adequate notions describing the mechanisms of physico-chemical processes occuring in such systems. A number of effects observed in strong electric fields (long-time current relaxations, nonlinear volt-ampere characteristics (VAC) *etc*.[2]) and their relation with spatial inhomogeneity of the samples have already been mentioned[3], though the direct analysis of experimental data with regard to spatial disorder of objects, in particular, by means of percolation theory methods, has never been conducted.

The aim of the present work was the study of electrophysical properties of thin polycrystalline films of a new OMS - dibenzotetraazaannulene - in an effort to verify the applicability of the theory of nonlinear percolation conductivity (NPC) to the description of charge transfer processes in OMS in strong electric fields.

EXPERIMENTAL

Thin films of 5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine (H_2TAA) have been fabricated by means of thermovacuum deposition (*ca.* $5\cdot10^{-4}$ Pa) on the glass supports with the raster electrodes (SnO_2, effective length $l=3\cdot10^{-2}$ m, interelectrode distance $d=2\cdot10^{-4}$ m). The deposition rate was *ca.* 20 nm/min with the final thickness of the films equal to 300±20 nm. The measurements were carried out in air (*ca.* $1\cdot10^{5}$ Pa) and "*in vacuo*" (133 Pa) with positive (PP) and negative (NP) polarities of high-potential electrode relatively to "earthed" low-potential one.

RESULTS AND DISCUSSION

Long - time Current Relaxations (LCRs) and Nonlinear VAC

Fig.1 shows the dependences of current density J *vs* time t through the surface structure $SnO_2/H_2TAA/SnO_2$ at different electric field strengths E applied. LCRs are observed only at $E > E_{min}$ ($E_{min} \approx 1.0\cdot10^{4}$ V/m) and correspond to the growth of conductance with time. *In vacuo* LCRs are fully reversible up to $E_{max} \approx 3.0\cdot10^{6}$ V/m, whereas in air the destruction of samples is observed at E *ca.* $1.5\cdot10^{6}$ V/m. The shapes of relaxation curves depend on both the value and sign of electric field applied, and air pressure (dioxygen concentration $[O_2]_{gas}$) in measuring unit: the characteristic times decrease and quasi-stationary values of J increase with increasing of E and decreasing of $[O_2]_{gas}$.

The approximation of experimental dependences with elementary functions shows that at $t < t^*$ (where t^* is dependent on both field applied and $[O_2]_{gas}$) the data obtained are described well by the exponential function $J = a\cdot\exp(b\cdot t)$, whereas at $t > t^*$ the function has the form $J = c\cdot\ln(t) + d$. The values of parameters a, b, c, d and their dependence on E allow us to establish the functional relationship between J and E in the form $J = J_o\cdot E^{2.2\pm0.1}$ (at $t < t^*$ and $E < E_{crit}$) *in vacuo* and $J = J_o\cdot\exp(\beta\cdot E^{1/2})$ in all remaining cases, with $E_{crit} \approx 5.0\cdot10^{5}$ V/m.

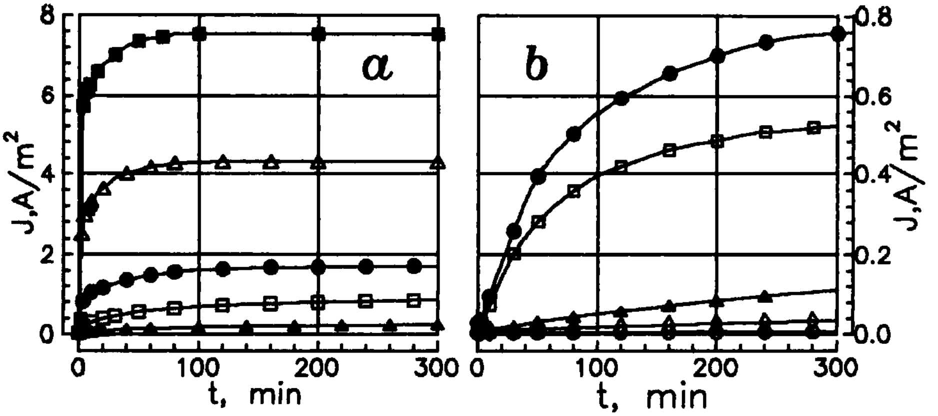


FIGURE 1 Dependences of current density J *vs* time t *in vacuo* (a, NP) and in air (b, PP) at different electric field strengths E (· 10^{-5} V/m) applied: ○ – 1.5, ◊ – 3, ▲ – 4.5, □ – 7.5, ● – 10.0, △ – 15.0, ■ – 20.0.

