Russian Chemical Reviews **63** (2) 103 – 123 (1994)
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UDC 541.64:537.31

Electron transport and electroluminescence in polymer layers

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Abstract. We shall discuss the transport of charge carriers (electrons and holes) in disordered polymeric dielectric matrices and electroluminescence phenomena in transport layers of various structures, and also the injection of charges into transport layers through a boundary bearing a solid layer of a different type. The temperature, field, and concentration dependences of the mobility of the carriers will be considered, as well as the effect of the structure of the polymer matrix and of the transport centres on the mobility. The most reliable theoretical models of charge transport in these media will be examined. The bibliography includes 150 references.

I. Introduction

Significant advances in the study of the electronic properties of organic materials have been made in recent years. Attention has been focussed mainly on the electric conductance and on the electron transport properties of these materials. Some of the studies were aimed at developing organic materials having electronic properties close to those of inorganic semiconductors. Since organic materials (and, principally, polymeric) display a great variety of chemical structures and physico-mechanical characteristics, and since they can be prepared by a variety of methods, an improvement of their parameters to the level achieved in inorganic semiconductors would reveal a new world in microelectronics. The use of organic polymeric photoconductors in electrophotography is the first (and, so far, the only) example of the wide-scale industrial application of these materials in order to exploit their unique electric properties.[1] We need only to note that at present most of the photocopying ('Xerox') devices, laser printers, and other electrophotographic (EP) equipment use organic polymeric photoreceptors as the main active element. These photoreceptors usually consist of two polymer layers: a photogeneration layer and a transport layer. The photogeneration layer, deposited on an electrically conducting substrate, is a dispersion of a pigment in a polymer binder, and the transport layer is an amorphous (polymeric) dielectric containing electron transport centres.[2]

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Received 12 October 1993
Uspekhi Khimii **63** (2) 107 – 129 (1994); translated by J I Carasso

The principle of the operation of these receptors is the following. The surface of the transport layer is negatively charged by a corona discharge. When the sample is exposed through a mask photons are absorbed in the generation layer of the illuminated parts of the photoreceptor, with formation of electron – hole pairs. Free holes are injected into the transport layer and drift through it under the influence of the electric field, discharging the surface of the transport layer. As a result, a potential contour (latent image) is formed on the surface of the transport layer: this is a replica of the spatial distribution of optical density in the original mask.

We should stress that the charges must cross the whole thickness of the layer until they reach the surface, and therefore we are dealing with electron transport not accompanied by mass transport. The quantitative characteristic of this process is the time of flight of the charge carriers t_τ through the transport layer. The time of flight is a critical parameter which determines the operating speed of the whole apparatus, since it must be shorter than the time interval between exposure and development, which is usually a fraction of a second. The fundamental technological problem is to develop organic polymer layers with the smallest possible t_τ.

We should stress that the transfer of a charge between adjacent transport centres during its drift through the film is an elementary redox reaction between a neutral molecule and its cation radical (for hole transport) or its anion radical (for electron transport).[3] Surprisingly, electron transfer can take place between particles not in direct contact (at distances up to 20 Å, determined by the concentration of transport centres in the sample).

However, interest in thin polymer layers showing electronic transport phenomena has been stimulated not only by their transport properties but also by their electroluminescence (EL) properties, which allow them to be used as the elements of flat, flexible colour displays, luminescent and television screens, electrically pumped lasers, etc.[4] Again, the transport of the charge carriers is the factor which determines the effectiveness of the conversion of electric into light energy.

The distinguishing feature of EL layers (as compared with EP layers) is that their transport centres act also as luminescence centres. The essential component of an EL diode is a polymer layer sandwiched between two electrodes, one of which injects holes while the other injects electrons. The injection of charges into the transport layer through a phase boundary is an operating stage common to EP and EL systems.

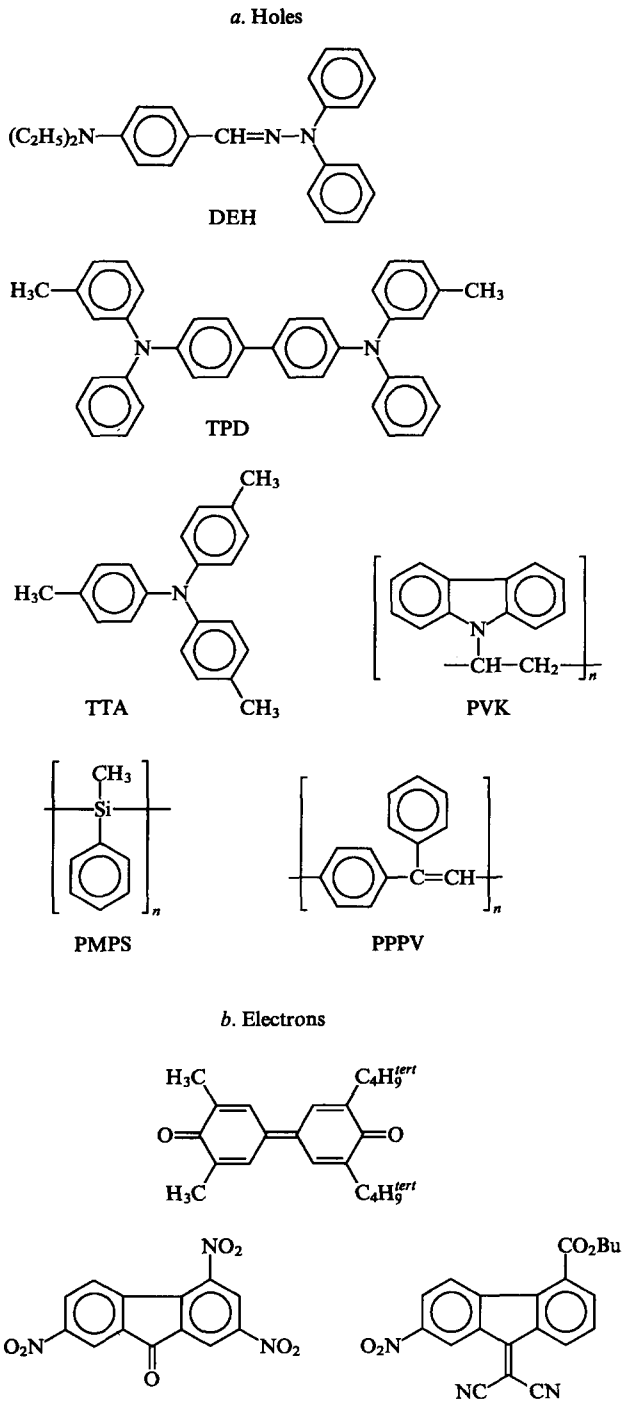


Figure 1. Typical compounds used as transport centres in polymer matrices containing mobile holes or electrons.

Electron transport phenomena in dielectric polymers are also responsible for the photorefractive effect (recently discovered in nonlinear optical polymers doped with molecules having electron transport properties[5-7]). Thus, holograms can be phase recorded by irradiating photorefractive polymer layers in a strong electric field. This four-step process includes: (1) the photogeneration of mobile charge carriers, (2) the transport and separation of charges of opposite sign, (3) the trapping of mobile charges and the generation of a nonuniform electric field by the space charge, (4) the modulation of the refractive index by the nonuniform electric field through the electro-optical effect. Uniform irradiation of the layer with a strong light erases the hologram and makes the recording process reversible.

In the present review we shall discuss only the special features and the mechanisms of charge transfer processes in polymeric transport layers, and also their electroluminescence. Photorefractive polymers lie beyond the scope of this article because their study is only beginning.

In spite of the many recent experimental and theoretical publications on electron transport in dielectric polymers a generally accepted theoretical model able to explain the basic experimental findings is still awaited. We shall examine the most significant experimental results on the temperature, field, and concentration dependence of the carrier mobility, and the effects on the mobility resulting from the structure of the polymer matrix and of the dopants introduced into the polymer and not contributing directly to the carrier transport, from the electroluminescence of transport layers of different structures, from the injection of charges into the transport layer through a boundary with a different solid layer, and also the most reliable theoretical models of charge transport in polymeric dielectric layers, i.e. models able to explain the total fund of experimental results.

II. Main characteristics of the transport of charge carriers

The polymers in which the mobility of the charge carriers can be measured by the direct time of flight method can be classified into the following groups: (1) molecularly doped polymers such as aromatic amines [triphenylamine (TPA), tritolylamine (TTA), etc.] and polyesters; (2) carbon chain polymers with chromophoric aromatic side substituents such as polyvinylcarbazole (PVK) and polyepoxypropylcarbazole (PEPK); (3) polymers with transport centres in the main chain such as polyhydroxyaminoethers (PHAE); (4) σ- and π-conjugated polymers [polysilylenes, polyphenylenevinylenes (PPV), etc.]

Some members of the different classes of transport centre are shown in Fig. 1. In groups 1–3 the localised transport centres are nitrogen atoms conjugated with phenyl groups, whereas in polymers of group 4 the transport centres are ordered parts of the polymer chains or the so-called effectively conjugated segments.[8]

Our discussion of the experimental data will invariably assume (unless accompanied by a statement to the contrary) that the transport of charge carriers is nondispersive, i.e. the injected charges are in thermal equilibrium with the medium, since this hypothesis makes the characteristics of the transport process of interest much easier to extract from the experimental results without complications from complementary factors. Detailed descriptions of dispersive (stochastic) transport can be found in existing reviews and monographs.[9-11]

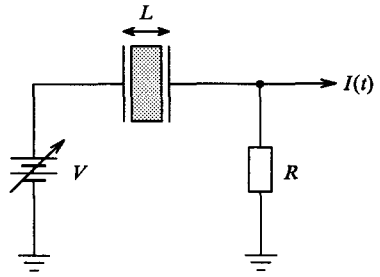


Figure 2. Scheme of the time of flight experiment.

Let us examine the basic information on transport discovered experimentally. The great majority of the data was obtained by the so-called time of flight experiment, shown schematically in Fig. 2. Charge carriers, injected (by a laser pulse or electric discharge) on one side of a flat sample of the dielectric

polymer exposed to a transverse electric field corresponding to a potential difference V, drift towards the opposite electrode. The dependence of the current I of carriers on the time t is determined experimentally. In the ideal case, when all the carriers move at the same speed, the $I(t)$ dependence is stepped: for $t < t_\tau$ the current is independent of time, but for $t > t_\tau$ it decreases rapidly with time. The transport properties of the carriers are usually defined through their mobility μ, where

$$\mu = \frac{L^2}{Vt_\tau}, \tag{1}$$

which in the ideal case is independent of the sample thickness L. The real $I(t)$ dependence has a more complex form: the sharp step is replaced by a shoulder, followed by a more gradual decrease. The latter feature shows that carrier transport in disordered systems is always to some extent dispersive. Nevertheless, when the position of the shoulder (identified with the time t_τ) is linearly dependent on L, we can confidently assume that the transport is mainly nondispersive and can be described in terms of a mobility independent of L.

The most important of the parameters which influence the transport of charge carriers are the temperature T, the electric field strength F, the concentration of transport centres c, and also the structure of the transport centres and of the polymer matrix. Many papers have been published on these topics, and we shall discuss only the most important. For a more detailed description the reader is referred to recent reviews [12-14] and to Borsenberger and Weiss's exhaustive monograph.[1] All the systems listed above have more or less similar dependences of μ on T and F.

Let us first consider the temperature dependence. The great majority of workers conclude that the temperature dependence of the mobility denotes activation control:

$$\ln\mu \propto -\frac{E_a}{T}, \tag{2}$$

where E_a is the activation energy (which we shall express in units for which the Boltzmann constant k_B is unity). However, the problem has not yet been finally solved. Recent publications by Borsenberger and coworkers [15-19] argue that the temperature dependence of the mobility is better described by an equation of the form

$$\ln\mu \propto -\left(\frac{T_0}{T}\right)^2. \tag{3}$$

(The physical significance of T_0 is examined in detail below.) A similar dependence had been proposed earlier,[20] but later work showed [12] that this observation was due to the erroneous inclusion of temperatures above the glass transition temperature, where the activation energy usually decreases steeply without a corresponding decrease in the mobility, thus stimulating a dependence such as Eqn (3). The experimentally accessible temperature range is not usually wide enough to allow an unambiguous distinction between the dependences (2) and (3). Therefore the choice of one of these functional $\mu(T)$ dependences is usually based on other considerations.[15]

In the vast majority of cases the dependence of the carrier mobility on the strength F of the electric field takes the form

$$\ln\mu \sim \text{const} + bF^{1/2}, \tag{4}$$

where b is a temperature-dependent coefficient. This is known as the Poole–Frenkel relationship because it was first proposed by Poole [21] and by Frenkel [22] in an attempt to describe the effect of an external field on the rate of escape of charge carriers from a Coulomb trap. The Poole–Frenkel model ascribes the dependence (4) to a lowering of the activation energy by the external field (Fig. 3), which gives

$$\ln\left(\frac{\mu}{\mu_0}\right) = -\frac{E_0 - \beta_{PF}F^{1/2}}{T},$$

$$\beta_{PF} = 2\left(\frac{e^3}{\varepsilon}\right)^{1/2}, \tag{5}$$

where E_0 is the depth of the potential well (trap) in a zero external field, e is the elementary charge, and ε is the permittivity of the medium. It is now generally thought that the Poole–Frenkel mechanism cannot be realised in disordered organic matrices because of the absence of significant numbers of transport centres in the great majority of organic materials.[13,23-25] Surprisingly, however, the Poole–Frenkel model gives a correct estimate of the proportionality coefficient in Eqn (4) though the experimental values of β are usually 2–3 times lower than those calculated by Eqn (5). Many experimental results show that in the majority of systems with nondispersive charge transport the overall dependence of μ on T and F is satisfactorily described by the equation

$$\mu = \mu_0 \exp\left[-\left(E_0 - \beta F^{1/2}\right)\left(T^{-1} - T_0^{-1}\right)\right], \tag{6}$$

proposed by Gill [26] and (in a slightly different form) by Pfister [27]. According to this equation the temperature dependences of the mobility measured in various electric fields should intersect at the temperature T_0, while the field dependences of μ for different temperatures have the common point $F_0 = (E_0/\beta)^2$. This behaviour has been observed in many systems of the first and second group,[1] in polyhydroxyaminoethers (third group),[28] and also in various polymers with a system of conjugated bonds in the main chain.[29,30]

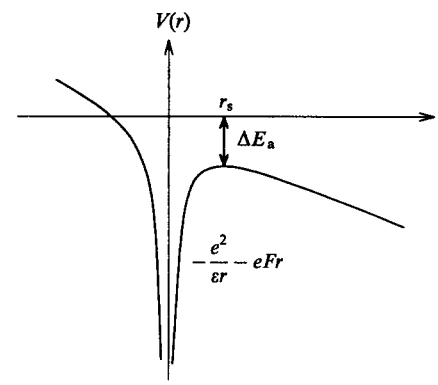


Figure 3. Lowering of the activation energy (ΔE_a) for the emission of a charge from a charged trap in an external electric field (Poole–Frenkel effect). r_s is the position of the saddle point in the potential energy.

