Electron Trapping in N,N′-bis(1,2-dimethylpropyl)-1,4,5,8-Naphthalenetetracarboxylic Diimide Doped Poly(styrene)

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Abstract

Electron mobilities have been measured in N,N′-bis(1,2-dimethylpropyl)-1,4,5,8-naphthalenetetracarboxylic diimide doped poly(styrene) containing a series of acceptor traps: 4-(cyanocarboethoxymethylidene)-2-methyl-1,4-naphthoquinone (MNQ), 3,5-dimethyl-3′,5′-diisopropyl-4,4′-diphenoquinone (DPQ), 4*H*-1,1-dioxo-2,6-di-*tert*-butyl-4-(dicyanomethylidene)thiopyran (TBS), N,N′-dicyano-2-*tert*-butyl-9,10-anthraquinonediimine (DCAQ), and 4*H*-1,1-dioxo-4-dicyanomethylidene-2-*p*-tolyl-6-phenylthiopyran (PTS). From reduction potential measurements, the trap depths of MNQ, DPQ, TBS, DCAQ, and PTS are 0.19, 0.19, 0.20, 0.35, and 0.40 eV, respectively. The mobilities decrease with increasing trap depth and trap concentration. The results are discussed within the framework of the Hoesterey-Letson formalism and the recent simulations of Wolf et al. and Borsenberger et al.

Introduction

Molecularly doped polymers contain an electron donor or acceptor molecule in a polymer host. Hole or electron transport occurs by charge transfer between adjacent donor or acceptor molecules, respectively. This can be described as a one-electron oxidation or reduction process between neutral molecules and their charged derivatives.[1-4] Due to their widespread use as xerographic photoreceptors,[5-11] there is considerable interest in transport phenomena in these materials. The mobilities are very low, strongly field and temperature dependent, as well as dependent on the dopant molecule, dopant concentration and the polymer host. For a review, see Borsenberger and Weiss.[11]

Many recent studies have been described by a formalism based on disorder, due to Bässler and coworkers.[12-17] The formalism is premised on the argument that transport occurs by hopping though a manifold of localized states that are distributed in energy. The key parameter is σ, the energy width of the hopping site manifold or DOS (density-of-states). The principal predictions are the field and temperature dependencies of the mobility where simulations predict $\ln\mu \propto \beta E^{1/2}$ and $-(T_0/T)^2$ relationships.[18] Here, E is the field, T temperature, and β and T_0 coefficients that increase with decreasing temperature and decreasing field, respectively. These agree with results reported for a wide range of molecularly doped polymers, as well as pendant and main chain polymers and vapor-deposited molecular glasses.[19]

Recently, Wolf et al.[20] and Borsenberger et al.[21] extended the formalism to include effects of trapping. In the treatments of Wolf et al. and Borsenberger et al., traps are considered to be neutral when empty and charged when occupied. The site energies are taken as the total energy of the dopant molecule with a hole or excess electron on that site, relative to that of the uncharged molecule. The simulations show that the presence of a distribution of shallow traps, offset from the intrinsic DOS by an energy E_t, does not change the basic phenomenology of transport, as revealed by the temperature and field dependencies of the mobility. The characteristic $\ln\mu \propto \beta E^{1/2}$ and $-(T_0/T)^2$ relationships are retained. The effect of trapping can be quantitatively accounted for by the replacement of σ with an effective width σ_{eff}. Relating the trap-controlled mobility to the trap-free mobility by an expression due to Hoesterey and Letson[22]

$$\mu(c) = \mu(c = 0)\, f^{-1} = \mu(c = 0)\{1 + c[\exp(E_t/kT)]\}^{-1} \tag{1}$$

yields a relationship between σ_{eff}^2 and the trap depth and the logarithm of the trap concentration c as

