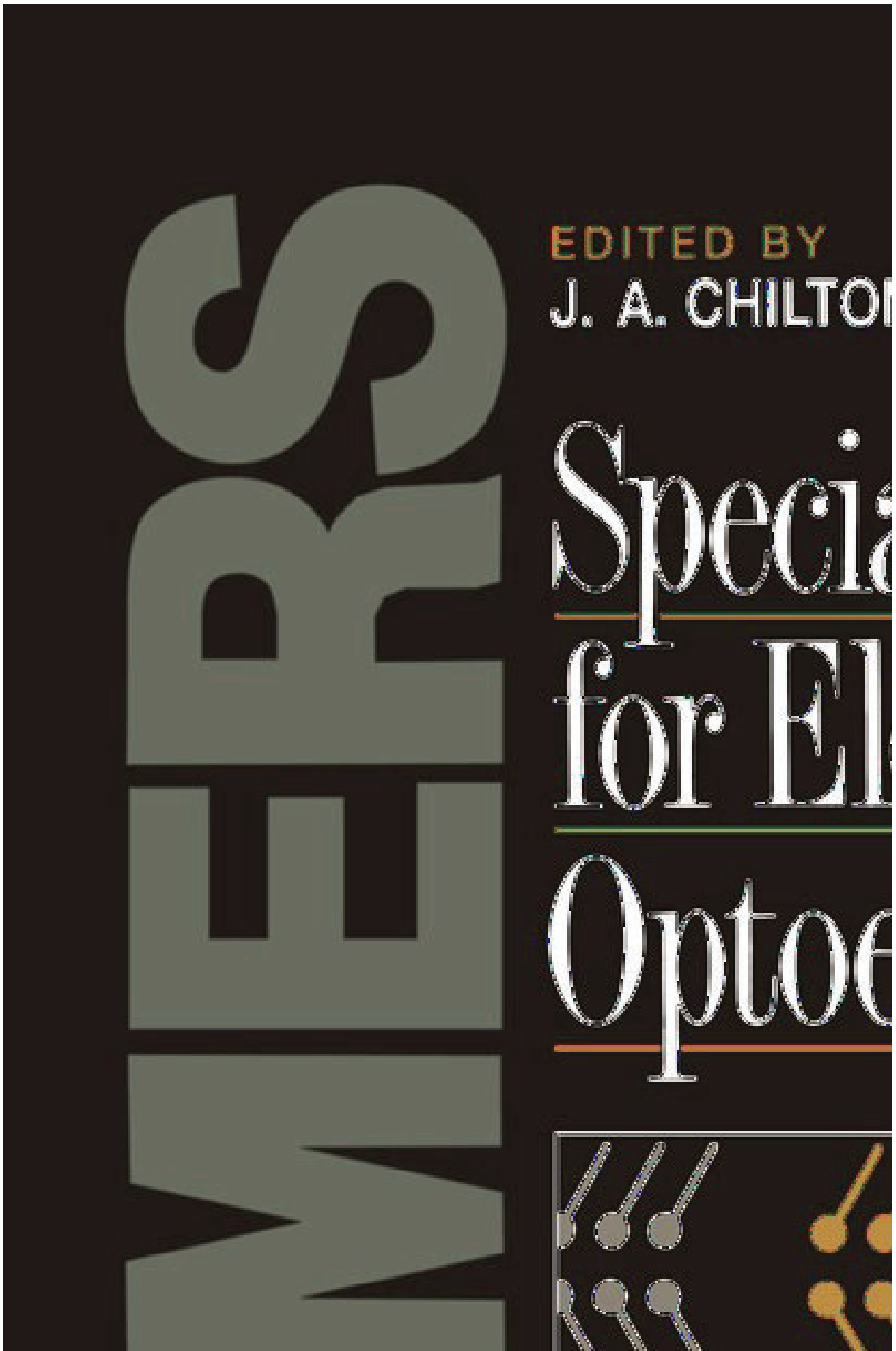




Special Polymers for Electronics and Optoelectronics

Special Polymers for Electronics and Optoelectronics

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Photoconductive polymers

M. Stolka

8.1 INTRODUCTION

Photoconductivity is the increase in electrical conductivity of a material caused by absorption of electromagnetic radiation. Photoconductive polymers are typically very good insulators in the dark, when the carrier(s) of electricity, free electrons and/or holes, are virtually absent. They become more conductive when exposed to light. In order to become a photoconductor, the polymer must satisfy two major requirements:

1. It must absorb light and thus allow photoexcitation of electrons from the ground state. The vacancy left behind (a hole) and the photoexcited electron form a pair of charge carriers, which can be separated by the action of an electric field.
2. It must allow migration of either photoexcited electrons or holes, or both, through the polymer in the electric field towards the appropriate electrodes. Since no ions move and matter is not displaced, the conduction process is wholly electronic, with no ionic contribution.

Polymers that do not absorb light of a particular wavelength can still support migration of charge carriers generated in an adjacent material. In such a case the polymers act merely as charge-transporting media. Since most known organic photoconductive polymers absorb only ultraviolet radiation, extrinsic photogeneration of charges has to be employed to make those polymers active in visible light, and in most practical organic photoconductors the polymers are only charge-transporting media for charges photogenerated in adjacent photoconductors.

Photoconductive and charge-transporting polymers can be either p-type or n-type, depending on the 'majority' carrier. Only in the special cases discussed below can polymers be bipolar, i.e. capable of trans-

porting both electrons and holes with comparable mobilities. However, most known photoconductive polymers are p-type; they can transport only holes.

One of the often neglected factors that influences the performance and efficiency of polymeric photoconductors is the nature of the electrodes used. Some electrodes, typically those with low work functions, can inject holes into photoconductive and charge-transporting polymers. With these so-called 'Ohmic' electrodes, the system will exhibit electronic conduction due to migration of injected charges even in the dark when no free carriers are generated in the polymer. In the presence of light that is absorbed by the polymer, the injected carriers add to those that are photogenerated in the bulk of the polymer. Alternatively, when 'blocking' electrodes are used, i.e. those that do not inject charges into the polymer, the same polymer may appear to be a good insulator in the dark and a good conductor in the light.

For each known photoconductive polymer, there exists a whole spectrum of electrodes ranging from perfectly Ohmic to perfectly blocking. Therefore in studies of steady-state photoconductivity one has to determine the role of electrodes before making any judgement about the quality of the photoconductor.

The development of organic polymeric photoconductors was stimulated by the discovery that poly(*N*-vinylcarbazole) (PVK, Fig. 8.1), sensitized by certain dyes and pigments, displays high enough photoconductivity [1] to be usable in electrophotographic photoreceptors.

Since then, hundreds of photoconductive polymeric compositions have been disclosed in the patent and open literature (for references see the reviews [2]). Unfortunately, the description of photoconductivity in these polymers was often limited to statements indicating that the polymers show photoconductivity 'as good' or 'better' than PVK, or at best some steady-state measurements were performed, often without reference to the nature of electrodes, the light source etc. Only in the past two decades have the basic parameters of photoconductivity (the

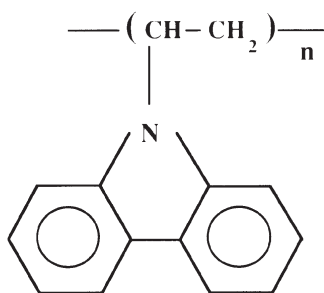


Fig. 8.1 Poly(*N*-vinylcarbazole) (PVK).

quantum efficiency of carrier generation and the carrier mobility) and their dependence on electric field, temperature, concentration etc. been analysed and functional models developed. PVK often served as a model material for these studies.

It should be noted that photocurrents usually observed in organic polymers are small, primarily because of the very low charge-carrier mobilities. The charge drift mobilities μ (defined as the velocity per unit electric field) are typically 10^{-12} – $10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ at the normally used electric fields of 10^6 – 10^8 V m^{-1} . For comparison, carrier mobilities in crystalline anthracene are near $10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and those in silicon are even higher, depending on the nature and the concentration of the dopant, etc. The small carrier velocities observed in polymers are perhaps sufficient for use in electrophotographic photoreceptors, some sensors or charge-coupled devices, but not for applications where typical semiconductor or conductor carrier velocities are required.

8.2 GENERAL BACKGROUND

8.2.1 Photoconductivity

Photoconductivity is a phenomenon involving the following sequence of steps.

