Charge Carrier Mobility in Transport Layers of Different Structure

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Abstract

A survey of experimental and theoretical results on charge carrier transport in molecularly doped polymers recently obtained is presented. A key transport parameter, drift mobility, measured using conventional time-of-flight techniques is discussed.

A number of polymers (polycarbonate, polystyrene, polyimide) and charge transport molecules (pyrazoloquinaline, picrylarylamine, cyanine dyes) is considered. The doped polymer systems exhibited monopolar or bipolar transport depending on electronic properties of both a dopant molecule and polymer matrix. The experimental data are compared with current theoretical models and they well fit a correlated disorder model for a dipole medium when energetic features of the transport molecules are also taken into account. The results are important for development of the most optoelectronic devices (e.g. electroluminescent, photorefractive, photovoltaic, xerographic etc.) whose operation relies critically on charge transport layers.

Introduction

In recent years charge transporting layers (CTL) based on polymers have been studied extensively due to their wide use as a key element in modern information systems. Photoreceptors based on the layers of such kind are used in photocopiers, laser printers,[1-3] organic light-emitting diodes for flexible displays and flat panels,[2,4,5] photorefractive films for reversible hologram recording with a diffraction efficiency up to 100%,[6,7] photovoltaic converters of light energy into electrical one.[8] For operation of the above mentioned systems, polymer layers have to possess charge transport capability. This condition is fulfilled by doping a polymer layer with low-molecular weight transport molecules or introducing transport substituents into macromolecules. The transport ability is intrinsic to strong donor or acceptor molecules (moieties) which as a rule are dipoles. The mechanism of the carrier transport in organic materials is generally accepted to involve a process where charge carriers move through the CTL by hopping between the transport sites.

Aromatic polyimides (APIs) are characterized by significant photoelectric sensitivity originating from the electron donor-acceptor interaction between the electron acceptor diimide fragments and the electron donor arylene rests of diamines. It was suggested that the charge carriers transport in the APIs is defined not only by the presence of both electron donor and electron acceptor units in the polymer chains, but by peculiarities of the chemical structure and also the APIs solid state structure.[9] It was found out[10] that electroluminescent cyanine dye associates, known as J-aggregates, may be formed at certain conditions in polymer CTLs especially in APIs. In present report, the results of an investigation of the electron and hole transport in some APIs (Fig.1) and their composites with dye J-aggregates are described.

Another type of CTL is based on low weight organic molecules dispersed into inert polymer matrix. In such molecularly doped polymers, it is evident that charge mobility depends on chemical structure of the dopant molecules. In the work, an influence of the electronic structure of charge transporting molecules on the charge drift mobility is studied and discussed. APIs, polycarbonate (bisphenol A) (PC) and polystyrene (PS) were used as a polymer binder and pyrazolo[3,4-b]quinoline (PAQ), picrylarylamine (PAA) and cyanine dyes (DC) were used as a dopant.

Experimental

Charge drift mobility was measured using conventional time-of-flight (TOF) techniques.[1] Details of the experiment may be found in Ref.9. Sandwich type samples the CTL thickness, ranged between 2 and 10 μm, were prepared for the measurements. The transit time, t_T, was determined from the intersection of the asymptotes to the plateau and the trailing edge of the nondispersive transient. At an electric field strength F, the drift mobility is given by $\mu = d/t_T F$.

In the case of insoluble API-1 - API-4, a corresponding poly(amic acid) solution was cast onto ITO coated glass substrates, heated to 80-90 °C and exposed to thermal imide formation in vacuum by raising the temperature to 320 °C for 1 h. Films of the soluble API-5 - API-7 were prepared by coating the API solution in a mixture of 1,1,2,2-tetrachlorethane and chloroform onto substrates, and drying under normal conditions.[9] The soluble APIs doped with the DC were also prepared by the same way.

