# Hole Mobility in Substituted N,N'-bis-(m-tolyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD) Derivatives Doped into Poly(styrene)

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## Abstract

Hole transport molecules have long been exploited for xerographic photoreceptors and recently in OLED's, photovoltaic cells, or photorefractive polymers. Hole mobilities in substituted N, N'-bis-(m-tolyl)-N-N'-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD) derivatives doped in polystyrene (PS), were analyzed by the time-of-flight technique to determine the effect of altering the geometric and electronic structure of TPD. Data were collected as a function of applied field and temperature to yield the energetic and positional disorder parameters defined in the disorder formalism. The impact of the molecular dipole moment on transport properties was also evaluated. The larger molecular dipole moments of the derivatives correspond to an increase in the energetic disorder, which contributes to their lower mobilities.

## Introduction

Due to the widespread use of molecularly doped polymers for xerographic photoreceptors and electroluminescent devices, there has been considerable interest in charge transport phenomena in doped polymers in recent years.[1,2] Recently, their range of applications significantly widened with the advent of organic opto-electronic devices such as OLED's, photovoltaic cells, and photorefractive systems.[3-8] The structure of organic transport molecules can be altered to produce small variations in the oxidation potentials and the stability of the radical cation, potentially influencing both the photogeneration efficiency and the mobility.[9] The effect of tailoring the electronic structure of these molecules on the charge mobility is therefore of interest for the development of new organic opto-electronic materials. Recent advances in methodologies for synthesis of triarylamines compounds have made possible the synthesis of a variety of new substituted molecules.[10-13] Several derivatives of the well-known hole charge transport material, N, N'-bis(N-m-tolyl-N-phenylamino)biphenyl (TPD), have been developed.[12-18] The three new derivatives of TPD shown in Figure 1 were synthesized and studied using the time-of-flight technique to determine the effect of substitution on hole mobility. The time-of-flight technique allows for direct measurement of charge carrier mobilities. Many recent studies have been interpreted using a formalism based on disorder, developed by Bässler, Borsenberger, and coworkers,[19-21] which yields a correlation between mobility values and physical parameters of the materials. In the disorder formalism, it is assumed that charge propagation occurs by hopping through a manifold of localized states with superimposed energetic and positional disorder. A key observation is that mobility decreases in the presence of large energetic disorder, such as that introduced by dipole-dipole interactions in highly polar molecules. For hole transport it is preferable that the molecules be electron donors when neutral, form stable radical cations, and exhibit reversible redox reactions in the solid state. Charge transport is an electronic process and no mass displacement is involved. The addition of alkoxy- (compounds I and II) and fluoro- (compound III) substituents to TPD influences both the oxidation potentials and the dipole moments of these molecules. Therefore, the dipolar contributions to the energetic disorder are analyzed within the framework of the disorder formalism.

## Experimental

### Synthesis

The TPD derivatives II and III were synthesized as described previously.[11] Molecule I was synthesized using the same methodology.
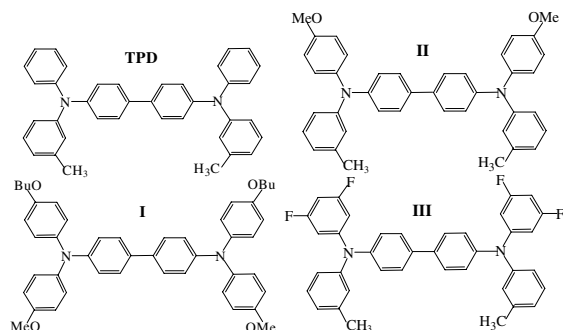
*Figure 1. TPD and derivatives.*

## Sample Preparation

Samples were prepared by dissolving TPD (*50 mg*) and PS (*50 mg*) in dichloromethane and syringe-filtered through *0.2 μm* pore size filter. The solvent was evaporated under reduced pressure on a rotary evaporator. The mixture was dried for *24 h* in a vacuum oven at *50 ºC*. The dried material was repeatedly melted and mixed mechanically between two large glass slides to rid the film of trapped air bubbles. A small piece of this transparent, bubble-free film was melted carefully between two ITO-coated glass slides at *150 - 190 ºC*. Calibrated glass spacers of *10 μm* were used to ensure a uniform sample thickness. Finally, samples were sealed with quick setting epoxy adhesive. Mixtures of I and II were prepared analogously, using a weighted amount of the derivative to yield the same molecular loading as TPD in PS; however the mixture of III in PS was prepared using a 50:50 weight ratio to enhance film quality.