An interesting property of Eqn (6) is the presence of the parameter T_0, which usually lies between 400 and 500 K. Formally it follows from Eqn (6) that for $T > T_0$ the mobility should decrease as the field is increased. This behaviour has been observed in recent experiments.[15,31-33] Furthermore, it was found that the mobility can be a nonmonotonic function of the field: it decreases with increasing F in weak fields and begins to increase in stronger fields.[13,34] An atypical variation of the mobility (increasing in moderately strong fields, and decreasing above $F = 10^6$ V cm^{-1}) has been reported.[35] We believe this to be an artefact, arising from the determination of the time of flight by different methods in experimental data for $F > 10^6$ and $F < 10^6$ V cm^{-1}, since the nondispersive component [the

plateau in the $I(t)$ dependence] could not be detected at high fields in those measurements. On the whole, individual instances of unusual field dependences of the mobility have been reported [with a sign inversion of b, or not consistent with Eqn (6)], but according to the Gaussian model (see below) the sign inversion of b at high temperatures and the decrease of μ in weak fields should be a common occurrence. Whether this is the case can be established only when additional experimental information becomes available.

The study of the transport properties of systems of the first group offers a unique opportunity to establish the dependence of the mobility carriers on the concentration of the transport centres, i.e. (effectively) on the average distance between the transport centres centres. It has been established that mobility decreases rapidly as the concentration of transport centres decreases.[36-38] The concentration dependence of the mobility will be discussed in more detail in the description of the various transport models given below.

The completely analogous dependence of the mobility of the two types of carrier (electrons and holes) on the temperature, field, and concentration is a fundamental experimental fact. Since the oxidation products of organic compounds have a relatively high electron affinity and act as deep traps it is easier to obtain polymer systems with hole conduction; nevertheless many systems with electron conduction have been studied in depth. Data on the transport of electrons in matrices with transport centres of the acceptor type (for example, quinone or nitrile derivatives) suggest that Eqn (6) is usually obeyed in these systems.[16,26,39] We can therefore assume that the same mechanism applies to transport by electrons and by holes.

Aromatic molecules containing nitrogen, which have low ionisation potentials (IP), have been used as transport centres for holes (see Fig. 1). A low IP is needed because fortuitous impurities with an even lower IP would act as traps for the holes. Correspondingly, molecules with the highest possible electron affinity are chosen to optimise the electron transport. It can be seen from Fig. 1 that the hole centres usually contain several nitrogen-containing $>N-C_6H_5$ groups. This facilitates the transport of positive charge within the relatively large transport centre. Kitamura and Yokoyama[40] have proposed the concepts of intramolecular and intermolecular charge mobility. The large linear size of the $>N-C_6H_5$ groups increases the intermolecular mobility, because under these conditions the length of the intermolecular jumps for a given concentration of molecules is decreased.[3] The intramolecular 'mobility' is a maximum when the density of positive charge is the same on the two functional groups of the cation radical, i.e. in symmetrical molecules.

Layers with bipolar carrier transport can sometimes be obtained, though the formation of charge transfer complexes (CTC) between donor and acceptor components strongly lowers the mobility. A well known example is PVK doped with trinitrofluorenone (THF).[26] Bipolar conduction has been observed[41] in polycarbonate (PC) doped with an alkyl derivative of diphenoquinone and tetra(*m*-tolyl)-1,3-diaminobenzene. Because of their bulky alkyl substituents the acceptor molecules cannot interact strongly with the donor molecules, and a CTC is not formed. Bipolar transport was observed also[42,43] in poly-[phenylenedi(phenoxyphenol)vinylene] (DPOP–PPV), one of the systems of the fourth group, without the addition of low-molecular-mass dopants. As will be shown below, bipolar transport is responsible for the very efficient electroluminescence of DPOP–PPV layers.

Important information is provided by data on the effect of the polarity of the matrix on the transport characteristics of the charge carriers. The existence of this effect, which shows that the role of the polymer matrix is not confined to providing sites for the transport centres, was first established in our laboratory.[44,45] The polarity of the medium can be varied either by adding chemically inert polar molecules (usually various isomers of dinitrobenzene or dinitrotoluene),[43-49] or be replacing the polymer matrix itself (for example, polystyrene by polycarbonate).[19,49] An increase in the dipole moment (or in the concentration) of the polar dopant usually lowers μ and increases β,[45,47,49] though other situations have also been observed[43,46,48] (usually in cases of strongly dispersive transport of the carriers).

In recent years the effect of the dipole moment of the transport centre on the transport characteristics of the charge carriers has been intensively studied. The most detailed contributions were made by Borsenberger and Fitzgerald[50] and by Sugiuchi and Nishizawa,[51] who studied the properties of fifteen different transport centres with dipole moments between 1.5 and 5.5 D. It was shown that an increase in the dipole moment of the centre lowers the absolute value of the mobility and increases the coefficient β.

III. Models of the transport of charge carriers in disordered organic matrices

Three main models of charge transport in disordered organic matrices have been proposed so far: the model of hopping transport over centres with a Gaussian distribution of energy levels, the polaron model, and the dipolar traps (transport centres) model. The situation is far from clear, and even the nature of the charge carriers in these matrices is still controversial.

1. Hopping transport over centres with a Gaussian distribution of energy levels

Bässler and coworkers[52-57] developed in greath depth the following model for the motion of the charge carriers. The organic matrix with the added transport centres is modelled by a cubic lattice with edge a with a transport centre located at each lattice point. The position of the energy level E involved in the charge transport is an independent, random quantity in each centre because of the random and noncorrelated effect of the surroundings. The corresponding density of states is described by the Gaussian distribution

$$\rho(E) = (2\pi\sigma^2)^{-1/2} \exp\left(-\frac{E^2}{2\sigma^2}\right). \tag{7}$$

Additional grounds for this choice of $\rho(E)$ are provided by the experimentally observed Gaussian form of the absorption and fluorescence bands of many polymers[58,59] and by the assumption that the central limit theorem must apply to some extent: the physical meaning of this model is that the overall energy of the interaction of the centre with the surroundings is the sum of many independent terms having not very different probability densities. The frequency of the jumps between the centres i and j is expressed in the form proposed by Miller and Abrahams:[60]

$$\nu_{ij} = \nu_0 \exp\left(-2\gamma a \frac{\Delta R_{ij}}{a}\right) \begin{cases} \exp\left(-\dfrac{E_j - E_i}{T}\right), & E_j > E_i \\ 1, & E_j < E_i \end{cases}. \tag{8}$$

Here ν_0 is the pre-exponential frequency factor, γ is the decrement of the wave function, and ΔR_{ij} is the distance between the centres. In the case of a nonzero external electric field an electrostatic contribution is included in the energy E_i:

$$E_i = E_i^0 - e\boldsymbol{F}\boldsymbol{R}_i. \tag{9}$$

The function $\rho(E)$ describes the effect of the energy disorder. The geometric disorder can be described phenomenologically by introducing the arbitrary parameter γa. It was assumed that

$$2\gamma a = \Gamma_{ij} = \Gamma_i + \Gamma_j, \tag{10}$$

where Γ_i and Γ_j are independent Gaussian arbitrary quantities having a dispersion σ_Γ, and the dispersion of Γ_{ij} is $\Sigma = 2\sqrt{\sigma_\Gamma}$.

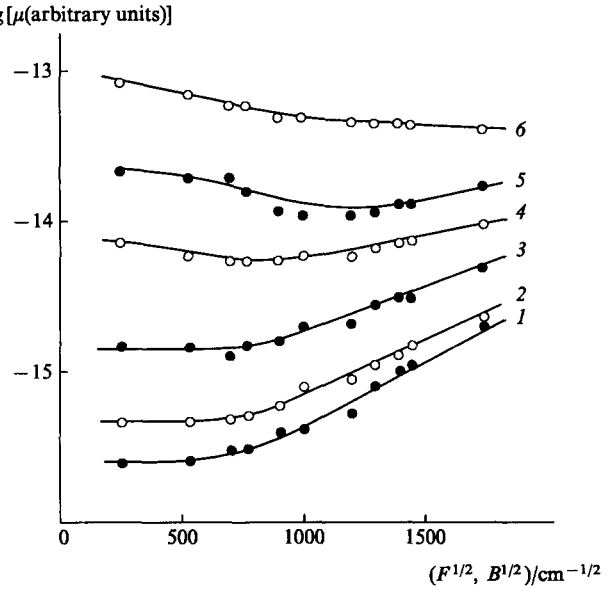


Figure 4. Field dependence of the carrier mobility in the Gaussian model (Monte Carlo calculation).[56] $\sigma/T = 3.0$; Σ: 0.00 (*1*), 1.41 (*2*), 2.12 (*3*), 2.54 (*4*), 2.80 (*5*), 3.26 (*6*).

Specific calculations by this model were possible only by the numerical modelling (Monte Carlo) method. The field dependence of the mobility is S-shaped (Fig. 4), and its middle part corresponds approximately to a linear dependence of $\ln\mu$ on $F^{1/2}$. However, this region is much narrower than the region covered by the experiment. The explanation proposed[61] for this discrepancy in terms of the difference in the definition of the mobility (through the average time of flight in the numerical experiment and through the time for the signal to fall to one half of its value at the plateau, or through the intersection of the corresponding asymptotics in the real experiment) is incompatible with the experimental results, according to which all these times have the same field dependence.[12] The calculation of the geometric disorder ($\Sigma > 0$) in terms of this model produces an interesting corollary: the mobility becomes a nonmonotonic function of the field, decreasing at first and then increasing as the field is increased.[56] This behaviour corresponds to the experimental observations of Borsenberger[34] and of Abkowitz[13].

The temperature dependence of the mobility in a zero field is not of the Arrhenius type, and is described by Eqn (3), with

$$T_0 = \tfrac{2}{3}\sigma\,. \tag{11}$$

In sufficiently strong fields the overall dependence of μ on T and F for $\Sigma \geqslant 1.5$ can be written[17]

$$\mu = \mu_0 \exp\left[-\left(\frac{2\sigma}{3T}\right)^2\right] \exp\left(-C\left[\left(\frac{\sigma}{T}\right)^2 - \Sigma^2\right]F^{1/2}\right), \tag{12a}$$

and for $\Sigma \leqslant 1.5$

$$\mu = \mu_0 \exp\left[-\left(\frac{2\sigma}{3T}\right)^2\right] \exp\left(-C\left[\left(\frac{\sigma}{T}\right)^2 - 2.25\right]F^{1/2}\right), \tag{12b}$$

where C is a universal constant equal to 2.9×10^{-4} cm$^{1/2}$ V$^{-1/2}$. However, the universality of this constant seems doubtful. In particular, Bässler's most recent paper[14] stresses that the field F should be interpreted as the dimensionless effective field

$$F_{\text{eff}} = \frac{eF\rho}{2T}, \tag{13}$$

where ρ is the average distance between the transport centres of the matrix. This replacement produces a change in the temperature dependence of μ. It is stated[14] that this change is unimportant in relation to the experimentally accessible temperature range. Nevertheless when using formula (12) we must treat the parameter C as a function of temperature rather than as a constant. Since in previous papers[16,34] the satisfactory consistency of the experimental 'constant' C with the calculated value had been repeatedly stressed in the comparisons with experiment the whole of the comparison procedure becomes open to doubt. This is a serious shortcoming, especially because of the recent tendency to treat the model of hopping transport over a system of levels normally distributed in density of states as the most promising candidate for the correct description of the transport of charge carriers in disordered organic matrices. Therefore the following list of the main weaknesses of the model could be useful.

1. The range of fields in which the mobility is linearly dependent on $F^{1/2}$ is much narrower than the experimental range. The suggested explanation[61] of this discrepancy is not consistent with experiment.

2. Nondispersive transport of the carriers is observed experimentally under conditions for which the model predicts dispersive transport (i.e. for $\sigma/T > 4.4$).[12]

3. The temperature independence of the parameter σ at temperatures below the glass transition temperature T_g of the matrix is difficult to understand, especially when σ and T have similar values: for example, $\sigma \approx (6-7) \times 10^{-2}$ eV and $T \approx 300$ K.[48] As expected, for $T > T_g$ the parameter σ begins to increase with T (see Abkowitz et al.[62]).

4. The following is probably the most serious deficiency of the model. The results (temperature and field dependence of the mobility) are to a large extent based on a specific (Gaussian) form of the density of states function. However, if $\sigma/T \gg 1$ (for example, if $\sigma/T \approx 4-6$) the main contribution to the carrier transport is provided by the decrease in the density of states in the region of $E/\sigma \gg 1$. The functional form of the density of states in this region does not have to be Gaussian. Whereas in the neighbourhood of the maximum a Gaussian distribution function can be produced by the central limit theorem, an additional decrease in the density of the distribution usually arises from infrequent fluctuations in the surroundings,[63-66] and the central limit theorem does not apply under these conditions.

Many specific problems of this type are met during familiarisation with the above model. For example, to what extent can the Miller–Abrahams model [Eqn (8)] be justified, and in particular the stipulated temperature independence of the probability of a jump giving a decrease in energy? How valid is the modelling of an organic matrix as a regular cubic lattice with transport centres at the corners? How are the results affected by the specific choice of an expression such as Eqn (10) to describe the geometric disorder?

Nevertheless at present the Gaussian model offers the most correct description of the transport of charge carriers, because it allows an integrated description of all its characteristics, including the transition from nondispersive to dispersive transport induced by a decrease in temperature, and it also allows the direct modelling of the current curve in the time of flight experiment.[34,67] It is interesting to note that the Gaussian model describes the time dependence of the stochastic transition current in a form different from that of the standard Scher–Lax–Montroll theory[68-71] of stochastic transport:

$$I(t) \sim \begin{cases} t^{-(1-\alpha)}, & t < t_\tau \\ t^{-(1+\alpha)}, & t < t_\tau \end{cases}. \tag{14}$$

This difference makes possible, in principle, an additional test of the model, though the experimental precision which has been achieved so far is not yet adequate for such a test.

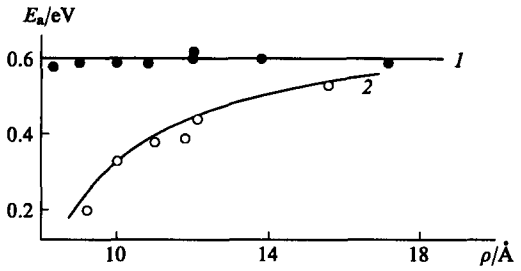


Figure 5. Dependence of the activation energy on the average distance between the transport centres in the DEH/PC (*1*) and TPD/PC (*2*) systems.[72]

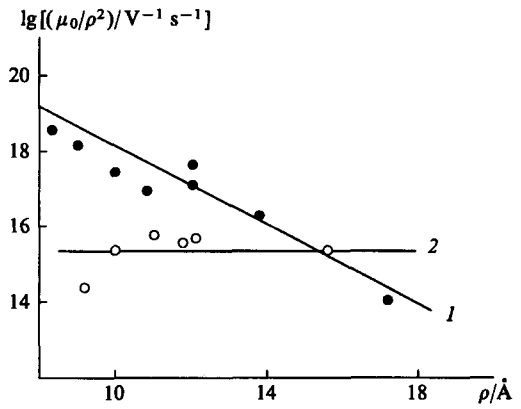


Figure 6. Dependence of the pre-exponential factor in Eqn (15) on the average distance between the transport centres in the DEH–PC (*1*) and TPD–PC (*2*) systems.[72]

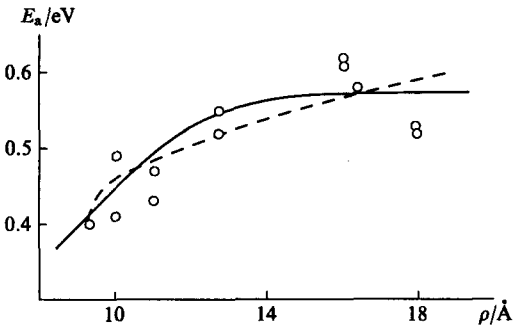


Figure 7. Dependence of the activation energy on the average distance between the transport centres in the TTA–PC system.[74]

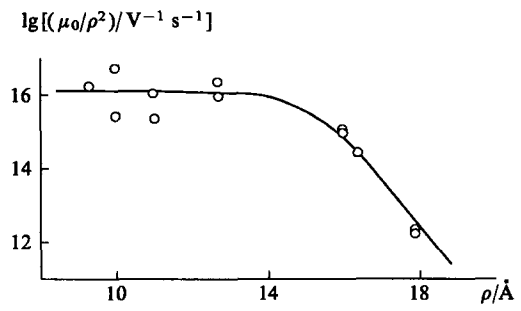


Figure 8. Dependence of the pre-exponential factor in Eqn (15) on the average distance between the transport centres in the TTA–PC system.[74]

2. The polaron model

Schein and coworkers[72–74] have actively developed the concept that the current carriers in disordered organic matrices are small polarons. As we know, the polaron is a bound state of a charge carrier and a vibrational mode (intramolecular, or involving phonons) which can move in a solid as a single entity. Those workers consider that a polaron is formed by the interaction of a carrier with an intramolecular vibrational mode.