1. *Absorption of radiation and formation of excitons.* To generate charge carriers, the polymer must absorb light. Transparent, non-absorbing polymers must therefore be sensitized to visible light. This is accomplished by adding dyes or pigments or additives that form charge-transfer complexes.
2. *Generation of charge carriers.* The excitons are captured at donor or acceptor sites, the functional groups are polarized and separate charges are formed. These sites can be either inherent to the polymer structure or be present as additives or impurities.
3. *Separation of charge carriers.* The electric field assists the separation of charges, electrons and holes. Some fraction of the hole–electron pairs, however, may undergo geminate recombination.
4. *Migration (transport) of charges.* Either electrons or holes or both drift towards electrodes in the presence of an electric field. Random diffusion of carriers will result in zero current.
5. *Recombination.* Coulombic forces will eventually cause recombination of free electrons and holes at recombination sites in the circuit.
6. *Trapping.* Migrating charges can be temporarily or permanently immobilized in shallow or deep traps. The terms ‘shallow’ and ‘deep’ are only relative, and refer to the release times. Shallow traps are those from which carriers are released in the time of the experiment.

7. *Charge injection.* When extrinsic photogenerators are used the charge injection efficiency also becomes important in controlling the photocurrent. Charge injection, as well as photogeneration and charge transport, is electric-field-dependent.

The photocurrent depends primarily on the density of carriers and their velocity under given field and temperature conditions. One therefore has to consider the rates with which the carriers are generated and the pathways with which they are temporarily or permanently immobilized in traps or entirely lost by recombination.

Suppose that when a photoconductive polymer is subjected to radiation that is absorbed by the polymer, f free carriers (those that have already escaped geminate recombination) are produced per unit volume per unit time. With constant illumination, the steady-state concentration of free carriers is then $n_0 = f\tau$, where τ is the average time between generation and recombination of the carrier, the so-called recombination time. For the simple case of a one-signed carrier system, the steady-state photocurrent conductivity σ is

$$\sigma = n_0 e \mu = f \tau e \mu \quad (8.1)$$

where e is the electronic charge and μ is the drift mobility. The value of n_0 is the carrier density before the photoconductor is connected into a circuit. Measurements of photocurrent can, however, be made only when the photoconductor is in a circuit. Application of voltage across the sample to measure photocurrent may result in changes in the density of carriers, depending on the nature of the electrodes, and therefore the measured values may have no relationship to the above basic parameters n_0 , μ and τ . With Ohmic contacts (the existence of purely Ohmic contacts is, however, the exception rather than a rule), the steady-state carrier density n_0 is unchanged after connection into a circuit and application of a voltage. As one carrier leaves the device, another is injected at the opposite electrode to maintain n_0 . The steady-state photocurrent density with Ohmic contacts is then

$$J_{st} = \sigma E = e f \mu \tau E \quad (8.2)$$

The number of photogenerated free carriers f is given by

$$f = \frac{\phi I}{L} \quad (8.3)$$

where I is the total absorbed intensity of radiation per unit area per unit time, ϕ is the quantum efficiency of photogeneration (number of carriers generated per number of photons absorbed) and L is the film thickness. This means that the steady state photocurrent density with Ohmic

contacts may also be written as

$$J_{st} = e \frac{\phi I}{L} \mu \tau E \quad (8.4)$$

Since equation (8.4) contains the fundamental parameters ϕ , μ and τ characterizing the photoconductor, steady-state photocurrents are often used for their determination. However, erroneous results are obtained if the contacts are not perfectly Ohmic. It should also be noted that both μ and ϕ depend on E , and therefore the variation of Ohmic current with electric field is complex.

When both carriers are mobile, since the mobility may be written as $\mu = L/tE$ (where t is the transit time), the steady-state photocurrent density (with Ohmic electrodes) becomes

$$J_{st} = ef(\mu_n \tau_n + \mu_p \tau_p) E = efL \left(\frac{\mu_n \tau_n}{L} + \frac{\mu_p \tau_p}{L} \right) E = efL \left(\frac{\tau_n}{t_n} + \frac{\tau_p}{t_p} \right) \quad (8.5)$$

With blocking electrodes, i.e. contacts that do not permit injection of charge into the polymer, but let the photogenerated charge leave the material under the influence of an electric field (assuming that the recombination time is far greater than the transit time: $\tau \gg t_{Tr}$), the steady-state photocurrent density is

$$J_b = \phi I e = efL \quad (8.6)$$

Thus the current is proportional to the rate of carrier generation. From the above, it is obvious that greater photocurrents can be drawn with Ohmic electrodes in the circuit than with blocking electrodes. With the latter, the current saturates if the two free carriers can reach the electrodes without recombination. Figure 8.2 shows schematically the maximum photocurrent densities that can be reached with Ohmic or blocking contacts respectively in the absence of space-charge effects.

Ohmic contacts, as indicated above, are those that can supply all the carriers that the bulk demands for any applied voltage. With Ohmic contacts, the current varies linearly with voltage – but only at low electric fields. At higher fields it varies as the square of the voltage. At these voltages the carrier density in the bulk is larger than the value that existed before the application of the voltage. The migration of this excess space charge results in a current that is higher than the simple Ohmic current. The overall observed current is then referred to as space-charge-limited current (SCLC), for which, in the simple case of a system without traps and one moving carrier type (situations typical of most photoconductive polymers), the following relationship has been derived [3]:

$$i_{scl} \propto \frac{CV}{t_{Tr}} \propto \frac{9}{8} \frac{\epsilon_0 \epsilon_r \mu E^2}{L} \quad (8.7)$$

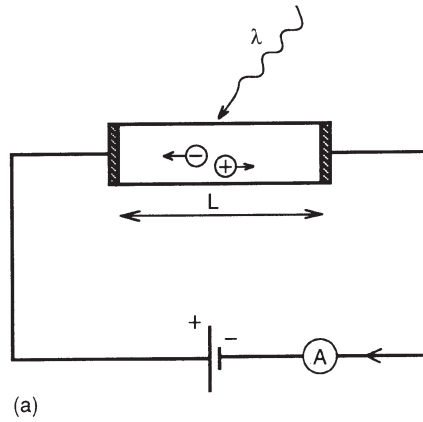
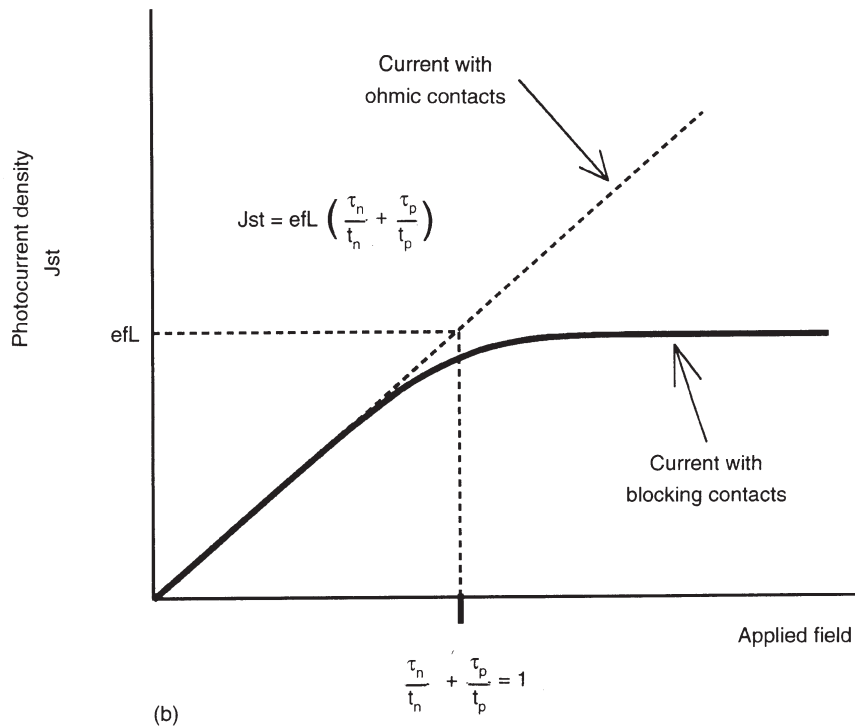


Fig. 8.2 (a) Schematic representation of the flow of photocurrent in a photoconductive insulator. (b) Steady-state photocurrents in insulating photoconductors with blocking and Ohmic electrodes. With blocking electrodes, the current saturates when both sign carriers reach the respective electrodes without recombination.

where C is the capacitance of the polymeric film and $\epsilon_o \epsilon_r$ is the permittivity. For a constant applied field, the low-field Ohmic current is independent of thickness (see equation 8.2), whereas the SCLC is inversely proportional to the thickness of the sample (see equation 8.7). For cases with both carriers mobile and for media containing charge traps, more complex relationships have been derived [4].

SCLC can be drawn even in systems with blocking electrodes if the incident light is so intense that bulk charge greater than CV_o is produced for times $t \ll t_{Tr}$.

The most important characteristic parameters of each photoconductor are the quantum efficiency of photogeneration ϕ and the carrier mobility μ . In most examined unsensitized polymeric photoconductors $\phi < 10^{-1}$, even at high electric fields.

Let us now discuss in some detail the key events that control the photocurrent: charge-carrier generation, injection and transport.

