

# Effect of Polar Molecules on the Transport and Localization of Charge Carriers in Molecular Materials\*

Juliusz Sworakowski

*Institute of Physical and Theoretical Chemistry,  
Technical University of Wrocław,  
50-370 Wrocław 51, Poland*

Received 23 March, 1998; received in revised form 20 August, 1998

The influence of polar species on the transport of charge carriers in molecular solids is reviewed. Guest molecules with permanent dipole moments introduced into molecular crystals can act as traps localizing carriers provided certain energetic conditions are fulfilled. In this case their polar character may manifest itself in a field-dependent decrease of the trap depth. Moreover, irrespective of the positions of their energy levels, polar impurities may locally modify the polarization energy thus creating traps on neighbouring molecules. The effect of polar dopants in disordered molecular solids can be described within the model due to Bässler: the presence of polar species broadens the density-of-states function thus decreasing the effective mobility of charge carriers.

## I Introduction

Research on electrical properties of molecular solids has been carried out for over half a century in many laboratories: early studies were carried out predominantly on polycrystalline or amorphous materials, often of natural origin (e.g., carnauba wax [1,2]) and aimed at gathering basic information about generation, transport and storage of charge carriers in these materials (see, e.g., [3-7] for extensive reviews). The research carried out in the sixties and seventies on systems of controlled purity and structural perfection helped to answer many questions related to microscopic models of charge generation and transport (cf. [8-10]). The last 10-15 years have witnessed a revival of the interest in disordered molecular solids and polymers, stimulated by numerous current and emerging applications of these materials in, e.g., electrophotography, nonlinear optics, electroluminescent devices etc. [11-15].

The role of localization of charge carriers in determining the electrical properties of molecular materials has been recognized quite early, resulting in numerous papers devoted to the determination of parameters of centres that localize carriers [8,9,16]. The localization of electrons and/or holes influences in a direct way the

transport of the carriers, hence a way to determine parameters of local centres is to employ direct methods of determination of the carrier mobility and its dependence on such parameters as biasing field, temperature etc. One should invoke the commonly used time-of-flight (TOF) technique, applicable in its simplest modification to photoconducting solids. The principle of the technique, first employed to organic solids by Kepler [17] and LeBlanc [18], has been described in several monographs [4,8-10,22]. Typically, a plane-parallel photoconducting sample is sandwiched between a semi-transparent electrode and a collecting one, and is connected to a system capable of recording the temporal evolution of the current in the time scale of the experiment. The experiment itself consists in illuminating the sample with a pulse of a strongly absorbed light through the semitransparent electrode and following the evolution of the photocurrent transient. Within the small-signal regime, the mobility is determined from the equation

$$\mu = \frac{L^2}{V t_{tr}} \quad (1)$$

$L$  standing for the sample thickness,  $V$  for the biasing voltage, and  $t_{tr}$  for the transit time.

---

\*Dedicated to Professor Bernhard Gross.

In the introductory discussion, let us consider the situation in crystalline solids, in which the charge transport can be described within the band model [8- 10]. The presence of local centres manifests itself in the TOF experiment in changes of the shape in the time dependence of the transient currents. For the purpose of the present discussion, it would be useful to introduce two characteristic parameters describing the transport of charge carriers in a sample containing local centres: time of localization (residence in a local state)  $\tau_t$  and free carrier lifetime  $\tau_f$ . If  $t_{tr} \gg (\tau_t, \tau_f)$ , carriers are subject to multiple trapping events before traversing the sample length; the centres fulfilling these conditions are often referred to as shallow traps. Another limiting case is that of deep traps: in this case  $\tau_t \gg t_{tr}$ , and carriers, once localized, are not released within the time scale of the experiment. If additionally  $\tau_f \ll t_{tr}$ , the determination of the transit time becomes impossible.

One of the questions which should be addressed in this context is the one concerning the nature of local centres. Based on the electrostatic model due to Lyons [19, 4], Silinsh [20] and Sworakowski [21] put forward a model explaining the appearance of traps for charge carriers (see also the discussion in [9,22,23]), whose basic features will be invoked in the following section of this article.

The situation in disordered molecular solids is more complicated as their behaviour can seldom be described (even for a qualitative description) within models developed for nearly-perfect single crystals. Here, basic ideas stem from the pioneering work of BäSSLer and his collaborators (see [24,25] and references therein) who put forward a model describing the transport of charge carriers in disordered molecular solids. Principal results confirming the validity of this model have been reviewed in several books and articles (see, e.g., [12, 24-27]).

The aim of this article is to present a short review of papers devoted to studies of the influence of polar molecules on the transport and localization of charge carriers in molecular solids - both in single crystals and in highly disordered systems such as glassy samples and molecularly doped polymers.

## II Centres localizing carriers in single-crystalline solids

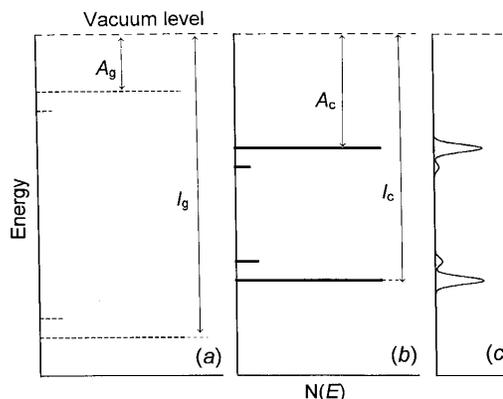


Figure 1. Energy levels in an isolated molecule (a), in a nearly-perfect molecular solid (b), and in a disordered molecular solid (c). Indicated are also the positions of energy levels of guest molecules which may act as chemical traps.

A discussion of the theories describing the transport of charge carriers in perfect molecular solids is beyond the scope of this article, and the reader is referred to a rich literature existing on the subject (e.g., [8,10] and references therein). For the purpose of the present discussion it is sufficient to mention that the theory predicts that the transport of charge carriers in perfect molecular solids occurs in narrow bands, the carriers being strongly coupled to lattice phonons. Experimentally determined room-temperature mobilities are of the order of  $10^{-1} - 10^0$  cm<sup>2</sup>/Vs, and are weak functions of temperature. A good example of such a behaviour is the temperature dependence of the drift mobility of holes and electrons in single crystals of polycyclic hydrocarbons. Careful measurements performed on high-purity single crystals (see the list in [28]) demonstrate that the mobilities ( $\mu_0$ ) follow a  $T^{-n}$  dependence, with  $0 < n \leq 3$  but mostly ranging between 0 and 1.5. Temperature dependences measured in anthracene by Probst and Karl [29] are shown in Fig. 2.

Doping of molecular solids with a small amount (of the order of  $10^{-7} - 10^{-4}$  mole/mole) of suitably chosen guest molecules may give rise to a dramatic reduction of the effective drift mobilities due to trapping of charge carriers. In case of shallow traps controlling the transport, the effective mobility ( $\mu_{eff}$ ) is reduced by the factor  $\tau_f/(\tau_t + \tau_f)$ , which leads to the expression for its

temperature dependence [30]

$$\mu_{eff} = \frac{\mu_0}{1 + x_g \exp(E_t/kT)} \quad (2)$$

where  $x_g$  is the mole fraction of the guest molecule, and  $E_t$  stands for the depth of the trap formed by the dopant (assumed monoenergetic). It follows from the equation that at low temperatures the mobility should be temperature-activated with a slope determined by the trap depth, whereas at sufficiently high temperatures it should attain its "lattice" value equal to that in a pure crystal. The results shown in Fig. 2 demonstrate that this is indeed the case.