A very large number of publications have dealt with the development of a theory of polarons as current carriers in solids of various types, such as semiconductors and organic crystals (see recent reviews, including a monograph[75–78]). In the limit of a weak external field the mobility of a polaron can be expressed as:[79]

$$\mu = \frac{e\rho^2}{T} P \frac{\omega}{2\pi} \exp\left(-\frac{\frac{1}{2}E_p - J}{T}\right), \tag{15}$$

where P is the probability of the transfer of a charge carrier from site to site in the lattice for identical energy levels in the two sites, ω is the frequency of the vibrational mode, E_p is the binding energy of the polaron, and J is the two-centre resonance integral. The function P has a complex form,[76] but a much simpler description can be used in the two limits of large and of small J. In the former (adiabatic regime) we have

$$P = 1, \tag{16}$$

and in the latter (nonadiabatic regime)

$$P \propto J^2 \propto \exp(-2\gamma\rho). \tag{17}$$

As has been pointed out[73] it follows from Eqn (15) that in the former case the activation energy increases with the average distance between centres (since J decreases), and in the latter it is almost independent of the distance (since J is small). An attempt was made to confirm this behaviour experimentally by studying the change in the mobility of the charge carriers in molecularly doped polymeric matrices as a function of the concentration of the dopant. Polycarbonate was used as the matrix, and the dopants included diphenylhydrazone-*p*-diethylaminobenzaldehyde (DEH)[72] and tri-*p*-tolylamine (TTA).[74] Results obtained in earlier work[38] with *N*,*N*′-bis(*m*-tolyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (TPD, see Fig. 1) were also discussed. It was found that in the DEH–PC system the activation energy is independent of the average distance between the transport centres, whereas the parameter P decreases exponentially as ρ increases, whereas in the TPD–PC system the activation energy increases with ρ but (conversely) P is independent of ρ (Figs 5 and 6). This difference was interpreted as a manifestation of nonadiabatic and of adiabatic polaron transport respectively. Since the resonance integral decreases exponentially with increase in ρ it follows that decreasing the concentration of transport centres in any system must sooner or later induce a transition to nonadiabatic transport. Schein et al.[74] claim to have detected this transition experimentally in the TTA–PC system (Figs 7 and 8). The different response observed in DEH, TPD, and TTA to a change in ρ (covering the same range) was ascribed to differences in geometry of the dopant molecules, leading to different packing in the polymer matrix and therefore to differences in the overlap of the π electron systems of the molecules.

Thus the experimental data are formally consistent, as a whole, with a polaron transport scheme. However, there are also some discrepancies. Firstly, the values obtained for J, E_p, and ω [0.25 (or more), 0.5, and 1 eV respectively] are unacceptably high in the case of J and ω. One obvious reason is the failure to allow for the disorder of the system. It was particularly stressed[74] that the concentration dependence of the activation energy and of the pre-exponential in Eqn (15) is explained by the polaron model without explicitly allowing for disorder effects.

The suggested explanation was that the activation energy in Eqn (15) is much greater than typical fluctuations in the position of the levels, i.e. the parameter σ as defined in the language of the Gaussian model. In this sense the suggested approach and the Gaussian model are totally incompatible. Furthermore Eqn (15) is not an exact formula but is essentially an interpolation (qualitative) expression. Kenkre and Dunlap[80,81] looked for a stricter expression for μ which also allowed for disorder effects through fluctuations in the energy levels (but not through fluctuations in the transition probability arising from geometric factors). This gives a slightly different functional dependence of the carrier mobility on the concentration for the TTA–PC system, but still as consistent with experiment as the earlier results[74] (see Fig. 7, broken curve). It was also suggested[80,81] that nonadiabatic polaron transport takes place in all the molecularly doped organic systems examined, since no transition to adiabatic transport was observed in the TTA–PC system. The same workers described[80,81] experimental data for the TPD–PC system by using their model. However, their model fails to describe satisfactorily the DEN–PC system, for which the activation energy is independent of ρ.

The proposed[80,81] modification of the polaron model did not eliminate its initial shortcoming: unacceptably high values of J were still obtained (of the same order as in the previous work[74]). Kenkre and Dunlap[81] stressed the fact that even in organic crystals, where the distance between the molecules is smaller than in molecularly doped polymers, the parameter J is at least an order of magnitude smaller than the values given by the model. Furthermore Bässler[14] correctly points out that the conclusions of Schein et al.[74] on the transitions between adiabatic and nonadiabatic transport regimes are based on the hypothesis of a temperature dependence of the mobility, undoubtedly of the Arrhenius type [see Eqn (2)], though this hypothesis now seems unjustified. For example, it yields (from the experimental data[74]) values of the pre-exponential factor in Eqn (15) of 100 $cm^2 V^{-1} s^{-1}$ and higher, which are unacceptably high for the hopping mechanism of mobility.

A recent paper[82] describes another attempt to choose between the polaron and the Gaussian model on the basis of the effect of small additions of diethylaminobenzaldehyde methylphenylhydrazone (DEMPH) on the transport of holes in the DEH–PC system. The transport level in DEMPH is located just below the corresponding level in DEH, and therefore it was suggested[82] that according to the Gaussian model a small addition of DEMPH should produce only a small widening of the distribution (7), whereas according to the polaron model the DEMPH molecules should act as shallow traps. As reported,[82] the observed increase in the activation energy can be explained only by adopting the polaron model. We do not agree that such an equivocal conclusion is justified, since the appearance of impurity levels in the low-energy region is essential to the transport of carriers in the Gaussian model for $\sigma/T \gg 1$ (see above). We suggest that the assumption of an effective widening of the distribution (7) as the only result of small additions of DEMPH is incompatible with the Gaussian model.

Thus it is impossible at present to produce unambiguous arguments for the occurrence of a transition from adiabatic to nonadiabatic polaron transport upon increasing ρ. The same must be said of the possibility of realising the polaron mechanism in general. The reason is that the main shortcoming of the polaron model (at least, in its present form) is its inability to account for the observed field dependence of the mobility. In the polaron model[79]

$$\mu \propto F^{-1} \sinh\left(\frac{e\rho F}{2T}\right), \tag{18}$$

which is totally incompatible with the experimental dependence (4). We believe that the ability to reproduce the field dependence of the mobility is the decisive test of the validity of any model of charge transport. Indeed, the temperature dependence of the mobility has an Arrhenius or similar form in the majority of the models which have been used, but the narrowness of the experimentally accessible temperature range makes it impossible to distinguish even between dependences of types (2) and (3). Different concentration dependences give an impression of artificiality, and often need to be combined with various extrapolation procedures.[14] Furthermore the extraction of unambiguous information from the concentration dependences is complicated by the frequent presence of large concentrations of dopant (10% or more), which make the separation of the system into transport centres and an inert medium an arbitrary decision. In fact a different effective medium corresponds to each concentration of dopant. Under these conditions the field dependence of the mobility offers a unique opportunity to test various models by a relatively simple experiment, using ranges of field strength covering two orders of magnitude in recent experiments.[23] This is why we believe that the strongest argument against the polaron model of charge transport is its failure to offer a correct description of the field dependence of the mobility.

Vannikov and coworkers[44,45,47] have tried to use the theory of Marcus[83] to describe the transport of charge carriers in polymers. In practice this meant allowing for the interaction of the charge carrier both with the intramolecular vibrations and with the vibrational modes of the medium in the polaron model. This approach allowed the activation energy of the carrier transport process to be related to parameters of the medium, such as the static relative permittivity, and thus to explain the influence of added inert polar molecules of the *o*-dinitrobenzene type on various characteristics of the transport. Unfortunately this variant of the polaron model suffers from the same serious shortcoming: as before, it gives Eqn (18) for the field dependence of the mobility.

3. The dipolar traps (transport centres) method

The dipolar traps method[84–88] is still only in the initial stage of its development. Nevertheless the results so far achieved show considerable promise. The model was first proposed in order to account for the field dependence of the mobility, which neither the Gaussian nor the polaron model could explain. However, it was later found that the new model offers interesting information as well on the temperature dependence of the mobility.

The model is based on the following considerations. Let the mobility be determined by the rate of emission of charge carriers from the traps (the transport centres). This state of affairs can be realised if the transport occurs (for example) by jumps of the carriers in a system of relatively shallow traps, and the rate of emission of the carriers from the transport centres determines their concentration in the mobile 'transport' state. Basically this idea underlies the Poole–Frenkel model,[21,22] but in addition that model also stipulates that the transport centres are charged even in the absence of charge carriers. Unfortunately, in the vast majority of matrices so far examined charged traps cannot exist in significant concentrations. Furthermore, as has been pointed out,[23] the distance from which the carrier is emitted from the charged trap according to the Poole–Frenkel model (i.e. the position of the saddle point in the potential energy surface, which determines the decrease in the activation energy, see Fig. 3) takes values of 50–400 Å in typical fields of 10^4–10^6 V cm^{-1}, i.e. it is unrealistically large. Since the transport traps are usually aromatic compounds or groups containing nitrogen they often possess sizeable dipole moments. Therefore it was suggested[84,85] that the effect of the field on the rate of emission of the charge carriers from a dipolar trap can explain the experimentally observed dependence of the mobility on the field strength. In the simplest case this effect can be evaluated through the lowering of the activation energy barrier to the emission of a carrier caused by an external electric field.

We assume that the carrier emerges from the trap in a region close to the saddle point, where the activation energy is a minimum, so that averaging over the different emergence directions becomes unnecessary, and quantum effects can be ignored. The interaction of a charge with a point dipole is described by the well known expression

$$V(r) = \frac{edr}{\varepsilon r^3} - eFr\,, \tag{19}$$

where d is the dipole moment of the trap. This leads to a dependence of the type

$$\Delta E_0 \propto F^{2/3}\,, \tag{20}$$

and therefore to $\ln\mu \propto F^{2/3}$, which is not consistent with experimental data. However, the decrease in the activation energy ΔE_0 depends also on the mutual orientation of the dipole and the field. By assuming that the orienting influence of the field on the dipolar transport centre is similar to its influence for a free dipole, we obtain the following expression for the mobility after averaging over the orientations of the dipole:

$$\mu = \mu_0 \int_0^\pi \sin\alpha \exp\left(-\frac{E_0 + \Delta E_0(\alpha, F) - dF\cos\alpha}{T}\right)\mathrm{d}\alpha\,,$$

where

$$\Delta E_0(\alpha, F) = -e\left(\frac{dF^2}{\varepsilon}\right)^{1/3} G(\alpha)\,, \tag{21}$$

$$\begin{cases} G(\alpha) \approx \alpha, & \alpha \to 0 \\ G(\alpha) \approx \dfrac{3}{2^{2/3}}\left[1 - (\pi - \alpha)^2/9\right], & \alpha \to \pi \end{cases},$$

and α is the angle between the vectors d and F. In a weak field this expression gives

$$\ln\mu = \ln\mu_0 - \frac{E_0 - \beta_1 F^{2/3}}{T}\,,$$

$$\beta_1 = \frac{3}{2} e\left(\frac{2d}{\varepsilon}\right)^{1/3}\,, \tag{22}$$

whereas in a strong field

$$\ln\mu = \ln\mu_0 - \frac{E_0 - \beta_2 F^{1/3}}{T}\,,$$

$$\beta_2 = \frac{1}{2} e^2\left(\frac{1}{d\varepsilon^2}\right)^{1/3}\,. \tag{23}$$

The change from Eqn (22) to (23) is brought about by the orientation of the dipoles in the external field, and takes place in fields of magnitude $F_t \approx 0.01 e^3/\varepsilon d^2$. Thus an increase in the field strength produces a change from the $\ln\mu \propto F^{2/3}$ to the $\ln\mu \propto F^{1/3}$ dependence. In the relatively wide intermediate range of field strength the change in mobility is satisfactorily described by Eqn (5) with

$$\beta = 0.36\beta_{\mathrm{PF}}\,. \tag{24}$$

Furthermore the distance between the dipole and the saddle point of the potential surface (19) is 10–40 Å, which is a reasonable value. An attempt[85] to describe the experimental data[23] by means of Eqn (21) gave good agreement between experiment and theory, though the adjustable parameters had to be given unreasonably high values (d_{opt} = 18 D and $\varepsilon_{\mathrm{opt}}$ = 7.5). In order to resolve this discrepancy an attempt was made[86,87] to allow for the dynamics of the motion of charge carriers in the trap by assuming that the motion is stochastic and can be described by a Markov controlling equation of the form

$$\frac{\partial P}{\partial t} = \int_{E_{\min}}^{\infty} \left[K(E, E')P(E', t) - K(E', E)P(E, t)\right]\mathrm{d}E' - k_{\mathrm{d}}(E)P(E, t)\,, \tag{25}$$

where $K(E, E')$ is the probability of the transition from a state of energy E' to a state of energy E in unit time, $P(E, t)$ is the distribution function over the energies of a charge bound in a trap, $k_{\mathrm{d}}(E)$ is the rate constant of the dissociation of the bound state of the charge in the trap, and $E_{\min}$ is the position of the bottom of the potential well. The nucleus $K(E, E')$ was chosen as a phenomenological Bhatnagar–Gross–Krook (BGK)[89] nucleus, for which in $\Gamma = (\mathbf{r}, \mathbf{p})$ phase space the function $K(\Gamma, \Gamma')$ takes the form

$$K(\Gamma, \Gamma') = \nu\delta(r - r')P_{\mathrm{eq}}(p)\,, \tag{26}$$

where ν is the characteristic frequency of the interaction with the external medium, r is the coordinate and p is the momentum of the charged particle, and $P_{\mathrm{eq}}(p)$ is the equilibrium distribution function over the momentum. The use of the BGK nucleus implies that every collision leads to a completely stochastic momentum distribution without change in the spatial coordinates. Intuitively this stipulation seems correct in the case of effective collisions of short durations, and therefore the BGK nucleus is often used to analyse and to model the dynamics of various systems.