8.2.2 Charge-carrier generation

The carrier generation can be intrinsic, i.e. by photons absorbed by the polymer itself, or extrinsic, by photoexcitation of photosensitive material that is mixed with, or adjacent to, the polymer, such as dyes or pigments. The existence of truly intrinsic photogeneration has been doubted, however, for light energies lower than 4.6 eV (≈ 270 nm) [5]. Some authors suggest that incidental electron acceptors must be present as impurities or known acceptors added to effect photogeneration in donor-like polymers, and vice versa. The currently accepted mechanism [5, 6] for intrinsic photogeneration is that illustrated in Fig. 8.3.

The first step is photoexcitation of the light-absorbing group, followed by migration of the exciton to an acceptor site, where an encounter

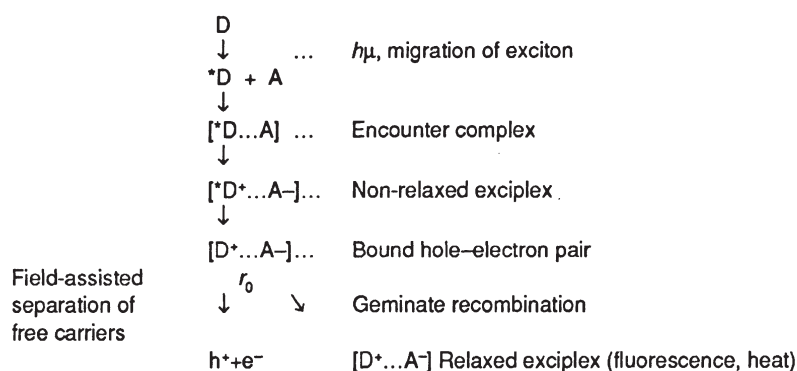


Fig. 8.3 Mechanism of intrinsic photogeneration of charges in amorphous photoconductors: D = electron donor site; A = electron acceptor site. (From [6].)

complex is formed. What constitutes the acceptor site is still under discussion. A variety of possibilities have been proposed, such as an oxidized carbazole moiety [5] (in the case of PVK), acceptor impurities, structural defects or even oxygen molecules. The key process determining the photogeneration efficiency is the competition between field/temperature-assisted carrier separation and geminate recombination. A theory originally developed by Onsager [7] for dissociation of ion pairs in weak electrolytes was used [8] to describe the photogeneration efficiency as a function of electric field, temperature and the separation distance r_0 of the bound hole–electron pair.

According to this theory, the overall photogeneration efficiency $\phi(E)$ is given by

$$\phi(E) = \phi_0 \int p(r, \Theta, E) g(r, \Theta) d^3 r \quad (8.8)$$

where $d^3 r$ is a volume element, ϕ is the primary quantum yield (number of bound electron–hole pairs produced by one absorbed photon), $p(r, \Theta, E)$ is the probability that a hole–electron pair separated by a distance r at an angle Θ to the direction of electric field escapes geminate recombination, and $g(r, \Theta)$ is the spatial distribution function between ions, assumed to be an isotropic delta function, so that $g(r, \Theta) = (1/4r_0^2) \delta(r - r_0)$, where r_0 is the characteristic thermalization length. Solution of equation (8.8) gives

$$\phi(E) = \phi_0 \exp \left[- \frac{r_c(T)}{r_0} \right] \left[1 + \frac{e}{k_B T} \frac{1}{2!} r_c E + \left(\frac{e}{k_B T} \right)^2 \frac{1}{3!} r_c [(1/2)r_c - r_0] E^2 + \dots \right] \quad (8.9)$$

where r_c , the critical Onsager distance, is

$$r_c = \frac{e^2}{4\pi\epsilon_r \epsilon_0 k_B T} \quad (8.10)$$

After neglecting the small terms, $\phi(E)$ becomes a relatively simple function of the electric field E , temperature T , the permittivity of the medium, the material-dependent thermalization length r_0 and ϕ_0 , which can also be thought of as the maximum photogeneration efficiency at an infinite field E and high temperature T .

For PVK at wavelengths between 310 and 350 nm, $\phi_0 = 0.11$ [9]. At realistic fields and temperatures the photogeneration efficiency is obviously much lower. For example, at room temperature and $E = 10^6 \text{ V m}^{-1}$, $\phi \approx 10^{-4}$. The theory is in excellent agreement with the experimental data on PVK [9] (at least for electric fields above about $3 \times 10^6 \text{ V m}^{-1}$), solid solutions of *N*-isopropylcarbazole (NIPC) in polycarbonate [10] and triphenylamine (TPA) in polycarbonate [11] (Fig. 8.4).

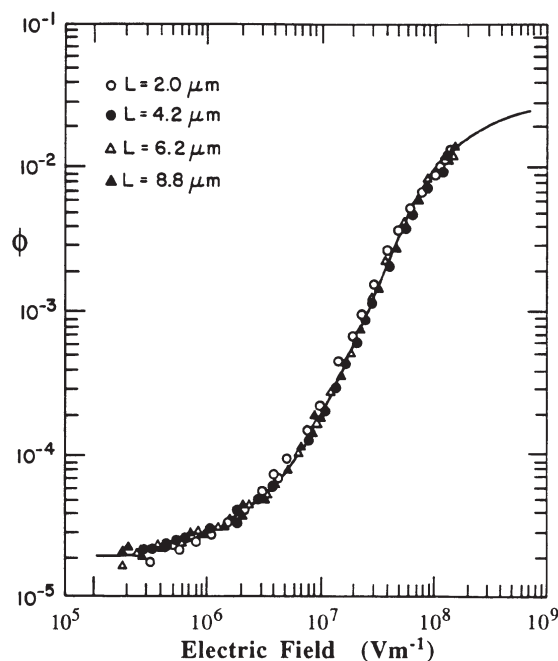


Fig. 8.4 Photogeneration efficiency in TPA (40 wt % in polycarbonate) as a function of electric field. The solid line is calculated from the Onsager theory using $r_0 = 0.25$ nm and $\phi_0 = 0.026$. (From [11].)

The primary quantum yield ϕ_0 also depends on the concentration of active species, as demonstrated in the NIPC/polycarbonate system [10]. In PVK the concentration of the carbazole groups is fixed to near 87 wt%, while in the NIPC/polycarbonate and TPA/polycarbonate systems the content of the active molecule is variable.

As equation (8.9) indicates, ϕ is a function of the parameter r_0 , which in turn depends on the excitation wavelength λ . ϕ increases in steps with increasing incident light energy (Fig. 8.5). Discontinuities occur at the onset of the transition between the ground state of the carbazole group in PVK and the first, second and third excited singlet states [9] or near the corresponding absorption peaks (Fig. 8.6). The stepwise increases in ϕ are due to increases in the thermalization distance r_0 (Table 8.1).

Similar discontinuities were found in the NIPC/polycarbonate photoconductor [10]. However, in PVK doped with the electron acceptor dimethyl terephthalate ϕ_0 was found to be independent of λ [5]. As expected, however, ϕ_0 scales with the concentration of the acceptor [5], and at wavelengths between 280 and 340 nm it can be as high as 0.9. A value of $\phi_0 = 0.23$ has been obtained for PVK mixed with 2,4,7-trinitro-

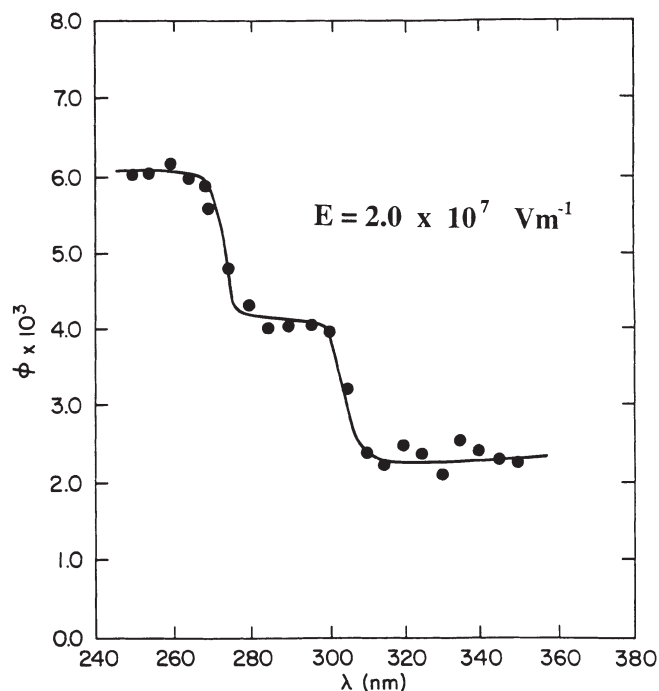


Fig. 8.5 Discontinuities in the wavelength dependence of the carrier generation efficiency in PVK at 25 °C and $E = 2.0 \times 10^7 \text{ V cm}^{-1}$. (From [6].)