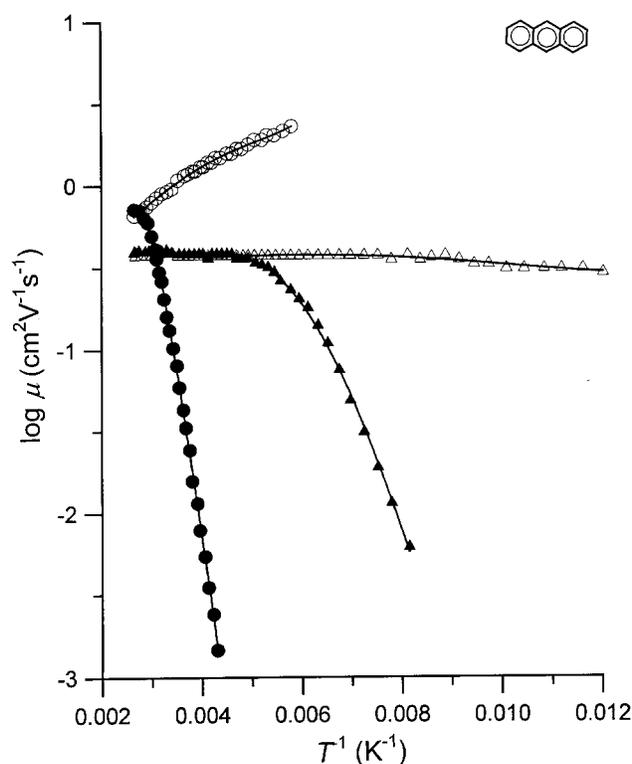


Figure 2. Temperature dependences of the drift mobilities of electrons (triangles), and holes (circles), in pure anthracene crystals (open symbols), and in tetracene-doped anthracene (closed symbols, dopant mole fraction amounting to ca.  $10^{-7}$ ). Data taken from [29].

The depths of chemical traps (i.e. traps formed by guest molecules introduced into a host lattice) determined from such experiments can be compared with respective values estimated from a Haber-Born type cycle based on the electrostatic model of Lyons [19]. It was pointed out [20-23,31,32] that electrons can be localized on crystal sites (molecules) exhibiting a local electron affinity ( $A_c^{loc}$ ) greater than the respective value in a perfect crystal ( $A_c$ ). Similarly, a molecule in

a crystal can act as a hole trap if its local ionization energy ( $I_c^{loc}$ ) is smaller than that in a perfect crystal ( $I_c$ ). The trap depths for electrons and holes ( $E_t^e$  and  $E_t^h$ , respectively) are given by simple relations

$$\begin{aligned} E_t^e &= A_c - A_c^{loc} \\ E_t^h &= I_c^{loc} - I_c \end{aligned} \quad (3)$$

(throughout this paper, we shall adopt the convention according to which the depths of local states are positive values). The values of  $A_c$  and  $I_c$  are related to the respective molecular ones ( $A_g$  and  $I_g$ , respectively) by the relations

$$\begin{aligned} A_c &= A_g - P \\ I_c &= I_g + P \end{aligned} \quad (4)$$

The parameter  $P$  ( $P < 0$ ), referred to as the polarization energy, is the energy of interaction between a charge localized on a given site and the surrounding polarizable medium; in many non-polar crystals its value ranges between -1.5 and -2.5 eV [19,4,9]. It becomes evident from Eqs. (3) and (4) that molecules will localize charge carriers if their molecular ionization energy is smaller and/or their electron affinity greater than the respective values of the host molecules (i.e., if they are chemically different from the host ones),

$$\begin{aligned} E_t^e &\approx A_c^{guest} - A_c^{host} \\ E_t^h &\approx I_c^{host} - I_c^{guest} \end{aligned} \quad (5)$$

or if the absolute value of the polarization energy is locally greater than that in a perfect crystal (i.e., if a carrier encounters a physical defect of the crystal structure containing regions in which distances between the host molecules are smaller than in the perfect lattice).

$$E_t^e \approx E_t^h \approx P^{perfect} - P^{local} \quad (6)$$

These are two limiting cases of purely chemical traps formed by guest molecules whose presence does not change the polarization energy, and of purely structural traps created by host molecules in the vicinity of defects of the crystal structure. In the former case, the above model can be easily verified by comparing experimentally determined trap depths with respective differences of ionization energies or electron affinities; despite its simplicity, the calculated values were in a surprisingly

good agreement with experimental results obtained for doped anthracene crystals (cf. tables in [21-23]).

Of particular interest to the main topic of this article is the situation when a crystal consisting of non-polar molecules is doped with polar guest molecules. One may envisage the following effects associated with the presence of polar dopants in a non-polar lattice:

- (i) If the electron affinities and/or ionization energies of the host and guest molecules fulfil at least one relation given by Eq. (5), then the guest molecule itself may act as a chemical trap. In this case the detrapping of charge carriers from such traps may be field-enhanced due to a charge-permanent dipole interaction.
- (ii) Independently of the positions of the energy levels of the guest molecule with respect to those of the host, its permanent dipole moment locally modifies the polarization energy due to a contribution to the local field acting on a localized carrier, resulting in the appearance of local states in the vicinity of the dopant.
- (iii) If the shape of the dopant molecule is different from that of the guest, then one should expect an additional local modification of the polarization energy due to a (static) distortion of the crystal lattice. This effect is equivalent to the appearance of a structural trap [9,20,31,32] and will not be discussed here.

### III Polarization energy in the vicinity of a polar dopant

The energy of polarization of the lattice by a charge localized on a  $k$ -th molecule can be expressed as

$$P_k = -\frac{1}{2} \sum_{j \neq k} \mathbf{F}_j p_j \quad (7)$$

where  $p_j$  is the total (permanent + induced) dipole moment of a  $j$ -th molecule, and  $\mathbf{F}_j$  is the field acting on the molecule, consisting of contributions from the ion, other permanent and induced dipoles, higher-order multipoles etc. Methods of calculation of the polarization energy were discussed by Silinsh et al. [33,9,10], and by Bounds and Munn [34,35]. For a semi-quantitative discussion it is, however, sufficient to adopt a simpler

method first employed by Lyons [19,4]: the polarization energy can be expressed as a sum of interactions between a localized charge and multipoles (permanent and induced), and between multipoles of various orders, and it is sufficient to retain only the lowest terms. Such an approach was used in model calculations reported in [36,37], performed on a cubic lattice of non-polar globular molecules characterized by a scalar polarizability  $\alpha$ , with some sites replaced by polar molecules possessing a permanent dipole moment  $\mathbf{m}$ . The polarization energy of the perfect lattice was calculated by taking into account only interactions between the charge and induced dipoles ( $P_{id}$ ), with numerical values of relevant parameters chosen so as to mimic the situation in anthracene crystals doped with guest molecules of various polarities; in particular, the lattice constant was assumed to be equal to 0.62 nm

$$P = P_{id} = -\frac{\epsilon^2 \alpha}{2} \sum_{j \neq k} r_{jk}^{-4} \quad (8)$$

where  $r_{jk}$  is the distance between the charge situated on the  $k$ -th molecule, and a neutral polarizable  $j$ -th molecule. This procedure, neglecting the contribution of higher terms, overestimates the polarization energy by some 20-30% [4,19]. Within the model, introduction of polar dopants results in the appearance of additional terms in the expression for the local value of the polarization energy, describing interactions between the permanent dipole(s) and the charge ( $P_{im}$ ), and between the permanent dipole(s) and the induced ones ( $P_{md}$ )

$$P^{loc} = P_{id} + P_{im} + P_{md} \quad (9)$$

The results obtained in [36,37], shown in Fig. 3, demonstrate that the presence of an isolated dipole perturbs the polarization energy within several lattice constants. Consequently, a set of spatially connected sites is created which may act as a "macrotrap", whose presence in molecular crystals has been postulated by Kalinowski and Godlewski [38-40]. The spatial extension of the perturbation (i.e., the zero-field effective trapping cross-section) strongly depends on the dipole moment of the guest molecule, as does the trap depth (i.e., the largest difference between the local and the average polarization energies associated with the dipole). The latter parameter obtained from the calculations described in [36,37] was found to be in reasonable agreement with the results obtained for doped anthracene

crystals from low-temperature thermally stimulated luminescence (TSL) experiments [41]. It should be noted that the presence of dipolar impurities necessarily disturbs the electrostatic interactions between charges and the crystal lattice and is likely to result in the creation of local states even though the guest molecules themselves do not act as traps.

