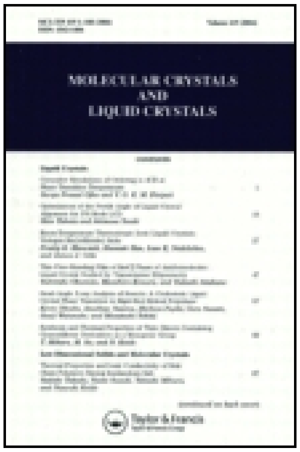

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CHARGE TRANSPORT PROCESSES IN MOLECULARLY DOPED POLYMERS : *Interaction effect between charge transporting molecules and polymers*

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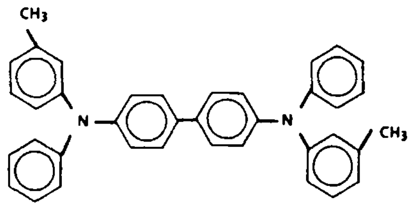
Abstract Hole transport has been investigated in films of solid solutions of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) and a structural variant of TPD in bisphenol A polycarbonate, polystyrene and phenoxy. Rather than being 'inert' as previously assumed, the binder plays a major role in influencing the rate of charge exchange between molecules. It is found that the absolute values of the drift mobilities, their electric field dependence and the activation energies are strong functions of the binder polymer employed to cast the film. At equivalent molecular concentrations but with two different binder polymers, the mobilities can vary by as much as two orders of magnitude. In some instances mobility decreases as the electric field is increased. The role that binder plays is related to the dispersibility of the diamine molecules in the polymeric binders. It is concluded that the the best molecular dispersion is observed when polystyrene is employed.

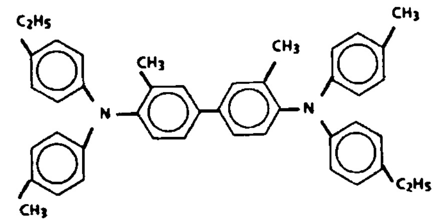
INTRODUCTION

The concept of molecular doping of organic polymers has received considerable attention in the last few years. This concept has found important application in transporting charges in organic photoconductors employed in the reprographic industry. The concept is also scientifically powerful in that it is believed that one can vary, at will, the density and type of localized states associated with the dopant molecules. Since charge transport involves charge exchange between neighboring molecules, the concept provides a simple and elegant way of studying properties of organic disordered state. In most of the exhaustive studies reported thus far, very little attention has been paid to understand the role of the polymer or binder that is employed to solvent cast the films. One reason for this is the underlying assumption that the binder is 'inert' or plays no role in the transport. The second reason may be that on a practical level it is found that molecules can be dispersed and form amorphous films in very few polymers. Bis phenol A polycarbonate is one of the universal binders in which most of the molecules which have found application in the reprographic industry can be dispersed. The polymer employed in the scientific studies is invariably bisphenol A polycarbonate. This paper will compare drift mobility results obtained by employing three binders; bisphenol A polycarbonate, polystyrene and phenoxy. The doner molecules employed are N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) and a variant known as ETPD.



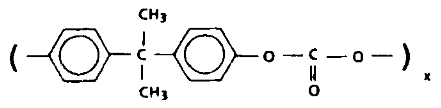
TPD

N,N'-Diphenyl-N,N'-Bis(3-Methylphenyl)-[1,1'-Biphenyl]-4,4'-Diamine

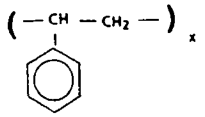


ETPD

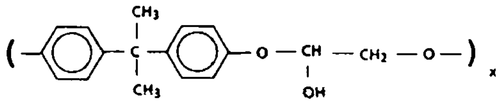
N,N'-Bis-(4-methylphenyl)-N,N'-Bis(4-Ethylphenyl)-[1,1'-3,3'-dimethyl-Biphenyl]-4,4'-Diamine



Polycarbonate



Polystyrene



Phenoxy

EXPERIMENTAL

The drift mobilities are measured by the time of flight technique on layered devices. To fabricate the device, an aluminum substrate is first coated with a one micron thick charge generation layer of Vanadyl Phthalocyanine dispersed in polyester. A thicker (≈ 20 microns) layer of a solid solution of the molecule TPD or ETPD in the polymeric binder is solvent coated on top of the generation layer. Five different concentrations of the solid solution (10, 20, 50, 75 and 100 %) are prepared. The 10 % loading is equivalent to the molecular concentration of 1.4×10^{20} molecules/cm^3. The 100 % loaded film contains no polymer binder. Methylene chloride employed to coat the film is removed by heating the film to 80°C under vacuum for several hours. A semitransparent gold electrode (100 Å thick) is then vacuum deposited on top of the film to form the sandwich structure.