9-fluorenone (1:1) at 23 °C and with a separation distance of 3.5 nm at $\lambda \approx 550 \text{ nm}$ [13].

PVK and all other known photoconductive donor-like polymers transport only holes, even though crystalline model compounds such as NIPC or anthracene are known to transport both holes and electrons. There is no definitive answer to the question of what happens to electrons photogenerated in a medium that is only hole-transporting. It can be speculated that trapped electrons recombine with holes thermally generated elsewhere in the system, which may diffuse freely through the bulk of the polymer, or with transiting photogenerated holes, thus effectively reducing the overall efficiency. If an electron acceptor is involved in the photogeneration process, as suggested by some authors [5], the 'free' electron could add to the acceptor molecule. With some added strong electron acceptors such as trinitrofluorenone (TNF), the explanation appears to be simple: photogenerated holes move by hopping via the donor carbazole groups while electrons migrate via the TNF molecules [14], which when dispersed in an inert polyester binder have been shown to be electron-transporting [15].

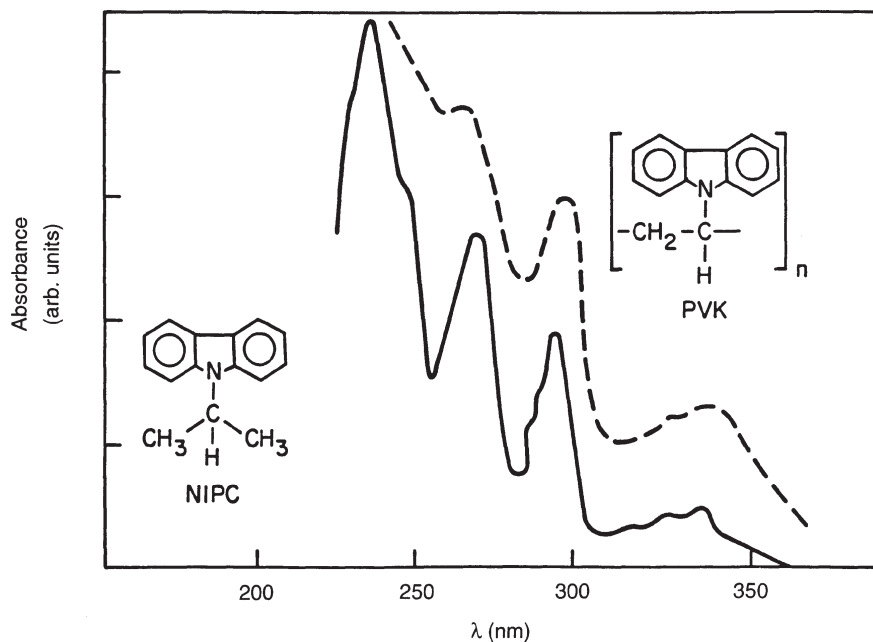


Fig. 8.6 Absorption spectra of thin films of PVK and NIPC in CH_2Cl_2 .

This method of sensitization by acceptors can be considered intrinsic, since the same material that supports charge transport is involved in the photogeneration process.

Many other carbazole polymer/acceptor combinations have appeared in the patent literature, but none have been studied as extensively as the PVK/TNF complex.

The addition of a photoconductive dye or pigment to a polymer such as PVK is another way of extending the spectral response to the visible range. When sensitized by pyrylium dyes [16], PVK has a quantum efficiency of photogeneration as high as $0.56 \text{ at } 10^8 \text{ V m}^{-1}$.

Table 8.1 Thermalization distance r_0 in PVK

Excitation wavelength (nm)	r_0 (nm)	Ref.
310–350	2.6	9
270–300	2.8	9
250–270	3.0	9
X rays	6.0	12

A variety of azo and methine dyes and pigments have been examined in conjunction with PVK and other polymers, but the patent literature indicates that virtually any dye or pigment can sensitize the photoconductivity of PVK into the visible range. When photogeneration proceeds via electronic transitions involving both the polymer and the dye (such as a charge-transfer complex between PVK and the acceptor part of the dye), the process is also considered intrinsic. When these transitions proceed within the dye molecules or pigment particles, the process is termed extrinsic.

The concept of extrinsic photogeneration was extended to the concept of layered photoconductors illustrated schematically in Fig. 8.7. In these devices carriers are generated in a very thin, highly absorbing layer of a photoconductive material such as amorphous selenium (a-Se) or in an organic pigment, while the adjacent thicker polymer layer serves only as a carrier-transport medium. This concept allows maximum utilization of useful properties of the materials, such as the flexibility and toughness of the polymer and the high photogeneration efficiency of the generation layer. Other frequently mentioned photogenerator layers are made of trigonal selenium (t-Se), Se-Te alloys, solvent-coated or evaporated dyes or pigments, CdS, etc.

The first layered photoconductive device with a polymeric transport layer consisted of a thin layer of a-Se and hole-transporting PVK [17]. The device is biased negatively by a semitransparent electrode or a corona charge. Visible light penetrates the thick PVK layer and is absorbed in the a-Se layer, which is only thick enough to absorb most incident radiation. Photogenerated holes are injected into and drift through PVK to the upper electrode, and electrons leave the device at the bottom electrode. Continuous currents can be drawn through the device. The value of current depends on temperature, electric field, the nature of the bottom electrode and space-charge conditions.

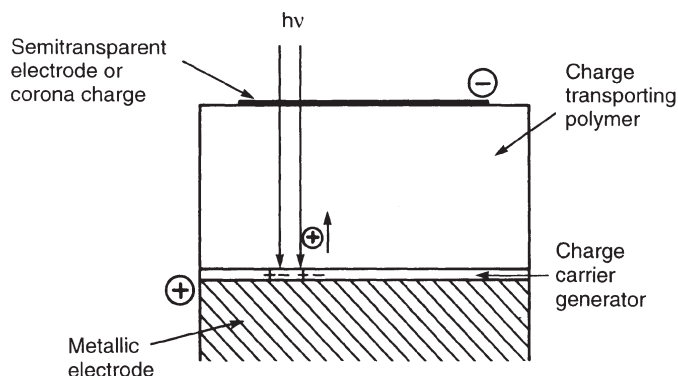


Fig. 8.7 A scheme for a layered photoconductor.

8.2.3 Charge injection

Efficient injection of charge into the transport polymeric layer is another important requirement for the operation of a photoconductor with an extrinsic photogeneration layer. The process of charge injection can be described qualitatively in the following manner [18]. The incident photons that are absorbed in the photogenerator layer generate carriers at a rate ϕI , where I is the light intensity in photons per unit area per second. The density of free carriers in the generation layer (i.e. those that escaped geminate recombination) is reduced by (i) recombination at a rate $\gamma_r n^2$ (where n is the concentration of free carriers) and (ii) injection at a rate $\gamma_i n$ (where γ_r and γ_i are the recombination and injection rates respectively). Under quasi-steady state conditions, i.e. under constant electric field,

$$\frac{dn}{dt} = \phi I - \gamma_r n^2 - \gamma_i n \approx 0 \quad (8.10)$$

Assuming that once the charges cross the interface they will not return, the photoinjection efficiency Y becomes [18]

$$Y = \frac{\gamma_i n}{I} = \delta \left[\left(1 + \frac{2\phi}{\delta} \right)^{1/2} - 1 \right] \quad (8.12)$$

where $\delta = \gamma_i^2 / 2I\gamma_r$. For large δ (low barrier for injection) or low recombination rates, $Y = 0$, in which case the photoinjection efficiency is determined solely by the generation efficiency. For a small δ , $Y = (2\delta\phi)^{1/2}$, which means that the photoinjection efficiency will depend on the injection rate, γ_i , or in a practical sense, on the choice of the transport-layer polymer. Figure 8.8 illustrates how the injection efficiency for a layered photoconductor using a 'Chlorodiane Blue' generator can be greatly improved by replacing PVK with a pyrazoline-based transport material [18].

8.2.4 Charge transport

Charges photogenerated in extrinsic photoconductors are injected into the transport materials. Hole injection, or transfer of holes into the transporting medium, can be viewed as an oxidation step resulting in a formation of cation radicals (or polarons). Similarly, electron injection is a reduction process. Once injected, the charges (not the molecules) migrate through the transport medium to reach the opposite electrode. It is now commonly accepted that migration of charge carriers, electrons or holes or both, involves 'hopping', i.e. a sequence of transfers of charges among localized sites [14]. These localized sites are associated with individual molecules or functional groups or with segments of the polymer chain.