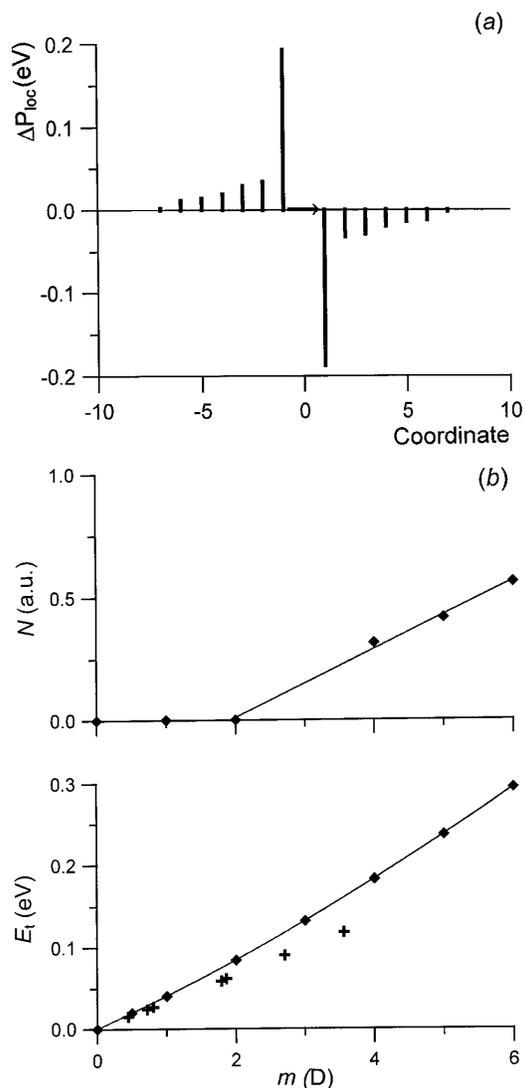


Figure 3. (a). Local values of the polarization energy in a model crystal due to the presence of an isolated dipole [36,37]. The diagram represents a cross-section through a three-dimensional perturbation. The heights of the vertical bars are proportional to differences between the local values of the polarization energy and the value calculated for a perfect crystal. The dipole is directed along one of the principal crystal axes, its permanent moment amounting to 4 D. (b). Depths of traps (upper curve), and number of molecules perturbed by the presence of an isolated dipole, i.e. a parameter related to the cross-section for trapping (lower curve). The diamonds and full lines are the results of the calculations [36,37], crosses are experimental results obtained on doped anthracene crystals [41].

## IV Transport of Charge Carriers in Disordered Molecular Solids

Experiments performed on intentionally doped molecular crystals have been rather scarce and limited to a few model systems, usually with anthracene serving as the host. This is due to difficulties with growing doped single crystals of a good and controlled quality on one hand, and to their limited use on the other. At the same time, a widespread use of disordered molecular solids (predominantly polymers) in electrophotography [12], as well as their emerging applications in non-linear optics [11,13] and electroluminescence [14] has stimulated continued interest in the electrical properties of this class of materials.

Most of the experimental results reviewed in this section have been obtained on so-called "molecularly doped polymers" (MDP) and on glassy charge-transporting materials. MDP are amorphous solid solutions of molecules of electron- or hole-transporting materials (electron acceptors or electron donors, respectively) dissolved in a polymer hosts acting as a binder. Typically, the concentrations of charge-transporting materials in the "molecularly doped polymers" range between a few % and several tens of % (often significantly exceeding 50%), one should therefore realize that in this case the notion of "doping" differs from that employed in conventional solid state physics.

Early results, reviewed in [42,43], indicated that the mobilities in disordered molecular solids are field- and temperature-dependent, the dependences being well described by the empirical equation

$$\mu = \mu_0 \exp\left(-\frac{E_{a,0} - \beta F^{1/2}}{kT_{eff}}\right) \quad (10)$$

where  $\mu_0$  and  $\beta$  are constants,  $E_{a,0}$  is the zero-field activation energy, and  $T_{eff}$  is an "effective temperature":  $1/T_{eff} = 1/T - 1/T_0$ ,  $T_0$  being a constant. This equation has been used also in recent years by several investigators [44-57]. Values of the constants, obtained by fitting experimental results with Eq. (10), were found to depend on the nature of the charge-transporting material (e.g., [56,57], see infra) but also on the polarity of the polymer [51-55]. These features: field dependence of the mobility, and non-Arrhenius temperature dependence have been observed for several disordered

molecular solids differing in physical order, chemical structure and the nature of conducting moieties.

In recent years, most of the rich experimental material have been interpreted within the model due to BäSSLER (see [24,25] and references therein, [58-60]). The model assumes that, due to disorder, energies of interaction of an excitation with the surrounding medium may be locally modified in a molecular solid. In case of charge carrier transport, this translates into local (random) modifications of the polarization energy. As a result, narrow energy bands in which the transport of charge carriers occurs in molecular single crystals split into a manifold of local states, the transport between them occurring via hopping. Additionally, the spread of intersite distances ( $r_{ij}$ ) must inevitably influence the respective transfer rates. BäSSLER [24] assumed that the jump rate between  $i$ -th and  $j$ -th sites can be described by an expression, originally proposed by Miller and Abrahams [61],

$$\nu_{ij} = \nu_0 f(\Delta E_{ij} r) g(r_{ij}), \quad (11)$$

where,

$$f(\Delta E_{ij}) = \begin{cases} \exp\left(-\frac{E_j - E_i}{kT}\right) & \text{for } E_j > E_i \\ 1 & \text{for } E_j \leq E_i \end{cases} \quad (12)$$

and

$$g(r_{ij}) = \exp(-2\gamma \cdot r_{ij}). \quad (13)$$

The functions  $f(\Delta E_{ij} r)$  and  $g(r_{ij})$  describe a Boltzmann probability of thermally assisted jumps between sites of different energies, and an overlap of the electronic wave functions of the initial and final states, respectively. In the above equations,  $\nu_0$  and  $\gamma$  are constants representing a frequency factor and the wave function decay constant, respectively. Apart from assuming explicitly the validity of the Miller-Abrahams equation, the BäSSLER's model also assumes that (i) distributions of intersite distances and site energies are Gaussian ones (cf. Fig. 1c); (ii) the process is incoherent; (iii) polaronic effects are insignificant although there exists a sufficient coupling to the lattice vibrations. The latter assumption is equivalent to neglecting the influence of dynamic disorder (polaronic effects) on the transport of charge carriers. The condition (i) defines the shape of the density-of-states (DOS) function

$$N(E) = \frac{N_{tot}}{(2\pi\sigma^2)^{1/2}} \exp\left(-\frac{(E - E_m)^2}{2\sigma^2}\right), \quad (14)$$

$N_{tot}$  standing for the total density of states,  $E_m$  for the energy of the distribution maximum, and the dispersion  $\sigma$  being a measure of the disorder; typically,  $\sigma \sim 0.1$  eV. The distribution of site energies is often referred to as due to diagonal disorder, whereas the distribution of intersite distances is due to an off-diagonal disorder. One can show that the parameters characterizing the diagonal and off-diagonal disorder are not independent. For example, assuming that the material under study consists of non-polar molecules and employing Eq. (8), one may relate the latter parameter to the polarization energy and the distribution of molecular positions [20,24]; qualitative estimation yields

$$\sigma = 4P \left\langle \frac{\Delta r}{r} \right\rangle, \quad (15)$$

where  $\langle \Delta r/r \rangle$  is the average relative fluctuation of the intersite distances.

Analytically, the BäSSLER's model is tractable only under special conditions [62,63] and solutions are not given in a closed analytical form. Thus most results have been obtained from computer simulations employing the Monte Carlo technique. The calculations were performed on a primitive cubic lattice built of non-polar isotropic molecules, with the lattice constant equal to 0.6 nm. The main results are [24,25,58-60,64,65]:

- (i) the diagonal and off-diagonal disorder contribute independently to the mobility,
- (ii) at sufficiently high temperatures, time-of-flight signals should be non-dispersive, changing to dispersive at a transition temperature whose parameters are determined by the disorder and the sample thickness.
- (iii) biasing fields, modifying the transfer probability may influence the mobility.

