PHOTOCONDUCTIVE POLYMERS

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Abstract – The fundamental aspects of charge carrier photogeneration and transport in organic polymeric photoconductors are discussed. Both pro- cesses are governed by the molecular nature of these solids and by the chemical and physical disorder associated with the amorphous polymeric state. Transport of electronic charge (holes/electrons) is considered in terms of localized electron transfer reactions between appropriate mole- cular functions. The low carrier mobilities observed in polymeric photo- conductors, and their dependence on electric field, temperature and con- centration of active component, are considered and current theoretical models are presented.

INTRODUCTION

The development of photoelectrically active polymers was originally stimulated by the dis- covery of Hoegl[1] that poly-N-vinylcarbazole (PVK) and sensitized PVK exhibited high enough levels of photoconductivity to be of utility in practical electrophotographic processes. Much of the subsequent effort was focused on the synthesis of vinyl type addition polymers possessing pendant aromatic and heterocyclic groups, and most of the published information on materials and devices is to be found in the patent literature. Other polymers, e.g., condensation type, have also been investigated but clearly at a much lower level of activity.

A photoconductive material is defined as one which exhibits an increase in electrical con- ductivity upon illumination. Many organic materials, including polymeric systems, have been reported to exhibit photoconductive properties. Very few, however, possess the level of activity required in commercial applications. In most practical devices the system is required to be insulating in the dark and conductive (by a change of several orders of mag- nitude) in activating light. The direct effect of the absorbed photons is to generate charge carriers in the material which contribute to the current. In the classical inorganic photoconductors, e.g. Se, Si, where conduction bands exist, the photogeneration step involves direct excitation of an electron from a filled valence band into the empty conduction band, provided $h\nu$ > forbidden gap energy. In organic solids, which are molecular in nature, the photogeneration mechanism is considerably more complex. Photoproduction of charge carriers is limited by the many competitive photophysical processes which are possible in molecular organic solids. The generation step is strongly electric field dependent and varies widely for different materials. Smith and Sharp[2] have reviewed this process and have concluded that no single mechanism can account for the photogeneration of charge carriers in organic solids in general.

The molecular nature of the organic solid state, i.e., week Van der Waals intermolecular interactions, also results in much lower charge carrier mobilities than are encountered in the inorganic semiconductors. The mobilities are also very strongly field and temperature dependent and vary over several orders of magnitude depending on the physical state of the system. Measured electron drift mobilities in liquid, amorphous and crystalline 2,4,7- trinitrofluorenone (TNF) and in TNF/polymer dispersions are presented in Table 1.

The mobilities measured in single crystals of aromatic and heterocyclic molecules (anthra- cene[4], N-isopropylcarbazole[5]) are generally in the range $10^0$ to $10^{-2}$ $cm^2V^{-1}sec^{-1}$ for both holes and electrons and are very clearly defined. In contrast to this, vinyl polymers pos- sessing the same pendant chromophore (vinylanthracenes[6], vinylcarbazoles[7]) generally exhibit only efficient hole transport, with mobilities in the range $10^{-5}$ to $10^{-9}$ $cm^2V^{-1}sec^{-1}$. The mobilities in these disordered amorphous polymers are also poorly defined (highly dispersive current signals). The inability to detect electron transport in these and other similar polymers has been attributed[8] to the complications arising from the presence of oxygen and oxidative impurities which effectively trap the electrons, rather than any intrinsic limita- tion of the materials.

TABLE 1.  Electron drift mobilities in TNF systems[3]

| Sample | $\mu_-$ $(cm^2V^{-1}sec^{-1})$ | $E_o$(ev)* |
|---|---|---|
| Crystal | $6 \times 10^{-2}$ | $\sim 0.1$** |
| Amorphous | $2 \times 10^{-6}$ | 0.63 |
| Liquid | $4 \times 10^{-4}$ (173°C) | $0.35$** |
| TNF:PVK[†] (0.1:1) | $\sim 10^{-9}$ | $\sim 0.7$ |
| (0.5:1) | $\sim 10^{-7}$ | $\sim 0.7$ |
| (1:1) | $\sim 10^{-6}$ | $\sim 0.7$ |
| TNF:Polyester[†] (0.4:1) | $\sim 5 \times 10^{-8}$ | $\sim 0.7$ |
| (3:1) | $\sim 5 \times 10^{-7}$ | $\sim 0.7$ |
| (5:1) | $\sim 10^{-6}$ | $\sim 0.7$ |

Applied field $E \sim 10^5 V\ cm^{-1}$, T = 25°C

\*      $E_o$ = zero field activation energy.

\*\*   Mobility was found to be independent of applied field.

†      TNF molecules dispersed in a polymer matrix.


In this presentation I will attempt to cover some of the more recent and significant findings in the areas of charge carrier photogeneration and transport in some of the better defined organic materials, with particular reference to polymeric systems.  Both processes are fundamentally related to the molecular (electronic) structure and to the physical (morphological) structure and, where they exist, these correlations will be presented.  Very recently, considerable progress has been made in the theoretical understanding of charge generation and transport in disordered systems and references to these models are included.


### PHOTOGENERATION

Photogeneration can be an intrinsic property of the polymeric photoconductor, but may also occur in a separate photoactive component which subsequently injects the charge into the polymer.  Studies of photogeneration in polymer systems are experimentally challenging.  It is very difficult to separate the effects associated with generation and transport, and to establish unambiguously the field and temperature dependence of the actual photogeneration process.  Virtually all of the work in this area has been carried out on the PVK and doped PVK systems.  The application of xerographic charge decay and transient current techniques, coupled with a good understanding of the transport characteristics, has provided key insights into intrinsic and extrinsic (including injection) photogeneration processes.

Pai[9] and Regensburger[10] studied charge generation and transport in PVK.  The photogeneration was shown to be electric field dependent with a quantum efficiency for carrier production in the range $10^{-1}$ to $10^{-2}$ at fields of $10^6$ V $cm^{-1}$.  Hughes[11] showed that with bulk x-ray excitation techniques the efficiencies were much lower, the implication being that surface phenomena play a significant role with strongly absorbed light.  Williams and Pfister[12] clearly established the importance of surface states, oxidative impurities, etc. on the photogeneration in PVK.  Even in the purest available samples of polymer, extrinsic effects dominate the photogeneration process.