A solution of Eqn (25) has been obtained[86–88] by two numerical methods: direct modelling of the random walk over energies of a charge carrier in the trap, by using the Monte Carlo method to calculate the rate constant for the dissociation of the bound state through the reciprocal mean time to reach the dissociation threshold, and by the direct calculation of the quasistationary solution of Eqn (25), whose decrement defines the rate of dissociation of the bound state. The latter method can be used for the low-temperature region, which is not accessible to the Monte Carlo method because of its unreasonable requirements of computer time. The two methods gave satisfactorily consistent results. The mobility of the carriers was also calculated by averaging the rate constant $k_{\mathrm{e}}(\alpha)$ over the angle α, using both a chaotic distribution and the distribution corresponding to Eqn (21).

Calculations showed[86–88] that in moderately weak fields the field dependences of the mobility have the typical Poole–Frenkel form (Fig. 9), irrespectively of the assumed distribution of the dipoles over the orientations. This effect is attributed to the fact that the parameter $\ln k_{\mathrm{e}}(\alpha)$ is linearly dependent on $F^{1/2}$ for strong enough fields (Fig. 10). The suppression of the $\ln k_{\mathrm{e}}(\alpha) \propto F^{2/3}$ dependence, indicated by the calculation of the rate constant, can be explained through a decrease in the activation energy. This is because the field F has a double influence on the motion of the charge carrier in the potential well. The strongest effect is a lowering of the activation energy. However, there is also a second effect which limits the space available for the motion of the particle, and therefore the application of a nonzero electric field converts the long-range potential of the dipole into a short-range potential. This ensures that at energies just below the threshold value the particle spends much less time in a state of low kinetic energy (a typical situation for a long-range potential), i.e. the average kinetic energy of the particle (the charge carrier) increases. In our mechanism, which assumes interaction of the particle with the thermal fluctuations of the surroundings, this leads to an increased rate of dissipation

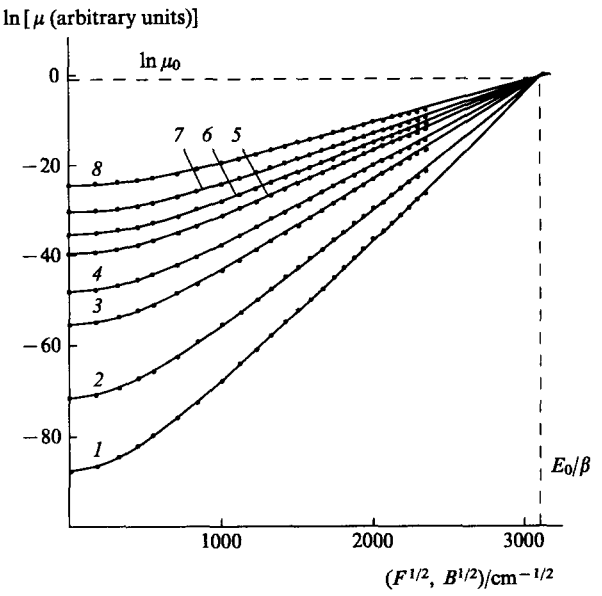


Figure 9. Field dependences of the mobility for different temperatures.[88] T/E_0: 0.01 (*1*), 0.012 (*2*), 0.015 (*3*), 0.017 (*4*), 0.02 (*5*), 0.022 (*6*), 0.025 (*7*), 0.03 (*8*). Calculated for $E_0 = 0.8$ eV, $T = 0.01E_0$, $d = 5$ D, and $\varepsilon = 1$.

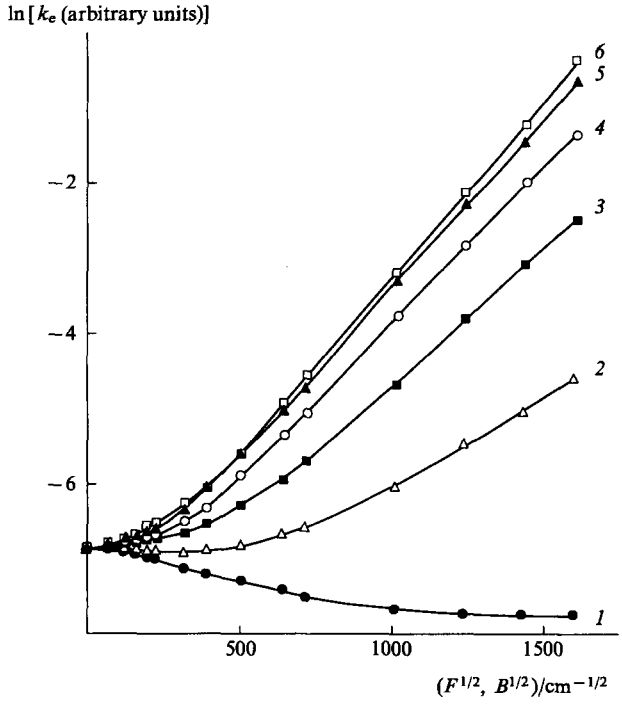


Figure 10. Field dependences of the rate constant k_e for different values of the angle α.[86] α/rad: 0 (*1*), $\pi/5$ (*2*), $2\pi/5$ (*3*), $3\pi/5$ (*4*), $4\pi/5$ (*5*), π (*6*). Calculated for $E_0 = 0.4$ eV and $T = 300$ K, other parameters as in Fig. 9.

of energy for a particular close to the threshold, and therefore to a decrease of $k_e(\alpha)$. This effect is most clearly seen for $\alpha = 0$, when there is no lowering of the activation energy and therefore $k_e(0)$ decreases as F increases.

The temperature dependence of the mobility was shown to be a complex phenomenon of the Arrhenius type at low temperatures and approaching the dependence described by Eqn (3) at high temperatures (where high temperatures are defined by the condition $T/E_0 > 0.03$, Fig. 11). Additional

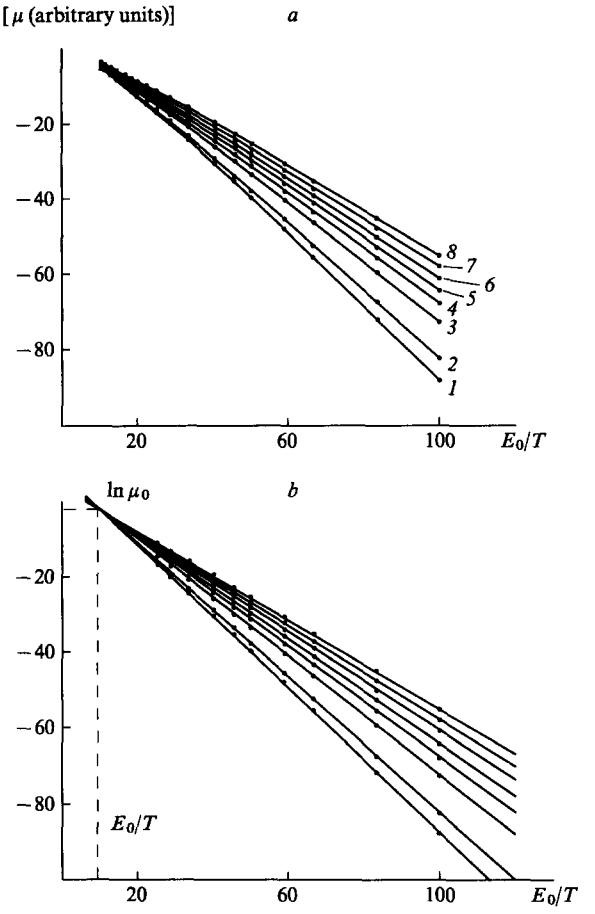


Figure 11. Temperature dependences of the mobility (*a*) for different values of the electric field,[88] and temperature dependences averaged by least squares (*b*) for temperatures not exceeding $0.05E_0$. $(10^{-5}E)$/V cm^{-1}: 0 (*1*), 2 (*2*), 7 (*3*), 10 (*4*), 12.5 (*5*), 15 (*6*), 17.5 (*7*) 20 (*8*). All the other parameters as in Fig. 9.

confirmation of the Arrhenius form of the $\mu(T)$ dependence is provided by the equality of the activation energy and of the depth of the trap (which depends on F).

The overall dependence of μ on F and T in not very weak fields is accurately described by the Gill–Pfister Eqn (5) (see Figs 9 and 11). It follows from Fig. 11 that a crude estimate of the temperature T_0 can be obtained by the formula

$$T_0 \approx 0.1\,E_0\,. \tag{27}$$

Evidence that the temperature T_0 is determined only by the parameter E_0 has been obtained.[88] The estimate (27) agrees reasonably well with experimental data,[24,39,40,90,91] especially if its approximate nature is not forgotten. Another interesting conclusion follows from the calculations: the constant μ_0 of the Gill–Pfister Eqn (5) corresponds approximately to the limit value of the mobility at $T \to \infty$, which is independent of F, whereas it follows formally from Eqn. (5) that

$$\mu(T \to \infty) = \mu_0 \exp\left(\frac{E_0 - \beta F^{1/2}}{T_0}\right). \tag{28}$$

For $F = 0$ we find from Eqns (27) and (28) that Eqn (5) gives a value of the limiting mobility too high by a factor of 2×10^4. Of course, the approximation (27) is quite arbitrary and has a low precision, and it is clear that it overestimates the limiting mobility by several orders of magnitude. Therefore the choice of the dependence (3) [rather than (2)] on the grounds that (2) gives an unreal value of the mobility as $T \to \infty$ is not justified.[15,92]

At the same time, in the light of the dipolar traps model, the relative advantages of the expression (2) or (3) are arguable. Depending on the temperature interval chosen the mobility can be better described by Eqn (2) or by Eqn (3).

To conclude this section we shall discuss the sign inversion at high temperatures[15,31-33] of the coefficient b in the field dependence of the mobility [Eqn (4)], which was mentioned above. This behaviour follows formally from Eqn (5) for $T > T_0$. The dipolar traps model in its most recent variant cannot account for this behaviour, and this is, in fact, its most serious shortcoming. Nevertheless we should stress that the Gill–Pfister formula applies with satisfactory precision to almost all the systems so far examined, whereas in practice the sign inversion has been established experimentally only in a few cases. For the great majority of compounds the temperature T_0 is found to lie well above the glass transition temperature of the matrix, and is therefore not experimentally accessible. Therefore we believe that the temperature T_0 is not directly related to the sign inversion of the coefficient b of Eqn (4), and is only a parameter which describes the deviation of the temperature dependence of the mobility from the Arrhenius form. From our point of view the sign inversion of b must be explained by the action of some specific and (obviously) rarely met mechanism. The same is true of the nonmonotonic field dependence of the mobility.[13,34] This dependence is a very rare exception. Only future work can show whether this is really the case, or whether these effects are unavoidable characteristics of charge transport in disordered organic matrices.

The dipolar traps model also offers a natural explanation of the effect of inert polar additives on the transport of charge carriers. It is reasonable to assume that the dipoles can form aggregates of various compositions and geometries with the transport centres, and that the effective dipole moment of these aggregates can vary within defined limits. Clearly, the dipole moment of the aggregates is directly correlated with the bond energy of the carrier, since the electrostatic interaction of the charge with the dipole adds a substantial contribution to the total energy of the bond. Since the number of carriers is usually small in comparison with the number of traps, the charge transport is dominated by the deepest traps, i.e. by the traps with the largest dipole moment. This decreases the absolute value of the mobility as a result of the increase in E_0, but it also increases β since an increase in d strengthens the long-range interaction of the charge with the dipole, which is responsible for the emission of the charge from the trap.[88] Similar arguments apply to the changes in dipole moment of the transport centre itself.

We note that an increase in d without a change in the depth of the trap results in an increase in μ as a result of the accompanying strengthening of the long-range interaction. This effect can be used to explain an interesting experimental observation:[45] the carrier mobility in the polystyrene–triphenylamine system is decreased by a factor of 320 after doping with *o*-dinitrobenzene, whereas allowing only for the change in the activation energy should lower the mobility by a factor of 5×10^4.

The most characteristic difference between the dipolar traps model and the Gaussian or the polaron models is the substantial role played by the medium (the polymer matrix). The latter two models treat the polymer matrix as a nontransport medium whose function is to accommodate the transport centres at a well defined mutual distance and which affects the transport only indirectly by acting on the parameters of the centres. Transport directly through the polymer matrix is excluded.

In the dipolar traps model the controlling step is the emission of the charge carrier from an isolated transport centre. In this case the transition to a neighbouring centre requires a stage of transport along the polymer matrix. Data on the radiation-induced electric conduction in polymers show that this mode of transport can easily account for the transport of the charge carrier for the required distance. We know that the radiation-induced electric conduction in polymers, which has undoubtedly an electronic nature, includes an instantaneous and a delayed component,[93,94] and that the instantaneous component γ_m (defined by the drift of the charge carrier between its generation and its capture by a trap) bears a direct relationship to the motion of the carriers in the polymer matrix between neighbouring transport centres. The instantaneous component is characterised by the constant K_m. Under these conditions $\gamma_m = K_m R_0$, where R_0 is the dose rate. If γ_m is expressed in C m^{-1}, and R_0 in Gy s^{-1} we can write

$$G\mu_0\tau_0 = 0.1\,\frac{K_m}{g}, \tag{29}$$

where G is the radiation-chemical yield of charge carriers per 100 eV of absorbed energy; μ_0 and τ_0 are the mobility of the carrier in the free state and the time elapsing before its capture by a deep trap; $\mu_0\tau_0$ is the specific path, m^2 V^{-1}; g is the density of the polymer, g cm^{-3}. In organic substances, including polymers, $G = 1$. In polycarbonate, the polymer matrix most often used in electron transport layers, $K_m = 1.6 \times 10^{-15}$ F m^{-1} Gy^{-1}, whence $\mu_0\tau_0 = 1.6 \times 10^{-12}$ cm^2 V^{-1}. The interval usually obtained for the change in F is 10^5–10^6 V cm^{-1}, i.e. the charge carrier travels a distance of 16–160 Å before being captured by a deep trap, whereas the average distance between the transport centres is usually 10–20 Å.

The dipolar traps model in its current form is only a model of a single trap, not a model of the transport process as a whole. Therefore it cannot claim to describe characteristics of the transport such as the various concentration dependences and dispersion phenomena. Nevertheless it can be used to give descriptions of field and temperature dependences in good agreement with experiment.