The following heuristic equation, based on the results of the simulations and valid in the non-dispersive transport region, has been put forward

$$\mu = \mu_0 \exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right] \Psi(T, \sigma\Sigma), \quad (16)$$

where

$$\Psi(T, \sigma \Sigma) = \begin{cases} 1 & \text{for } F < F_{tr} \\ \exp\{C[(\sigma/kT)^2 - \Sigma^2]F^{1/2}\} & \text{for } F > F_{tr}, \Sigma \geq 1.5 \\ \exp\{C[(\sigma/kT)^2 - 2.25]F^{1/2}\} & \text{for } F > F_{tr}, \Sigma < 1.5 \end{cases} \quad (17)$$

In the above equations,  $F_{tr}$  is a transition voltage between the low-field and high-field regimes (typically,  $F_{tr}$  is of the order of  $10^5$  V/cm),  $C$  is a temperature- and field-independent constant being a function of the intersite distance and assuming the value of  $2.9 \times 10^{-4}$  (cm/V) $^{1/2}$  for the distance equal to 0.6 nm, and  $\Sigma$  is a temperature-independent parameter related to the dispersion of the function  $g(r_{ij})$  describing the off-diagonal disorder (Eq. 13). A similar equation, valid for the dispersive transport, has also been derived, differing essentially in the  $\sigma$ -dependence of the mobility [64,65].

The above equations predict that (i) at high fields, the mobility should be field-dependent, following a Poole-Frenkel-type dependence, *independently of the polarity of the molecules in the material*; (ii) temperature dependences of the mobility should be non-Arrhenius; (iii) the zero-field mobilities are dependent on the diagonal disorder only, following a  $\ln \mu_0 \propto T^{-2}$  dependence. Thus, analyzing the field and temperature dependences of the drift mobility of holes in a disordered photoconducting material, one should be able to extract information concerning both diagonal and off-diagonal disorder. It is necessary to point out that the model predicts the high-field mobilities to obey a Poole-Frenkel type dependence without directly assuming any Coulombic interaction between the local centres and the carriers.

The model presented above provides a basis for interpreting the ample experimental material published so far. Experiments performed by several groups [66-115] are at worst in qualitative agreement with the model, in most cases following quantitatively its predictions. The experimental material gathered during recent years was obtained on MDP using in most cases polystyrene (PS) and bisphenol-A-polycarbonate (PC) as binders (other polymers have been used less frequently), and several groups of donors [66-84,103-107, 109-115] and acceptors [85-89,108] as charge transport

materials. Similar experiments have also been performed on glassy films of the charge-transporting materials [84,90-102]; bearing in mind the concentrations of the charge-transporting materials in the MDP samples, it comes as no surprise that results obtained on the latter systems would not be qualitatively different from those obtained using molecular glasses.

Results obtained on 1,1-bis((di-4-tolylamino)phenyl)cyclohexane (TAPC - see insert to Fig. 4) by Borsenberger, Bässler and Pautmeier [67,68], shown in Fig. 4, are a good example of the agreement between the predictions of the model and the experiment: measured mobilities indeed follow the  $\ln \mu \propto F^{1/2}$  and  $\ln \mu_0 \propto T^{-2}$  dependences. It should be noted that the experimentally determined values of the parameters of the model: pre-exponential mobility  $\mu_0$ , and the disorder parameters  $\sigma$  and  $\Sigma$  were found to depend on the nature of the polymer used as binder: for TAPC dissolved in polar PC the mobilities were orders of magnitude inferior to those obtained on glassy TAPC, and TAPC in a weakly polar PS. This feature points to a role of the polarity of the components in both MDP and molecular glasses in controlling the transport of carriers.

## V Effect of Polar Species on the Transport of Carriers in Disordered Molecular Materials

The role of the polarity of dopants in molecular materials has been discussed in several papers. Early research carried out on single crystalline materials has been mentioned in Sections II and III of this paper. Results obtained on MDP (for example, those shown in Fig. 4b) also indicate that the presence of dipoles manifests itself in modifying the carrier mobilities. Systematic studies carried out by Borsenberger et al. [67,69-89], Young

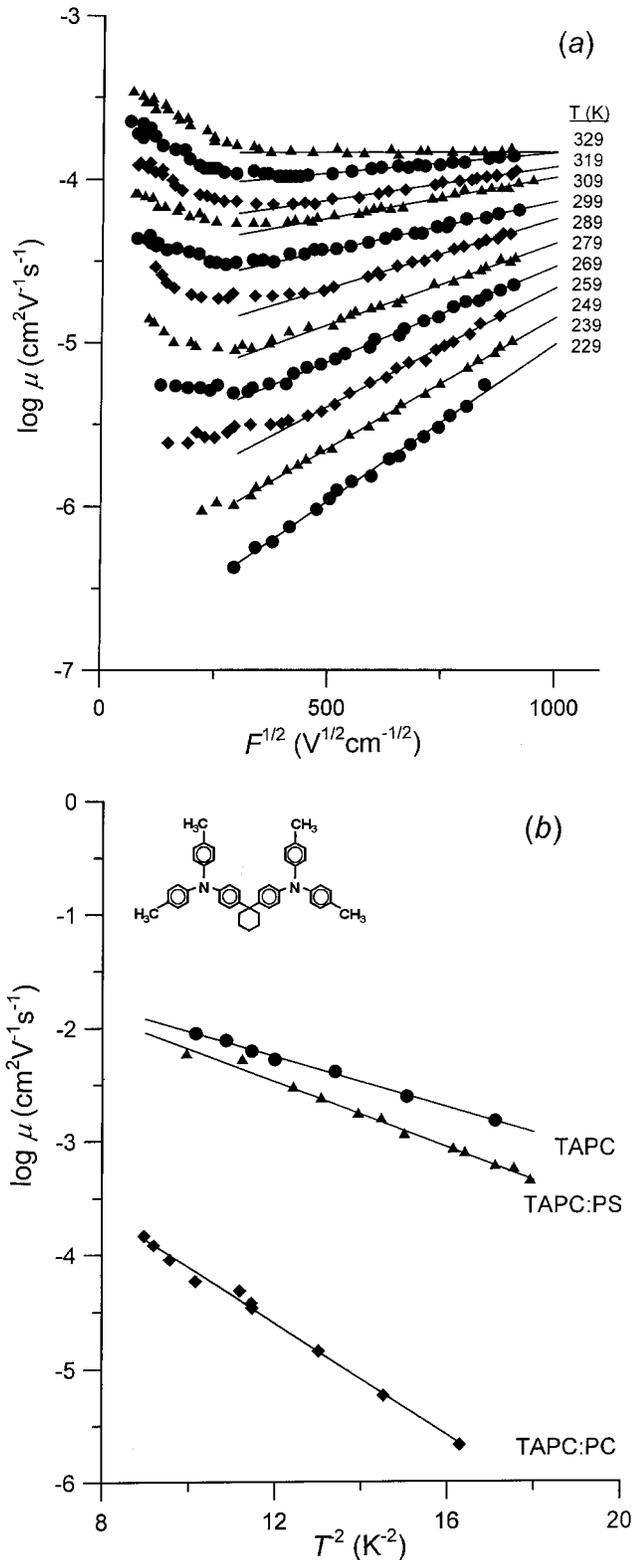


Figure 4. Field and temperature dependences of drift mobilities of holes in TAPC-containing polymers. (a). Field dependence of the mobility in bisphenol-A-polycarbonate: TAPC ( $w_{\text{TAPC}} = 0.75$ ) at various temperatures [66]. (b). Temperature dependence of the zero-field mobility in bisphenol-A-polycarbonate: TAPC ( $w_{\text{TAPC}} = 0.75$ ), polystyrene: TAPC ( $w_{\text{TAPC}} = 0.75$ ), and glassy TAPC [67].