Figure 1 shows the spectral dependence of the generation efficiency in commercial and purified PVK (1) and in the related polymers, poly-2-vinyl-N-ethylcarbazole (P2VK, 2) and poly-3-vinyl-N-ethylcarbazole (P3VK, 3).  The efficiency of carrier production in purified PVK, P2VK and P3VK increases in a stepwise fashion with decreasing wavelength, the steps coinciding with the next higher lying electronic states in the carbazole chromophore, i.e. $\sim 3100 A°$ and $2850 A°$.  Within the same electronic state the efficiency is roughly independent of wavelength.  This contradicts previously published work on PVK in which the carrier generation efficiency was claimed to closely follow the absorption spectrum.
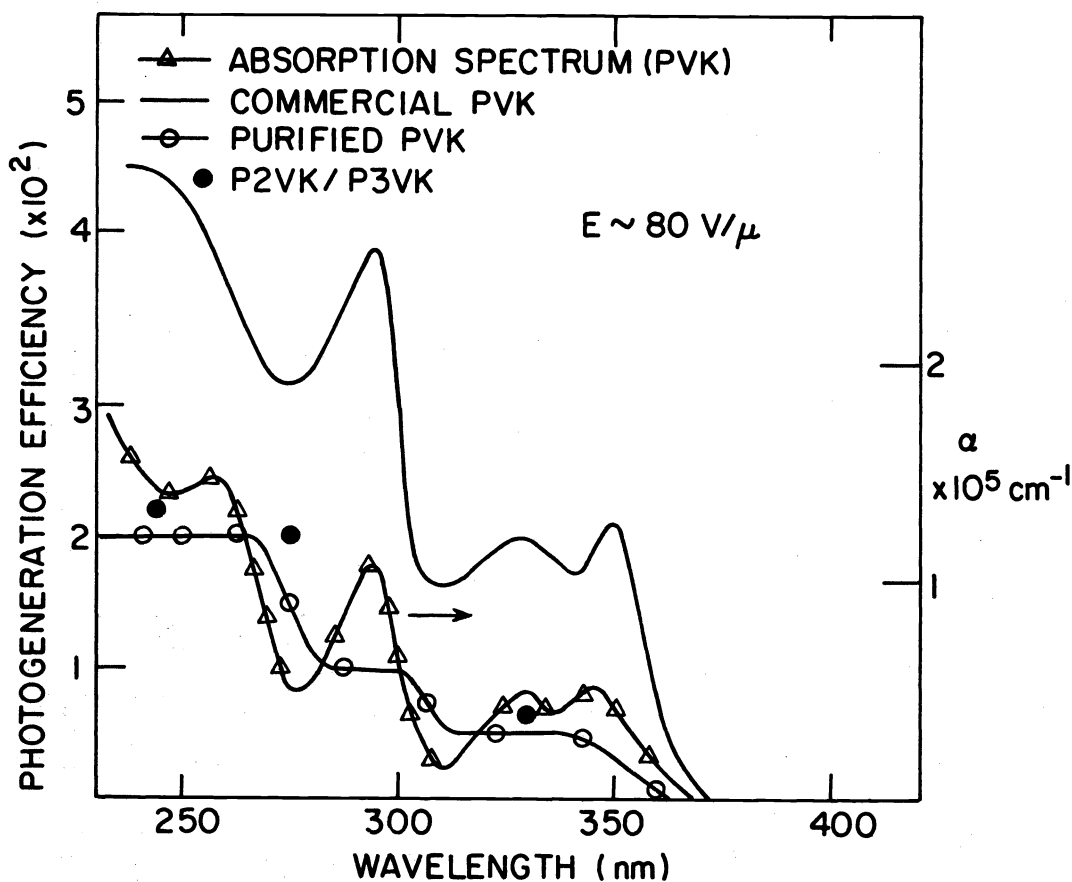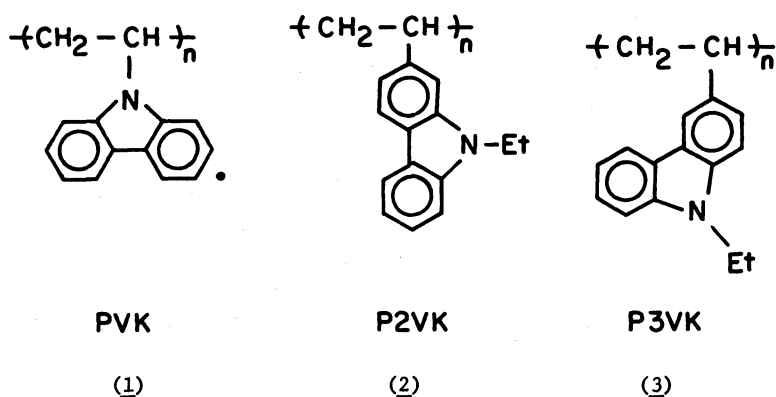
Fig. 1.  Carrier generation efficiency in vinyl carbazole polymers.

The scheme presented in Figure 2 summarizes the currently accepted mechanism for the photo-generation process in polymers such as PVK.  The excited state (singlet/triplet manifold) of the carbazole chromophore, $m^*$, can undergo radiationless decay back to the ground state, m, diffuse into an excimer state, $e^*$, or form a charge transfer state, $\underset{\sim}{m}^*$.  The lowest lying state in this $m^*$ manifold corresponds to the situation where the electron - hole pair resides on neighboring molecules.  One of the states will eventually attain a charge separation such that their Coulomb interaction is of the order of kT and free charge carriers will be produced.  Radiationless deactivation and excimer formation processes are, therefore, competitive with carrier generation.  In this general scheme, carrier formation via singlet-triplet and triplet-triplet annihilation is considered unlikely because of the short exciton diffusion lengths (few hundred angstroms) encountered in vinyl polymers.  In the presence of an

external electric field, the geminate recombination of the electron-hole pair is reduced and, therefore, the rate of carrier production will exhibit some appropriate field dependence, as observed experimentally in all organic photoconductors.
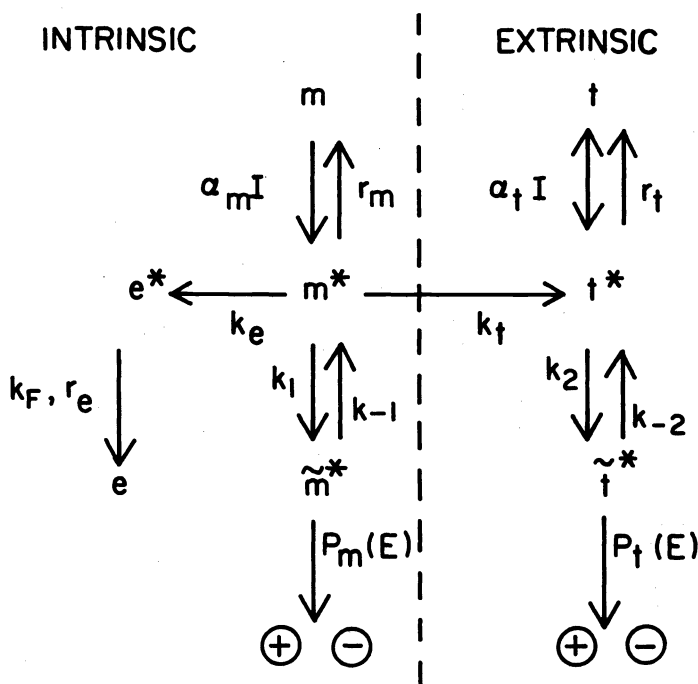


Fig. 2.   General mechanism for carrier photogeneration in PVK.

The question whether charge carriers are produced via the $m^*$ or $e^*$ states can be answered by considering the emission characteristics of polymer films. Emission from solid PVK films is almost exclusively from excimer ($e^*$) states[13-14]. In the precence of an electric field it has been demonstrated[15] that charge carriers are produced at the expense of fluorescence. Also, the relative decrease of the fluorescence intensity is of the order of the saturation efficiency for carrier generation ($\lesssim 0.15$). Recent studies of Hatch[16] have confirmed this observation and he has further shown that while the fluorescence efficiency decreases with increasing electric field, the lifetime ($\tau$) of the emitting state remains constant. Carrier production, therefore, occurs through the $m^*$ rather than the $e^*$ manifold, at least in the purified vinylcarbazole polymers.