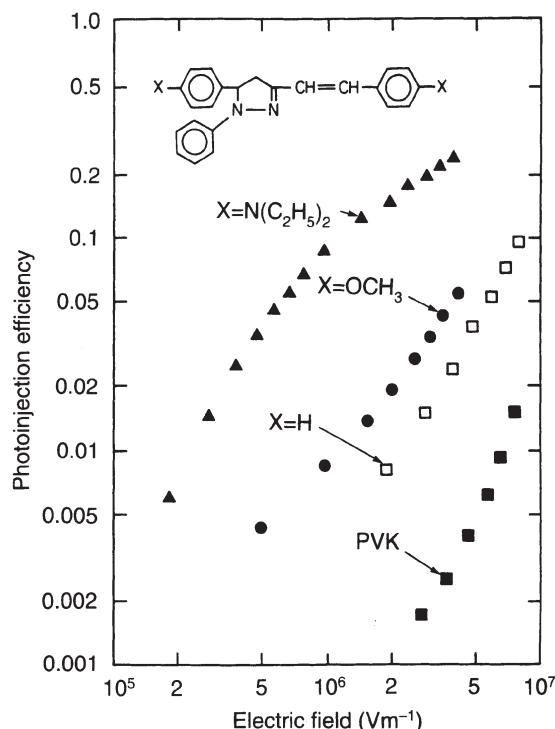


Fig. 8.8 Photoinjection efficiency from 'Chlorodiane Blue' to PVK and pyrazoline-based transporting molecules (illuminated with 550 nm light with an intensity of 10^{15} photons $\text{m}^{-2} \text{s}^{-1}$). (From [18].)

The prevalent feature of all known photoconductive polymers is that they all either

1. have an extended π -electron system in the backbone or in groups pendant to the chain; or
2. are σ -conjugated, as in the case of silicon backbone polymers (polysilylenes).

These features guarantee delocalization, and therefore stabilization of transiting charges. Hole-transporting photoconductive polymers are electron donors; they contain groups with large π -electron clouds such as anthracene and pyrene, or strongly donating groups such as aromatic amines. On the other hand, linear highly conjugated polymers with extended π -electron systems that encompass large segments of the macromolecule, such as in polyacetylene, are typically too conductive in the dark to be of interest as photoconductors (Chapter 1). The best known photoconductive polymers are those where π conjugation extends over a limited number of atoms, as in condensed aromatic rings or single

aromatic rings with adjacent amine groups. Since these structural elements are isolated from one another, classical semiconductor theories of band transport do not apply.

The transport-active groups can be part of the polymer backbone structure, they can be covalently linked as pendant groups to a vinyl or similar chain such as carbazole groups (substituted aromatic amines) in PVK, or need not be covalently attached to the polymer backbone at all. Indeed, solid solutions of NIPC in polycarbonate display hole mobilities that are comparable to those in PVK [19, 20]. The polymer backbone in PVK does not contribute to transport, but merely ties the transport-active groups together. Similarly, both solid solutions of triphenylamine (TPA) in polycarbonate [21] and poly(methacrylate) with pendant triphenylamine groups [22] display photoconductivity and charge transport.

The velocity v of migrating charge carriers in organic polymers depends on the electric field E , the temperature T and the intersite distance q [21]:

$$v = \mu(E, T, q) E \quad (8.13)$$

An early phenomenological model [14] had

$$\mu \approx \mu_0 \exp \left(- \frac{\Delta_0 - \beta E^{1/2}}{k_B T_{\text{eff}}} \right) \quad (8.14)$$

where $T_{\text{eff}} = 1/T - 1/T_0$, k_B is Boltzmann's constant, Δ_0 is the zero-field activation energy, β is a constant that depends only on the dielectric constant of the medium, and T_0 is a characteristic temperature at which the Arrhenius plots of μ for different fields intersect. At T_0 , therefore, μ should be field-independent. This has indeed been observed with poly(di-n-butylgermylene) [23]. It was also suggested that a correlation exists between the shift factor T_0 and the glass transition temperature T_g , although they were not exactly coincident [24]. The relatively abrupt change in the temperature dependence of μ near T_g has been seen in several systems [25–27]. The activation energy of transport at $T > T_g$ is always smaller than below T_g .

Simple Arrhenius behaviour of μ is also predicted by the redox rate model [28, 29], which describes transport as an electric-field-biased succession of diffusional (random walk) electron self-exchange reactions between neutral molecules or groups and their charged counterparts (cation radicals in hole transport).

A computer simulation of hopping transport in a disorder-induced distribution of localized states with a Gaussian spread of energies, however, predicted [30] that

$$\mu = \mu_0 \exp \left[- \left(\frac{T_0}{T} \right)^2 \right] \quad (8.15)$$

where μ_0 is the mobility in a system with no disorder. The question of which temperature dependence of μ applies has not been resolved, because in both representations approximately linear fits have been obtained. The temperature ranges studied were too narrow to permit differentiation between the two models. Recent studies on PMPS, however, confirmed the simple Arrhenius behaviour of μ below T_g of the polymer [23].

Activation energies of transport in organic polymers, including 'molecularly doped' ones below T_g (assuming the process is simply thermally activated), are typically 0.2–0.7 eV, and decrease with increasing electric field. At $T > T_g$ the activation energies are typically smaller than below T_g . This behaviour is similar in detail to that already reported for glassy selenium [31].

The relationship between μ and E has also not been completely elucidated. The empirical exponential dependence of μ on $E^{1/2}$ shown in equation (8.14) [14] has been most often applied to analyse transport data in a variety of systems. However, it failed to explain many subsequent experimental observations. A modification of this formula was proposed [21], but it was not general enough to explain all observed data.

The computer simulation model [30] mentioned above predicts that $\mu \approx \exp(E/E_0)$, which has been observed in several cases [32–34]. In other cases, however, μ was found to be proportional to $E^{1/2}$, which is consistent with the Poole–Frenkel formalism of field-lowering of hopping barriers [14, 35]. In many cases, however, the graphic representation cannot differentiate between the models owing to difficulties in assessment of the linearity or nonlinearity of the field dependence over a narrow field range.

Recent details analysis [35] leads to a functional relationship of the form

$$\mu = \mu_0 \exp\left(-\frac{T_0}{T}\right)^2 \exp\left[E^{1/2}\left(\frac{\beta}{T} - \gamma\right)\right] \quad (8.16)$$

(where γ is a fitting parameter) which fits data obtained on DEH (*p*-diethylaminobenzaldehyde diphenylhydrazone) in polycarbonate, but it assumes the non-Arrhenius behaviour of transport.

The redox migration model [29] predicts a more complex relationship between μ and E :

$$\mu E \propto r_h A' \exp\left(-\frac{\Delta G_0}{RT}\right) \left\{ \exp\left(\frac{\alpha n F r_h E}{RT}\right) - \exp\left[-\frac{(1-\alpha) n F r_h E}{RT}\right] \right\} \quad (8.17)$$

where r_h is the mean hopping distance, and A' is a pre-exponential factor that may be further expanded in terms of electronic, vibrational and nuclear terms [36]. This factor also contains the intersite distance

relationship according to which μ decreases exponentially with increasing intersite distance. ΔG_0 is the free energy of activation, F is the Faraday constant and α is a measure of the symmetry of the energy barrier near the intersection of the of the product and reactant curves – a value typically between 0.5 and 1.

In the low-field exploration of equation (8.17) μ is independent of E ,

$$\mu \propto A' r_h^2 \frac{nF}{RT} \exp \left(- \frac{\Delta G_0}{RT} \right) \quad (8.18)$$

and at very high fields an exponential dependence of μ is predicted:

$$\mu E \propto r_h A' \exp \left(- \frac{\Delta G_0}{RT} \right) \exp \left(\frac{\alpha n F \lambda E}{RT} \right) \quad (8.19)$$

It is conceivable that in the intermediate field range (in most cases this is the only experimentally accessible range) μ may appear to scale linearly with $E^{1/2}$. Good agreement with this model has been obtained at least in one case [29]; however, the issue of the field dependence of the mobility remains unresolved.

An empirical relationship between μ and the average intersite hopping distance q has been proposed [21]:

$$\mu \propto q^p \exp \left(- \frac{2q}{q_0} \right)^q \quad (8.20)$$

where q_0 is the so-called empirical charge-localization radius. Empirical values of $p=2$ and $q=1$ were proposed and supported by many experiments (see e.g. Fig. 8.9). The exponential dependence on the intersite distance was also explained by the small-polaron hopping theory [37] and phonon-assisted hopping [38]. The redox migration model predicts that the exponent p (in effect) rises from 1 to 2 as the electric field decreases from the point where hopping against the field is unimportant to the low-field diffusion limit. The original relationship [21] (equation (8.20)) of course does not recognize the field dependence of p .