IV. Electroluminescent polymer layers

In recent years studies of radiative recombination and the preparation of flat, flexible polymer diodes which emit light upon the application of an electric potential difference have become one of the leading new areas in applied science.[4,95,96] The main part of these electroluminescent diodes is a polymer layer located between two electrodes: the cathode injects electrons and the anode injects p-type carriers. Metals having a low work function (ϕ) are used for the cathode (Al, In, Ca, or Mg), whereas the hole-injecting anode is a compound having a high electron affinity: In_2O_3/SnO_2 (ITO), or a polyaniline (PAn) film in the form of the conducting (acid-doped)[97,98] emaraldin salt, or oligothiophen.[99] When a voltage is applied the injected electrons and holes move into the layer from opposite directions and recombine (when they meet) with emission of light:

$$p^{+\cdot} + e^{-\cdot} \longrightarrow {}^{1,3}(p^{+\cdot}\cdots e^{-\cdot}) \longrightarrow$$

$$\xrightarrow{25\%} S_1 \longrightarrow h\nu^{fl} + S_0 + \text{phonons} \tag{30a}$$

$$\xrightarrow{75\%} T_1 \longrightarrow S_0 + \text{phonons}. \tag{30b}$$

In keeping with the multiplicity of the states S_1 and T_1 25% of the charges which collide in reaction (30) recombine through a singlet excited state, and 75% through a triplet state.[100] Electrophosphorescence was not observed in these diodes. As will be shown below, the triplet excitons T_1 contribute to the electroluminescence by virtue of the reaction (30c) in competing processes:

$$T_1 + T_1 \longrightarrow S_1 \longrightarrow h\nu^{fl} + S_0 + \text{phonons} \tag{30c}$$

$$T_1 + T_1 \longrightarrow S_0 + \text{phonons}. \tag{30d}$$

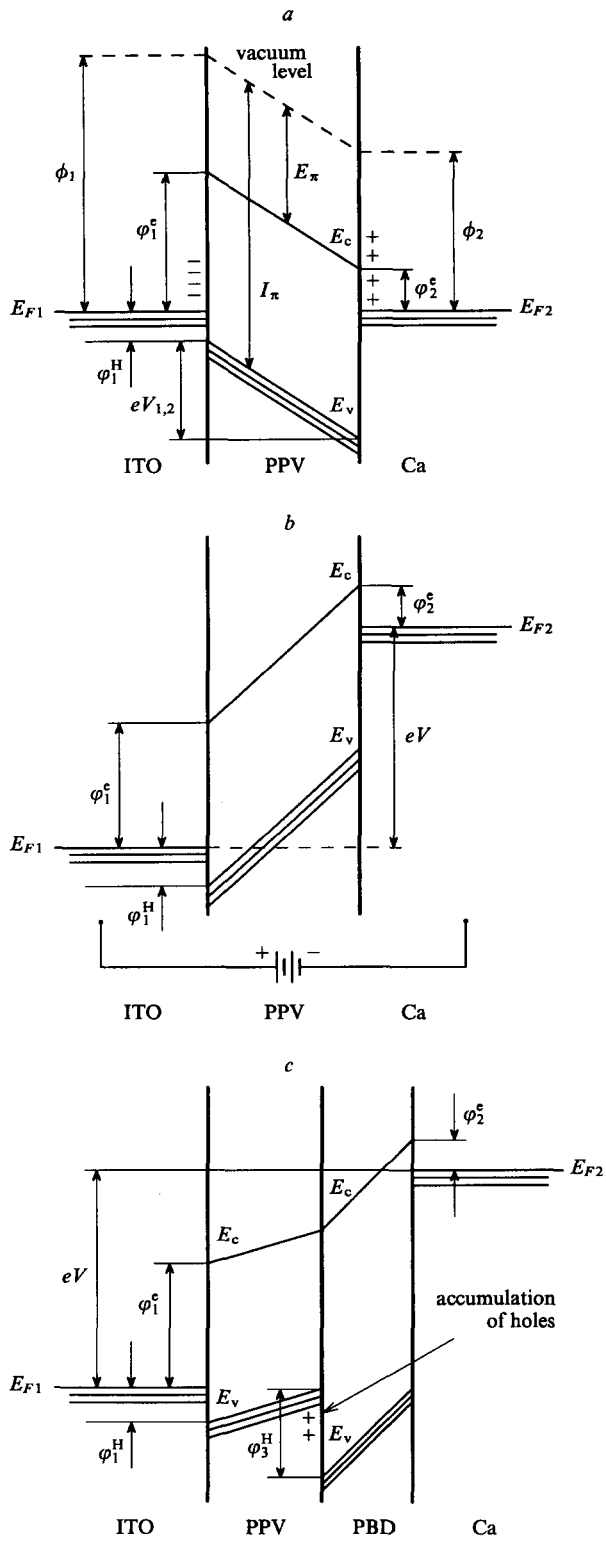


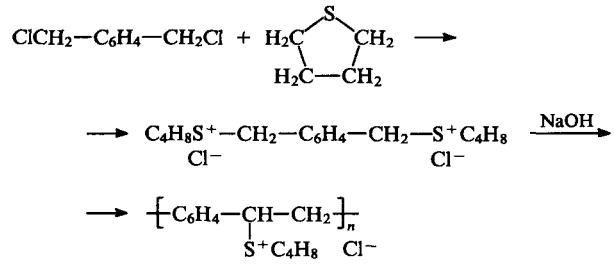
Figure 12. Energy diagram of the processes in single-layer (*a*, *b*) and in bilayer (*c*) electroluminescent diodes (symbols defined in text). Applied potential difference $V = 0$ (*a*), V (*b*, *c*).

Two types of system have been examined so far. The first type includes single-layer systems with one or more components. The one-component systems rely on polymers with conjugated bonds, in which charge transport and light emission can take place simultaneously (PPV and its derivatives,[4,95,97,98,101-107] poly-3-alkylthiophens,[100,108,109] poly-*p*-phenylene,[110] etc.). A typical example of a single-layer multicomponent system is a composition consisting of PMMA with a dissolved triphenyldiamine additive (TPD, see Fig. 1) responsible for the transport of holes, and the organoaluminium complex (Alq_3), responsible for the transport of electrons and for the emission of light.[112] An energy diagram of the processes in single-layer systems is shown in Figs. 12*a* and 12*b*, where ϕ_1 and ϕ_2 are the work functions of the anode and of the cathode respectively; I_π and E_π are the ionisation potential and the electron affinity of the polymer layer in the solid phase [respectively, the distance from the vacuum level to the upper edge of the valence band (E_v) and to the lower edge of the conduction band (E_c)]. Under these conditions $h\nu^{fl} \approx I_\pi - E_\pi$. In PPV I_π is equal to 6.2 eV and E_π to 2.5 eV.[113] The strength of the EL is determined by the effectiveness of the radiative recombination channel, by the energy barriers which the electrons and holes must overcome before recombining, and also by the transport of electrons and/or holes, all of which contribute to the encounter of electrons and holes in the polymer.

Systems of the second type include structures consisting of two (or more) polymer layers (see Fig. 12*c*), one of which (PPV) is responsible for the transport of holes while the other [PPMA containing 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD)] is responsible for the transport of electrons.[104,114-117] In these systems the emission of light takes place from the contact region of the two layers.[104,114-117] Structures in which the polymeric transport layer is in contact with a sputtered layer of a low-molecular-mass compound have also been prepared. The transmission of electrons through interlayer boundaries is discussed in detail in Section V.

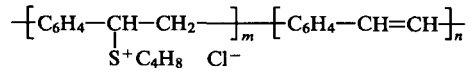
1. Electroluminescence of PPV derivatives

In the method widely used to synthesise PPV its precursor is first obtained from α,α′-dichloro-*p*-xylene in the form of the polyelectrolyte **1**, for example by reaction with tetrahydrothiophen (THT).[118]



1

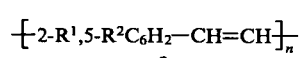
The polymer **1** is unstable, and conjugated phenylenevinylene portions of the chain are formed in the molecule during lengthy storage at elevated temperatures (160-300 °C).



2

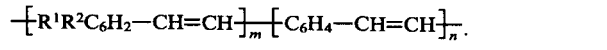
The polymer **2** is completely converted into PPV when stored in vacuum at 300 °C for several hours.[118]

If substituted α,α′-dichloro-*p*-xylenes [$ClCH_2-2\text{-}R^1,5\text{-}R^2.C_6H_2-CH_2Cl$ (R^1 and R^2 = CH_3O, NO_2, or other groups)] are used in the synthesis derivatives of PPV are obtained,



3

or copolymers of the structure



As will be shown below, PPV has a weak EL, and polymer **2** is most often used in the preparation of diodes. Since the conversion of polymer **2** into PPV continues in the prepared diode it is difficult to control the degree of development of the unsaturated chains in PPV. This may be the reason for the large scatter of the characteristics of the EL obtained in different laboratories. Changes in the region of the Schottky barrier caused by the interaction of the cation material (for example, Ca) with the sulfur-containing impurity produced during the conversion of the polymer **2** into PPV also contribute to the scatter of the results.[119]

The position of the EL band is determined mainly by the size of the system of conjugated bonds, and also by the structure of the side substituents in the polymer chain and by other factors which control the position of the energy levels contributing to reaction (30). The optical absorption of the PPV film lies in the energy range above 2.4 eV and has a maximum at ~3.0–3.2 eV (410–390 nm).[118–120] The long-wave threshold of the optical absorption of the polymers **3** is bathochromically shifted by the introduction of donor substituents from ~2.4 eV in PPV ($R^1 = R^2 = H$) to 2.18 eV for R^1 and $R^2 = OCH_3$ and to ~2.1 eV for R^1 and $R^2 = O-(CH_2)_7-CH_3$, or $R^1 = O-CH_2-CH(CH_2CH_3)-C_4H_9$, $R^2 = O-CH_3$; or for $R^1 = R^2 = O-(CH_2)_5-CH_3$.[121] A hypsochromic shift of the spectrum has been observed for the oligomeric analogues of PPV ($n = 3$) with $R^2 = NO_2$.

The EL spectra are usually similar to the photoluminescence (PL) spectra of the polymers. The similarity is due to the fact that in both cases the formation of an exciton is an intermediate stage, and the same excited states take part in the radiative transitions. As an example we show in Fig. 13 the photoluminescence spectra of poly[1,4-phenylene-1,2-di-(4-phenoxy-phenyl)vinylene], DPOP–PPV, measured at room temperature,

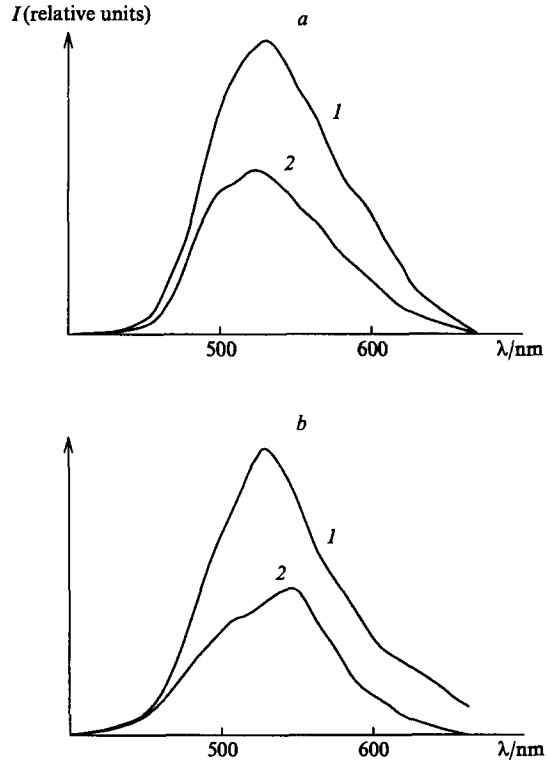
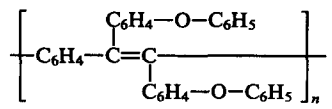


Figure 13. Photoluminescence spectra (*a*) of a layer of DPOP–PPV ($\lambda^{exc} = 370$ nm) and electroluminescence spectra (*b*) of a layer of DPOP–PPV in an ITO/PAn/DPOP–PPV/Al cell ($V = 12$ V) without (*1*) and with 10 wt.% of *o*-DNB (*2*).



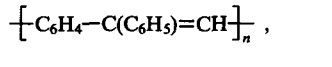
and their electroluminescence spectra, measured in an ITO/PAn/DPOP–PPV/Al cell with an applied voltage of 10–20 V. It can be seen that the EL and PL spectra lie in the same region (450–650 nm) and have a maximum at ~530 nm (2.34 eV) in the absence of additives.[98] The spectral changes produced by the addition of *o*-DNB are discussed below. In cells of this type the brightness of the EL is proportional to the density of the current flowing through the sample when the voltage is applied. The heating of the sample at high current densities shifts the EL spectrum towards shorter wavelengths.[105]

2. Photoluminescence of PPV derivatives

The fluorescence excitation and emission spectra of PPV are similar in form to those of *trans,trans*-1,4-distyryl benzene $C_6H_4(CH=CHC_6H_5)_2$,[123,124] bispropylstilbene[124] $C_3H_7-(C_6H_4-CH=CH)_2-C_6H_4-C_3H_7$ or oligomeric analogues having the structure $H-(C_6H_4-CH=CH)_n-C_6H_5$, $n = 3-7$.[125,126] In all these compounds the PL spectrum has a well resolved fine structure. The energy of the $S_1 \rightarrow S_0$ 0–0 transition (ΔE), measured from the fluorescence spectra in frozen (6 K) solutions of the oligomeric analogues of PPV, depends on the size of the π conjugation system (n) and corresponds to the Kohn potential box model[122,125–127]

$$\Delta E = \Delta E_\infty + \frac{\text{const}}{n}. \qquad (31)$$

An analysis of the optical absorption spectra of polyphenylphenylenevinylene (PPPV),



during the oxidation of the polymer (in contact with $SbCl_5$) showed[127] that, as the polymer was consumed by being converted into the oxidised form, the optical absorption maximum was hypsochromically shifted from 25×10^3 to 30×10^3 cm^{-1}. These changes, which suggest a nonuniform broadening of the spectra, were ascribed[126] to a nondegenerate energy ground state, i.e. to a weak exchange interaction of the overall collection of segments of the polymer with different effective lengths of conjugated bond systems. In this case the nonuniform broadening of the spectrum is due to the contribution of the optical transitions from conjugated segments having different n values [see Eqn (31)]. The longest conjugated segments are oxidised first, because they have the lowest ionisation potential. This results in a lowering of the optical density at the low-energy absorption edge of the initial polymer and in the appearance of three optical absorption bands belonging to the oxidised form. As the oxidation proceeds, increasingly short conjugated chains begin to contribute to the reaction (i.e. n decreases), and this produces a gradual hypsochromic shift of the spectra of both the initial polymer and its oxidation products.

By comparing the ΔE energies in the polymers and the oligomer analogues with the known values of n we can calculate by Eqn (31) the maximum length of the system of conjugated bonds in the polymers: it is found to be $n \simeq 5-7$ in PPPV and ~10 in PPV.[122,126,127] The value $n \simeq 4$ was obtained for the average length of the conjugation chain in PPPV,[127,128] and in other derivatives of PPV,[128] and this was ascribed to a nonplanar structure of the polymer chain. It was suggested[127] that because of the weak exchange interaction the photoexcitation generates a Frenkel exciton, delocalised within one particular conjugated region. During its random motion (spectral diffusion) the exciton

gradually loses energy and migrates towards more extensive regions of effective conjugation: thus, radiative transitions take place with a higher probability from the regions with the highest n value.

These concepts are consistent with the lack of dependence of the maximum in the fluorescence emission spectra on the energy of the exciting light $h\nu^{ex}$, which has been established experimentally for PPV and PPPV, if $h\nu^{ex} \geqslant h\nu^{loc}$, where $h\nu^{loc}$ depends on the morphology of the polymer and lies in the region of 2.5–2.36 eV [$\nu^{loc} \sim (20.2-19) \times 10^3$ cm^{-1}].[126,129] Lowering ν^{ex} into the region below ν^{loc} at 6 K produces uniformly broadened radiative transitions, resulting from the local excitation of the largest π conjugated segments.[126,129] Since the diffusion of low-energy excitons is hindered, the absorption and the emission of light take place in the same fragment. A dependence of the displacement between the maxima of the excitation and radiation PL spectra (Stokes shift) upon the degree of order in the polymer chains has been established for this case. This effect justifies the conclusion that the Stokes shift is determined by a change in conformation of the polymer chain in the photoexcited state[129] rather than by the electron–photon interaction, as had been suggested previously.[126] The Stokes shift is 500 cm^{-1} (0.062 eV) in PPPV, but it depends on the extent of conversion of the polymer **2** into the conjugated PPV, decreasing from ~100 cm^{-1} for $n \simeq 10$ (see Mahrt et al.[125]) to zero for $n \simeq 20$ (see Heun et al.[129]). In the highly oriented PPV crystals the Stokes shift is close to zero,[130] and singlet excitation extends over more than seven monomer units of the chain. These observations led to the conclusion that the electronic excitation in ordered crystalline PPV corresponds to the Wannier type of exciton.[130]

The PL quantum yield in 1,4-distyrylbenzene at room temperature[120,124] is ~94%. It is substantially lowered by changing to polymer analogues, and in PPV it is variously reported to be $\leqslant 0.1\%$ at room temperature[120,123] and ~4%–0.4% in the 10–293 K region.[124] Separating the basic π conjugated chains by introducing bulky side substituents in the change to PPPV increases the quantum yield at 10–293 K to 20%–10%, and if the PPPV is additionally diluted with polycarbonate the yield increases to 32%–25%. On these grounds it was concluded that a competition between radiative and nonradiative recombination is occurring. The nonradiative disappearance of the excitons is due to their capture by randomly distributed traps, formed by the interaction of the π conjugated chains of the polymer. The effectiveness of the capture of excitons by these traps is increased by the increase in their rate of migration at higher temperatures.