In commercial or unpurified PVK samples the generation process is dominated by impurities, i.e. extrinsic in nature. The impurities can be physical (e.g. defects, chain folds, etc.) or chemical (e.g. process or oxidative contaminants, surface states, etc.) and in some cases impossible to remove even using standard polymer purification techniques. Mikawa[21] studied the emission/photocurrent relationship in PVK doped with the weak acceptor molecule, dimethyl-terephthalate. These authors showed that the exciplex fluorescence is quenched by application of an electric field. The quenching was interpreted in terms of a mechanism involving a field assisted thermal dissociation of the exciplex into free carriers, i.e.,

$$(D, A)^* \rightarrow (D^{\delta+} \cdots \cdots A^{\delta-})^* \rightarrow D^{\ddot{+}} + A^{\dot{-}}$$

This mechanism is consistent with carrier production via the $t^*$ manifold in the general scheme in Figure 2.

In practical systems it becomes necessary to utilize extrinsic sensitization in order to extend the spectral response of the photoconductor into the visible region of the spectrum. This is generally achieved by addition of dyes/pigments or by formation of charge transfer complexes. It is now reasonably well established[17,18] that the sensitization process involves electron rather than energy transfer processes. Charge carriers (electrons/holes) are

formed via electron transfer reactions between the excited states of the sensitizing mole-
cules and the molecular chromophore in the host material. Depending on the relative energy
levels of the appropriate states in the sensitizer (S) and the matrix (T), either electrons
or holes can be injected into the transporting polymer binder. This is shown schematically
in Figure 3. Electrical measurements in PVK have clearly established[17,18] that holes are
generated by electron transfer to the photoexcited dye molecules. The holes are subsequently
transported through the PVK films while the electrons remain trapped at the dye site and can-
not move. In an electron transport matrix the holes will be trapped and in an ambipolar
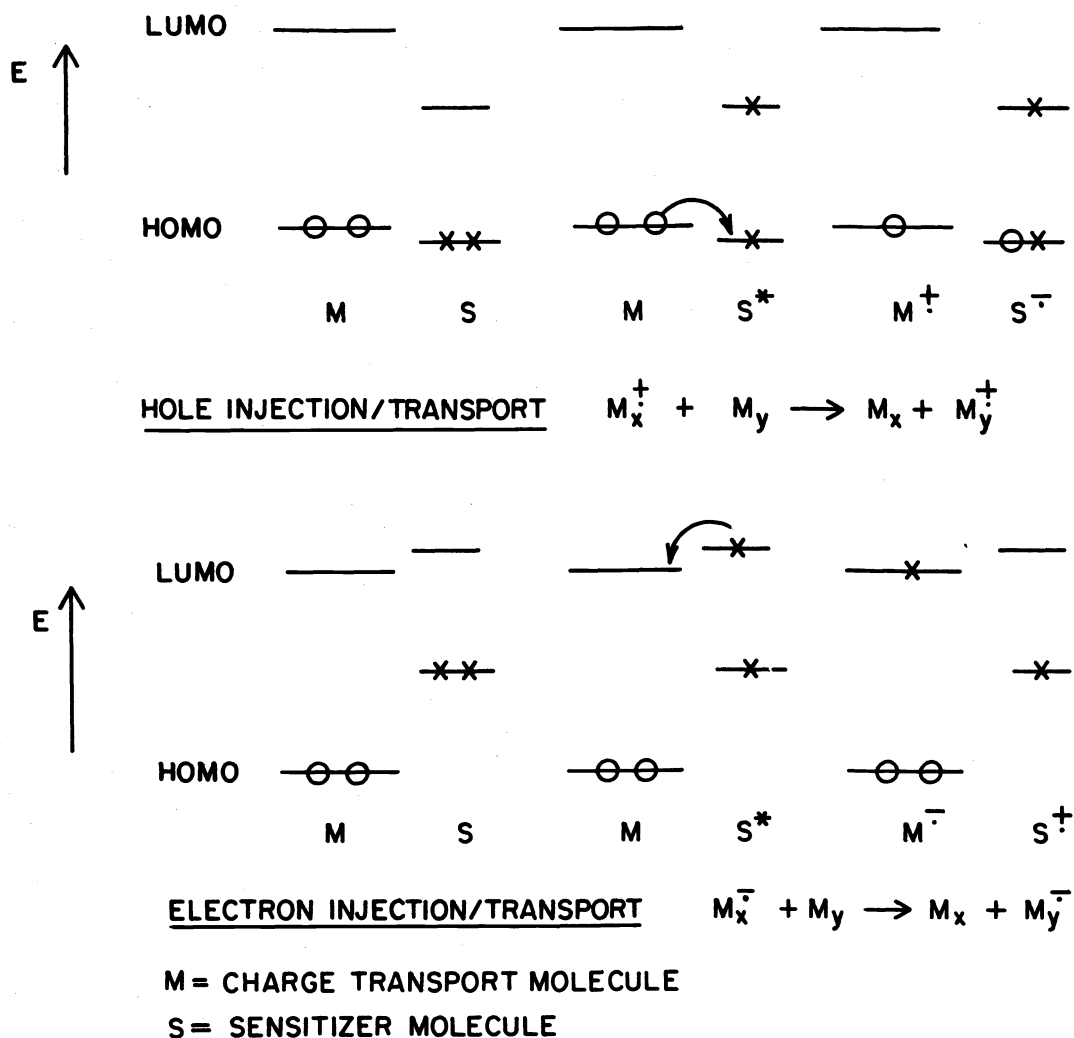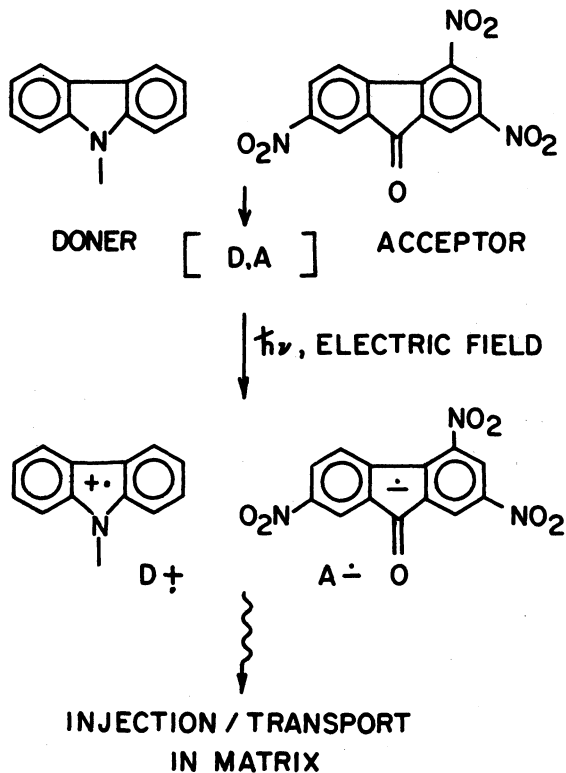matrix both holes and electrons can be transported.



Fig. 3. Mechanism of dye sensitization of organic photoconductors.

This mechanism is appropriate to both molecular solutions and microcrystalline dispersions
of sensitizing agents and also to layered structures of sensitizers and polymeric photocon-
ductors. The polymer functions primarily as a transport medium in these sensitized struc-
tures.