In photoconductive polymers the intersite hopping distance is not variable; it is determined by the structure and morphology of the polymer. In 'molecularly doped' polymers the average hopping distance can be varied at will, simply by changing the concentration of the transport-active species in the host polymer. In the PVK/TNF bipolar system there is evidence that holes move via uncomplexed carbazole groups, while electrons move via both complexed and uncomplexed TNF molecules [14]. The hole mobility decreases and the electron mobility increases as the TNF concentration increases [14] (Fig. 8.10).

It is interesting to note that polymers in which the active groups are fixed in position, by covalent bonding to the backbone, show lower

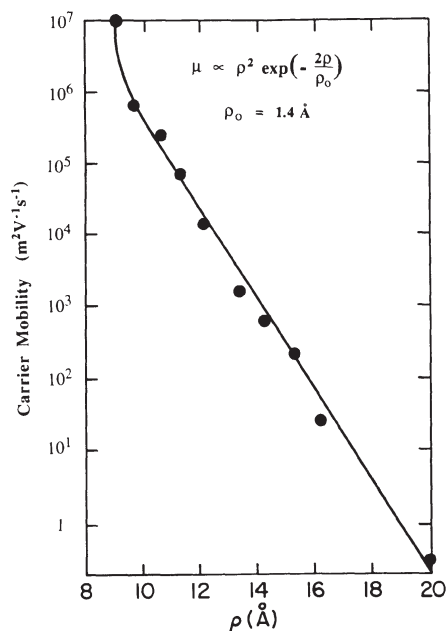


Fig. 8.9 Hole mobility in TPD/polycarbonate as a function of the average intersite hopping distance. (From [34].)

mobilities than one would obtain with small molecules, dissolved in inert host polymers at correspondingly high concentrations of the transport-active groups. Thus PVK with around 87 wt% carbazole has about the same hole mobility [39] as NIPC with only 40 wt% in polycarbonate [20]. According to equation (8.20), at 87 wt% NIPC, μ would be several orders of magnitude higher. Similarly, TPA at 30 wt% in polycarbonate [21] has even higher mobilities than a polymer made of TPA-containing methacrylate with around 71 wt% TPA groups in the monomer unit [22].

Charge-carrier mobilities in amorphous disordered organic photoconductive polymers that include 'molecularly doped polymers' are typically near or below $10^{-1} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $E \approx 10^7 \text{ V m}^{-1}$ and $T \approx 295 \text{ K}$. σ -Conjugated silicon backbone polymers under similar conditions display hole mobilities around $1 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ [40, 41].

Another important issue related to charge transport is the velocity distribution of transiting charges. The relative dispersiveness as manifested in the shape of time-of-flight (TOF) transients varies with temperature, electric field, sample thickness and the details of the injection or photogeneration steps. Ideally, when a sheet of charge carriers is injected into deep-trap free-transport material, constant current should be observed in TOF experiments as the sheet of charges

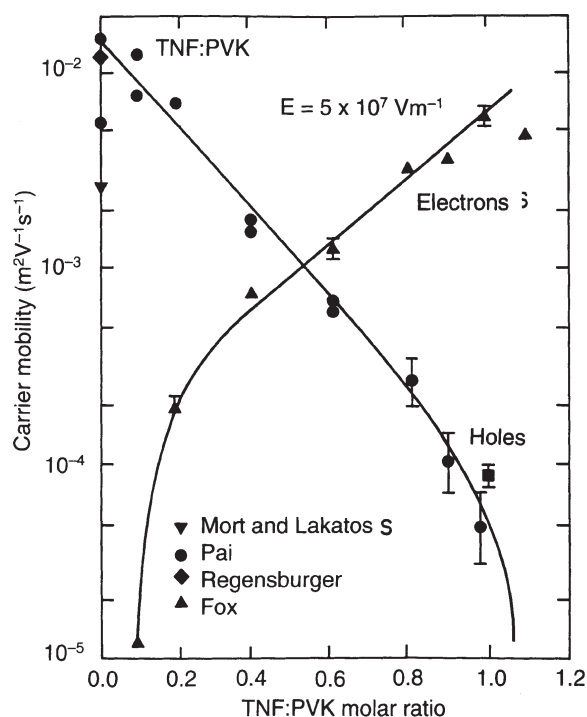


Fig. 8.10 Hole and electron mobilities in PVK/TNF as functions of the PVK/TNF molar ratio. (From [14].)

migrates towards the counter-electrode. The current should drop to zero when the carriers reach the collecting electrode as a coherent sheet. In practice, however, rounding of the transit pulse is always observed, because dispersion is induced by thermal diffusion and Coulombic repulsion. In addition to these minimal effects, there exist other dispersion phenomena, related to the degree of geometrical (positional) and energetic disorders, sometimes referred to as off-diagonal and diagonal disorders respectively. Hopping transport can be interpreted as a chain of discrete redox steps where each event is associated with a waiting time on a given site. When the waiting-time distribution function is Gaussian, the mean position of the packet of transiting carriers is proportional to time (the current in TOF measurements is constant), and the width of the spread increases only as the square root of time. Gaussian dispersion of charge carriers has indeed been observed in N,N' -diphenyl- N,N' -bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD)/polycarbonate [42] and in PMPS [43].

In many cases dispersive-looking transients cannot be identified with anomalous scaling. The latter is believed to be a direct consequence of the

presence of a very broad algebraic distribution of carrier waiting times, broad enough to impinge on the timescale of TOF measurements. For the cases where the waiting-time distribution is very broad (so that leading-edge carriers reach the counter-electrode while a large fraction of carriers are still close to the plane of injection), it was suggested [44] that the time-resolved transient current would acquire two algebraic branches, which intersect at some statistically defined t_{Tr} . The transient current should then be

$$i(t) \propto t^{-(1-\zeta)} \quad \text{for } t < t_{Tr} \quad (8.21a)$$

$$i(t) \propto t^{-(1+\zeta)} \quad \text{for } t > t_{Tr} \quad (8.21b)$$

where ζ is the dispersion parameter. The theory also predicts that

$$t_{Tr} \propto \left(\frac{E}{L} \right)^{1/\xi} \quad (8.22)$$

where L is the sample thickness. The latter expresses the anomalous thickness dependence of mobility. Plots of $\log i$ versus $\log t$ normalized to transit times at various fields should superimpose, exhibiting the phenomenon of ‘universality’. This theory of dispersive transport implies that ζ for $t < t_{Tr}$ (denoted by ζ_1) equals ζ for $t > t_{Tr}$ (denoted by ζ_2): $\zeta = \zeta_1 = \zeta_2$. Studies on PMPS [43] and TPD/polycarbonate [34, 42], however, show that in neither case was the universality of the log-log plots or the anomalous thickness dependence or the equality of ζ_1 and ζ_2 observed. Transport in these systems is therefore ‘non-dispersive’. Time- (or thickness-) independent mobility has also been demonstrated in other systems [46]. Dispersive transport in terms of the above theory has, however, recently been observed on polysiloxane with pendant carbazole groups [45].

The dispersion of transiting holes can be artificially broadened by doping polymers with molecules that can be charge-transporting themselves, but have a lower oxidation potential $E_{ox}^{1/2}$ than the host polymer [47, 48]. Depending on the relative amounts of the dopants, the system can undergo transition from pure hopping to single-trap controlled hopping [49]. At low densities of charge traps (at low concentrations of the low- $E_{ox}^{1/2}$ additives) charge transport is dominated by slow release of charges from the trap sites back to the host medium. This leads to broadening of the dispersion of the carrier packet [49], and eventually to a reduction in drift mobility, sometimes by several orders of magnitude [47–49], depending on the concentration of traps and the relative position on the energy scale. As the concentration of the additives is increased, so that it becomes comparable to the concentration (density) of transport states, the probability of hopping directly among the hole trap sites becomes higher, and eventually, at high concentrations of the

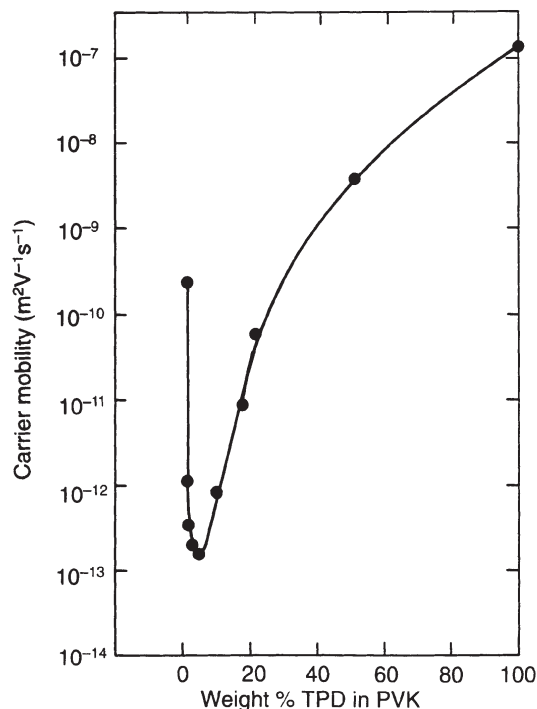


Fig. 8.11 Hole mobility in PVK doped with varying amounts of TPD at 22 °C and $E = 5 \times 10^7 \text{ V m}^{-1}$. (From [48].)

trapping additives, new transport channels via the additive sites are created [47, 48]. The hole mobility then increases with increasing additive concentration. The role of the host polymer such as PVK is eventually reduced to that of an inert binder [48] (Fig. 8.11). The spatial distribution of the transiting carriers is also affected by the trapping additives. The transport changes from non-dispersive to highly dispersive and back to non-dispersive as the concentration of the trapping additive is increased [49].