The EL and PL spectra of polyphenylenevinylene lie at ~2.6–1.8 eV, with a maximum at ~2.1–2.4 eV,[105,108] and they have similar fine structures with a resolution of ~0.16 eV.[120] However, in the partially conjugated polymer **2**, with segments containing the saturated precursor PPV, the PL and EL emssion spectra were found[118] not to be exactly identical: in particular, differences were noted in the relative intensities of the fine structure bands. These differences were tentatively ascribed to contributions to the PL and EL from different parts of the polymer chain.[118] The main contribution to the PL is provided by portions of the chain with a high content of nonconjugated segments, since on the conjugated segments the emission is preferentially quenched by nonradiative recombination processes. On the other hand, in EL the oppositely charged species can approach each other to within a distance which allows recombination within the conjugated regions, where the charge carriers have their highest mobility.[118]

Measurements of the EL and PL in DPOP–PPV are consistent with these arguments. As is shown in Fig. 13, the addition of *o*-DNB to the polymer (which increases the hole mobility[42]) lowers the intensity of both the EL and the PL, and therefore the *o*-DNB is acting as a quencher of the singlet excitation of the polymer. The suppression of the intensities is accompanied by a hypsochromic shift of the maximum of the PL spectrum and by a bathochromic shift of the maximum of the EL spectrum (see Fig. 13). These changes can be explained in terms of nonuniform broadening of the spectrum. Evidently, the displacement of the PL towards higher energies is associated with preferred interactions giving a CTC of the quencher with the most extensive π conjugation regions, which have the lowest I_π. The bathochromic shift in the maximum of the EL spectrum may be due to a simultaneous increase in the mobility of the charge carriers upon the addition of *o*-DNB, which increases their time of residence in regions with a more developed system of conjugated bonds.

According to published results EL and PL have different characteristic times. Thus, the application of nanosecond voltage pulses to a PPV film produces a decrease in the EL intensity which can be described by two exponentials with time constants of <11 and 60 ns respectively.[105] The slow component is determined by the distortion of the electric pulse by the *RC* constant of the sample, and the fast component by the EL process itself, which suggests the possibility of fabricating fast EL devices by optimising their geometry. Another important result of the pulse measurements was the observation of a proportionality between the current density and the brightness of the EL, up to current densities of the order of 10 A cm^{-2}. In the absence of limitations associated with the geometry of the sample the PL can be measured in the picosecond range. The decay of the PL also involves two components. Initially the PL intensity decreases 2.7-fold in PPV and PPPV at 10 K in ~135 and 430 ns respectively, and at room temperature in ~70 and 120 ns. Diluting the PPPV with polycarbonate increases this time to 780 ns and eliminates the temperature dependence. The slow component has a time constant of 1.1–1.4 ns,[124] which coincides with the 1.3 ns time constant measured in 1,4-distyrylbenzene.

3. Role of the spin constants in electroluminescence

Data on the electronic processes which accompany reaction (30) in EL diodes based on PPV and its derivatives were obtained by measuring the electric conductivity (σ) and the EL,[131] and also the PL [131,132] under conditions of paramagnetic resonance of the species which contribute to the process (electrons, holes, triplet excited states). These characteristics were measured at 20 K in diodes placed in the resonator of an ESR spectrometer, in which the magnetic field was scanned in the region of spin allowed ($\Delta m_s = 1$, $g \approx 2$) and of spin forbidden transitions ($\Delta m_s = 2$, $g \approx 4$). The increase in the PL intensity is accompanied by the appearance of a narrow signal ($\Delta H_{1/2} = 13$ *G*) with a g factor of 2.0023. Under paramagnetic resonance conditions the Boltzmann distribution of the population of Zeeman levels is perturbed as a result of the reorientation of the spins, and the fractional number of charged particles for which the charge recombination process (30a) becomes spin allowed is increased:

$$^3(p^{+\cdot}\uparrow \cdots e^{-\cdot}\uparrow) \xrightarrow{PMR} {}^1(p^{+\cdot}\uparrow \cdots e^{-\cdot}\downarrow) \quad p^{+\cdot} + e^{-\cdot} \qquad (32a)$$

Swanson et al.[131] assume that the increase in the PL under conditions of resonant change in spin orientation is due to the participation in reaction (30a) of the triplet pairs $^3(p^{+\cdot} \cdots e^{-\cdot})$, and that [as shown in the scheme (32a)] under spin forbidden conditions and in the absence of resonance these pairs dissociate into the free current carriers which are responsible for the photoconduction.[133] A broad spectrum (from 2600 to 4200 G) due to the increased fluorescence intensity produced by the reactions of the triplet excitons T_1 is superimposed on the narrow signal. The appearance of this spectrum shows that the probability of reaction (30c) in the competing processes

(30c) and (30d) is increased under paramagnetic resonance conditions.[131,132] For this reason the PL increases also in the region of forbidden transitions with $\Delta m_s = 2$, $g = 4.07$.

In contrast to the PL, a decrease in the electric conductivity σ and in the EL brightness was observed in the region of resonance spin transitions with $\Delta m_s = 1$. This effect is due to the possible existence, in equilibrium with the singly charged particles, of doubly charged particles with zero spin (depending on the chosen model, they have been called PPV^{2-} and PPV^{2+})[122,125-127] or bipolarons[121,131,132] bp^{++} and bp^{--}. As a result of the reorientation of the spins at resonance by the schemes (32b) and (32c) the probability of formation of doubly charged particles by scheme (32d) should increase:

$$p^{+\cdot}\uparrow + p^{+\cdot}\uparrow \xrightarrow{\text{PMR}} p^{+\cdot}\uparrow + p^{+\cdot}\downarrow \qquad (32b)$$

$$e^{-\cdot}\uparrow + e^{-\cdot}\uparrow \xrightarrow{\text{PMR}} e^{-\cdot}\uparrow + e^{-\cdot}\downarrow \qquad (32c)$$

$$p^{+\cdot}\uparrow + p^{+\cdot}\downarrow \rightleftharpoons bp^{++}$$
$$e^{-\cdot}\uparrow + e^{-\cdot}\downarrow \rightleftharpoons bp^{--} \qquad (32d)$$

According to Swanson et al.[131] the bipolarons have a much lower mobility than the singly charged current carriers, and therefore the decrease in σ and in EL under paramagnetic resonance conditions is interpreted as a confirmation that the reaction (32d) is taking place in the forward direction. In the region of forbidden transitions ($\Delta m_s = 2$) we find marked differences in the dependence of the EL and of σ on the magnetic field. Both these dependences demonstrate the two resonant transitions of the triplet excitons (low-field at 1.61 kG and high-field at 1.63 kG). Whereas σ is increased as a result of the two transitions the EL signal falls in the 1.61 kG region and rises at 1.63 kG. In agreement with reaction (30a) 75% of the charged particles form triplet excited states in their interaction. As in the case of the PL the increase in the EL is due to the increased probability of reaction (30c) under PMR conditions. It is assumed that the low-field triplet excitons with a resonance at 1.61 kG are more localised than the high-field excitons, and therefore that the process (30c) to which they contribute takes place in the immediate vicinity of the cathode surface. The S_1 singlet formed in the interaction with the electrode surface either undergoes nonradiative deactivation or rapidly decomposes into p^+ and e^-, the p^+ being discharged on the electrode. These changes lower the EL and increase σ under resonance conditions at 1.61 kG.[131]

Thus we conclude from the above discussion that the derivatives of PFV are usually characterised by a greater hole mobility, and that the reaction (30a) takes place in the space adjacent to the negatively charged electrode. The most serious problems are the decreased rate of the forward hole discharge reaction on this electrode, the equalisation of the concentrations of electrons and holes injected into the layer, and the limitation by the deactivation of excited S_1 states as a result of interaction with the electrode.

4. Quantum efficiency of the electroluminescence

The quantum efficiency η of the electroluminescence, defined as the ratio of the number of photons $h\nu$[f1] produced by the reactions (30) to the number of injected charges, depends on the mechanism of the motion of the charged particles, and also (as in the case of the PL) on the factors which affect the deactivation of the excited states.

It has been established[118] that the brightness of the EL in the ITO/polymer **2**/calcium cell depends on the degree of conversion of the saturated sulfur-containing precusor **1** into the π conjugated PPV, i.e. it is determined by the temperature and duration of the heat treatment of the precursor during the synthesis of the PPV. The quantum efficiency is 0.08% if the polymer **1** is heated for 2 h at 140 °C. If the two-hour heat treatment is increased the efficiency η initially increases to a maximum of 0.75% at 160 °C and then falls again to ~0.05% at 300 °C. Increasing the time of heating at 300° C to 20 h lowers η further to $\leqslant 0.003\%$. The PL intensity shows similar dependences on the temperature and time of the heat treatment. A substantial lowering of the PL and EL intensities upon increasing the length of the conjugated bond system has been ascribed[118,120] to an increase in the rate of diffusion of the excitons and in the mobility of the charge carriers, which increases the probability of their migration to sites responsible for the nonradiative recombination.

An analysis of the dependence of the mobility of holes on the degree of thermal conversion of the polymer **1** into the π conjugated PPV, or of other precursors in which the $S^+(C_4H_8)Cl^-$ group is replaced by chlorine, dimethyl-, or diethyl sulfide, or by the methoxy or butoxy group, has been reported.[134] In all the polymers prepared by this method, and whatever their degree of conversion, the hole mobility exceeds the mobility of electrons by more than two orders of magnitude. In spite of a marked lack of reproducibility of the results, increasing the number of conjugated segments in the polymer **2** produces an unmistakable increase in the mobility of holes, but this increase is suppressed by lengthy storage of the sample at room temperature or by heat treatment of the precursor above 150 °C.

Antoniadis et al.[134] were unable to detect the motion of charge carriers through a film of polymer having a high level of conjugation prepared by heat treating **2** for 2 h at 250° C. They showed that increasing the heat treatment temperature increases the dispersion of the time of flight of the charge carriers through the sample. These results were ascribed to the formation (after heat treatment at 150 °C) of polymer **2**, in which the regions of π conjugation include 2–3 phenylene-vinylene units. As was pointed out in Section II, the hopping model of transport, characteristic of many amorphous polymers, is applicable to this polymer containing isolated transport centres. As the extent of conversion of polymer **2** into PPV is increased, the size of the system of conjugated bonds also increases, and so does the dispersion of the times of flight through the transport layer, since the longest π conjugated segments (which have the lowest ionisation potentials) are hole traps. Furthermore, segments with a large n tend to form crystalline domains whose inclusion into an amorphous polymer produces an additional increase in the dispersion of the time of flight of the holes.[134]

In the copolymer of phenylenevinylene (PV) and 2,5-dimethoxy-*p*-phenylenevinylene (CH_3O–PV)[102] the EL spectrum is the same as in PPV, but the quantum efficiency increases more than 30-fold, reaching 0.3% for $m:n = 1:9$ in the ITO/copolymer/Al structure. Burn et al. point out[102] that the quantum efficiency can be increased to $\eta > 1\%$ by controlling the $m:n$ ratio during the synthesis through an appropriate choice of components:

$$-\{C_6H_4-CH=CH\}_n-\{C_6H_2(OCH_3)_2-CH=CH\}_m-$$

(CH_3O–PV)

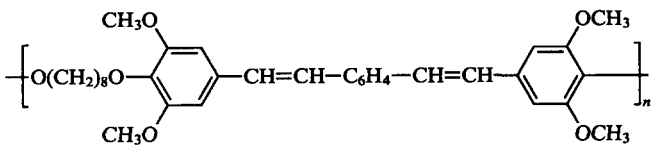
The PL radiation from this copolymer is characterised by two spectra with maxima at 555 and 608 nm, resulting from the different emissions of the PV regions in CH_3O–PV. In contrast to the EL, the PL intensity decreases on passing from PPV to the copolymer. As the $m/(m+n)$ ratio is increased from 0 to 0.33 the PL intensity decreases by about a factor of 8 and takes a constant value, characteristic of CH_3O–PV ($n = 0$).[135] It is suggested that the PL quenching in a copolymer is due to the photodissociation of excitons as a result of the transfer of an electron between parts of the chain of different nature.[135]

In the copolymer

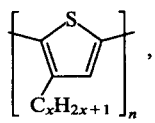
$$-\{C_6H_4-CH(OCH_3)-CH_2\}_m-\{C_6H_4-CH=CH\}_n-$$

the conjugated structures are also separated by segments containing different bonds. The maximum of the emission spectrum corresponds to 508 nm (2.44 eV). At this light energy the quantum efficiency of the EL is 0.02% in the ITO/polymer (1000 Å)/Al structure.[103]

The electroluminescence lies in the blue region, and has a maximum near 470 nm (2.64 eV), in a polymer whose chain is divided into short segments of conjugated bonds by longer chains of single bonds:[107]

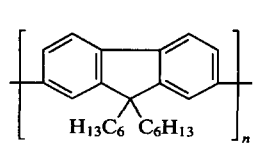


Attempts to prepare EL diodes on the basis of poly-(3-alkylthiophens) (PAT) have been reported: [100, 108, 109]



where $x = 8$ (see Ref. 100), 12, 18, and 22 (see Refs 108, 109). The electroluminescence is characterised by a broad spectrum with a maximum at 620–640 nm (1.9–2.0 eV). The position of the maximum in this spectrum is unaffected by the size of the neutral C_xH_{2x+1} side groups.[100, 108, 109] In the system based on poly(3-octylthiophen), replacing a Ca cathode by an In cathode increases the voltage needed to generate EL, but this does not affect the quantum efficiency of the reaction (30a) to a significant extent: in the diode based on Ca the parameter η lies in the range $10^{-4}\% - 10^{-3}\%$ [for working strengths of the electric field of $(0.2-0.7) \times 10^6$ V cm^{-1}], whereas in an In diode it lies in the range $(1-3) \times 10^{-3}\%$ [for fields of $(1-3) \times 10^6$ V cm^{-1}].[100] These low values of η were explained in terms of the presence in the final polymer of an impurity of $FeCl_3$, which is used in the synthesis and generates defects leading to the nonradiative recombination of the current carriers. A 4-fold increase of η upon increasing the length of the alkyl side chain x from 12 to 22 has been demonstrated.[108, 109] This observation led to the conclusion that the intermolecular interaction of the main chains containing the conjugated structures, which is weakened by an increase in x, is responsible for the nonradiative recombination of the charge carriers in these polymers as in the case of PPV. In PAT an increase in the applied voltage and in the current flow produce an anomalous superlinear increase in the EL.[108, 109] This effect is attributed to the increase in temperature and to the corresponding (temperature-induced) twist rotations of the main chains, leading to a shortening of the effective conjugation chain. The final result is a weakening of the intermolecular interaction of the main chains and a decrease in the rate of the nonradiative processes.