The polymeric complex of PVK with TNF has been the most extensively studied charge transfer
type sensitizer. Photogeneration has been investigated over a very wide TNF:PVK composition
range (0.1:1 to 1:1 molar ratio) and quantum efficiencies as high as 0.25 were measured. On
the basis of detailed absorption and electroabsorption measurements on thin amorphous poly-
meric complex films, Weiser[19] concluded that appreciable charge transfer takes place in the
excited state of the carbazole/TNF complex. The photogeneration step can be visualized as
an electron transfer reaction to produce the corresponding oxidized/reduced couple, i.e. ion
radical species,

NO$_2$

O$_2$N                              NO$_2$

O

DONER     [  D,A  ]     ACCEPTOR

$\hbar\nu$, ELECTRIC FIELD

NO$_2$

+·

N

O$_2$N                              NO$_2$

D$\underset{\bullet}{+}$          A$\dot{-}$  O

INJECTION / TRANSPORT
IN MATRIX

Depending on the composition of these films either hole transport via the carbazole or electron transport via the TNF molecular states is observed[20]. This particular system is somewhat unique in that at TNF:PVK compositions in the range 0.5 to 0.7:1, both holes and electrons are mobile and charge carrier trapping encountered in most sensitized polymers is not prevalent.

The field enhanced carrier photogeneration in both inorganic and organic photoconductors (both molecular crystals and polymeric materials) is best discussed[22] in terms of the Onsager model (which was originally developed to account for geminate recombination of ions in solution). This model has been very successful in predicting the photogeneration characteristics of PVK and doped PVK films[12] and of the PVK:TNF systems[23] in both the low and high field regimes.

### TRANSPORT

The study of electronic transport in insulating, low mobility solids presents many experimental problems. It is only within the last few years that reliable charge transport measurements (carrier concentrations, mobilities) have become available and the number of materials studied has precluded the establishment of any meaningful molecular structural/electrical correlations.

Two techniques have proven highly successful in characterizing transport phenomena in polymeric photoconductors. Xerographic charge decay experiments have been used to study vinylcarbazoles[10,7] and other vinyl type polymers[6]. One particular modification of this technique has been widely used in our laboratories for screening potential photoconductors and obtaining carrier mobility values. A film of polymer on a conductive substrate is overcoated with a thin layer of a very efficient photogenerating material such as selenium. The structure is charged to some potential (V) with a corona unit and exposed to an appropriate illumination source. From the decay in the surface potential, (dV/dt), and utilizing a modified version of Child's Law, the carrier mobilities can be estimated. This measurement also provides information on charge carrier trapping, and on the detailed relationships between transport and generation of latent electrostatic images in xerography. The second type of measurement is the transient current or time of flight technique and this has been used to study mobilities in PVK[9], the PVK:TNF[20] polymeric complex and TNF dispersions in polyester matrices[3].

Regensburger[10] first reported the mobility of holes ($\mu_+$) in PVK. He found that the hole mobility was field dependent ($\alpha E^2$) with an activation energy of 0.4-0.7eV. Subsequent independent studies have confirmed these results and hole mobilities within the range of $10^{-6}$ to $10^{-7}$ $cm^2V^{-1}sec^{-1}$ at a field of 5 x $10^5V$ $cm^{-1}$ have been reported for PVK[7,9,20,24]. These mobilities were measured by both xerographic and transient techniques and the agreement is remarkable considering the probable variations in polymer purity and retained coating solvents. Generally the higher mobilities are found in carefully vacuum degassed samples.
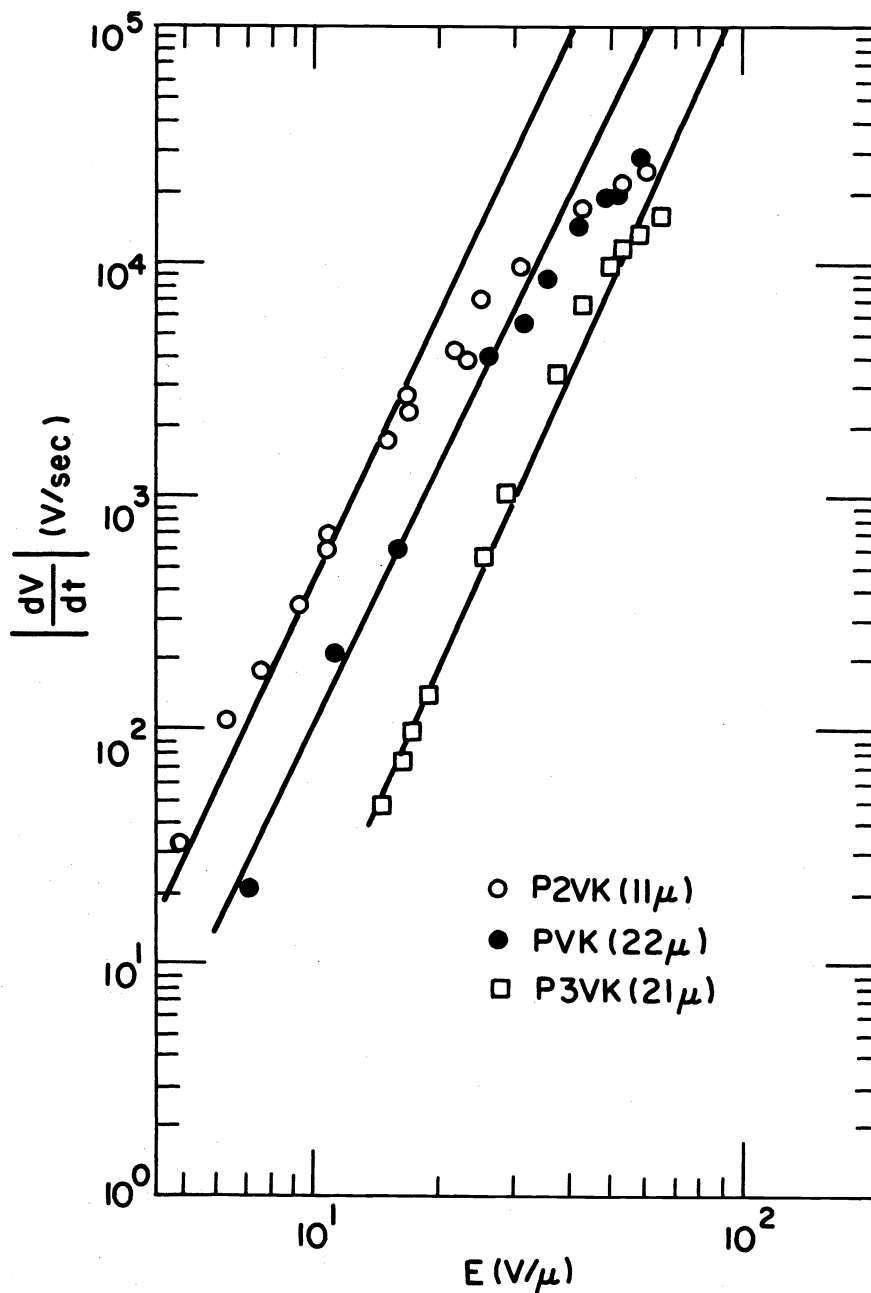


Fig. 4. $|dv/dt|$ as a function of applied field (E) for a series of vinylcarbazole polymers.