## Time of Flight Technique

Hole mobility was measured by the conventional time-of-flight method.[22, 23, 1] A low-noise high voltage power supply (Keithley 248) was used for applying the bias voltage. The photocurrent generated by irradiation with *6 ns* pulses from a $N_2$ laser (*337 nm*) was amplified using a low noise preamplifier (SR560) and monitored with a digital oscilloscope (Agilent 54815A). In order to keep $RC \ll t_t$ (transit time), resistance values were $10^2 - 10^4$ $\Omega$. *C* represents the total capacitance of the electrical circuit. Sample capacitance values were on the order of *10 pF*. All measurements were made in air. The samples were mounted inside of a Ransco (model 924-1-6-SR) temperature controlled unit. Neutral density filters were used when necessary to avoid excess charge accumulation in the samples that creates non-uniformity in the electrical field across the sample.

## Results And Discussion

### Time-of-Flight Results

Figure 2 shows typical normalized transient photo-currents ($j_{ph}$) as a function of time (*t*) measured at different applied fields and temperatures. At most temperatures and applied fields, transient photocurrents were non-dispersive for all the derivatives and the transit times were determined directly from the double linear plot of the transient photocurrent vs. time. For dispersive signals, the transit times were determined from the intersection of two straight lines with different slopes at short and long times of the photocurrent transients, in a double log plot. The hole drift mobility $\mu$ was calculated from the transit time $t_t$ according to the equation $\mu = d^2/t_t V$, where *d* is the sample thickness and *V* the applied voltage. It was found that the mobility is highest for the regular TPD and decreases down the series I, II, III at room temperature, corresponding to the increase in molecular dipoles (*vide infra*).

The electric field and temperature dependencies of the hole mobilities of *bis*-triarylamine doped polymers were analyzed in terms of the disorder formalism as described by equation (1):

$$\mu = \mu_0 \exp\left[-\left(\frac{2\sigma}{3k_BT}\right)^2\right]\exp\left[C\left\{\left(\frac{\sigma}{k_BT}\right)^2 - \Sigma^2\right\}E^{\frac{1}{2}}\right] \qquad (1)$$

where $\mu_o$ is the hypothetical disorder free mobility, *E* is the applied electric field, *T* is the temperature, *C* is an empirical constant with a value of $2.9 \times 10^{-4}$ $(cm/V)^{1/2}$, and $k_B$ is the Boltzmann constant. The formalism assumes that charge transport occurs by hopping through a manifold of localized states with superimposed energetic and positional disorder and that the distribution of both the hopping-site energy (diagonal or energetic disorder $\sigma$) and $\pi$-electron overlap between adjacent molecules (off-diagonal or positional disorder $\Sigma$) are Gaussian. Hole mobilities were measured at several different applied electric fields and temperatures to determine the parameters $\mu_o$, $\sigma$, $\Sigma$, and the value of *C* for these new molecules doped into PS.

Figure 3 shows the electric field dependencies of the hole mobilities for TPD and its derivatives at room temperature. For TPD:PS 50:50 *wt. %*, our results are consistent with those reported previously.[1] The mobilities exhibit traditional "Poole-Frenkel" type electric field dependencies, i.e. $\mu = \mu' exp(\beta E^{1/2})$, where $\beta = C[(\sigma/k_BT)^2 - \Sigma^2]$ as defined by the disorder formalism. The hole drift mobility at zero electric field ($\mu'$) and the coefficient $\beta$ were obtained from linear plots of $log\ \mu$ *vs.* $E^{1/2}$ at several temperatures. We did not observe any negative electric field dependence, which means that over the temperature range used $\hat{\sigma} = \sigma/k_BT > \Sigma$.