$$(\sigma_{eff}/\sigma)^2 = 1 + (3kT/2\sigma)^2(E_t/kT + \ln c) \tag{2}$$

Here, $\mu(c)$ is the trap-controlled mobility, $\mu(c = 0)$ the trap-free mobility, f a term that describes the increase of the transit time by the time spent by a carrier in traps, σ the width of the DOS in the absence of traps, and k Boltzmann's constant. For $c[\exp(E_t/kT)] >> 1$, Eq. (1) predicts the mobility scales with trap concentration as c^{-1}. For a series of arylamine donor molecules doped with traps of different depths, the work of Veres and Juhasz23 and Borsenberger et al.[21,24-26] yield $c^{-1.0}$ to $c^{-1.5}$. The results further show that the coefficient of the concentration dependence increases with increasing trap depth. For hole trapping, the results thus suggest that while the Hoesterey-Letson formalism may provide a meaningful description for shallow traps, it may not hold for traps of moderate depth. For electron trapping, the only literature reference is the work of Borsenberger et al.27 of N,N′-bis(1,2-dimethylpropyl)-1,4,5,8-naphthal-enetetracarboxylic diimide (NTDI). In agreement with the simulations of Wolf et al., a plot of $(\sigma_{eff}/\sigma)^2$ versus trap depth showed a linear dependence. The slope, however, was considerably lower than predicted. The dependence on trap concentration was not described.

To further investigate electron trapping in these materials, we have extended our earlier work with NTDI to include the effects of trap concentration. The traps were 4-(cyanocarboethoxymethylidene)-2-methyl-1,4-naphthoquinone (MNQ), 3,5-dimethyl-3′,5′-diisopropyl-4,4′-diphenoquinone (DPQ), 4*H*-1,1-dioxo-2,6-di-*tert*-butyl-4-(dicyanomethylidene) thiopyran (TBS), N,N′-dicyano-2-*tert*-butyl-9,10-anthraquinonediimine (DCAQ), and 4*H*-1,1-dioxo-4-dicyanomethylidene-2-*p*-tolyl-6-phenylthiopyran (PTS). The polymer host was poly(styrene). From reduction potential measurements, the trap depths of MNQ, DPQ, TBS, DCAQ, and PTS are 0.19, 0.19, 0.20, 0.35, and 0.40 eV, respectively.

Experimental

Figure 1 shows the molecular structures of NTDI, MNQ, DPQ, TBS, DCAQ, and PTS. Samples were prepared by dissolving different ratios in dichloromethane, then coating the solutions on Ni-coated poly(ethylene terephthalate) substrates that had previously been coated with an 0.30 μm layer of α-Se. The solids concentration of the coating solutions was 10%. All samples contained 40 wt% NTDI, equivalent to 1.0 x 10^{-3} moles of NTDI/cm^3. The trap concentrations are expressed as the mole fraction of the traps to NTDI and correspond to the parameter c in the work of Wolf et al.[20] and Borsenberger et al.[21] The molecular weights, reduction potentials, and trap depths are summarized in Table 1. A detailed description of the techniques used for the reduction potential measurements has been given in Ref. 25. From cross-section photomicrographs, thicknesses of the doped polymer layers were between 10 and 12 μm.

The mobilities were measured by conventional time-of-flight photocurrent transient techniques. For a review of the method, see Melnyk and Pai.[28] In brief, the displacement of a sheet of electrons, created in the α-Se layer by 3 ns exposures of 440 nm radiation, is time-resolved. The exposures were derived from a N_2-pumped dye laser. The photocurrent transients were measured with a transient digitizer. The mobilities were derived from the conventional expression, $\mu = L^2/t_0V$, where L is the sample thickness, t_0 the transit time, and V the applied potential. All measurements were made at room temperature.

Table 1. Molecular weights, reduction potentials, and trap depths of compounds used in this study.

Compound	M(g/mole)	E_{RED}(V)	E_t(eV)
NTDI	406	-0.596	
MNQ	267	-0.403	0.19
DPQ	296	-0.403	0.19
TBS	304	-0.392	0.20
DCAQ	312	-0.245	0.35
PTS	358	-0.194	0.40

The reduction potentials were measured in dichloromethane versus saturated calomel by Osteryoung square wave voltammetry. A detailed description of the technique is given in Ref. 26. The uncertainties in the potentials are estimated as ±0.004 V.

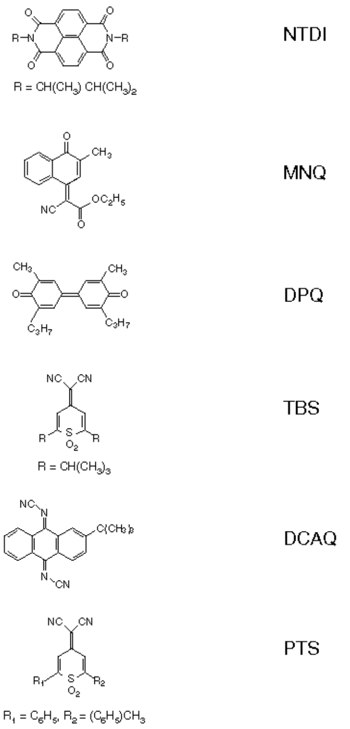

Figure 1. The molecular structures of molecules used in this study.