It is known that in strong electric fields (E > kT/e·a, where a is the average crystallite size) the conductivity of polycrystalline systems, which is limited by the heights ξ (in kT units) of intercrystalline barriers, nonlinearly depends on the value of E applied and is described within the scope of percolation theory by the expression[4]:

$$J = J_o \cdot \exp(\beta \cdot E^{1/2}); \ \beta = (\mathrm{const} \cdot \frac{e \cdot a}{k \cdot T} \cdot f(\xi))^{1/2} \qquad (1)$$

where J_o is the value of "pre-relaxation" current density weakly depending on E and $f(\xi)$ is a function which characterizes a degree of spatial disorder of the system (*i.e.* dispersion of intercrystalline barrier heights). An estimataion of this dispersion[3] gives, for our samples, the value *ca.* 0.3 - 0.4 eV, suggesting a large spread in ξ - values.

Fig.2 presents VAC constructed as a temporal cross-section of the curves shown in Fig.1. The linearity of VAC as ln J - $E^{1/2}$ plots and the dependence of their slopes β on $[O_2]_{gas}$ indicate the applicability of the model of NPC for polycrystalline OMS samples in strong electric fields (for "pre-relaxation" VAC obtained when the re-population processes of impurity states (IS) can be neglected, $\beta_{air} = 3.3 \cdot 10^{-3}$ $(m/V)^{1/2}$ and $\beta_{vac} = 4.9 \cdot 10^{-3}$ $(m/V)^{1/2}$, "pre-relaxation" VAC are symmetric about the sign of the field).

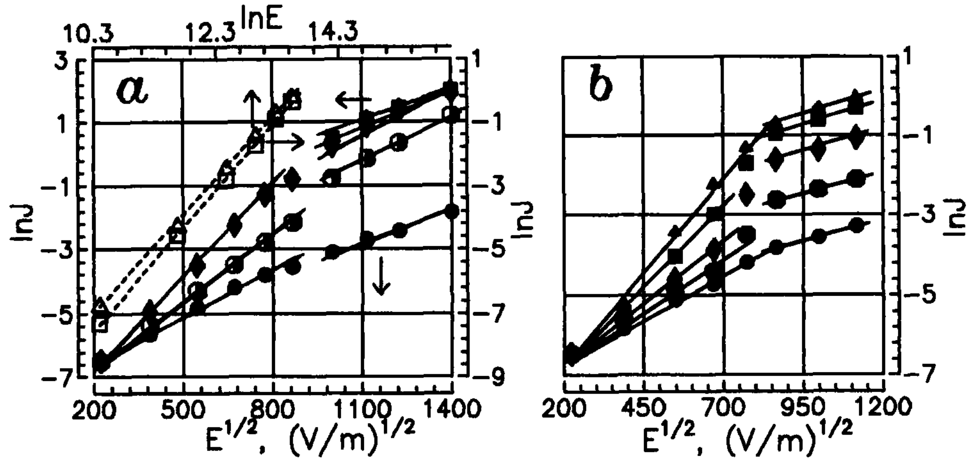


FIGURE 2 VAC of the samples *in vacuo* (a, NP) and in air (b, PP) at different times after application of external field. Time (min): ● - 0.02 ("pre-relaxation"); ◐ - 1; ● - 10; ♦ - 30; □ , ■ - 100; △ , ▲ - 300.