An electroluminescence with $\lambda_{max} = 470$ nm (2.5 eV) has been measured in a cell based on poly(9,9-dihexylfluorene):[111]



5. Effect of the material of the injecting layer

The efficiency of the EL can be improved by lowering the energy barriers which the electrons and holes have to surmount during injection. The quantum efficiency in single-layer diodes based on the derivatives of polyphenylenevinylene with p-type mobile carriers increases when cathodes such as Al (($\phi_2 = 3.8$ eV, see Fig. 12*a*)[136] or In ($\phi_2 = 4.2$ eV) are replaced by an electrode with a much lower work function, for example Ca ($\phi_2 = 3$ eV).[101] In a diode based on unsubstituted PPV [ITO/PPV (1000Å)/Al] the quantum efficiency (photons per electron) has been variously reported to be 0.01% (Refs 102, 103) or 0.05% (Ref. 100). When the aluminium cathode is replaced by a calcium cathode in this structure the quantum efficiency increases to 0.1%.[104]

In a diode based on poly[2-methoxy, 5-(2-ethylhexoxy)-1,4-phenylenevinylene], MEG–PPV [structural formula **3**, where $R^1 = O-CH_3$, $R^2 = O-CH_2-CH(CH_2CH_3)-C_4H_9$], ITO/MEG–PPV/In(or Ca), an electroluminescence in the spectral region between ~1.6 and 2.3 eV with a maximum at ~2.15 eV (at 300 K) or two maxima at 2.03 and 1.88 eV (at 90 K) is produced at voltages above 1.8 V.[97, 101] For a constant diode current density of 2 mA cm^{-2} the quantum efficiency is 0.05% and 1% (photons per electron) in the case of an In or a Ca cathode respectively.[101] In both diodes the increase in η is due to the fact that lowering the electronic work function strengthens the injection of electrons into the polymer for a constant hole current. It should also not be forgotten that in polymers with mobile carriers of a single sign (holes) the injected electrons are captured in traps directly on the metallic electrode, and recombination with formation of excited states by reaction (30) also takes place on the cathode. Under these conditions the nonradiative dissipation of the exciton energy on the metallic surface can compete effectively with the radiative $S_1 \rightarrow S_0$ transition (30).

Attempts to solve these problems have been made by synthesising derivatives of polyphenylenevinylene in which charge carriers of both signs are mobile,[42, 43, 98, 137, 138] and their recombination by reaction (30a) takes place not only in the immediate vicinity of the electrode but also throughout the polymer layer. For example, charges of both signs are mobile in the polymer DPOP–PPV. At 20 °C the quantum efficiency of reaction (30), measured at the emission maximum (530 nm, see Fig. 13) in ITO (or PAn)/DPOP–PPV (3000 Å)/Al cells for a constant voltage of 20–40 V, was 0.13% in the case of the ITO anode ($\phi_1 = 4.1$ eV,[97] see Fig. 12), and was increased to 0.38% by changing to a PAn anode ($\phi_1 = 4.3$ eV,[97]).[98] In the latter case the energy efficiency of the transformation of electric into light energy is 0.32%. As can be seen, when polymers with mobile carriers of both signs are used the anode material also has a marked effect on the quantum efficiency of the EL. In contrast, in a cell based on the MEG/PPV polymer, in which only the holes are mobile, the quantum efficiency of the EL is unaffected by replacing ITO by PAn: the current through the cell is increased by a factor of 10^3-10^4 for applied voltages below 1.5 V, but it ceases to be a function of the anode material at voltages above 1.8 V, where the EL is produced in the bulk of the polymer.[97] In this case, as was pointed out above, the controlling processes are those taking place directly on the cathode and involving its material.

6. Molecularly doped polymers

Molecularly doped polymers, in which compounds with both donor and acceptor properties are introduced into the polymer matrix to generate transport at both holes and electrons,[112] are a special class of electroluminescent layer. Poly(methyl methacrylate) (PMMA) is often used as the polymer matrix. Direct measurements of the mobility of the excess charge carriers in PMMA in the absence of additives or in the presence of a donor (triphenylamine, TPA) and an acceptor (chloranil, CA) showed[139] that the polymer matrix itself is reactive towards the excess electrons. Dissociative electron capture by the polymer

matrix competes effectively with all electron transport processes, and no electron drift from the generation region can be observed. No motion of holes is detected in the undoped PMMA because of the presence of structural traps (T), which capture holes according to the scheme

$$T + p^{+\cdot} \longrightarrow T^{+\cdot}.$$

The drift of holes begins at temperatures above 50 °C and 80 °C in the presence of TPA and CA respectively, but it is observed at room temperature in the simultaneous presence of TPA and CA. The formation of donor–acceptor complexes was not detected even at the maximum concentration of the dopants, which corresponded to an average intermolecular distance of ~20 Å. It was therefore concluded that the effect of the dopants on the drift of the holes was additive. It was suggested[139] that the drift of holes takes place by a hopping mechanism (between TPA molecules):

$$TPA^{+\cdot} + TPA \longrightarrow TPA + TPA^{+\cdot}.$$

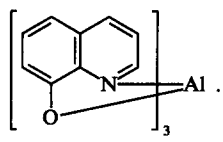
Under these conditions the structural traps terminate the transfer by the scheme

$$TPA^{+\cdot} + T \longrightarrow TPA + T^{+\cdot}.$$

Chloranil interacts with defects of the hole trap type, lowering their concentration and thus increasing the drift mobility of the holes:

$$CA + T \longrightarrow CA^{-\cdot} + T^{+\cdot}.$$

The donor *N,N'*-bis(*m*-tolyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD, see Fig. 1) was used to provide transport centres for p-type carriers in a single-layer EL diode based on PMMA, and the aluminium complex of tris(8-hydroxyquinoline) (Alq_3) was used as the acceptor:[112]



In systems based on two evaporated layers (a donor and an acceptor) the EL spectrum is shifted towards lower energies with respect to the PL spectrum of the individual component as a result of the formation of a charge transfer complex (responsible for the emission) or of an exciplex.[140] In a system consisting of a PMMA matrix containing TPD and Alq_3 the EL spectrum coincides with the PL spectrum of the complex of Alq_3 in PMMA and has a maximum at 510 nm (2.44 eV). Steric hindrance to the formation of an exciplex with the donor (TPD)[112] may be created by the octahedral configuration of the metal in the Alq_3.

The following jump model of the bipolar transport of charge carriers in this composition, involving the oxidation–reduction reaction

$$TPD^{+\cdot} + TPD \longrightarrow TPD + TPD^{+\cdot}$$
$$Alq_3^{-\cdot} + Alq_3 \longrightarrow Alq_3 + Alq_3^{-\cdot},$$

has been proposed, followed by the recombination

$$TPD^{+\cdot} + Alq_3^{-\cdot} \longrightarrow Alq_3^{*} + TPD$$
$$Alq_3^{*} \longrightarrow Alq_3 + h\nu^{fl}.$$

The luminescence of Alq_3 has been detected in the photoexcitation of the TPD in this composition, and therefore the possibility of the following reaction cannot be excluded:

$$TPD^{+\cdot} + Alq_3^{-\cdot} \longrightarrow Alq_3 + TPD^{*}$$
$$Alq_3 + TPD^{*} \longrightarrow TPD + Alq_3^{*}.$$

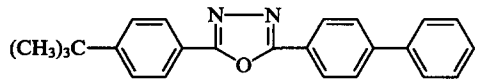
The diode current and the EL brightness are shown below for different TPD : Alq_3 ratios (by weight) in a diode based on ITO/TPD : Alq_3 : PMMA (1000 Å)/Mg with an applied voltage of 17 V and a ratio by weight of (TPD + Alq_3) : PMMA = 0.5.

TPD : Alq_3	0.43	0.67	1.0
i/mA cm^{-2}	60	170	90
EL/cd m^{-2}	180	920	430

7. Systems with separate transport layers

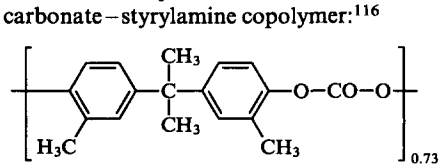
In order to minimise the direct discharge of the mobile current carriers on the electrodes, diodes consisting of two polymer layers (one providing electron transport, the other, hole transport) have been fabricated. We shall discuss them below, together with the characteristics of structures consisting of a polymer layer and an evaporated layer of a low-molecular compound. In these diodes the radiative recombination of injected charges is shifted from the cathode region to the region close to the boundary of the two polymer layers[96, 103–105, 107] (see Fig. 12*c*).

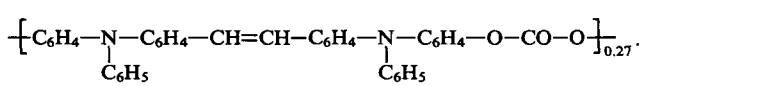
Brown et al.[104] have described the main characteristics of an EL diode consisting of PPV in contact with an electron transporting layer: 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD)



molecularly dispersed in PMMA. The EL spectrum of the structure ITO/PPV (3500 Å)/PBD in PMMA (300 Å)/Ca is identical to the EL spectrum of the PPV polymer. Hence the PPV layer is responsible for the emission of light in this two-layer system. The upper edge of the filled band in PPV lies ~1.5 eV above the highest occupied level of PBD, and the injected holes accumulate and contribute to reaction (30a) in the PPV layer near the PPV/PBD boundary (Fig. 12*c*). The accumulated holes create a large space charge which strengthens the electric field in the electron transport layer. This effect produces an increase in the number of injected electrons, and consequently an increased EL brightness. The quantum efficiencies of the two-layer and the single-layer structures (in the absence of PMMA containing PBD) for a current density of 1 mA cm^{-2} are, respectively, 1.1% and 0.07%, and at a current density of 15 mA cm^{-2} they are 0.8% and 0.1%. In the two-layer structure the ratio of luminescence brightness to current density is 0.85–0.6 cd A^{-1} over a wide range of current densities. In the one-layer structure this ratio is 0.017 cd A^{-1}, increasing to 0.034 cd A^{-1} when the current density is increased to 15 mA cm^{-2}.

The two-layer structures include a system based on a carbonate–styrylamine copolymer:[116]





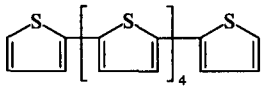
The self-repeating styrylamine segment is responsible for the transport of holes and the emission of light. An electron-transport layer of PBD was evaporated onto the polymer.[116] ITO and Mg were used as electron and hole injecting electrodes respectively. The electroluminescence was characterised by λ_{max} = 460 nm (2.7 eV), the brightness was 130 cd m^{-2} for a current of 80 mA cm^{-2} and an applied voltage of 11 V. The conversion of electric energy into light energy was 0.05 lm W^{-1} at 11 V.[116]

The evaporated electron-transport layer of PBD was studied[115] in conjunction with polymethylphenylsilane (PMPS, see Fig. 1) doped with a europium complex, tris(phenyltrifluoroacetonato)europium, responsible for the transport of holes and the electroluminescence. ITO and Mg were used as the anode and the cathode respectively. A weak EL was observed in the red region, the luminescence being brightest (0.3 cd m^{-2}) at 18 V: it was attributed to the fact that effective nonradiative recombination of charge carriers can take place in europium complexes.

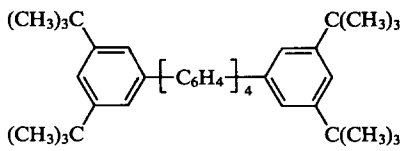
In the absence of additives the polymer PMPS is a p-type organic semiconductor, with a drift mobility of holes of 10^{-4} cm^2 V^{-1} s^{-1} at 20 °C. The ITO/PMPS (350 Å)/Alq_3 (1000 Å)/Mg system, in which a layer of Alq_3 had been evaporated onto the PMPS layer, produced EL with a maximum at 520 nm:[114] an applied voltage of 18 V produces a diode current density of 150 mA cm^{-2}, and the brightness of the electroluminescence rises to 1500 cd m^{-2}. Decreasing the thickness of the Alq_3 film to 600 Å lowered the brightness to 400 cd m^{-2}. Increasing the thickness of the PMPS layer from 350 to 460 Å did not affect the brightness, but decreasing it from 350 to 220 Å lowered the brightness approximately five-fold.

Studies of systems prepared from PMPS (350 Å) and Alq_3 (1000 Å) revealed a serious shortcoming of two-layer structures: the heating produced by high current densities through the device induces crystallisation of the evaporated film, which rapidly degrades the diode by disrupting the contact between the layers. It was established that at high enough voltages (20 V) the EL is irreversibly quenched in a period of a few seconds.

Alq_3 emission was observed[99] in cells having the structure ITO/T6 (200 Å)/TBP/Alq_3 (600 Å)/Mg, where T6 is the oligothiophen



(I_π = 5.2 eV, E_π = 2.9 eV), TBP is the tetrabutyl derivative of the six-ring polyphenyl



(I_π = 5.7 eV, E_π = 2.9 eV); EL was observed in the region of 450–700 nm with a maximum at 510 nm, due to the emission from Alq_3.[99] A linear dependence of the EL brightness on the device current density (i) and a superlinear increase of the current density with the applied voltage V were discovered: for $V > 4$ V, $i \propto V^n$, where $n > 9$. At voltages of 9 and 13 V the following characteristics were obtained for the EL cell with and without a TBP layer (300 Å thick).

	Without TBP	With TBP	
V/V	9	9	13
i/mA cm^{-2}	93	93	313
EL/cd m^{-2}	290	700	2300

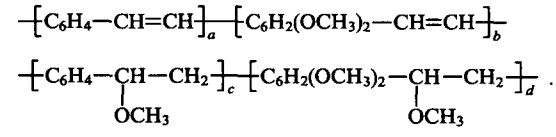
At V = 9 V the conversion of electric energy into light energy is 0.1 lm W^{-1} in the cell without a TBP layer and 0.32 lm W^{-1} when the TBP has been included. The large increase in brightness of the EL as a result of the insertion of a TBP interlayer is ascribed[99] to the suppression by the TBP of the penetration of electrons, which inhibits the transfer of energy from the emitter to the semiconductor polymer.

The brightest EL was obtained in a two-layer system, in which a film of Alq_3 was deposited by vacuum evaporation on a polymer layer of PMMA or polycarbonate (PC) doped with TPD (see Kido et al.[117]). An increase in EL brightness upon increasing the dopant concentration was observed in the diode based on ITO/TPD:PMMA (400 Å)/Alq_3 (500 Å)/Mg. At an applied voltage of 16 V the following dependences of the diode current density and of the EL brightness on the ratio by weight of TPD:PMMA were obtained:

TPD:PMMA	0.3	0.5	0.8
i/mA cm^{-2}	100	180	420
EL/cd m^{-2}	1400	2300	7400.