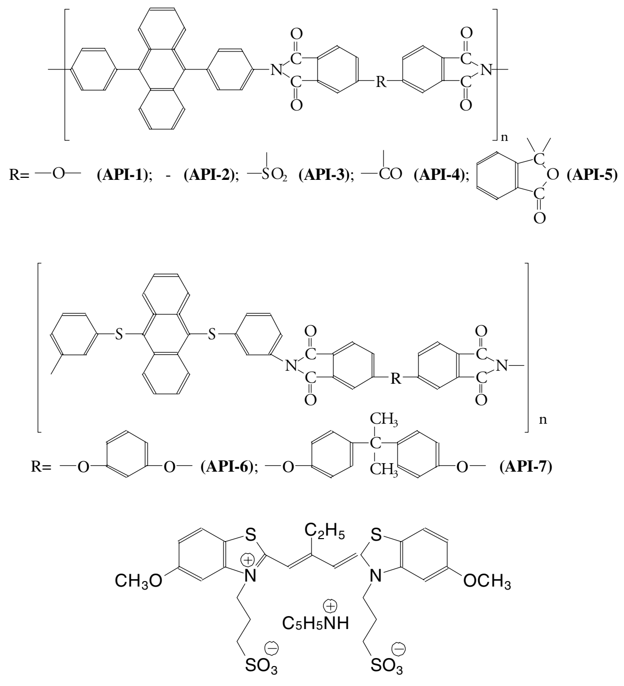


Figure 1. Structure of the APIs and the DC studied.

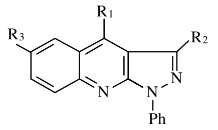


Figure 2. General structure of the PAQ derivatives

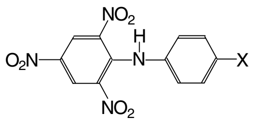
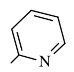


Figure 3. Structure of the PAA derivatives where
***X =-N(CH$_3$)$_2$** (PAA-I), **- CH$_3$** (PAA-II), **-OCH$_3$** (PAA-III).*

Table 1. Substituents of PAQ shown in Figure 2.

	R_1	R_2	R_3
PAQ4	CH_3	Ph	H
PAQ5	CH_3	CH_3	H
PAQ6	H		H
PAQ7	Ph	CH_3	Cl

Films of molecularly doped PS were produced by dissolving a mixture of PS and PAQ (8 wt.%) in toluene.[11] The solutions were coated onto quartz substrates with ITO electrode followed by drying at room temperature for more than twenty-four hours. CTLs of PAA/PC were prepared onto an aluminium substrate by the casting a solution of the PC doped with 10 wt.% PAA in chloroform. This was dried at room temperature overnight. A description for the preparation of the PAA derivatives can be found in Ref.12. PS from BDH and PC from Aldrich with a number average molecular weight of 120,000 and 20,000-25,000 respectively were used in our experiments. For quantum-chemistry calculations, the geometry of molecule was optimised by the restricted Hartree-Fock method for neutral molecules and the unrestricted Hartree-Fock (RHF) method for charged radicals using the semiempirical PM3 method. Molecular orbitals (MOs) were calculated by the RHF/ZINDO/S method. The computing was performed with the HyperChem program (Hypercube, Inc.).

Results and Discussion

The APIs possess both electron and hole mobility (Fig.4 and 5). In the insoluble API films including crystalline phase, the mobility is lower by one or two orders of magnitude compared to the soluble ones. The soluble APIs are the most remarkable among the APIs studied. In addition, the variation of R between phthalimides of a diimide moiety does not appreciably influence the charge mobility.

One may suppose that relatively high drift mobility in soluble APIs is connected with the absence of structure traps in fully amorphous films. Films of the insoluble APIs (API-1 - API-4) are prepared from poly(amic acid) by thermal imidization which causes the loss of two water molecules per one monomer link unit. This process may form microcavities, microcracks etc. disordering electron transport paths. It is known[16] that defects of up to 100-200 A in size are present in polyimide films prepared by thermal imide formation. The lower drift mobility of API-1 - API-4, compared with API-5 - API-7, is most probably due to these defects. For hopping charge carrier transport the following relationship for the drift mobility is valid:

$$\mu \propto R^2 exp(-2R/R_0) \qquad (1)$$

where R is the distance between the neighboring transport sites and R_0 is the wave function decay constant. In API-1 - API-4, the mean distance R is longer than that in other APIs. The assumption agrees with the microcavity structure of the insoluble films with crystalline phase. The transport properties of APIs changed drastically in the presence of J-aggregates formed by the cyanine dye (Fig.1). In the API/J-aggregate composites, the electron and hole mobility is ten times as large as for the pure API (Fig.6). The data indicate an active role of J-aggregate nanophase in the charge-carrier transport for the composites.