Within the limits of this model, for H_2TAA as p - type semiconductor with acceptor IS, the following equations may be written[4]:

$$J(t) \approx J_o (1+n(t)/\xi_o^{1/2})^{\nu} \cdot \exp\{2\cdot \xi_o^{1/2} \cdot n(t)\} \quad \text{at } N < N^* \qquad (2)$$

$$J(t) \approx J_o ((\theta^{1/2}+n(t))^2-\xi_o)^{\nu} \cdot \exp\{\xi_o - \theta\} \quad \text{at } N > N^* \qquad (3)$$

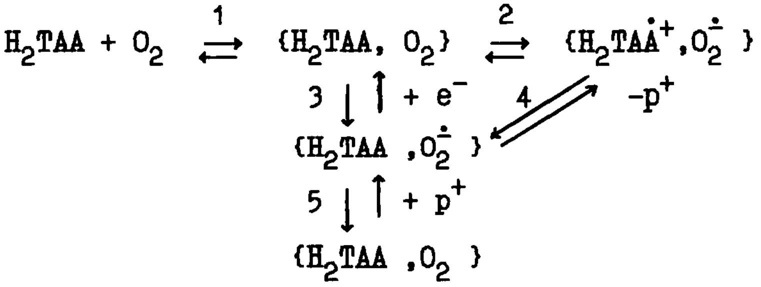
where ξ_o - "pre-relaxation" height of critical barriers; θ - the difference between the eletrochemical potential level ζ and energy level E_a of IS (in kT - units); $\nu = 0.88$; $N^* = \xi^{1/2} - \theta^{1/2}$. Assuming that the total concentration N of IS is time-independent, the concentration n(t) of charged form of IS equals $N\cdot[1-\exp(-t/\tau)]$, with τ as a parameter.[4]

Experimental curves obtained in air at positive polarity are good approximated by the dependences (2) at $E < E_{crit}$ and (3) at $E > E_{crit}$. However, the attempts to describe the relationship between J and t by eqs (2,3) in other cases examined were unsuccessful. The reason of this may lie in the fact that the value of N is no more independent on time - *in vacuo* due to the presence of non-equilibrium state between adsorbed and gaseous dioxygen, and in air because of negative electroadsorption effect when high-potential electrode has the negative sign.

Origin of Intercrystalline Barriers

Intercrystalline barriers which determine the conductivity of polycrystalline samples are originated from the diminution of the majority carriers concentration in the region of contacts between crystallites owing to their trapping by the structural and impurity levels, as well as due to recombination processes on surface. As was shown[5] , the filling of the structural levels, which are characterized by broad gaussian energy distribution centred on corresponding conductivity levels of molecular polarons M_p^+ and M_p^-, depends only slightly on external field E.

It is also well known[5] that the polycrystalline films of OMS always contain dioxygen, mainly in the form of superoxide anion-radical O_2^-. But low value of redox potential of O_2 insufficient for chemical oxidation of H_2TAA[6] and the data on its diffusion[7] in single crystals of OMS allow us to assume that in the absence of bending of M_p^+- and M_p^-- levels impurity dioxygen is in neutral form. In this case the charged dioxygen centres are located mainly in the near-surface layer where the impoverishing bend ξ of M_p^+ and M_p^- exists, and can act owing to their spatial and energy position as the recombination centres. Therefore the degree of filling of these centres may be very sensitive to the value of E because of rather small dispersion parameter of gaussian distribution of their energy. General scheme of dioxygen participation in different processes occuring in OMS is shown below:



1 - adsorption, 2 - chemical oxidation, 3 - electron trapping, 4 - hole thermolysation, 5 - recombination

Origin of E_{crit}

The application to the surface structures of external electric field upsets the balance of filling of IS as the consequence of field reduction of the barrier heights ξ. This, in its turn, leads to the transformation of initial heights distribution and to the changes in number of critical barriers determined by $f(\xi)$. These effects manifest themselves by changing in time of both the conductivity and the slope β of VAC (Fig.3). The growth of β at $E < E_{crit}$ corresponds to increasing of dispersion of ξ and is caused by transformation from charged to neutral form of that part of dioxygen centres for which, owing to decrease of ξ under influence of external electric field, the levelling of E_a and ζ occures. At the same time, at $E > E_{crit}$ the dependence of β *vs* t (Fig.3) indicates the transition of spatial-inhomogeneous structure in partially ordered state. The latter effect causes the "switchover" of samples in "high - conductive" state. The change in the functional dependence of J on t from (2) to (3) allows to suppose that in the present case the value of E is large enough for levelling of E_a and ζ as the consequence of field decrease of ξ. This means, that at $E > E_{crit}$ the dioxygen admixtures cease to play the role of recombination centres and exert no more the influence on the dispersion of ξ. It is necessary to mention that owing to more effective desorption of O_2 at negatively signed high-potential