In an attempt to probe the effect of steric interactions on the transport of holes in carbazole containing polymers, Williams et al. synthesized[25] and evaluated[8] poly-3-vinyl-N-ethyl carbazole (P3VK) and poly-2-vinyl-N-ethyl carbazole (P2VK). Hole mobilities for PVK, P3VK and P2VK were measured using the xerographic discharge technique and Figure 4 shows plots of $(dV/dt)_{t=0}$ (Vsec$^{-1}$) as a function of applied field E(V.$\mu^{-1}$) for the three polymers. Table 2

shows the mobilities at a field of $4 \times 10^5 V cm^{-1}$.

TABLE 2.  Hole drift mobilities in a series of vinyl carbazole polymers

| Polymer | $\mu_+(cm^2V^{-1}sec^{-1})$ | Exp. Method | Ref. |
|---------|------------------------------|-------------|------|
| P2VK | $1.4 \times 10^{-6}$ | Xerog. Disch. | 8 |
| P3VK | $2 \times 10^{-8}$ | Xerog. Disch. | 8 |
| PVK | $1.4 \times 10^{-7}$ | Xerog. Disch. | 8 |
| PVK | $\sim 10^{-6} - 10^{-7}$ | Transit time | 10 |
| PVK | $\sim 3 \times 10^{-7}$ | Transit time | 20 |
| PVK | $\sim 1 \times 10^{-7}$ | Transit time | 26 |
| PVK | $\sim 10^{-6} - 10^{-7}$ | Transit time | 9 |

Applied field $E \sim 10^5$ $Vcm^{-1}$, $T = 25°C$.

Nmr studies[27] of these three vinylcarbazole polymers revealed that the degree of shielding due to ring current effects (shift to higher $\tau$) of the aromatic protons in PVK and P2VK was substantially greater than in P3VK.  Because of the width of the nmr lines resulting from slow segmental motion in these polymers, it was not possible to fully interpret these proton spectra.  However, it can be qualitatively established that P2VK and PVK which exhibit the highest degrees of carbazole ring overlap also exhibit the highest mobilities.  It should be pointed out that this correlation is based on the solution conformations of the polymers, whereas the transport measurements are carried out on solid films.  The recent correlation[28] established between the photocurrent level in polymers such as poly-1-vinyl pyrene, poly-9-vinylacridine and chloro- and bromo- substituted poly-N-vinylcarbazoles and nmr upfield proton shifts does, however, lend support to this qualitative model.
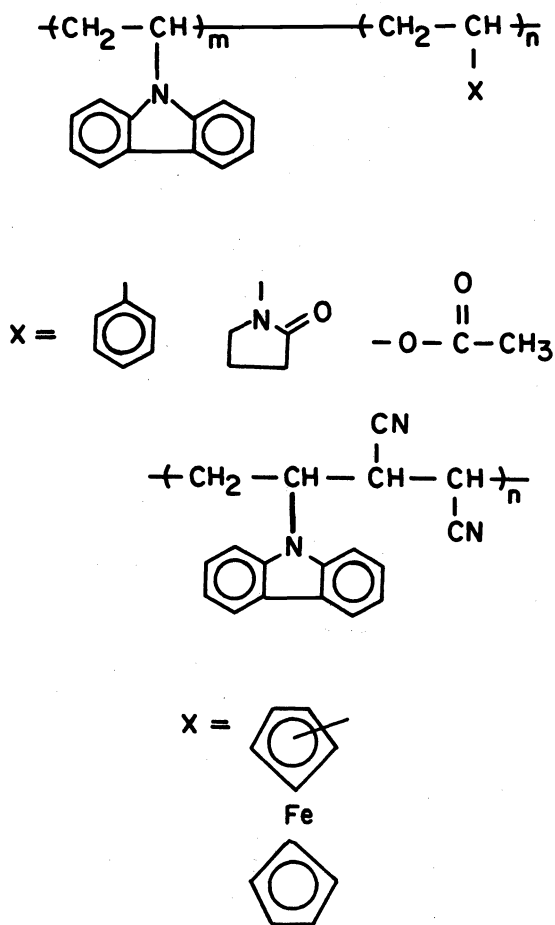
Okamoto[29] recently reported the photoconductive properties of another carbazole containing polymer, poly(β-N-carbazolylethyl vinylether, 4),

$$+ CH_2 - CH \mathbin{\rlap{+}{\phantom{|}}}_n$$
$$| $$
$$O$$
$$|$$
$$(CH_2)_2$$
$$|$$
$$N$$
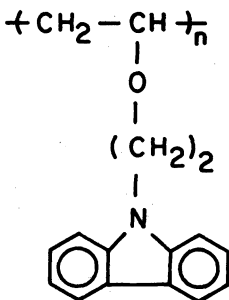
(4)

This polymer (oligomer) exhibited quite different behavior from the vinylcarbazole polymers, and the low photocurrents were attributed to poor transport properties resulting from the low degrees of interaction of the carbazole groups.

Mikawa et al.[30] investigated the photoelectric properties of copolymers of N-vinylcarbazole (NVK) possessing random and alternating structures.  In all cases the photocurrents were decreased.  Pittman[31] also found a lower photoconductivity in NVK - vinylferrocene copolymers.  Both authors concluded that the copolymers exhibited lower carrier mobilities due to perturbations in the active carbazole group interactions.  The role of comonomer on trapping was also recognized, although it must be pointed out that no mobility measurements were made on these materials.

$+CH_2-CH)_m \quad\quad\quad +CH_2-CH)_n$

with carbazole N-substituent on the m unit and X substituent on the n unit.

$X =$ phenyl; pyrrolidinone (N-C=O); $-O-\overset{\overset{O}{\|}}{C}-CH_3$

$+CH_2-CH-\overset{\overset{CN}{|}}{CH}-CH)_n$ with carbazole N-substituent and CN

$X =$ ferrocene (Fe)

The effect of molecular weight on the photoactivity of PVK was studied by Hatano[32]. These authors found a photoconductivity which was molecular weight dependent in the range $M_w \sim 10^3$ to $10^5$, becoming independent of molecular weight above $M_w \sim 10^5$. The phenomenon was attributed to end group induced perturbations of the carbazole group interactions which are critical for effective transport. Again, no actual mobility data was available.

The obvious conclusion that can be drawn from the mobility studies on PVK, P2VK and P3VK is that subtle changes in the steric environment of the active transport function (carbazole group) can produce significant changes in electronic mobility. The photocurrent studies of the carbazole vinylether, of the NVK copolymers and of PVK of different molecular weights are consistent with this picture. Unfortunately, our understanding of the purity and the detailed morphology of amorphous polymers and copolymers does not permit us to probe these structure/transport correlations in more depth.

Several groups have reported the crystallization and orientation of PVK, but unfortunately no electrical measurements were performed. Hermann[33] recently claimed orientation of PVK and PVK charge transfer complex (TNF, TCNQ and $I_2$) films by growth in electric and magnetic fields. Since oriented liquid crystalline materials are known to exhibit unusual dielectric and conductivity behavior, one might anticipate that these novel films will show enhanced charge transport properties.