Comparing these characteristics with those given above for the ITO/TPD:Alq_3:PMMA/Mg system shows that the change from a one-layer to a two-layer structure increases the brightness of the EL by almost an order of magnitude. A further increase in brightness was obtained by using a matrix of PC: for a component ratio of TPD:PC of 0.5 and an applied voltage of 14 V the diode current density reaches 420 mA cm^{-2}, and the EL brightness reaches 7700 cd m^{-2} (see Kido et al.[117]). It has been suggested that the improvement in the EL characteristics on replacing PMMA by PC is associated with the corresponding increase in the rate of hopping transport, resulting from the higher glass transition temperature and greater aromaticity of the PC. In the light of the results obtained with evaporated layers of low-molecular-mass compounds,[141] we can expect further improvements in the EL brightness by replacing the Alq_3 by other metal complexes, for example bis(10-hydroxybenzo-[h]quinoline)beryllium.

Electroluminescent diodes containing several mutually insoluble polymer layers are of considerable interest:[106] for example, MEG–PPV, or PPV and a copolymer having the structure



Structures of four types were studied:

A. ITO/copolymer/PPV (2300 Å)/MEG–PPV/Ca;
B. ITO/MEG–PPV/PPV (500 Å)/copolymer/Ca;
C. ITO/copolymer/MEG–PPV/PPV (1500 Å)/copolymer/Ca;
D. ITO/copolymer/PPV (300 Å)/copolymer/Ca.

In all the structures the thicknesses of the copolymer and of the MEG–PPV layers were 200 and 500 Å respectively. The quantum efficiency of reaction (30) was measured for light intensities of 5 cd m^{-2}: it was found to be η = 0.3%, 0.22%, 0.26%, and 0.16% (photons per injected electron) for the structures A, B, C, and D respectively. It was found that the structure A is the sole one for which only the (MEG–PPV) layer contributes to the EL spectrum (the characteristics of this spectrum are quoted above). Polyphenylenevinylene and the copolymer are responsible only for the transport of holes. Neither the electrons nor the excited states formed by reaction (30) extend beyond the (MEG–PPV) layer. The structure B is characterised by a broad emission spectrum, lying at 1.62–2.5 eV with a maximum at 2.13 eV. The intensity of the

radiation of light quanta with an energy of 1.75 eV is 15% of the maximum value (I_{max}). In this spectral region the MEG–PPV is the only luminescent component, and neither the copolymer nor the PPV emit radiation. At the same time the intensity of the emission of light quanta with an energy of 2.35 eV reaches 30% of I_{max}. This emission lies beyond the limits of the emission spectrum of MEG–PPV, and is due to the formation of excited states in the PPV or in the copolymer. The emission spectrum of the structure C is identical to that obtained for the structure B, confirming that both the intermediate MEG–PPV layer and the PPV (or the copolymer) layer are contributing to the process. The emission spectrum of the cell D also contains contributions from the radiation of the PPV and of the copolymer. Thus by allowing for the thickness of the individual layers we may conclude that the emission zone of the structures B–D extends over more than 500 Å. According to calculations the distance travelled by the charge carriers before their encounter is 2600 Å. The distance to which a neutral excitation can diffuse is $(Dt)^{1/2} \approx 50$ Å [D is the diffusion coefficient ($D \simeq 10^{-3}$ cm^2 s^{-1})], t is the lifetime of the excited state ($t \simeq 0.25$ ns)]. It can be seen that this distance is 10 times smaller than the emission zone. Thus the mobile species responsible for the fairly extensive emission zone are the charge carriers and not the excited states. The preparation of structures from layers emitting light in different spectral regions may provide a path to the development of EL sources of white light.

We may conclude from the above arguments that the best characteristics obtained from different structures are the following: quantum efficiency of the conversion, 1%;[118] brightness, $\sim 10^4$ cd m^{-2} (see Kido et al.[117]); stability of the parameters of the light-emitting polymer diode, 16 h.[118] The wide practical exploitation of EL layers now depends on the prospects of combining all these favourable characteristics into a single layer and of greatly increasing its operating and storage life.

V. Injection of charges into polymer transport layers

Our discussion has shown that in EP and EL systems the charge carriers can surmount various phase separation barriers: metal–polymer, inorganic semiconductor–polymer, and molecularly doped polymer–polymer with conjugated bonds.

In the EP layers light absorption in the generation layer produces charge carriers which are then injected into the transport layer. The properties of the contact (layer of molecules with developed regions of conjugated bonds)/(molecularly doped polymer layer), often used in EP and EL systems, have been extensively reviewed by Kanemitsu and Imamura[142] in the specific case of a polyester (PC), and of doped DEH/phthalocyanine. Like PPV, polythiophen (PT), and PAn, phthalocyanine contains a system of conjugated bonds which produces photosensitivity. This allows a given concentration of charge carriers to be generated in the material, providing quantitative data on the injection coefficient.[142] The sensitivity of the photoreceptor is defined as the ratio of the number of charges passing through the transport layer to the number of photons absorbed in the generation layer; for a given value of the electric field the injection coefficient of the carriers $\eta(F)$ is calculated as the ratio of the number of charge carriers (determined by electrophotographic or time of flight methods) passing through the molecularly doped transport layer to the number of photogenerated carriers which abandon the generation layer through its interface with the transport layer (photoacoustic method); the photoinjection coefficient η_f is the ratio of the number of carriers crossing the transport layer to the number of photogenerated free charge carriers.

Clearly, $\eta(F)$ is determined by the competition between the transport of charge carriers and their capture by deep traps at the interface, and it can be measured only by using pulse kinetic methods, whereas η_f depends on the rate of recombination of the photogenerated charges in the generation layer and on the rate of injection through the boundary. Since the ionisation potentials of DEH and phthalocyanine are almost identical (5.5 and 5.4 eV respectively) an interfacial barrier is not formed at the contact between the layers.

The parameter $\eta(F)$ increases markedly when F is increased: in a field of 10^5 V cm^{-1} $\eta(F)$ is 0.1, but it increases to 0.7 in a field of 10^6 V cm^{-1}. This effect is associated with the fact that the mobility of holes increases exponentially with F, as was shown in Section II, and their time of flight through the boundary and of capture by traps decreases correspondingly. It is interesting to note that increasing the concentration of the hydrazone DEH in the transport layer lowers $\eta(F)$ slightly. This effect is determined by the capture of holes at the interface by traps of an unspecified type, associated with the method of establishing the interface, of forming the charge transfer complexes between the hydrazone and the phthalocyanine, etc. Similar results were obtained in studies of the injection of positive charges from PPV into a transport layer consisting of polycarbonate molecularly doped with diaryldiamine (TPD).[134] In this case the injection coefficient in a field of 4×10^5 V cm^{-1} is equal to or greater than 0.25, and only a small trapping of carriers is observed at the interface of the two polymer layers at large F values.

These results suggest that in relatively high fields the interface between two polymer layers of different nature is permeable to the transfer of positive charge. However, in lower fields we must allow for the trapping of holes at the layer interface, leading to the formation of a barrier as a result of the passage of a sufficiently high electric current. Under stationary conditions $\eta(F) = 1$, and the barrier affects the value of η_f and the electric characteristics of the EP and EL devices. The interface between SeTeAs and a transport layer consisting of PVK or PC doped with pyrazoline derivatives has been examined in depth.[143–145] Under stationary conditions the following relationship is obeyed:[145]

$$\eta_f = a\left[(1 + 2\eta_c/a)^{1/2} - 1\right], \tag{33}$$

where $a = [k_i(F)]^2/2J_0k_r$ (k_i is the injection rate constant, k_r is the rate constant of the recombination in the bulk of the generation layer), η_c is the quantum yield of the photogeneration of free charge carriers. In large fields with $(2\eta_c/a) \ll 1$ it follows from Eqn (33) that $\eta_f \simeq \eta_c$, i.e. that all the generated charges are injected into the transport layer, and η_f is determined exclusively by η_c and is independent of the nature of the transport layer. In moderately large fields, when $(2\eta_c/a) \gg 1$, $\eta_f = (2a\eta_c)^{1/2}$ and η_f is determined, among other factors, by the function k_i, which depends on the height of the barrier formed at the interface as a result of the capture of holes by deep traps. It was found[145] that for a constant generation layer, and with a transport layer consisting of pyrazoline with $N(C_2H_5)$, OCH_3, and H as substituents, and also PVK, η_f decreases: for example an η_f value of 0.15 is reached in this series of compounds for $F = 1.7 \times 10^4$, 4×10^4, 1.2×10^5, and 2.5×10^5 V cm^{-1} respectively. In very strong fields ($F > 5 \times 10^5$) the differences between the field dependences for different layers disappear, and η_f becomes equal to 1. Thus in strong fields all the photogenerated charge carriers are injected into the transport layer, but in weak fields η_f depends on the nature of the transport layer, and in particular on the ionisation potential of the transport centres.

In multilayer EL systems the application of a potential difference introduces dark charge carriers into the luminescent layer, unlike the EP systems, in which photogenerated carriers are introduced into the transport layer. In EL diodes the energy efficiency of the conversion of electric current into light is strongly dependent (as it is in EP photoreceptors) on the

injection mechanism of charge carriers into the EL layer, but it should be noted that in this case dark charges are injected and the injecting layer should be transparent to the emitted light. In practice this means that ITO is used as a hole-injecting transparent and conducting layer. Let us examine in detail a typical ITO/PPV/Ca structure,[106] whose energy diagram is shown in Figs 12*a* and 12*b* . To make the discussion simpler and more meaningful we shall assume that the contacts between layers are neutral, i.e. that the PPV region, in direct contact with the interfaces, does not contain space charges.[146] In this case a potential difference $V_{1,2} = \phi_1 - \phi_2 = \varphi_1^e - \varphi_2^e$ is generated in the semiconductor: this impedes the access of electrons from the Ca and of holes from the ITO to the PPV layer, and the electric field is uniform in this layer ($F = V_{1,2}/L$). The barriers for electrons are given by the expression $\varphi_i = \phi_i - E_\pi$, and for $E_\pi = 2.5$ eV they take the values $\varphi_1^e = 1.6$ and $\varphi_2^e = 0.5$ eV (Fig. 12*a*). The application of a large external potential V (with its negative polarity on the electrode with the lower work function) produces a relative shift of the Fermi levels: ($E_{F1} - E_{F2} = eV$), and as can be seen from Fig. 12*b* the electrons and holes can easily overcome the barriers φ_2^e and φ_1^H. Since in PPV the holes are mobile but the electrons are captured by traps in the polymer near the metallic electrode, recombination takes place at the surface of the metal layer in parallel with the discharge of holes at the cathode.

The inclusion of an additional PBD electron transport layer between the Ca and the PPV (see Fig. 12*c*) creates a barrier to the motion of holes at the PPV/PBD boundary (φ_3^H), where the holes accumulate and recombine with the electrons drifting towards this barrier, with emission of luminescence. As was shown in the previous section, the PBD layer greatly improves the efficiency of the EL. Additional layers are added not only to create barriers opposing the escape of charges from the EL layer but also, conversely, to lower the barrier at the boundary of the EL layer. Thus, as was shown above, the insertion of oligothiophen[99] or PAn[97] between the EL layer and the metallic anode greatly increases the hole current because the edge of the valence band of the conjugated polymers lies only slightly above the Fermi level in the ITO. Evidently, neutral contacts are actually formed, in most cases, at the interface between polymer layers. A more complex state of affairs is found at the metal/polymer interface. The simple model of neutral contacts, though qualitatively consistent (in general) with experimental results, fails to explain many important observations. Since the work functions of Ca and Al differ by almost 1 eV we would not expect significant current flows at the PPV/Al interface because of the height of the φ_2^e barrier. Nevertheless, replacing the Ca by Al lowers the current (for the same bias) by only 1–2 orders of magnitude. Furthermore the neutral contact gives a linear current–voltage characteristic for both positive and negative bias.[145] In reality a rectification effect is observed at the metal/polymer boundary, and with forward bias the current is exponentially dependent on the potential, which is characteristic of a Schottky barrier.[147, 148] In this case a space charge is formed near the electrode in the polymer, and the applied potential is dropped mainly in the space charge region.

A Schottky barrier or an ohmic injecting contact can be formed at the contact between the metal and the polymer (doped with conjugated molecules or containing conjugated double bonds in the main chain), depending on the work function ratio of the metal and of the polymer. Metals with the lowest possible work function are chosen to inject electrons into an EL layer. A Schottky barrier is formed at the contact with In or Al, because these metals have a relatively high work function: $\phi = 4.2$ and 3.8 eV respectively. Changing to Ca ($\phi = 3$ eV) increases the EL by more than an order of magnitude. Nevertheless even in this case a barrier to electrons is formed. This is an important feature. A study of the metal/PPV interface by X-ray emission spectroscopy showed[119] that the bending of the bands in the PPV gradually increases, starting with an Al layer approximately 1 Å thick (monolayer), and reaching a constant value for an evaporated thickness of about 5 Å. No chemical interaction between the Al and the PPV is observed under these conditions. Conversely, when calcium is evaporated as an electrode the bands in the PPV begin to bend only when the thickness of the Ca layer reaches 8 Å, and at 15 Å the process goes to completion and the energy of the bond falls by 0.4 eV. As in the case of Al no interaction takes place between the Ca and the PPV. The behaviour can be explained by the presence on the surface of oxygen as hydroxyl groups and of sulfur as sulfide groups, formed during the synthesis of the polymer. These impurities protect the PPV macromolecules from attack by the calcium. Thus the real metal/polymer contact is a multilayer structure including metal oxides and other compounds.

Studies of polyacetylene, PAn, and other polymers with p-type conductivity have shown that a Schottky barrier is formed at the contact with metals having a work function $\varphi_M < 4.5$ eV. Because of the low charge mobility in polymers the electrons are transmitted through the barrier by a diffusion mechanism rather than by thermionic emission (as in extrinsic inorganic semiconductors).[147, 148]

For a sufficiently high potential difference the current is exponentially dependent on the temperature:

$$J_d = J_{0d}\left[\exp\left(\frac{eV}{nkT}\right) - 1\right], \tag{34}$$

where

$$J_{0d} = e\mu N_c F_g \exp\left(-\frac{e\varphi}{kT}\right),$$

and n is the ideality factor (in our case, close to 1), N_c is the effective density of states in the polymer, F_g is the electric field at the barrier, and φ is the height of the barrier at the metal/polymer contact, equal to the difference between the corresponding work functions.[147] The upper limit of the injection current is set by the resistance of the polymer layer, and therefore the smaller the thickness of the EL layer, the greater is the injected current, and the greater the energy efficiency of the transformation. The temperature dependence of the current through the aluminium/poly(3-octylthiophen) interface was used to establish[149] that an over-barrier transition takes place at temperatures above 340 K. At low temperatures the injected currents are greater than the values expected for a diffusion mechanism: this suggests a tunnel effect.

At the boundary between a metal with a high work function and a p-type semiconductor polymer, such as Au ($\phi = 5.2$ eV)/PPV, we find an ohmic contact[150] which efficiently injects holes into the transport layer. We should note that studies of the mechanisms of carrier injection from solid electrodes into polymer layers are much less widespread than the studies of transport and of electroluminescence: this state of affairs is inconsistent with the important role of injection in the processes which we have considered.

* * *

Our discussion has shown that the problems of electron transport in disordered dielectric layers are closely associated with a number of fundamental questions: the mechanism of electron transfer between identical centres in an organic medium, the effect of the physicochemical characteristics of the medium on the transfer, the formation of excited light-emitting recombination states, and the need to optimise the electric and the light-emission parameters of the organic layers used in newly developed and widely used optoelectronic devices. Studies in these directions should help the achievement of interesting new results and should assist the further progress of the problem as a whole.

This study was carried out with financial support from the Russian fund for fundamental research (project 93-03-5703) and from the American Physical Society (Sloan Foundation Grant).

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