A number of theoretical models have been developed in order to describe the charge carrier transport in disordered systems. The Gaussian disordered formalism14 and the correlated disorder (CD) model15 are the models of sufficient generality. The CD model consider the dipole nature of the medium. The Monte Carlo simulation of charge carrier transport in dipolar systems leads to the following relationship describing nondispersive mobility:

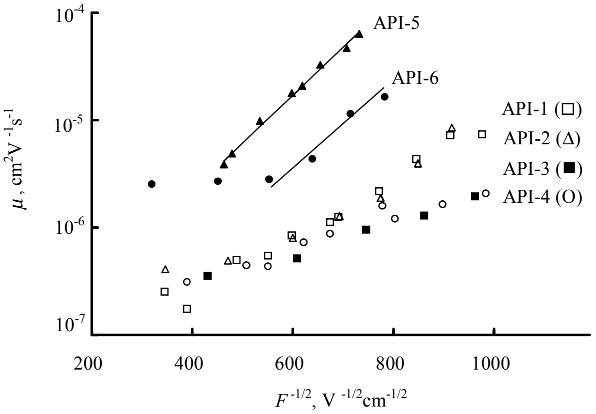


Figure 4. Field dependence of hole drift mobility in API films at 291 K. The data for API-7 are are similar to those for API-6.

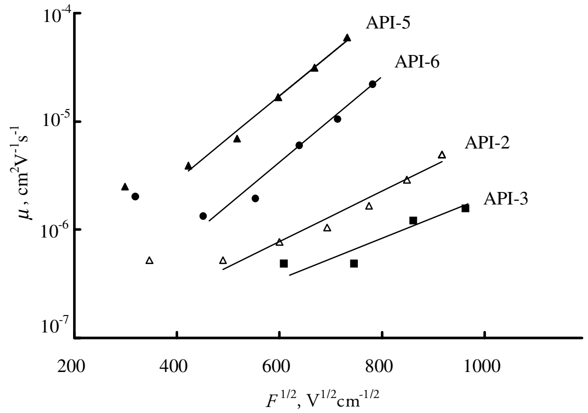


Figure 5. Field dependence of electron drift mobility in API films at 291 K.

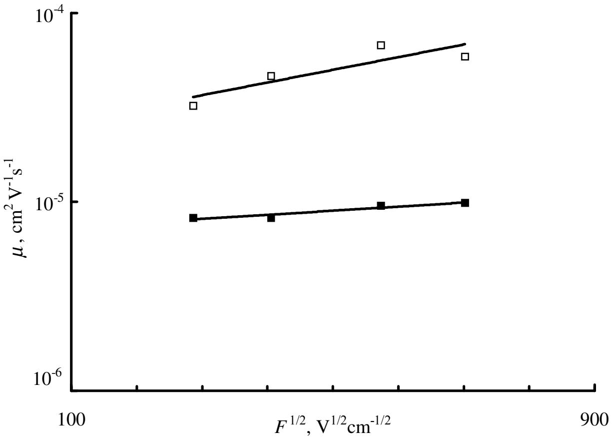


Figure 6. Field dependence of electron (empty squares) and hole (filled squares) drift mobility in API-6/ J-aggregate films.

$$\mu = \mu_0 \exp\left[-\left(\frac{3\sigma_d}{5\,kT}\right)^2 + C_0\left(\left(\frac{\sigma_d}{kT}\right)^{3/2} - \Gamma\right)\sqrt{\frac{e\,R\,F}{\sigma_d}}\right] \quad (2)$$

where C_0=0.78, Γ=2, μ_0 is the pre-exponential factor, R is the distance between transport sites, and σ_d is the root mean square width of the dipolar energetic disorder. The key parameter of the model, $\sigma_d \sim p/(\varepsilon\, a^2)$, is determined by dipoles existing in the system where p is the permanent dipole moment of molecule, ε is the dielectric constant of the medium, and a is the dipole-dipole separation. The CD approach is quite consistent with the structure of API molecules.[9] It can be invoked to explain the decrease of mobility when disordered dipole transport molecules are oriented along the external electric field.[16]

Table 2. Hole drift mobility μ extrapolated to F=0 in the PC layers doped with 10wt.% PAA and parameters of the PAA molecules computed at the "gas phase" approach.

	μ(F=0) ($cm^2V^{-1}s^{-1}$)	Dipole moment (Debye)	$\Delta_{HOMO-SOMO}$ (eV)	IP (eV)
PAA-I	2×10^{-6}	6.1	0.8	7.9
PAA-II	6×10^{-7}	4.7	0.8	8.5
PAA-III	9×10^{-7}	4.9	0.9	8.4

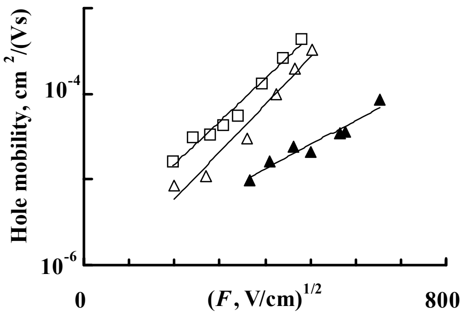


Figure 7. Field dependence of mobility in PC doped with 10 wt.% of PAA-I (empty squares), PAA-II (empty triangles), and PAA-III (filled triangles) at room temperature.