The examined samples are charged to and held at a constant voltage. A 5 ns laser flash (530 nm) is used to photogenerate charges in the photogeneration layer. Holes injected from the generation layer drift through the charge transport layer under the influence of a constant electric field. The induced current is monitored on a Biomation 4500 digitizing scope. All experiments are performed in a small-signal time of flight mode.

RESULTS

The transient time of flight signals are non-dispersive. This observation is consistent with the conclusions from our previous study[1] that a clean molecularly doped hole transport system does not show dispersive character. Therefore, our data indicate that the systems studied here are shallow trap free[2]. The drift mobility can be easily calculated from the transit time determined from the demarcation point between the plateau and the tail of the time of flight signal.

The drift mobility increases with the molecular doping level, as is usually observed in the molecularly doped system, indicating that the charge transport takes place by charge exchange between molecules and the polymer is not directly involved. However, the drift mobility also depends critically on the structures of the polymer binder. Figures 1 and 2 show that the mobility can vary by about two orders of magnitude by changing the polymer binder. This difference is most profound at low molecular doping levels. The effect of the binder at 10 % molecular doping concentration is shown in Figure 1. As the doping level increases, the binder effect on the magnitude of the mobility value decreases, but the trend remains unchanged. In a wide range of doping levels, higher drift mobilities are always observed with polystyrene as the binder . This is true for both TPD or ETPD doped systems. The mobility is higher for ETPD doped systems than for

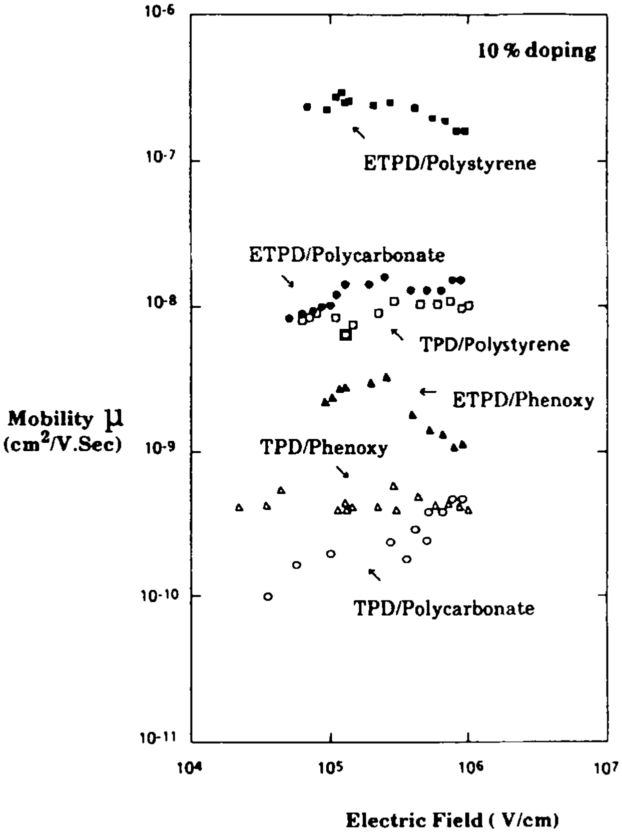


FIGURE 1. Drift mobility as a function of electric field for 10 % doping of TPD or ETPD in three different polymers.

TPD doped systems with the same polymeric binder. No data is reported here for doped phenoxy systems with the doping level higher than 10 %, due to incompatiblity of solid solutions at higher loading levels.

The drift mobility μ is as usual a function of temperature. However, the activation energy ε determined from the Arrhenius plot ($\mu \propto \exp(-\varepsilon/kT)$) depends not only on the doping level and electric field, as reported in most molecuarly doped polymeric systems[3], but also on the polymer binders. The activation energy, in general, follows the same trend as drift mobility. As shown in Figure 3, the ε value in polystyrene is always lower than that obtained in polycarbonate.. The difference in activation energies by replacing binders can range from 0.05 to as large as 0.15 eV. Such large