A more detailed description of the techniques used for sample preparation and the mobility measurements has been given in our earlier work.[20,21,24-27]

Results

For NTDI, the photocurrent transients are similar to those reported for a wide range of acceptor doped polymers. The transients feature an initial spike of very short duration, a plateau of variable temporal length, and a long tail. Plateaus were observed over the range of fields investigated. The width of the tail can be described by the tail-broadening parameter W, defined as $W = (t_{1/2} - t_0)/t_{1/2}$, where $t_{1/2}$ is the time for the photocurrent to decay to one-half its value at t0. Values of W were weakly field dependent, increasing with increasing field. At 3.6 x 10^5 V/cm, W was approximately 0.42. The features for NTDI containing MNQ, DPQ, TBS, DCAQ, or PTS were substantially different. The presence of PTS at concentrations of a few multiples of 10^{-7} erodes the transients. The initial spike is suppressed, the plateaus are less well defined, and W is increased. For concentrations in excess of 10^{-6}, transit times can be resolved only from double logarithmic transients. For concentrations in excess of 10^{-3}, however, the transients closely resemble those of NTDI, although with transit times that are very long, frequently in excess of a few s. For NTDI containing DCAQ, the transients were degraded only for concentrations in excess of approximately 10^{-5}. Transit times could be resolved from double linear transients at all concentrations. For NTDI containing MNQ, DPQ, or TBS, the transients were unchanged except for concentrations in excess of a few multiples of 10^{-4}. As with DCAQ, transit times could be derived from double linear transients for all concentrations.

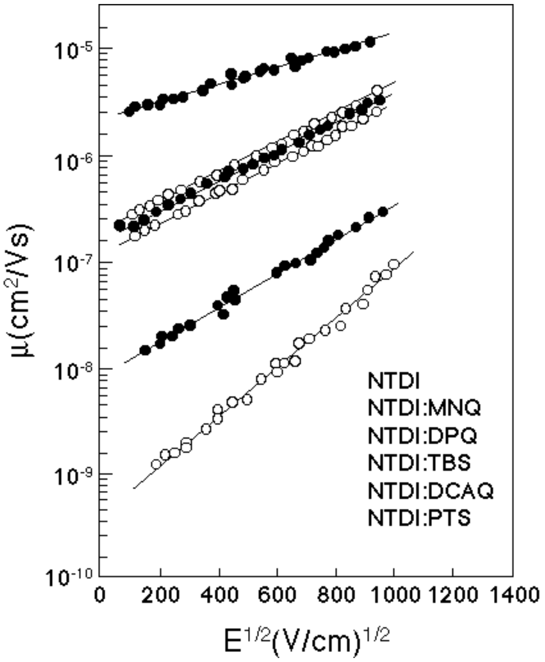

Figure 2. The field dependencies of the mobilities for NTDI and NTDI containing MNQ, DPQ, TBS, DCAQ, and PTS. The trap concentrations were 10^{-2}.

For both NTDI and NTDI containing MNQ, DPQ, TBS, DCAQ, and PTS, the field dependencies of the mobility can be described as $\ln\mu \propto \beta E^{1/2}$. Here, β is a coefficient that is weakly dependent on trap depth. Figure 2 shows the room temperature results for trap concentrations of 10^{-2}. Figures 3 to 7 show the room temperature mobilities versus trap concentration. For MNQ, DPQ, TBS, and DCAQ, the mobilities were derived from transients in double linear current versus time representation. For PTS, however, it was necessary to use double logarithmic transients. Table 2 summarizes values of $c_{1/2}$ and n derived from the results in Figs. 3 to 7. Here, $c_{1/2}$ is the trap concentration at which the mobility is reduced by a factor of two from its trap-free value. The parameter n is derived from the relationship $\mu(c) \propto \mu(c = 0)c^{-n}$ under the condition $c[\exp(E_t/kT)] >> 1$.