Figure 4 shows the temperature dependencies of the zero-field mobility (extrapolated from the "Poole-Frenkel" type plots). The parameters $\mu_o$ and $\sigma$ were determined from the linear plot of $log\ \mu\ (T, E = 0)$ *vs.* $T^2$ (see Eq. (1)). The energetic disorder values obtained for TPD and its three derivatives are shown in Table 1, along with room temperature mobilities at $4 \times 10^5$ *V/cm*. As expected, the TPD derivatives exhibit larger energetic disorder. The energetic disorder is larger for III, the fluoro-derivative, than for the alkoxy-derivatives I and II. Although the mobility of TPD is highest, the pre-exponential factor for compound I is five times greater (see Fig. 4). Derivative I has the lowest ionization potential of the compounds studied.
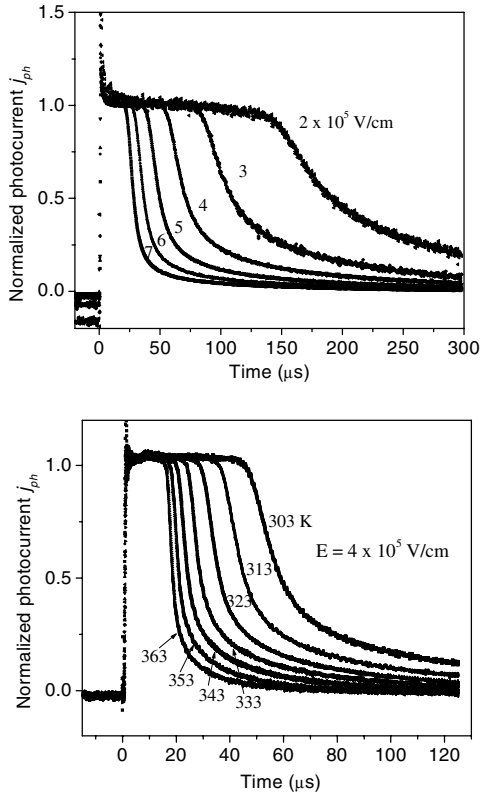
*Figure 2. Transient photocurrents for TPD/PS (1:1 wt. %) at 297 K and different applied fields: 2–7 x $10^5$ V/cm (top); and at 4 x $10^5$ V/cm at different temperatures: 303-363 K (bottom).*



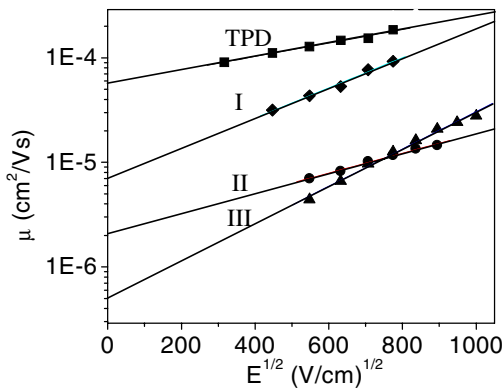*Figure 3.Room temperature electric field dependencies of hole mobilities in TPD, I, II, and III doped into PS.*

Figure 5 shows a typical plot of $\beta$ vs. $(\sigma/k_B T)^2$, which yields values for $C$ and $\Sigma$ from the slope and calculated from the intersect with the Y-axis, respectively. As predicted by Eq. (1), values of $\beta$ decrease with increasing temperature as the effect of trapping due to the energetic disorder decreases i.e., it becomes easier for hopping to occur

between molecules with slightly different energies. The random orientation of asymmetric molecules and fluctuations of their mutual distances cause positional disorder. $\Sigma$ is lowest for underivatized TPD ($\Sigma = 1.1$), and is greatest for I ($\Sigma = 3.6$), which is the largest molecule characterized in this study and contains four flexible substituents. $\Sigma$ is much smaller for the fluoro-substituted TPD, III ($\Sigma = 1.8$), as the two fluorine atoms are more rigidly locked in place in the molecule. Because of its high energetic disorder and low positional disorder, III exhibits a stronger dependence on temperature than I and II ($\Sigma = 2.7$). Although the room temperature mobility of III is lower than the mobility in II, the mobility in III is greater at temperatures greater than *45 °C*. Our values of $C$ are close to the empirically derived value of *$2.9 \times 10^{-4}$ (cm /V)$^{1/2}$*.
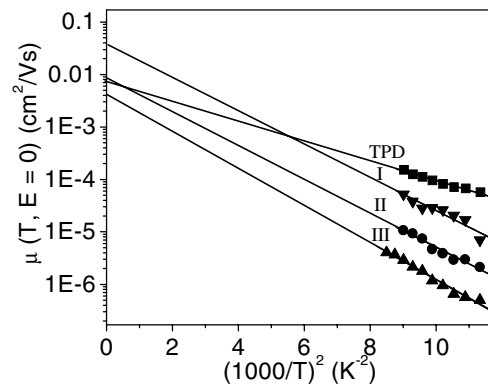


*Figure 4. Temperature dependencies of the hole mobilities in films of TPD, I, II, and III doped into PS at zero electric field.*
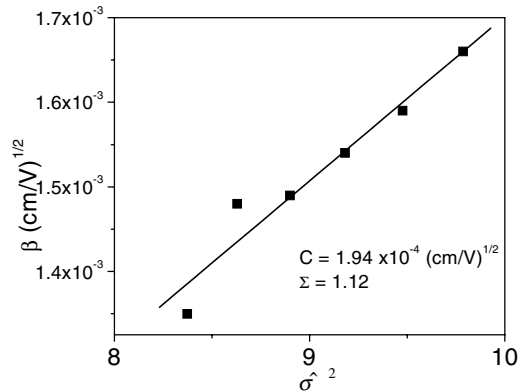