The charge transfer complex of PVK with TNF (over the composition range TNF:PVK 0.1:1 to 1:1) has been the most thoroughly investigated polymeric photoconductor. This particular combination is somewhat unique in that high TNF loadings can be accomodated into the amorphous polymer without phase separation and crystallization problems. Weiser[19] determined the film compositions and established that free carbazole, free TNF and charge transfer complexes were present. It is interesting to note that whereas some 70% of the TNF molecules are complexed in 0.1:1 TNF:PVK films, only 40% are complexed in the TNF:PVK 1:1 films. Parallel studies of the transport properties were carried out by Gill[20] using the time of flight method and independently by Mort[34] using the xerographic discharge technique. Both the hole and elec-

tron mobilities exhibited similar field and temperature dependences for films ranging from PVK to TNF:PVK 1:1. The magnitude of the drift mobilities was, however, very sensitive to the TNF:PVK ratio and the results are summarized in Figure 5.
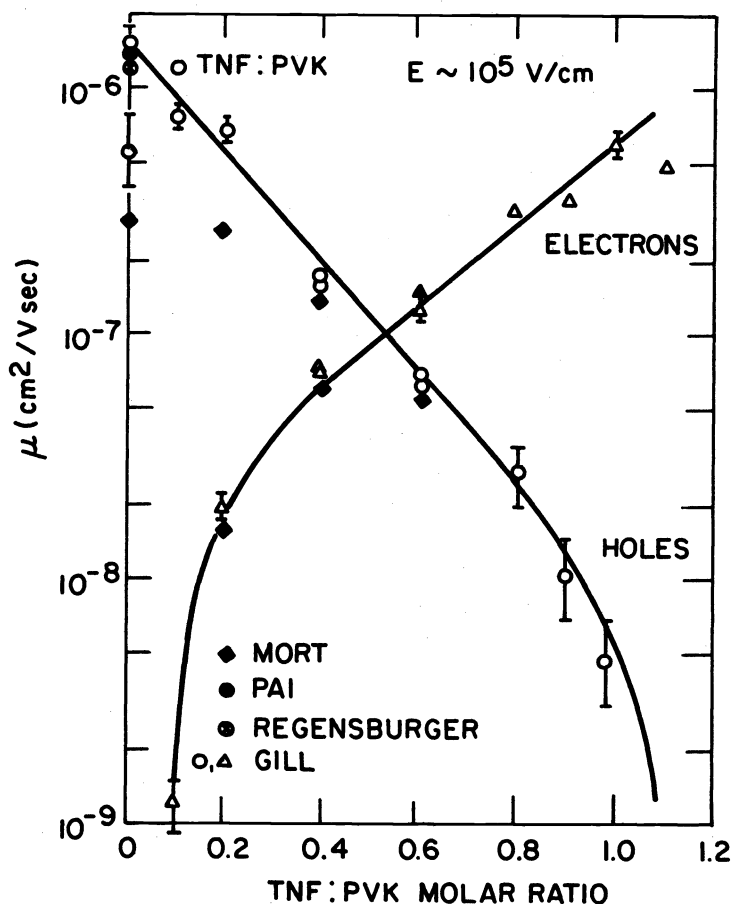


Fig. 5. Hole and electron drift mobilities in PVK:TNF as a function of TNF loading.

The hole mobility in PVK decreases as the TNF loading increases; $\mu_+$(PVK) $\sim 10^{-6}$ $cm^2V^{-1}sec^{-1}$, $\mu_+$(PVK:TNF 1:1) $\sim 10^{-9}$ $cm^2V^{-1}sec^{-1}$, both at a field of 5 x $10^5$ $Vcm^{-1}$. On the other hand, as the TNF content of the films increases the electron mobility increases; $\mu_-$(PVK) not measurable, $\mu_-$(PVK:TNF 1:0.1) $\sim 10^{-9}$ $cm^2V^{-1}sec^{-1}$, $\mu_-$(PVK:TNF 1:1) $\sim 10^{-6}$ $cm^2V^{-1}sec^{-1}$, all at a field of 5 x $10^5$ $Vcm^{-1}$. These results can be rationalized in terms of a mechanism in which hole transport is associated with the PVK (or carbazole) donor component and electron transport with the TNF acceptor component. Further, hole transport appears to involve only non complexed carbazole groups, whereas electron transport occurs via both free and complexed TNF molecules.

Exchange of holes between carbazole groups is dependent on the overlap between the appropriate highest occupied molecular orbitals (HOMO). All the results from the vinylcarbazole polymers and copolymers plus the PVK:TNF systems would indicate that this overlap is very sensitive to perturbation, either morphological or from other chemical species, e.g. comonomers, end groups, dopants. The exchange of electrons between TNF molecules in PVK:TNF occurs through the lowest empty molecular orbitals (LEMO). This is an antibonding orbital which is more spatially delocalized than the bonding orbital involved in hole transport in PVK. It is probable that these orbitals can tolerate larger separations/perturbations without impacting the local electron transfer reactions. Electron mobility is in fact exponentially dependent on the total TNF concentration in PVK:TNF, showing the importance of the overlap.

Figure 6 shows a plot of electron mobility as a function of the average separation (R) of the TNF molecules dispersed in PVK and in a non-complexing polyester matrix[35]. It can be concluded that complex formation in PVK does not impede electron transfer and the mobility is governed by the distribution of the available TNF molecules, both complexed and free. It is more difficult to construct a similar picture for hole transport in PVK:TNF systems. Here, the active carbazole component is covalently attached to the polymer backbone. If all the carbazole groups are involved in hole transport, then the presence of the TNF molecules should not greatly impact the hole mobility. The results, however, are more consistent with a scheme in which the carbazole/TNF complexes effectively dilute the carbazole concentration resulting in lower mobilities with increasing TNF loading. Even in PVK itself, it is likely that not all the carbazole groups are effective in hole transport. The mobility results[7] from the related P2VK and P3VK systems support this view. Some undetermined concentration of carbazole functions are rendered ineffective in transport of holes as a result of unfavorable conformations arising from polymer structure/morphology. Recent studies of Mort[41] on dispersions of N-isopropylcarbazole in polymers should shed some light on this issue.
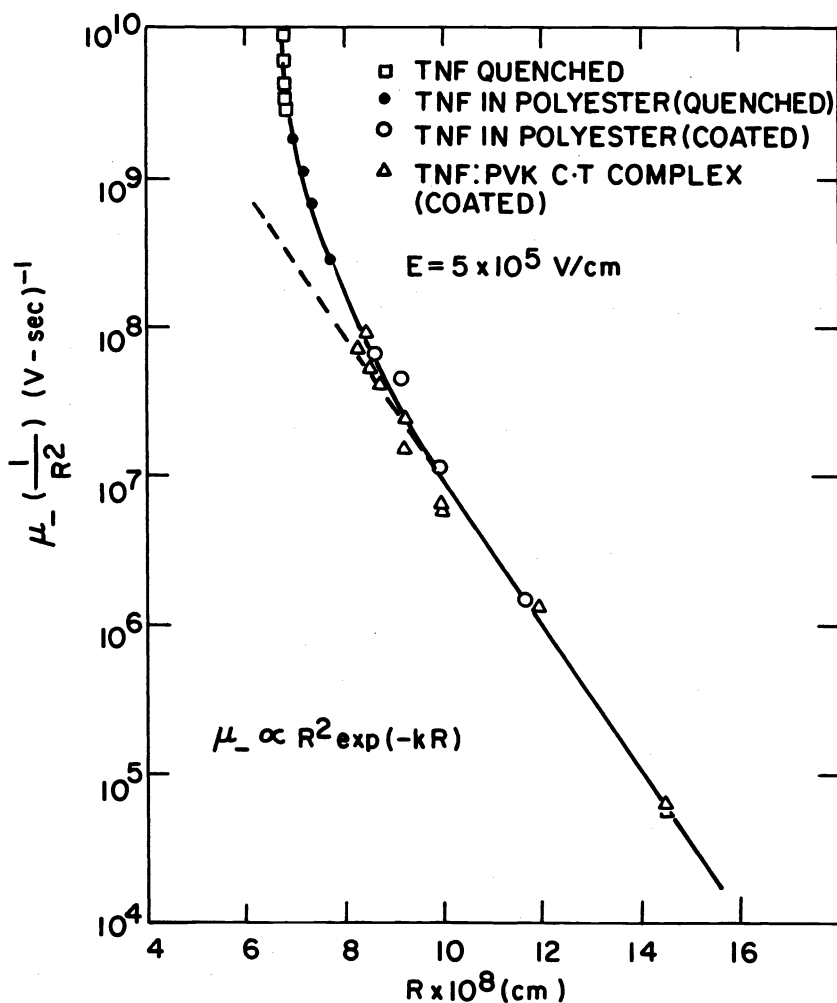