The claims that electronic transport in organic polymers is universally dispersive therefore appear to be incorrect. On the contrary, the above and other published examples [35] indicate that dispersive transport (with thickness-dependent μ and universality of the $\log i$ versus $\log t$ plots) in neat (i.e. impurity-free) materials is the exception rather than the rule. It is possible that systems exhibiting unusually broad dispersions were contaminated by transport-interactive impurities.

Even though charge transport in diverse materials (including silicon backbone polymers, a-Se, and even $\alpha\text{-Si:H}$) has many common features [23], no comprehensive theory of transport is available. At least three

alternatives for the development of a microscopic transport theory, potentially able to deal with all the experimental observations, have been suggested.

(a) Electric-field-assisted polaron hopping

A polaronic mobility is expected if sufficient configurational relaxation is stimulated by the transiting carrier during its residence on each transport site. Polaron models need to be developed further to account for the observed field dependence.

(b) Thermalization in a Gaussian distribution of localized states

If hopping occurs among iso-energetic sites, and the carriers do not relax with their surroundings to form a polaron during each wait at a discrete site, then transport should be temperature-independent, and the mobility should scale exponentially with the average intersite distance. In real materials, however, the active sites are subject to a site-variable disorder potential. This should cause site energies to reorganize to a Gaussian distribution, the width of which reflects the degree of disorder. The drift mobility is predicted to exhibit a non-Arrhenius behaviour with μ proportional to $\exp[-T_0/T^2]$, T_0 is the width of the Gaussian distribution in temperature units. However, recent data indicate that, for some systems, the mobility is proportional to $\exp(-T_0/T)$ over a wide range of temperature. Also, μ is predicted to vary exponentially with the electric field E , not the square root of the field as is commonly observed. The refined version of Bässler's disorder model that accounts for both spatial and energetic disorder deals with these discrepancies, and is now considered to be the most comprehensive and consistent model of charge transport [50].

(c) Rate models

These predict an exponential field dependence of mobility at high fields, field-independent mobility at low fields, normal Arrhenius behaviour, decreasing activation energy with increasing field, and an exponential decrease of mobility with increasing intersite distance. Even though a reasonably good fit with experimental data has been seen for at least one system, it remains to be seen if the model is generally applicable to all types of charge-transporting polymers.

8.2.5 Charge trapping

Migrating charges can be temporarily or permanently immobilized in trap

sites. If the traps are 'shallow', they may be referred to as 'transport-interactive'. Thus shallow traps (for holes) were introduced to PVK by the addition of small amounts of TPD [48]. Similarly, TPA acts as a shallow trap in NIPC [47], and a pyrazoline derivative, 1-phenyl-3-(4'-diethylaminostyryl)-5-(4''-diethylaminophenyl)pyrazoline (PPR) acts as a shallow trap for hole transport in TPD/polycarbonate [49]. All the hole-trapping species have lower oxidation potentials (i.e. they are stronger donors) than the host-transporting materials. A strong electron acceptor (e.g. TNF) is a trap for electron transport in polyesters [51].

In addition to the loss of carriers due to geminate recombination and recombination of carriers in the circuit, charges can be immobilized (trapped) as a result of redox-irreversible side-reactions involving the charged moiety (a 'carrier', cation radical in the case of hole transport) that can perhaps be best illustrated by the schemes shown in Fig. 8.12, where (a) depicts the trap-free migration (hopping) of a hole by a succession of redox (electron self-exchange) steps, involving neutral groups M and charged groups M^+ (cation radicals), while (b) shows that the intermittent species M^+ can, under certain conditions, undergo a side-reaction leading to a charged species X^+ that will not further exchange the charge with the neighbouring group M. The charge is thus immobilized at the site X, formerly M_j . The occurrence of such a process has been demonstrated [52] with bis[4-(diethylamino)-2-methylphenyl]phenylmethane, a well-studied hole-transporting molecule [32, 33].

8.3 MATERIALS

8.3.1 Polymers with conjugated C=C, C=N, N=N and C≡C bonds

These polymers are mainly known for their conductivity, particularly when doped with suitable electron donors or acceptors. Photoconductivity is marginal, and therefore these polymers are of limited interest for the study of this phenomena. Undoped and doped polyacetylene has been studied in some detail [53–57]. Undoped *cis*-polyacetylene is photoconductive in UV light [54]; doping with AsF_5 shifts the photoresponse to the visible range, but the polymer also becomes highly dark-conductive. Under certain conditions, the ratio of photo to dark

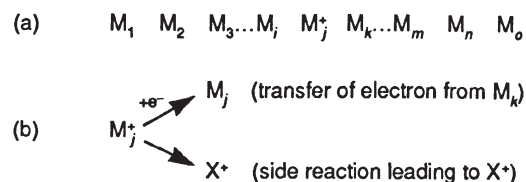
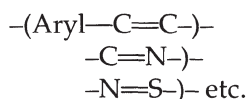


Fig. 8.12 Charge immobilization due to a redox-irreversible side-reaction.

current in *trans*-polyacetylene doped with I₂ or DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) is as high as 1000 [58]. Electrons are believed to be the majority carriers [58]; the transport mechanism is different from the hopping transport in PVK, and resembles band transport in inorganic semiconductors.

Crystals of poly[2,4-hexadiyne-1,6-diol bis(*p*-toluenesulphonate)] [59, 60] are highly photoconductive, with high carrier mobilities, near $20 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, even at low electric fields. This corresponds to drift velocities of about $2.2 \times 10^3 \text{ m s}^{-1}$, i.e. close to the velocity of sound in the material. It is interesting to note that the spectral dependence of photoconductivity (the so called action spectrum) in this and other polyacetylenes does not follow the absorption spectrum, but is shifted towards shorter wavelengths. Charge-carrier generation follows the Onsager one-dimensional model, at least for electric fields up to 10^6 V m^{-1} [60, 61].

A number of photoconductive polyarylene vinylenes of the general structure



have been described in the literature [62–64]. Some of these polymers form tough, flexible films, and generally are characterized by high thermal stability. Doping increases their conductivity. A polymer of this type with sulphur and benzidine groups exhibits a photoresponse in the near infrared range [63].

Photoconductive poly-*p*-phenylene sulphide [65] with hole mobility near $10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ is included in this category of polymers, even though it is not truly π -polyconjugated. Sulphur atoms in the chain separate the aromatic rings from each other. However, the free electron pairs on the sulphur atoms probably participate in charge delocalization.

Many other photoconductive polymers with extended polyconjugation of multiple bonds and complex structures have been described in the literature. In many cases, however, these polymers have low molecular weight, their structures are sometimes poorly characterized or they are insoluble. Moreover, direct comparison with well-studied polymers such as PVK is not possible owing to lack of data [2].

8.3.2 Polymers with polynuclear aromatic rings

Anthracene is one of the most thoroughly studied photoconductors, and numerous attempts have been made to synthesize high-molecular-weight materials or polymers containing similar groups. Poly(9-vinyl-anthracene) [66], poly(1-vinylanthracene) and poly(2-vinylanthracene)

[67, 68], poly[1-(2-anthryl)ethyl methacrylate] [69] and poly(vinyl-*p*-phenyl-9-anthracene) [70] are all photoconductive in UV light, but oxidatively unstable, brittle and generally difficult to synthesize.

Poly(vinylpyrene) [71, 72] (and D.M. Pai, personal communication) is also UV-photoconductive, with hole mobility at room temperature and $E = 2 \times 10^7 \text{ V m}^{-1}$ around $7.5 \times 10^{-11} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. Similarly, UV-photoconductivity has been seen in poly(pyrenyl methylvinyl ether) [73]. In this case a maximum photocurrent has been observed at 410 nm, while the peak absorption is at 376 nm.

Several other polymers with large pendant groups, such as poly-(9-vinylacridine) [74], also display some degree of photoconductivity.

The patent literature details many photoconductive resins made by polycondensation of aromatic compounds with formaldehyde and the like, but, typically, no fundamental measurements of charge generation or transport have been made.

8.3.3 Polymers with aromatic amine groups

Polymers with aromatic amine groups (and various substituents) comprise the most studied and best understood photoconductive and charge-transporting materials (Fig. 8.13). The arylamine transport-active groups are either part of the polymer structure or are mixed with the host polymer. One can easily recognize that PVK is a substituted aromatic amine.