Figures 7 and 8 show the field dependence of charge carrier mobility for the PC and PS doped with PAA and PAQ derivatives, respectively. The dipole moment of the PAA-I molecule is larger than that of the others and the hole mobility of the PC/PAA-I layer is found to be larger than that of the other layers (Table 2). To explain the apparent disagreement with eq. 2, it is necessary to look at the factor μ_0 more closely, in which molecule energy characteristics are implicitly included. The charge transport between active molecules is in fact an electric field driven chain of redox processes due to the one-electron transfer from HOMO of neutral molecules to single occupied MO (SOMO) of radical cations in the case of hole transport. Chemical reactivity of radical cations is inversely proportional to the energy gap $\Delta_{HOMO\text{-}SOMO}$ between the HOMO and SOMO. But the $\Delta_{HOMO\text{-}SOMO}$ values do not correlate to the data on $\mu(F=0)$ (Table 2). It is the ionization potential (IP) of the PAA molecules which is connected with the HOMO that correlates well with the $\mu(F=0)$ values and defines controlling step of the charge transport. So the factor μ_0 must take account of the ionization potential of the PAA molecules. The conclusion means that the PC molecules may be involved in the charge transport process.

As shown in Fig.8, the linear relation between $\lg\mu$ and $F^{1/2}$ is fulfilled in all three PAQ systems in agreement with eq. 2. The calculated dipole moment of PAQ4, PAQ5 and PAQ6 have values of 2.4, 2.7 and 3.4 D respectively. The dipole moment of the PAQ6 molecule is larger than that of the PAQ4 and PAQ5 and the mobility of the PAQ6/PS layer is found to be lower than that of two other layers. This is in good agreement with eq. 2. However, in a comparison between the PAQ5 and PAQ4, one may find a disagreement with the eq. 2. The electron transport is considered to be a chain of redox reactions due to the one-electron transfer from the single occupied molecular orbital (SOMO) of the radical anions to the lowest unoccupied molecular orbital (LUMO) of the neutral molecules. So an electron transport efficiency is defined by the energy gap $\Delta_{SOMO\text{-}LUMO}$ between these SOMO and LUMO. The calculated values of $\Delta_{SOMO\text{-}LUMO}$ explain well the obtained data on electron mobility in frame of the CD model.[11]

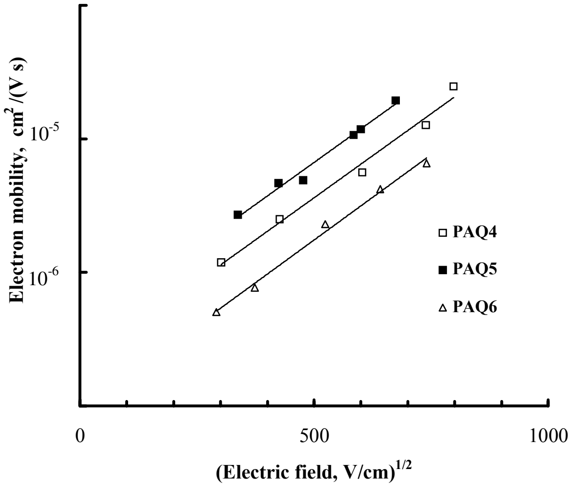


Figure 8. Field dependence of electron drift mobility in PS films doped with 8 wt.% of PAQ derivatives at room temperature.

Conclusion

The CD model fit well the field dependence of mobility in transport molecules and polymers with different electron donor and acceptor moieties when energetic features (HOMO, SOMO, LUMO, ionization potential) of the molecules are also taken into account.

Acknowledgments

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Biography

Anatoly Vannikov was graduated from the Moscow State University in 1959. Ph.D. (1965), Doctor of science degree in physical chemistry (1975), professor of physical chemistry (1978). Head of the Laboratory of charge transfer processes (from 1975), Deputy Director of Frumkin Institute of Electrochemistry of Russian Academy of Sciences (from 1983). He is a member of IS&T and SPIE. Scope of activity: electrophysics of organic dielectrics, semiconductors and metals, photochemistry and radiation chemistry of polymer systems, non-silver organic photographic systems, non-linear optical organic systems, polyfunctional polymers.