*Figure 5. Typical plot of $\beta$ vs. $\hat{\sigma}^2$ for TPD:PS 1:1 wt. %*

**Dipolar Contribution to the Energetic Disorder**

For molecularly doped polymers, the total energy width of the distribution of hopping states $\sigma$ (DOS), is given by the sum of independent contributions [24-27]:

$$\sigma^2 = \sigma_d^2 + \sigma_{vdW}^2 + \sigma_D^2 \qquad (2)$$

where $\sigma_d$ is the contribution due to dipolar interactions between the transport sites and the dopant molecule, $\sigma_{vdW}$ is the contribution due to local variations of the potential resulting from van der Waals interactions, and $\sigma_D$ is the dipolar contribution due to dipolar interactions between the transport sites and host molecules. Since the dipole moment of PS is near-zero, the polymer dipolar component, $\sigma_D$, can be neglected here. The dipolar component can be estimated by expressions derived by Dieckmann[28] and Young[29]:

$$\sigma_d = \frac{k_0 c^n p}{a^2 \varepsilon} \qquad (3)$$

where $c$ is the fraction of lattice sites occupied by dipoles (around *0.5* in our case[25]), $p$ the dipole moment (in debye), $a$ is the distance between two transport molecules (in Å), $\varepsilon$ the relative dielectric constant, $k_0 = 3.06$ and $n = 2/3$ (Dieckmann) or $k_0 = 7.05$ and $n = 1/2$ (Young). The numerical predictions in equation (3) due to Dieckmann and Young generally differ by a factor of *2* (larger from Young). From the lattice gas model, $a = (M_w/N_A c\rho)^{1/3}$ where $M_w$ is the molecular weight of the bis-triarylamine, $N_A$ is the number of Avogadro, and $\rho$ the sample mass density. The values of $\sigma_d$ due to Young, for derivatives II, III, and TPD are: *0.0056, 0.0356, and 0.0435 eV*. The dielectric constants were determined by measuring the sample capacitance. The dipole moment values were calculated previously:[30] $p_{TPD} = 0.72\ D$, $p_{II} = 2.34\ D$, and $p_{III} = 4.45\ D$. The mass density value of TPD is $\rho_{TPD} = 1.16\ g/cm^3$ [25, 31] and was used as an estimation of sample density for II and III. Heun *et al.*,[25] reported for TPD:PS 20:80 *wt. %*, a dipolar contribution of $\sigma_d = 0.027\ eV$ ($\sigma = 0.102\ eV$), and Heun *at al.*,[24] reported for TPD in the glassy state (*100 wt. %*), the value $\sigma_d = 0.037\ eV$ ($\sigma = 0.077\ eV$). $\sigma_{vdW}$ values were extrapolated from Eq. (2), they are close to *0.1 eV*, typical value for doped polymers (independent on dipole moment).[1]

## Conclusions

The hole mobilities of three new derivatives of TPD doped poly(styrene) have been studied by the time-of-flight technique. The mobility in the derivatives decreases from I to II to III. This trend is also evident in the values for the pre- exponential factor, $\mu_o$, and according to the analysis of the electric field and temperature dependencies, corresponds to an increase in positional disorder, $\Sigma$, and an increase in energetic disorder $\sigma$. The alkoxy tails in I and II lead to larger positional disorder due to the ability of the substituents to rotate freely around several bonds. The presence of larger energetic disorder and relatively low positional disorder for III yields a stronger temperature dependence than in either I or II. The molecular dipole moments of the derivatives increase their energetic disorder, which contributes to their lower mobilities relative to underivatized TPD.

**Table 1. Comparison of energetic disorder and hole mobility values at $E = 4 \times 10^5$ V/cm and T = 297 K.**

| Compound | $\sigma$ (eV) | $\mu$ (cm$^2$/Vs) |
|---|---|---|
| TPD:PS 1:1 *wt. %* | 0.083 | $1.5 \times 10^{-4}$ |
| I/PS 1.34:1 *wt. %* | 0.110 | $6.3 \times 10^{-5}$ |
| II/PS 1.12:1 *wt. %* | 0.110 | $8.2 \times 10^{-6}$ |
| III/PS 1:1 *wt. %* | 0.116 | $6.7 \times 10^{-6}$ |

## Acknowledgements

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