and Fitzgerald [103,104,108] Kanemitsu et al. [53,57,109-111], and Nishizawa et al. [54,113,114] demonstrate that the polarities of both, charge transporting materials [56,57,72,75,76,78,80-82,85,109,111,113] and the polymer binders [52-54,67,69,71,74,76,85,86,110] modify the mobilities. The effect has been explained by introducing a dipolar contribution in the DOS function: Dieckmann et al. [116] assumed that the width of the DOS is a superposition of a van der Waals component ( $\sigma_{vdW}$ ) and a dipolar one ( $\sigma_{dip}$ ); taking both of them being independent, and neglecting any possible displacements of the maxima of the two Gaussian distributions, one may write

$$\sigma^2 = \sigma_{vdW}^2 + \sigma_{dip}^2 \quad (18)$$

with the dipolar component related to the permanent dipole moment of the species ( $m$ ) and its concentration (expressed here as the mole fraction  $x$ )

$$\sigma_{dip} = \frac{\kappa x^b m}{\epsilon a_0^2} \quad (19)$$

where  $\kappa$  and  $b$  are constants,  $\epsilon$  is the relative electric permittivity of the medium, and  $a_0$  is the inter-site distance. According to Dieckmann et al. [116], for diluted systems  $\kappa = 3.06$ ;  $b = 2/3$ , approaching  $1/2$  at higher concentrations. Young [117] gives  $\kappa = 7.04$ ;  $b = 1/2$ , whereas according to Hirao and Nishizawa [114]  $\kappa = 8.35$ ;  $b = 2/3$ . These equations are implicitly valid in a system consisting of a polar charge-transporting molecules dissolved in a neutral non-polar medium; the situation is less clear when the polarities of both components are similar. This is, e.g., the case of the system TAPC: polymer: the dipole moment of TAPC amounts to ca. 1 D, whereas the group moments of PC and PS amount to ca. 1D and 0.5 D, respectively. The results shown in Fig. 5, based on those given in [70], clearly exhibit a concentration dependence but the system behaves as if the widths of DOS (calculated from the field dependences of the mobility - cf. Eqs. (16) and (17)) were influenced by the dipole moments of the polymer functional groups.

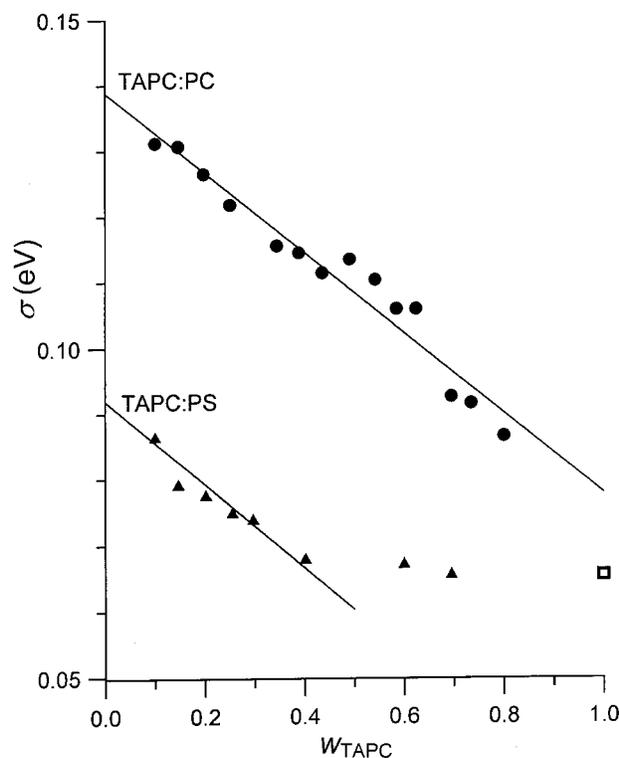


Figure 5. Concentration dependence of the width of the DOS function in TAPC-containing polymers. Data taken from [70]. The open square represents the value obtained for pure TAPC. The lines serve only to guide the eye.

Valerian et al [112] put forward a model attempting to rationalize experimental results obtained on poly(methylphenylsililene) (photoconducting by itself) doped at low concentrations ( $x \leq 0.072$ ) with highly polar 1-(benzamido)-4-nitronaphthalene ( $m \approx 6D$ ). The model qualitatively reproduces the concentration dependence of the width of DOS calculated from the experiment. It also comes from the model that the effect of polar additives should depend on their shapes: with input parameters mimicking those of the dopant, the reduction of the mobility should be more efficient for spherical molecules than for elongated ones.

The results obtained for one-component amorphous samples of charge-transporting materials are similar. The available experimental material, obtained by Borsenberger et al. [90-102] confirms qualitatively the applicability of the model. According to Eqs. (18) and (19), one should expect a linear dependence of  $\sigma^2$  on  $m^2$ . The dependence is reasonably fulfilled for several hole-transporting materials (donors), as is demonstrated in Fig. 6, the agreement between the model and the experimental results being much worse in the case of acceptors. Borsenberger et al. [98,99,101] explain the dis-

crepancy assuming that the width of the dipolar contribution should be associated with the group dipole moments rather than with the dipole moment of the molecule taken as a whole. This is essentially equivalent to admitting that the point dipole approximation breaks down in case of sufficiently large molecules, as was postulated by Kanemitsu and Sugimoto [111]. Another source of possible discrepancies are the differences in molecular packing resulting in differences of the van der Waals component (and also influencing the effective dipole moments of the molecules in glasses).

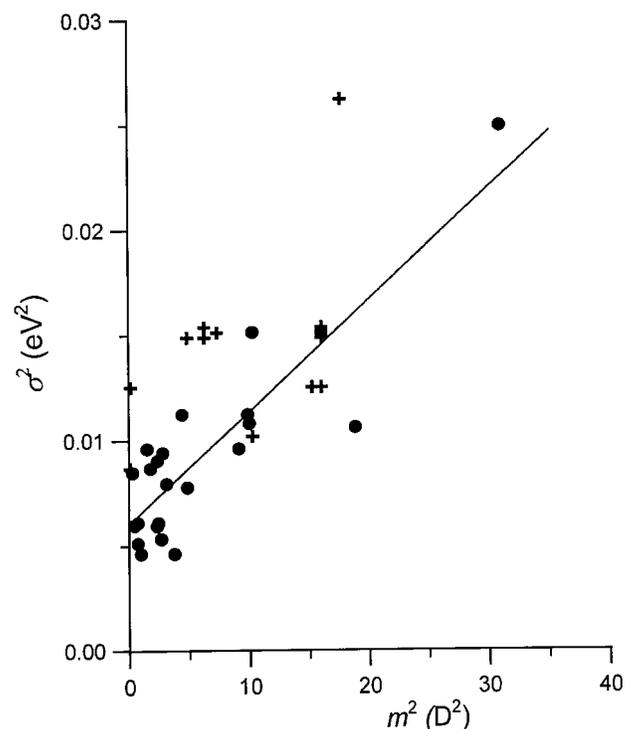


Figure 6. Influence of the dipole moment of the dopant on the width of the DOS function. Circles: hole-transporting materials (donors), crosses: electron-transporting materials (acceptors). The figure, similar to that shown in [94], contains experimental results collected from [84,90-102].

The role of dipolar disorder was also investigated by adding small amounts of (otherwise neutral) polar molecules to MPDs [105-107,115,118]. The results indicate that, at least to a first approximation, introducing polar additives results in an enhancement of the dipolar disorder and, consequently, to a decrease of the carrier mobilities. One should, however, point out that addition of even small amounts of a third component (in addition to the polymer and charge-transporting material) may result in creation of traps in the same way as in ordered molecular crystals (see Section II of this pa-

per). Due to disorder, the trap depths will also be distributed around a centroid, as is shown schematically in Fig.1c. The effect of chemical traps on charge transport in molecularly doped polymer was examined by Wolf et al. [83]. The results of computer simulations show that for sufficiently shallow traps their effect may be incorporated into an effective (broader) density of states: in other words, the trap free and shallow trap-controlled temperature dependences of mobilities should be indistinguishable, contrary to the situation in ordered solids. These conclusions are in agreement with experimental results obtained on tri-*p*-tolylamine:polystyrene system containing small amounts of tri-*p*-anisylamine which should act as a chemical hole trap ( $E_t \approx 0.24$  eV). It is therefore not unconceivable that at least some results reported in the literature contain a contribution of effects due to the presence of traps (introduced intentionally or - more often - unintentionally).

While highly successful in explaining most basic features of charge transport in disordered molecular solids, the BäSSLER's disorder model [24,25,58-60] fails in some cases to provide a *quantitative* explanation of differences (often quite small) between computer simulations and experimental results obtained on various systems. A detailed discussion of these differences is beyond the scope of this article, one should, however, point to at least two possible sources of discrepancies.