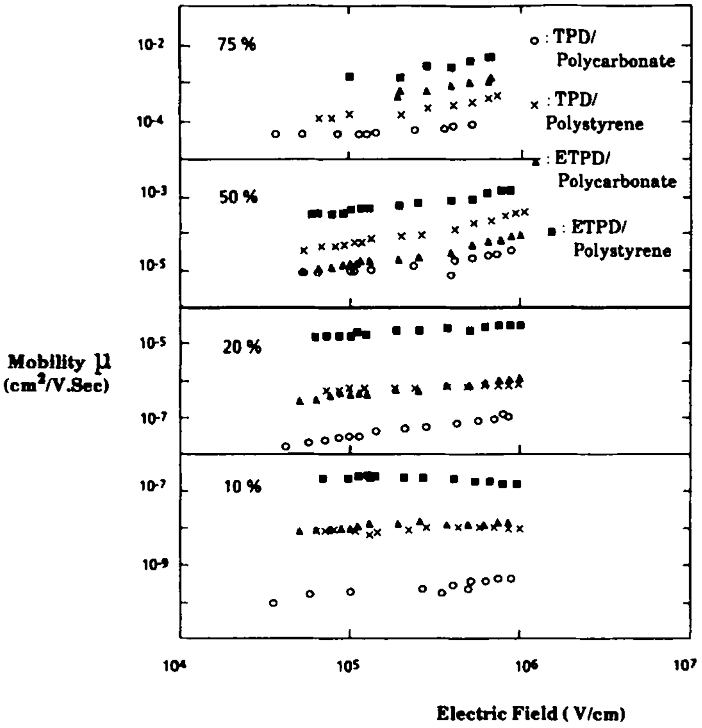


FIGURE 2. Drift mobility as a function of electric field for various doping levels.

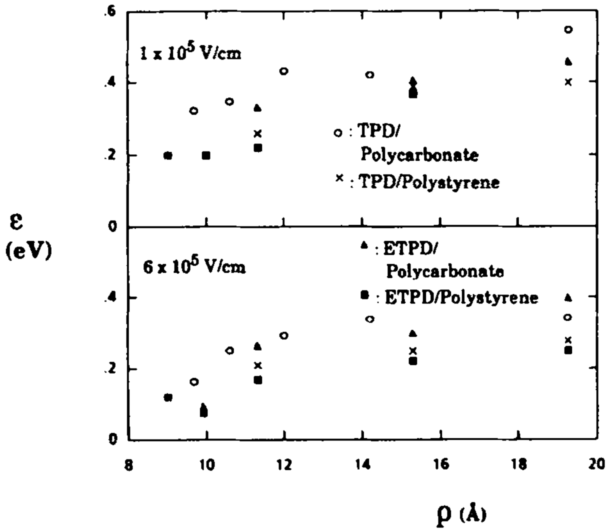


FIGURE 3. Activation energy as a function of average intermolecular distance.

activation energy differences can account for one to two orders of magnitude differences in the value of drift mobility at 295 °K. The mobility changes observed in Figure 2 are accounted for by the differences in activation energies.

The drift mobility is also a strong function of electric field in most of the systems. However, in some cases, the mobilities are almost independent of electric field. This is shown in Figure 1 for films containing 10 % TPD in phenoxy or polystyrene and in films containing 20 % TPD or ETPD in polystyrene. In addition, a negative field dependence is observed in some systems. This can be seen for films containing 10 % ETPD in polystyrene or phenoxy (Figure 1).

DISCUSSION

The large differences in the value of mobility and activation energies with different polymers clearly show that the polymer binder plays a very important role in the charge transport process. The mobility data correlate with the dispersibility of the transporting molecules in the polymer binders. The strong dipole-dipole interaction in polycarbonate and the strong hydrogen bonding in phenoxy make uniform dispersion of the organic molecules TPD or ETPD into these polymers more difficult. This is especially true at high doping levels (> 50 %). At these high doping levels, the difficulty in dispersibility will drive the doping molecules to coalesce. The dispersibility trend observed here is ETPD/Polystyrene > ETPD/Polycarbonate ≫ ETPD/Phenoxy; TPD/Polystyrene > TPD/Polycarbonate ≫ TPD /Phenoxy. The additional methyl and ethyl groups on the ETPD molecule as compared to the TPD, aid dispersibility.