Other carbazole-containing polymers are also photoconductive [2]. Among the carbazole polymers studied in detail are poly(*N*-epoxy-propylcarbazole) [75], poly[γ -(β -*N*-carbazolyethyl)-L-glutamate] [76] and poly[β -(*N*-carbazolyl vinyl ether)] [77]. Charge mobilities in these polymers are comparable to those in PVK, but they form tougher, less brittle films.

The photoresponse of arylamine-containing polymers can be extended to the visible range by copolymerizing the donor monomer with electron-accepting comonomers [78, 79]. For example, poly(*N*-methyl-3-hydroxy-methylcarbazolyl acrylate-co-acryloyloxy-3'-hydroxypropyl 3,5-dinitrobenzoate) extends the photoresponse through the visible to the near-infrared range [79].

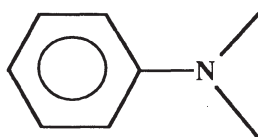


Fig. 8.13 The arylamine transport-active group.

The possible effect of spatial order on carbazole groups has been a subject of discussion. Isotactic poly[2-(*N*-carbazolyl)ethyl acrylate] exhibits a room-temperature hole mobility of $1.7 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $2 \times 10^7 \text{ V m}^{-1}$, which is considerably higher than that of the atactic polymer or PVK [80]. On the other hand, these values are very close to those obtained for NIPC/polycarbonate at a comparable concentration of the transport-active molecule, i.e. a system with no order. Experiments with other carbazole polymers have shown that changing the backbone (e.g. carbon vinyl to siloxy) [45], or spacing of carbazole groups from the chain, has only a secondary effect.

As in the case of polymers with polynuclear aromatic groups, all aromatic amine-containing polymers that have been examined for photoconductivity support charge transport and show at least signs of carrier generation in ultraviolet light. They also typically accept and transport charges from extrinsic photogenerators such as selenium. Numerous polymers belong to this category [2], e.g. poly(*p*-diphenylaminostyrene), poly(*N,N*-diphenylaminomethylstyrene), poly(*N*-vinylindole), poly(vinyldiphenylamine), a series of arylamine-containing methacrylate polymers, and a number of condensation products of carbazole derivatives. Hole mobilities measured in some of these polymers are similar to those seen in PVK [22].

Among other recently obtained photoconductive polymers containing donor groups and an extended π -electron system is electrochemically polymerized poly(thionaphthene-indole) [81].

Many photoconductive and hole-transporting 'molecularly doped' polymers (i.e. solid solutions of transport-active arylamine containing molecules in an inert polymeric binder, typically polycarbonate) have been studied in detail. Among them are triphenylamine [21, 46], *N*-isopropylcarbazole [19, 20], bis(4-*N,N*-diethylamino-2-methylphenyl)-phenylmethane [32, 33], *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl-4,4'-diamine) [34], 4-diethylaminobenzaldehyde-1,2-diphenylhydrazone [35], 2,5-bis(4-*N,N*-diethylaminophenyl)-1,2,4-oxadiazole [82] and 1-phenyl-3-(4-diethylaminostyryl)-5-(4-diethylaminophenyl)pyrazoline [18,82]. The carrier-generation efficiency, as determined in some of these (undoped) systems, is typically low and the carrier mobilities at 40–50 wt% concentrations of the active molecules are 10^{-10} – $10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$.

8.3.4 Inorganic polymers

Crystals of bis[*catena*-poly(methylarsenic)] are photoconductive when exposed to radiation with photon energy greater than 1.55 eV [83]; TNF-doped poly[bis-(2-naphthyloxy)phosphazene] and poly[bis(*p*-tolyl-

amino)phosphazene] [84] are also intrinsically photoconductive (the latter having $-(P=N)-$ repeat units in the chain).

High-molecular-weight silicon backbone polymers, polysilylenes, also exhibit high room-temperature hole mobilities, near $10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ [40, 41]. The independence of charge transport of the nature of the side-groups in polysilylene indicates that carrier migration involves the σ -bonded saturated backbone rather than the pendant groups. The side-groups may be either aromatic or aliphatic. The similarity of the transport characteristics and activation energies with those observed in disordered solids, where transport proceeds by hopping among discrete sites, suggests that charge transport in polysilylenes proceeds by the same mechanism, namely by hopping along segments of the silicon chain. Only hole transport has been seen in these saturated polymers. Polysilylenes with simple aliphatic or aromatic side-groups do not absorb in the visible range of wavelengths, and therefore are only UV photoconductors. The charge-carrier photogeneration efficiency ϕ is rather small, less than 10^{-4} .

Photoconductivity has also been detected in polymers prepared by glow-discharge polymerization of tetramethylsilane, tetramethyltin and tetramethylgermanium [85], polymers of copper phthalocyanine [86] and rhodium(I) aryldiisocyanide polymers [87].

8.3.5 Electron-transporting and bipolar polymers

References to electron-transporting polymers or small molecules are rare in the literature. The only organic substances in which electron transport has been observed are solid solutions of TNF in polyester [15] or PVK [14] and some TNF derivatives [88], of which 2-alkyltrinitrofluorene-9-ones [89] are perhaps closest to TNF in their transport capabilities. Recently, several substituted diphenylquinones have been added to the small inventory of electron-transporting molecules [90]. It is interesting to note that the best transport performance has been achieved with TNF derivatives in PVK or other carbazole polymer binders. A methacrylate with the TNF group attached was polymerized, but no electron transport was detected [91].

8.4 EXPERIMENTAL TECHNIQUES

Fundamental parameters in photoconductivity studies of solids are the quantum efficiency of photogeneration ϕ , the injection efficiency Y (where applicable) and the carrier mobility μ . These parameters are not directly obtainable from steady-state measurements, where ϕ and μ appear as products in the expression for photoconductivity. Independent experiments are therefore required [92]. Transient techniques such as time-of-flight (TOF) and xerographic discharge are best suited. Both

techniques require blocking (non-injecting) contacts. In the TOF technique the polymer or the layered system is sandwiched between two electrodes, at least one of which is semitransparent, and connected in a circuit with a voltage source and a resistance. If the contacts are blocking and the film is an insulator in the dark, the source voltage appears across the film. Charges are then produced in the film or in the adjacent photo-generator by a flash of light, the duration of which is much shorter than the transit time of the charges. In single-layer systems most of the charges are generated in the region of the film that is close to the semitransparent electrode, where most of the incident photons are absorbed. In order to resolve the migrating sheet of charges as a current pulse the condition $RC < t_{Tr}$ must be met, where R is the resistance, C is the capacitance and t_{Tr} is the transit time of the charges. For specimens without excessive charge dispersion, the obtained signal is (ideally) a rectangle with an amplitude

$$i_0 = \frac{e\phi N}{t_{Tr}} \quad (8.23)$$

where e is the electronic charge and N is the number of absorbed photons. When the charges reach the electrode, the current drops to zero, thus giving t_{Tr} . The carrier mobility is then

$$\mu = \frac{L}{Et_{Tr}} \quad (8.24)$$

where L is the film thickness. In materials with highly dispersive transport the transit time t_{Tr} is determined from the $\log i$ versus $\log t$ plots.

In the xerographic technique the corona-deposited charge plays the same role as the semitransparent electrode. The potential difference across the specimen is monitored by a capacitively coupled probe. In the absence of charge trapping, the rate of potential decay has the form

$$\frac{dV}{dt} \propto \frac{I'\phi}{C} \quad (8.25)$$

where C is the capacitance and I' is the number of absorbed photons per unit area per unit time. Free charges must be photogenerated slowly by using a weak light source, so that the total amount of charge (equal to the surface charge CV_0) is produced in a time much longer than t_{Tr} . By measuring the decay rate of the potential, μ and its field dependence can be obtained.

8.5 APPLICATIONS

The only commercial field where photoconductive or charge-transporting polymers have been applied successfully is electrophotography. Many

modern electrophotographic copiers, duplicators and laser printers employ layered organic photoreceptors with a polymeric charge-transport layer. The charge-transport layer is typically a solid solution of transporting molecules in an inert polymeric binder resin. The main advantages of organic photoconductors are panchromaticity, including near-IR sensitivity for solid state laser printers, flexibility for application in belt photoreceptors, simple fabrication by solution coatings and, most importantly, low cost. The best current organic xerographic photoreceptors are as sensitive as the common inorganic devices based on selenium.

Application in photovoltaic cells has been suggested many times, but the low conversion efficiency and particularly the high UV instability of the polymers have prevented their commercial utilization. Several other possible applications have been reported in the literature, but none have been exploited commercially. Among them are photothermoplastic imaging [93], holographic recording [94] and optical switching devices [95].

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