First, the BäSSLER's model assumes that both, diagonal and off-diagonal disorder are described by specific (Gaussian) functions, the inter-site transfer rates being given by the Miller-Abrahams function [61]; these equations, qualitatively correct, may not necessarily provide a good quantitative description of real cases [107,25]. Also, work of GARTSTEIN and CONWELL [119-121] points out to a sensitivity of the carrier transport to the model of off-diagonal (positional) disorder.

Secondly, the disorder model in its orthodox form neglects any influence of a dynamic disorder on the field and temperature dependences of the mobility. This assumption may hold in the case of rigid polymer networks doped with relatively small and rigid molecules, one may, however, intuitively suppose that for large and flexible dopants and/or for polymer binder around and above their glass transition temperatures the influence of vibrations (polaronic contribution) must not be neglected a priori.

The influence of polarons on the transport in disordered solids has been considered in several papers (see the literature cited in [26]). At present, both theoretical work [122,123] and experimental results (e.g., [124-127]) seem to indicate that the polaronic contribution should be taken into account as a significant but secondary factor to explain details of the charge transport in disordered molecular solids.

## VI Dipolar Traps

It has already been mentioned in Section II of this paper that polar character of a chemical trap should manifest itself in a dipolar analogue of the Poole-Frenkel effect [16]. Such an effect has been predicted several years ago [128,129]: the authors suggested that electrostatic interactions of a charge carrier released from a chemical trap with the permanent dipole moment of the molecule constituting the trap should result in a field-assisted lowering of the trap depth (cf. Fig. 7). Contrary to the "conventional" Poole-Frenkel effect, however, the effect should be directional, reaching its maximum value in the case when the biasing field is parallel to the orientation of the dipole. Moreover, the field dependence of the trap depth, reflecting itself in the field dependence of the carrier mobility, should be of the  $\ln \mu \propto F^{2/3}$  type. Such an effect has not been observed in experiments: no experimental results have been published to date reporting on the field dependence of the depth of chemical traps in single crystalline molecular materials intentionally doped with polar molecules, whereas almost all available experimental results obtained on disordered solids (molecularly doped polymers and glassy films) [43- 117] show that the mobility is either field-independent or, at high fields, follows a  $\ln \mu \propto F^{1/2}$  dependence. The latter dependence, taken in early papers for a signature of charged species acting as traps, is apparently an inherent property of the transport of charge carriers in disordered molecular materials, even those formed by non-polar molecular species [25].

The influence of dipolar traps on the transport of charge carriers in disordered materials was considered by NOVIKOV and VANNIKOV [130-137]. Their analytical treatment of the problem [130,131], based on the assumption that the dipoles are allowed to orient in the direction of the biasing field, the orientation being field

dependent, led the authors to the following conclusions: at low fields the lowering of the trap depth is proportional to  $F^{2/3}$ , changing into  $F^{1/3}$  at high fields. Thus there exists a sufficiently broad transition range where the field dependence becomes undistinguishable from the experimentally observed  $F^{1/2}$  dependence. This model implicitly assumes that there exist in abundance species in samples acting as chemical traps, which additionally possess a significant freedom of orientation. In view of a general validity of the  $F^{1/2}$  dependence in disordered solids, it seems that the effects taken into account by the dipolar trap model cannot be considered generally responsible for the field and temperature dependences of charge carrier mobilities in these materials. It is, however, worth mentioning that more recent Monte Carlo simulations of the carrier transport in disordered dipolar lattices carried out by the same authors [132,133] predict a temperature dependence of the mobility slightly differing from the  $T^{-2}$  one found by Bässler [24,25, 58-60]: Novikov and Vannikov obtain a  $(T^{-2} - T_0^{-2})$  dependence ( $T_0$  being a constant). Interestingly, such a dependence was found in the experiments reported by Mack et al [49].

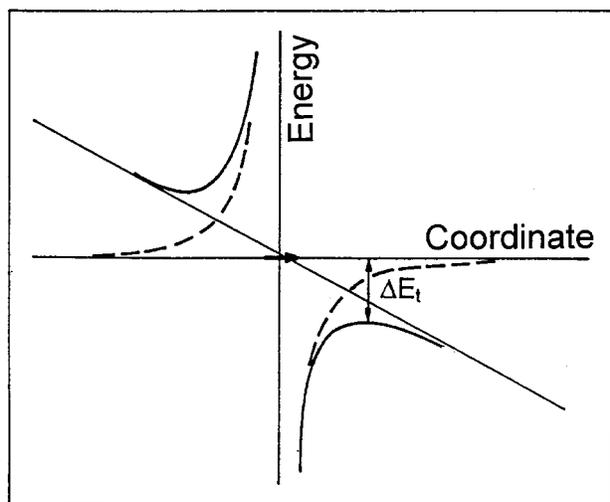


Figure 7. Field-induced modification of the depth of a chemical trap formed by a polar molecule. The field is parallel to the direction of the dipole.

## VII Final remarks

The purpose of the article was to review recent work carried out on ordered and disordered molecular solids containing polar species. The presence of polar

molecules in single crystalline materials should result in the appearance of traps localizing charge carriers on and/or in the vicinity of the dopant. The latter effect should be observed even if the dopant molecule itself does not act as a chemical trap.

The most convenient framework to describe the transport of charge carriers in disordered materials is the disorder model due to Bässler. The presence of polar species in disordered molecular solids - molecularly doped polymers and glassy samples - reflects itself primarily in increasing both the diagonal and off-diagonal disorder. Traps due to polar species are likely to be present in these materials but their effect on the transport cannot, in principle, be separated from the dominating effect of static disorder reflected in the broadening of the DOS function.

## Acknowledgements

The author wishes to express his thanks to H. Bässler, P.M. Borsenberger, A.K. Kadashchuk and N. Karl for permissions to use their results in the figures shown in this paper. The paper was supported by the Technical University of Wrocław.

## References

- 1 B. Gross, *Phys. Rev.* **67**, 253 (1945).
- 2 B. Gross, *J. Chem. Phys.* **17**, 866 (1949).
- 3 G. Gross, *Charge Storage in Dielectrics*, Elsevier, Amsterdam 1964
- 4 F. Gutmann and L.E. Lyons, *Organic Semiconductors*, J. Wiley, New York 1967; F. Gutmann, H. Keyzer, L.E. Lyons and R.B. Somoano, *Organic Semiconductors*, Part B, R.E. Krieger Publ., Malabar, FL 1983
- 5 H. Meier, *Organic Semiconductors*, Verlag Chemie, Weinheim 1974.
- 6 M. Kryszewski, *Semiconducting Polymers*, Elsevier, Amsterdam 1980.
- 7 Proc. Oji Int. Seminar on Org. Semiconductors - 40 Years, Okazaki 1988; *Mol. Cryst. Liq. Cryst.* **171** (1989).
- 8 M. Pope and C.E. Swenberg, *Electronic Processes in Organic Crystals*, Clarendon Press, Oxford 1982; M. Pope and C.E. Swenberg, *Annu. Rev. Phys. Chem.* **35**, 613 (1984).
- 9 E.A. Silinsh, *Organic Molecular Crystals*, their Electronic States, Springer Verlag, Berlin 1980.