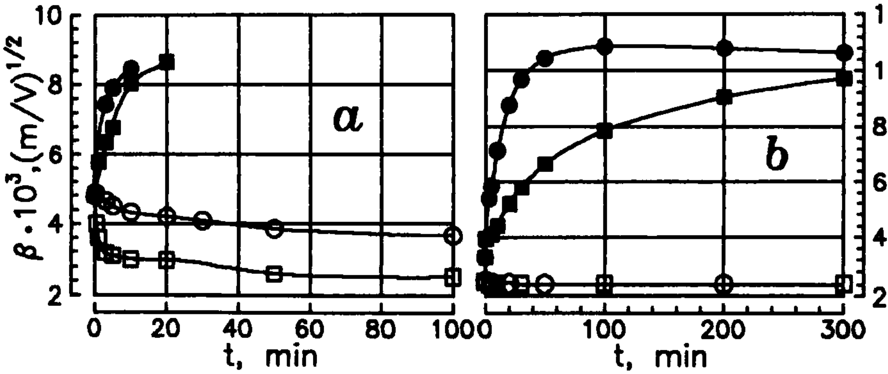


FIGURE 3 Plot β *vs* t *in vacuo* (a) and in air (b).
$E < E_{crit}$: ● - NP, ■ - PP; $E > E_{crit}$: ○ - NP, □ - PP.

electrode *in vacuo* the degree of order at $E > E_{crit}$ is lower than in other cases (Fig.3a).

At $t > t^*$ and $E < E_{crit}$ *in vacuo* the plots lnJ *vs* lnE are linear with the slope 2.2±0.1. This behaviour is characteristic of space-charge-limited current. Such transformation of charge-transfer mechanism is connected with homogeneous (uniform) distribution of field along the sample. The reason of this, apparently, is also the levelling of E_a and ζ which occures *in vacuo* at lesser potentials than in air because of a smaller number of critical barriers and greater dispersion of ξ in the former case.

CONCLUSION

Thus, our data show that the application of the theory of nonlinear percolation conductivity to description of the properties of thin polycrystalline films of H_2TAA allows to explain non-contradictory the assemblage of electrophysical effects observed in strong electric fields. The conclusion can be made that both the nonlinear VAC and the LCRs are determined by the variations of intercrystalline barrier heights. Therewith, in the field range $E_{min} < E < E_{crit}$ the nature of dioxygen centres exerts the principal influence on $f(\xi)$, whereas at $E > E_{crit}$ the conductivity of the samples is determined mainly by the structural defects.

REFERENCES

1. C. L. Honeybourne, J. Phys. Chem. Solids, 48, 109 (1987).
2. V. M. Mokshin and O. A. Postnikova, Chem. Phys., 4, 1327 (1985) (Russ.ed.).
3. A. M. Meshkov, Dissertation theses, Leningrad, (1986).
4. I. A. Myasnikov, V. Ya. Sukharev, L. Yu. Kupriyanov and S. A. Zavjalov, Semiconductor sensors in phisico-chemical studies (Nauka, Moskow, 1991), p.176 (Russ.ed.).
5. J. Simon and J.-J. Andre, Molecular Semiconductors (Springer-Verlag, Berlin, 1985), p.268.
6. H. Alt, H. Binder and G. Sandstede, J. of Catal., 28, 8 (1973).
7. H. Yasunaga, K. Kojima, H. Yohda and K. Takeya, J. Phys. Soc. Jap., 37, 1024 (1974).