Fig. 6.   Electron mobility as a function of average separation of TNF molecules dispersed in PVK and in a polyester binder.

Mort and Emerald[34], using a thin selenium layer to generate and inject charge into PVK:TNF films, were able to construct an energy level structure for the PVK:TNF combination. This is shown in Figure 7 and is the most definitive analysis of the transport states in any polymeric material to date.
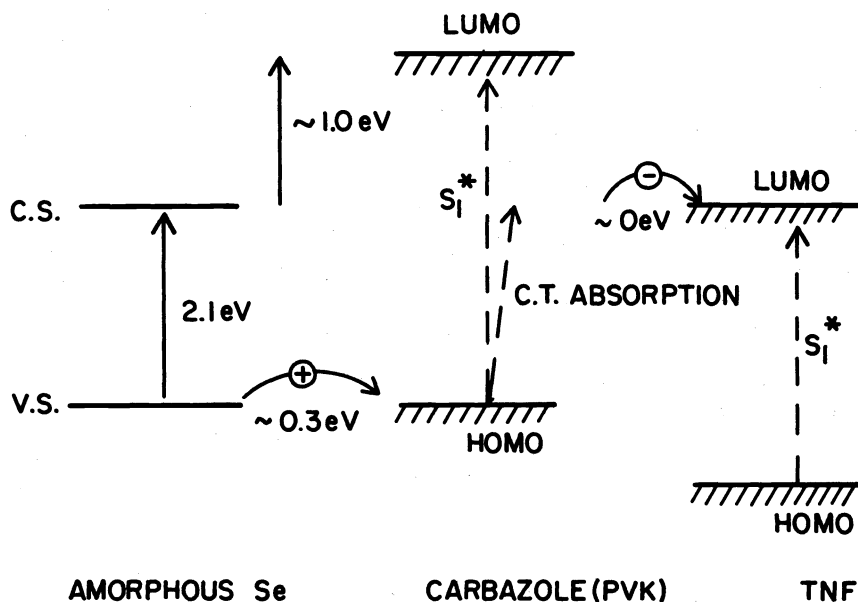
Fig. 7.  Relative energy level structure of PVK and the PVK:TNF complex.

Besides the PVK:TNF polymeric charge transfer complex, no other polymers are known which effectively transport electrons.  There appear to be two basic reasons for this observation; (1) few polymers are known which possess acceptor functions, and (2) the acceptor groups must have electron affinities high enough to compete with $O_2$ and oxidation products for the negative charge carriers.  Certainly vinyl monomers containing such electron acceptor moieties would be extremely difficult to polymerize by free radical and ionic methods.

Poly-2-vinylfluorenone (PVF) was recently synthesized[36] and shown to exhibit very low electron mobilities, $\mu_- < 10^{-8}$ cm$^2$V$^{-1}$sec$^{-1}$ at $E \sim 10^5$ Vcm$^{-1}$.  All attempts to nitrate this polymer were unsuccessful.  Reaction of PVF with malononitrile[37] introduced the corresponding 9-dicyanomethylene fluorene acceptor function into the polymer,
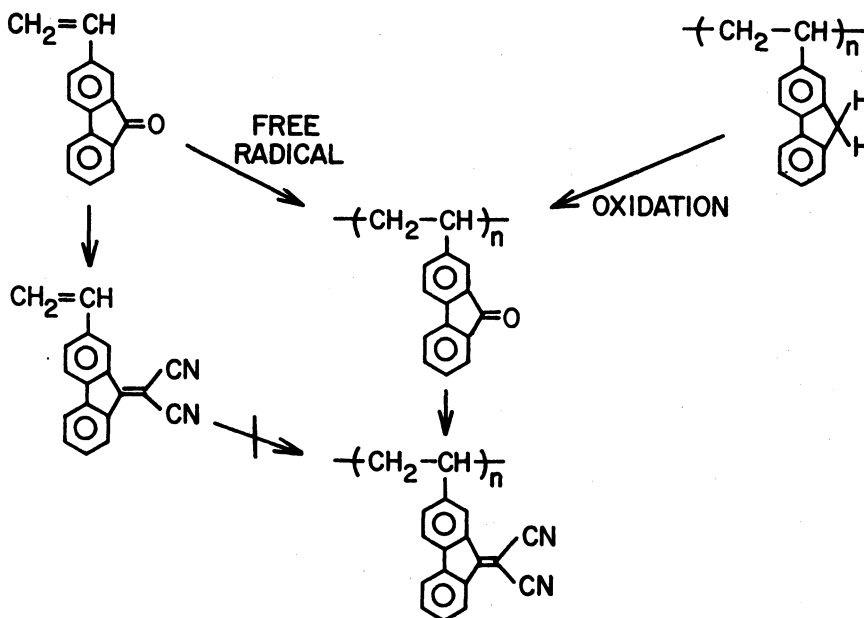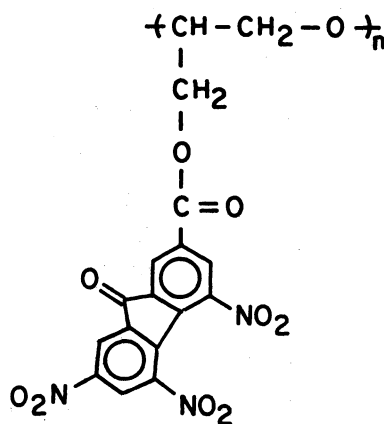
Unfortunately solubility problems precluded any detailed electron transport studies on this novel acceptor polymer.
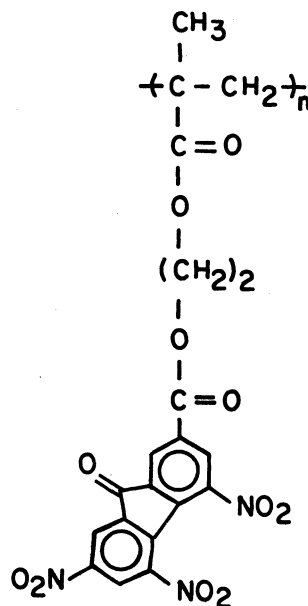
Turner[38] has prepared a number of interesting polymers containing the trinitrofluorene and trinitrofluorenone groups,
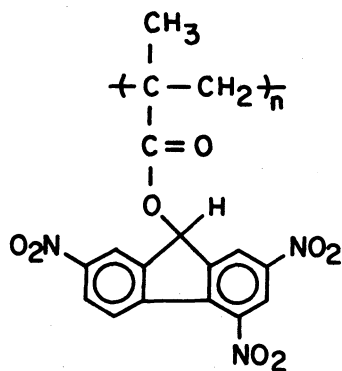


Of the three monomers, the 2,4,7-trinitro-9-fluorenyl methacrylate (5) was the most readily polymerized. The polymer, however, exhibited no electron transport capabilities. The TNF containing monomers, glycidyl-4,5,7-trinitrofluorenone-2-carboxylate, (6) and 2'-ethylmeth-acrylyl-4,5,7-trinitrofluorenone-2-carboxylate, (7) were difficult to polymerize and molecular weights were generally low. Both polymers were characterized by low electron mobilities, $\mu_- \sim 10^{-8}$ cm$^2$V$^{-1}$sec$^{-1}$ at E $\sim 10^5$Vcm$^{-1}$, and high levels of charge carrier trapping.