- 10 E.A. Silinsh and V. Capek, *Organic Molecular Crystals. Interaction, Localization and Transport Phenomena*, AIP Press, New York 1994.
- 11 P.N. Prasad and D.R. Ulrich (Eds.), *Nonlinear Optical and Electroactive Polymers*, Plenum Press, New York 1988.
- 12 P.M. Borsenberger and D.S. Weiss, *Organic Photoreceptors for Imaging Systems*, M. Dekker, New York 1993.
- 13 V. Shibaev (Ed.), *Polymers as Electrooptical and Photooptical Active Media*, Springer Verlag, Berlin 1996.
- 14 S. Miyata and H.S. Nalwa (Eds.), *Organic Electroluminescent Materials and Devices*, Gordon and Breach, London 1996.
- 15 F. Kajzar, V.M. Agranovich and C.Y.-C. Lee (Eds.), *Photoactive Organic Materials. Science and Application*, Kluwer Acad. Publ., Dordrecht 1996
- 16 K.C. Kao and W. Hwang, *Electrical Transport in Solids*, Pergamon Press, Oxford 1981.
- 17 R.G. Kepler, Phys. Rev. **119**, 1226 (1960).
- 18 O.H. LeBlanc, Jr., J. Chem. Phys. **35**, 1275 (1961).
- 19 L.E. Lyons, J. Chem. Soc. 5001 (1957).
- 20 E.A. Silinsh, Phys. Stat. Sol. (a) **3**, 817 (1970).
- 21 J. Sworakowski, Mol. Cryst. Liq. Cryst. **11**, 1 (1970).
- 22 N. Karl, Adv. Solid State Phys. (Festkörperprobleme) **14**, 261 (1974).
- 23 J. Sworakowski, Sci. Papers Inst. Org. Phys. Chem. Tech. Univ. Wrocław **6**, 3 (1974).
- 24 H. Bässler, Phys. Stat. Sol. (b) **107**, 9 (1981).
- 25 H. Bässler, Phys. Stat. Sol. (b) **175**, 15 (1993).
- 26 P.M. Borsenberger, E.H. Magin, M. van der Auveraer and F.C. de Schryver, Phys. Stat. Sol. (a) **140**, 9 (1993).
- 27 A.V. Vannikov, A.D. Grishina and S.V. Novikov, Uspekhi Khim. (Russian Chem. Rev.) **63**, 107 (1994).
- 28 N. Karl, *Organic Semiconductors*, in: Landoldt-Börnstein Numerical Data and Functional Relationships in Science and Technology, Group III, Vol. 17i, Springer Verlag, Berlin 1985.
- 29 K.H. Probst, thesis, Univ. Stuttgart 1974; K.H. Probst and N. Karl, Phys. Stat. Sol. (a) **27**, 499 (1975); erratum: Phys. Stat. Sol. (a) **31**, 739 (1975).
- 30 D.C. Hoesterey and G.M. Letson, J. Phys. Chem. Solids **24**, 1609 (1963).
- 31 J. Sworakowski, Mol. Cryst. Liq. Cryst. **19**, 259 (1973).
- 32 J. Sworakowski, Mol. Cryst. Liq. Cryst. **33**, 83 (1976).
- 33 A. Jurgis and E.A. Silinsh, Phys. Stat. Sol. (b) **53**, 735 (1972).
- 34 P.J. Bounds and R.W. Munn, Chem. Phys. **44**, 103 (1979).
- 35 R.W. Munn, Materials Sci (Poland) **7**, 61 (1981).
- 36 J. Sworakowski, Proc. 7th International Symposium on Electrets, Berlin 1991, p. 45
- 37 J. Sworakowski, Diel. and Related Phen'98, Proc. SPIE, in print.
- 38 J. Kalinowski, J. Godlewski and P. Mondalski, Mol. Cryst. Liq. Cryst. **175**, 67 (1989)
- 39 J. Kalinowski and J. Godlewski, Mol. Cryst. Liq. Cryst. **205**, 101 (1991).
- 40 J. Kalinowski, J. Godlewski, P.G. Di Marco and V. Fattori, Japan. J. Appl. Phys. **31**, 818 (1992).
- 41 A.K. Kadashchuk, N.I. Ostapenko, Yu. A. Skryshevskii, V.I. Sugakov and M.T. Shpak, Pis'ma v Zh.E.T.F. (USSR) **46**, 165 (1987); JETP Lett. **46**, 207 (1987).
- 42 W.D. Gill, in: J. Mort and D.M. Pai, (Eds.), *Photoconductivity and Related Phenomena*, Elsevier, Amsterdam 1976.
- 43 J. Mort and G. Pfister, in: J. Mort and G. Pfister (Eds.), *Electronic Properties of Polymers*, Wiley, New York 1982.
- 44 G. Pfister, Phys. Rev. B **16**, 3677 (1977).
- 45 M. Stolka, J.F. Yanus and D.M. Pai, J. Phys. Chem. **88**, 4707 (1984).
- 46 D.M. Pai, J.F. Yanus and M. Stolka, J. Phys. Chem. **88**, 4714 (1984).
- 47 A. Hirao, H. Nishizawa and M. Sugiuchi, Phys. Rev. Lett. **75**, 1787 (1985).
- 48 A. Hirao and H. Nishizawa, Phys. Rev. B **54**, 4755 (1986).
- 49 J. X. Mack, L.B. Schein and A. Peled, Phys. Rev. B **39**, 7500 (1989).
- 50 A. Peled, L.B. Schein and D. Glatz, Phys. Rev. B **41**, 10835 (1990).
- 51 M. Abkowitz, M. Stolka and M. Morgan, J. Appl. Phys. **52**, 3453 (1981).
- 52 T. Sasakawa, T. Ikeda and S. Tazuke, J. Appl. Phys. **65**, 2750 (1989).
- 53 Y. Kanemitsu and J. Einami, Appl. Phys. Lett. **57**, 673 (1990).
- 54 A. Hirao, H. Nishizawa and M. Sugiuchi, J. Appl. Phys. **74**, 1083 (1993).
- 55 H.-J. Yuh and D.M. Pai, Mol. Cryst. Liq. Cryst. **183**, 217 (1990).
- 56 T. Kitamura and M. Yokoyama, J. Appl. Phys. **69**, 821 (1991).
- 57 Y. Kanemitsu, H. Funada and Y. Masumoto,