When the dispersibility is higher, the interaction of the transporting molecules with the surrounding polymer is larger. This is in fact reflected in the value of localization radius ρ_0 obtained from the empirical equation $\mu \propto \rho^2 e^{-\rho/\rho_0}$[4]. The average intermolecular distance ρ is calculated by taking the cube root of the volume of the film per single molecule. The ρ_0 value follows the trend observed with the mobility and activation energy values. As seen in Figure 4, ρ_0 is 1.9 Å for ETPD/Polystyrene, 1.7 Å for ETPD/Polycarbonate and TPD/Polystyrene and 1.4 Å for TPD/Polycarbonate. Deviation from the straight line fit is observed at higher loadings ($\gtrsim$ 75 %) for ETPD/Polycarbonate, TPD/Polystyrene and TPD/Polycarbonate. This

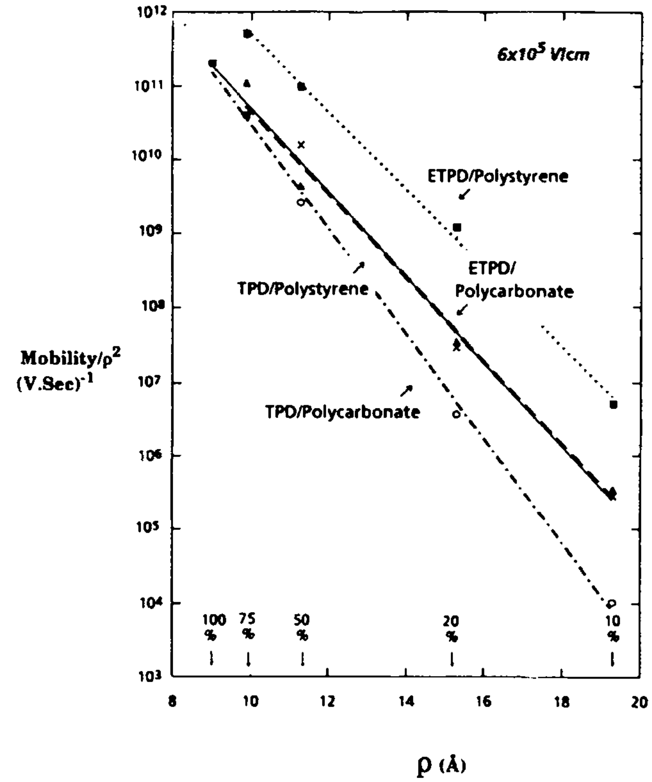


FIGURE 4. Plot of μ/ρ^2 vs average intermolecular distance ρ.

again may be due to the non-uniform dispersion of these systems. This is, however, not the case for the better dispersed system, ETPD/Polystyrene.

Charge delocalization can stabilize the molecular cations and lower the energies of the hopping states. This could lower the hopping activation energy. In addition, the polar groups on the polymer binder may hinder charge transport and raise the activation energy. The change in the activation energy accounts for the large differences in the mobility values. Therefore it is not surprising to observe similar trend in the values of mobility, the activation energy and the localization radius with the polymer structures.

As shown in Figures 5 and 6, a square root electric field dependence of drift mobility is observed in most instances. However, there is a large distribution in the values of the slope β (Figure 7). In some instances β is negative indicating a situation in which the mobility decreases as the electric field is

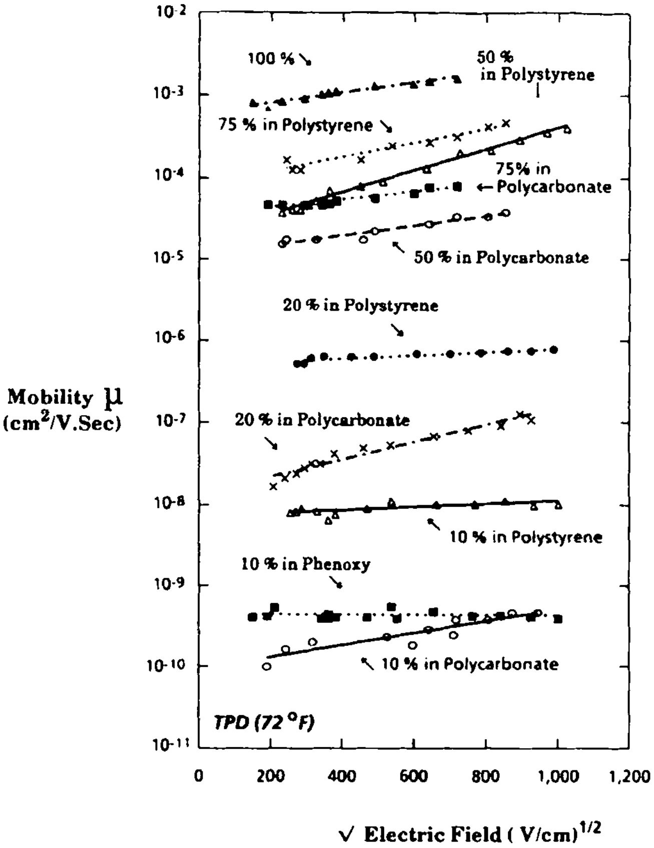


FIGURE 5. Drift mobility as a function of square root of electric field for various doping levels of TPD.

increased. In the best dispersed system, ETPD/Polystyrene, the slope appears to decrease linearly with the value of ρ. In a limited data base, the slope increases with decreasing temperature. Although, in the literature[5], the electric field dependence has been linked to the well-known Poole-Frenkel barrier lowering model, the origin of this square root field dependence is still not known. Also, it is difficult to calculate the proper theoretical β value, due to the problem of determining the dielectric constant. This is especially true when the charges are delocalized onto the surrounding polymer.