Two conclusions can be drawn from these results. First, the trinitrofluorene function does not transport electrons, and this can be rationalized by its lower electron affinity relative to trinitrofluorenone. The poor electron transport exhibited by the 4,5,7-trinitrofluorenone containing polymers can probably be explained by an unfavorable morphological structure or by a relatively low TNF content, both of which will result in unfavorable molecular and molecular orbital interactions.

Although the number of polymers for which reliable mobility data is avialable is very limited, a reasonably unified picture of the transport process is emerging. The magnitude, the activated behavior and the concentration (degree of orbital overlap) dependence of electron and hole mobilities strongly suggest a hopping type process involving highly localized charge carriers. Hole transport occurs via highest occupied and electron transport via lowest empty molecular orbitals, HOMO and LEMO respectively. Charge transport can be envisaged as a series of electron transfer reactions between ionized (radical anion or radical cation) and neutral neighboring molecules to distant electrodes. In amorphous materials, including polymers, these electron transfer steps will be governed by chemical and physical disorder in the system and will take place at varying rates. This variation will result from fluctuations in interchromophore separations and orientations which determine orbital overlap. The introduction of slow components into the electron exchange process is manifest in a very dispersive current signal. At the present time, our knowledge of the amorphous state of polymers, particularly those materials described in this review, is far too primitive to permit development of a more detailed structural analysis of the transport mechanism.

The theoretical problem of describing charge transport in amorphous materials requires an understanding of the microscopic and the statistical nature of the process. Small polaron theory attributes the transport to a hopping or tunneling between sites where the activation energy is associated with polarization and vibrational factors of the molecule and its environment. The charge carriers become coupled to the molecular vibrational modes and this has been examined experimentally and theoretically in molecular crystals[39].

A number of 'anomalous' features characteristic of the transport process have provided key insights into the statistical nature of electronic transport in disordered, low mobility

systems. Mobilities have been shown to be dependent both on sample thickness and on applied field. Hence, a mobility cannot be specified for any given material without specifying the sample thickness and measurement field. It is also implied that in sufficiently thick samples a photocurrent may not be observable, although the material is intrinsically capable of carrier transport. A second important feature which was noted from transient experiments was that the sheet of carriers produced at one electrode does not spread in a Gaussian manner as it traverses the sample to the collection electrode.

Scher[40] has developed a stochastic transport model for disordered systems. The detailed features of the transient photocurrents are accounted for by describing the dynamics of the charge carrier packet in terms of a biassed continuous time random walk in the presence of an electric field. The key to this treatment is the proper description of the distribution of waiting times between hopping events which govern the random walk. The model predicts that at longer times the carriers are more likely to encounter at least one longer waiting time at some site leading to the observed dispersion of transits. Transient photocurrents measured in amorphous inorganic photoconductors and in PVK and PVK:TNF and other polymer systems agree extremely well with calculated values.


## APPLICATIONS OF POLYMERIC PHOTOCONDUCTORS

In spite of the extensive studies which have been carried out on the electrical and photo-electrical properties of organic polymeric based materials, their commercial utilization has been very limited. Two currently active areas of research are electrophotography and photoelectric (solar energy) devices.

### Electrophotography
A schematic of the electrophotographic process is shown in Figure 8. In this particular configuration, electrons are transported through the bulk of the material to neutralize the charge on the rear electrode, e.g. PVK:TNF (1:1). Following generation of a latent electrostatic image on the surface of the photoconductor, the system is developed and the image transferred to a receiving sheet (paper) and fixed. In order to complete the cycle, the photoconductor is cleaned of residual developer (e.g. polymeric toner), and any remaining electrostatic pattern is erased. The device is then ready to start another cycle. Polymeric materials combine desirable mechanical and electrical properties with fabrication and cost advantages, making them attractive candidates for commercial exploitation.
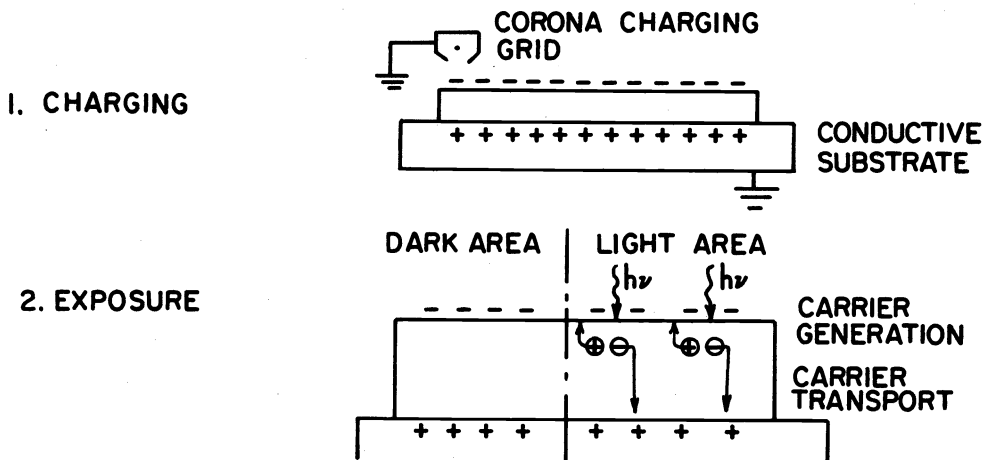


Fig. 8. Schematic of the electrophotographic process—electrostatic image formation.


### Photoelectric Devices
The development of cheap, functional photovoltaic cells for solar energy conversion is highly desirable and there is presently considerable interest in organic polymeric systems. Reucroft[42] has made a study of the PVK:TNF system and has concluded that conversion efficiencies of the order of $10^{-2}$ to 1% might be realized in thin (<1μ) films. For thicker films (>1μ) considerably lower efficiencies were achieved. These efficiencies compare very unfavorably with the present 10 - 15% levels available from silicon solar cells, and are primarily due to the low charge carrier photogeneration efficiencies encountered in organic materials. With the development of improved organic photogenerating molecules and optimized systems, functional devices may become a reality.

This rather limited utilization of polymeric photoconductive materials may appear somewhat discouraging. Their success, however, in the electrophotographic scene is an indication that these systems can compete very favorably with their inorganic counterparts. Significant applications in the important fields of medicine and energy are likely to follow.

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