- Appl. Phys. Lett. **59**, 697 (1991).
- 58 G. Schönherr, H. Bässler and M. Silver, Phil. Mag. **B44**, 47 (1981).
- 59 H. Bässler, G. Schönherr, M. Abkowitz and D.M. Pai, Phys. Rev. B **26**, 3105 (1982).
- 60 H. Bässler, Phil. Mag. B **50**, 347 (1984).
- 61 A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).
- 62 B. Movaghar, H. Grünwald, B. Riess, H. Bässler and D. Würtz, Phys. Rev. B **33**, 5545 (1986).
- 63 B. Riess, H. Bässler, H. Grünwald and B. Movaghar, Phys. Rev. B **37**, 5508 (1988).
- 64 P.M. Borsenberger, L.T. Pautmeier and H. Bässler, Phys. Rev B **46**, 12145 (1992).
- 65 P.M. Borsenberger, L.T. Pautmeier and H. Bässler, Phys. Rev B **48**, 3066 (1993).
- 66 P.M. Borsenberger, L. Pautmeier and H. Bässler, J. Phys. Chem. **94**, 5447 (1991).
- 67 P.M. Borsenberger and H. Bässler, J. Phys. Chem. **95**, 5327 (1991).
- 68 P.M. Borsenberger, R. Richert and H. Bässler, Phys. Rev B **47**, 4289 (1993).
- 69 P.M. Borsenberger E.H. Magin and J.J. Fitzgerald, J. Phys. Chem. **97**, 8250 (1993)
- 70 P.M. Borsenberger E.H. Magin and J.J. Fitzgerald, J. Phys. Chem. **97**, 9213 (1993).
- 71 P.M. Borsenberger and L.B. Schein, J. Phys. Chem. **98**, 233 (1994).
- 72 P.M. Borsenberger and M.B. O'Regan, Chem. Phys. **200**, 257 (1995).
- 73 P.M. Borsenberger, W.T. Gruenbaum, J.E. Kaeding and E.H. Magin, Phys. Stat. Sol. (b) **191**, 171 (1995).
- 74 P.M. Borsenberger, W.T. Gruenbaum, E.H. Magin and L.J. Sorriero, Chem. Phys. **195**, 435 (1995).
- 75 S. Heun and P.M. Borsenberger, Physica B **216**, 43 (1995).
- 76 P.M. Borsenberger, E.H. Magin M.B. O'Regan and J.A. Sinicropi, J. Polym. Sci. B **34**, 317 (1996).
- 77 P.M. Borsenberger, W.T. Gruenbaum and E.H. Magin, Physica B **228**, 233 (1996).
- 78 W.Gruenbaum, E.H. Magin and P.M. Borsenberger, Japan. J. Appl. Phys. **35**, 2704 (1996).
- 79 J E.H. Magin, W. Gruenbaum and P.M. Borsenberger, Japan. J. Appl. Phys. **35**, 3930 (1996).
- 80 P.M. Borsenberger and D.S. Weiss, J. Imaging Sci. Technol. **41**, 185 (1997).
- 81 P.M. Borsenberger, J.R. Cowdery-Corvan, E.H. Magin and J.A. Sinicropi, Thin Solid Films, **307**, 215 (1997).
- 82 W.T. Gruenbaum, L.-B. Lin, E.H. Magin and P.M. Borsenberger, Phys. Stat. Sol. (b) **204**, 729 (1997).
- 83 U. Wolf, H. Bässler, P.M. Borsenberger and W.T. Gruenbaum, Chem. Phys. **222**, 259 (1997).
- 84 J.A. Sinicropi, J.R. Cowdery-Corvan, E.H. Magin and P.M. Borsenberger, Chem. Phys. **218**, 331 (1997).
- 85 P.M. Borsenberger and L.J. Rossi, J. Chem. Phys. **96**, 2390 (1992).
- 86 P.M. Borsenberger, H.-C. Kan, E.H. Magin and W.B. Vreeland, J. Imaging Sci. Technol. **39**, 6 (1995).
- 87 P.M. Borsenberger, E.H. Magin and M.R. Detty, J. Imaging Sci. Technol. **39**, 12 (1995).
- 88 P.M. Borsenberger, W.T. Gruenbaum, M.B. O'Regan and L.J. Rossi, J. Polym. Sci. B **33**, 2143 (1995).
- 89 P.M. Borsenberger and W.T. Gruenbaum, J. Polym. Sci. B **34**, 575 (1996).
- 90 M. van der Auwerauer, F.C. de Schryver, P.M. Borsenberger and J.J. Fitzgerald, J. Phys. Chem. **97**, 8808 (1993).
- 91 P.M. Borsenberger and J.J. Fitzgerald, J. Phys. Chem. **97**, 4815 (1993).
- 92 S. Heun and P.M. Borsenberger, Chem. Phys. **200**, 245 (1995).
- 93 P.M. Borsenberger and J. Shi, Phys. Stat. Sol. B, **191**, 461 (1995).
- 94 P.M. Borsenberger, E.H. Magin and J. Shi, Physica B **217**, 212 (1996).
- 95 P.M. Borsenberger, W.Gruenbaum and E.H. Magin, Japan. J. Appl. Phys. **35**, 2698 (1996).
- 96 P.M. Borsenberger, W.T. Gruenbaum and E.H. Magin, Physica B **228**, 226 (1996).
- 97 P.M. Borsenberger, L.-B. Lin and E.H. Magin, Phys. Stat. Sol. (b) **204**, 721 (1997).
- 98 P.M. Borsenberger, W.T. Gruenbaum and E.H. Magin, Phys. Stat. Sol. (b) **190**, 555 (1995).
- 99 P.M. Borsenberger, M.R. Detty and E.H. Magin, Phys. Stat. Sol. (b) **185**, 465 (1994).
- 100 P.M. Borsenberger, E.H. Magin, M. van der Auwerauer and F.C. de Schryver, Phys. Stat. Sol. (b) **186**, 217 (1994).
- 101 M.B. O'Regan, P.M. Borsenberger, W.T. Gruenbaum, Phys. Stat. Sol. (a) **148**, 259 (1995).
- 102 P.M. Borsenberger, W.T. Gruenbaum, E.H. Magin and L.J. Rossi, Japan. J. Appl. Phys. **35**, 6135 (1996).
- 103 R.H. Young and J.J. Fitzgerald, J. Phys. Chem. **99**, 4230 (1995).
- 104 R.H. Young and J.J. Fitzgerald, J. Phys. Chem. **99**, 9497 (1995).

- 105 R.H. Young and J.J. Fitzgerald, *J. Chem. Phys.* **102**, 2209 (1995).
- 106 R.H. Young and J.J. Fitzgerald, *J. Chem. Phys.* **102**, 6290 (1995).
- 107 R.H. Young and J.J. Fitzgerald, *J. Chem. Phys.* **102**, 9380 (1995).
- 108 R.H. Young, Teh-Ming Kung, J.A. Sinicropi, N.G. Rule, J.J. Fitzgerald, J.E. Eilers, C.H. Chen and N.W. Boaz, *J. Phys. Chem.* **100**, 17923 (1996).
- 109 Y. Kanemitsu, H. Funada and Y. Masumoto, *J. Appl. Phys.* **71**, 300 (1992).
- 110 Y. Kanemitsu, *J. Appl. Phys.* **71**, 3033 (1992).
- 111 Y. Kanemitsu and Y. Sugimoto, *Phys. Rev. B* **46**, 14182 (1992).
- 112 H. Valerian, E. Brynda, S. Nespurek and W. Schnabel, *J. Appl. Phys.* **78**, 6071 (1995).
- 113 M. Sugiuchi and H. Nishizawa, *J. Imaging Sci. Technol.* **37**, 245 (1993).
- 114 A. Hirao and H. Nishizawa, *Phys. Rev. B* **56**, R2904 (1997).
- 115 A.V. Vannikov, Yu.A. Kryukov, A.G. Tyurin and T.S. Zhuravleva, *Phys. Stat. Sol. (a)* **115**, K47 (1989).
- 116 A. Dieckmann, H. Bässler and P.M. Borsenberger, *J. Chem. Phys.* **99**, 8136 (1994).
- 117 R.H. Young, *Phil. Mag. B* **72**, 435 (1995).
- 118 P.M. Borsenberger and H. Bässler, *Phys. Stat. Sol. (b)* **170**, 291 (1992).
- 119 Yu. N. Gartstein and E.M. Conwell, *Phys. Rev. B* **51**, 6945 (1995).
- 120 Yu. N. Gartstein and E.M. Conwell, *Chem. Phys. Lett.* **245**, 351 (1995).
- 121 Yu. N. Gartstein and E.M. Conwell, *J. Chem. Phys.* **100**, 9175 (1995).
- 122 D.H. Dunlap and V.M. Kenkre, *Chem. Phys.* **178**, 67 (1993).
- 123 D.H. Dunlap, P.E. Parris and V.M. Kenkre, *Phys. Rev. Lett.* **77**, 542 (1996).
- 124 L.Th. Pautmeier, J.C. Scott and L.B. Schein, *Chem. Phys. Lett.* **197**, 568 (1992).
- 125 M. Van der Auweraer, G. Verbeek, F.C. De Schryver and P.M. Borsenberger, *Chem. Phys.* **190**, 31 (1995).
- 126 B. Hartenstein, H. Bässler, S. Heun, P. Borsenberger, M. Van der Auweraer and F.C. De Schryver, *Chem. Phys.* **191**, 321 (1995).
- 127 S. Heun, H. Bässler and P. Borsenberger, *Chem. Phys.* **200**, 265 (1995).
- 128 J. Sworakowski, *Proc. Polish Conf. on Mol. Crystals*, Blazejewko 1979, p. 266.
- 129 P.A. Martin, B.G. Streetman and K. Hess, *J. Appl. Phys.* **52**, 7409 (1981).
- 130 S.V. Novikov and A.V. Vannikov, *Khim. Fiz. (Russia)*. **10**, 1692 (1991).
- 131 S.V. Novikov and A.V. Vannikov, *Chem. Phys. Letters* **182**, 598 (1991).
- 132 S.V. Novikov and A.V. Vannikov, *Khim. Fiz. (Russia)*. **12** [1], 90 (1993).
- 133 S.V. Novikov and A.V. Vannikov, *Chem. Phys.* **169**, 21 (1993).
- 134 S.V. Novikov and A.V. Vannikov, *Khim. Fiz. (Russia)*. **13** [3], 92 (1994).
- 135 S.V. Novikov and A.V. Vannikov, *J. Imaging Sci. Technol.* **38**, 355 (1994).
- 136 S.V. Novikov and A.V. Vannikov, *Khim. Fiz. (Russia)*. **13** [8-9], 47 (1994).
- 137 S.V. Novikov and A.V. Vannikov, *Synth. Metals* **85**, 1167 (1997).