In conclusion, we have demonstrated that the polymeric binder in the

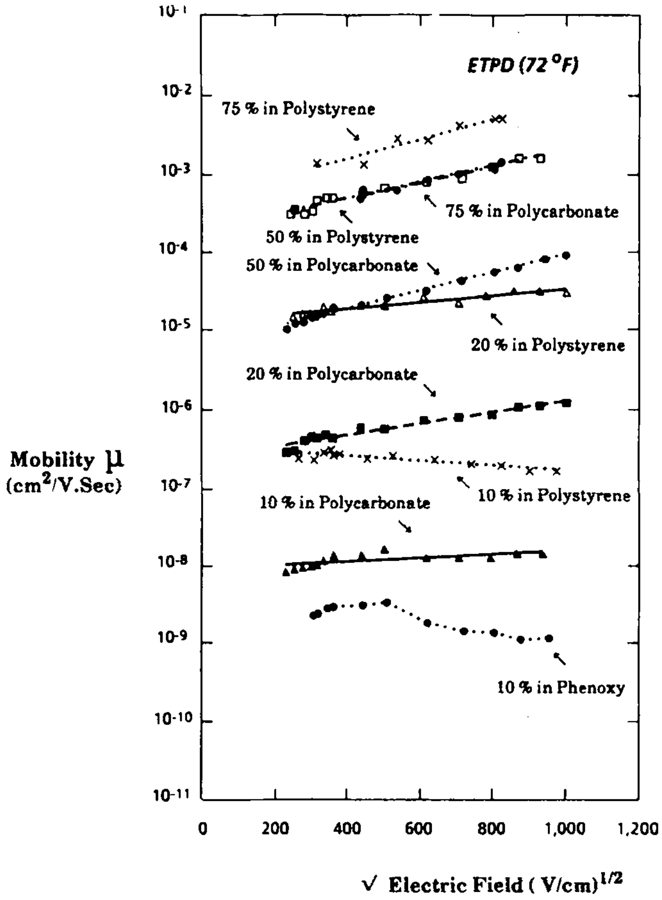


FIGURE 6 : Drift mobility as a function of square root of electric field for various doping levels of ETPD.

molecularly doped system plays a very important role in the charge transport process. Detailed study is in progress and will be presented in a further publication.

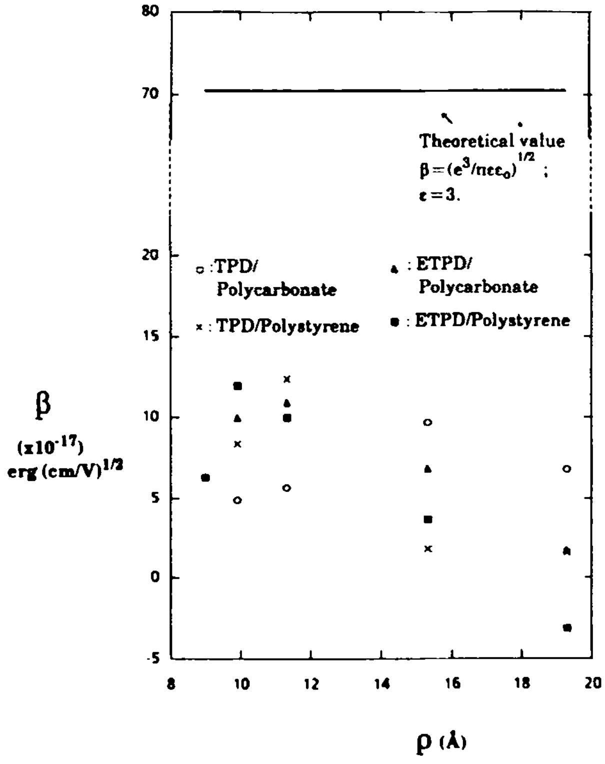


FIGURE 7. β value as a function of average intermolecular distance.

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