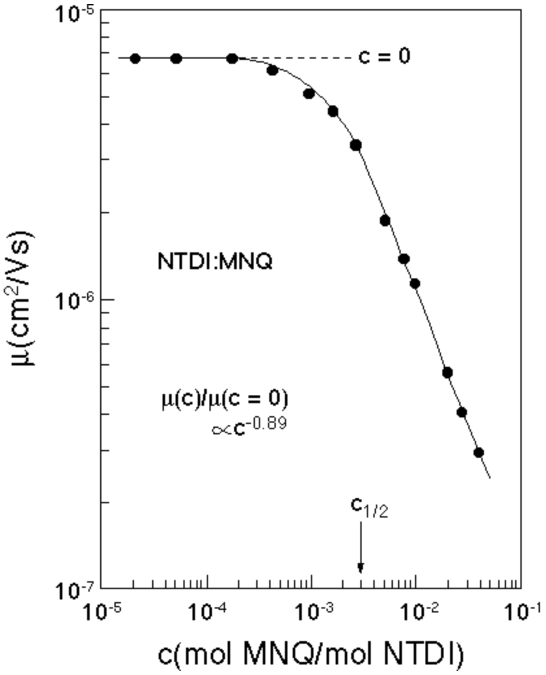

Figure 3. The mobility versus MNQ concentration. The field was 3.6 x 10^5 V/cm. The dashed line is the mobility in the absence of MNQ. The arrow indicates the trap concentration for which the trap-free mobility is reduced by a factor of two.

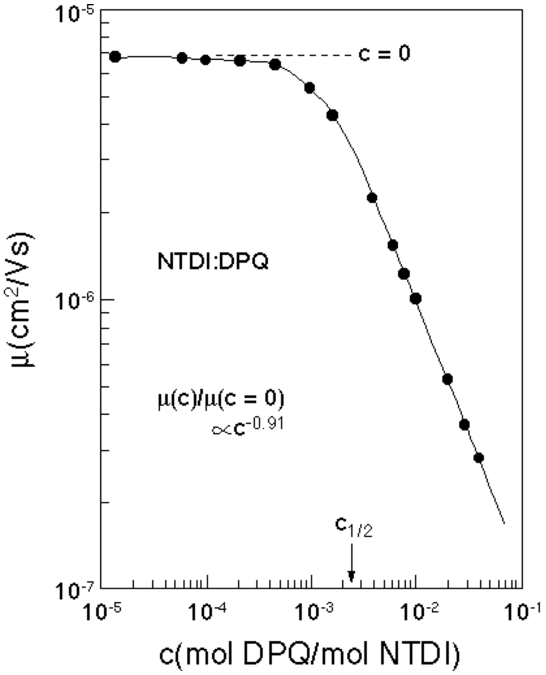

Figure 4. The mobility versus DPQ concentration. The field was 3.6 x 10^5 V/cm. The dashed line is the mobility in the absence of DPQ. The arrow indicates the trap concentration for which the trap-free mobility is decreased by a factor of two.

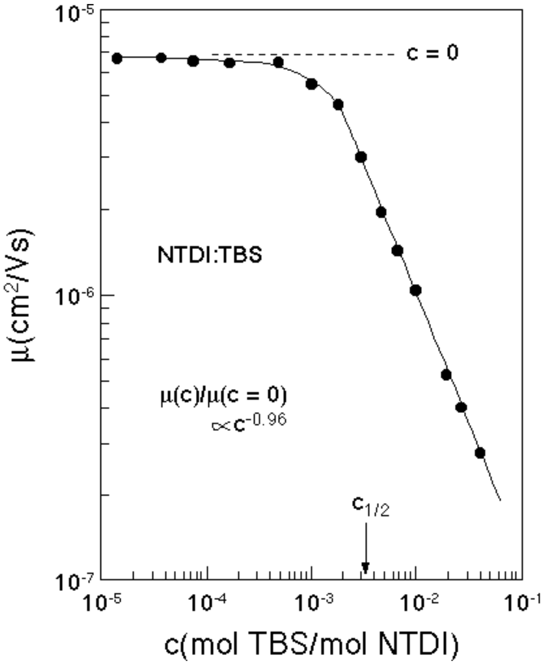

Figure 5. The mobility versus TBS concentration. The field was 3.6×10^5 V/cm. The dashed line is the mobility in the absence of TBS. The arrow indicates the trap concentration for which the trap-free mobility is decreased by a factor of two.

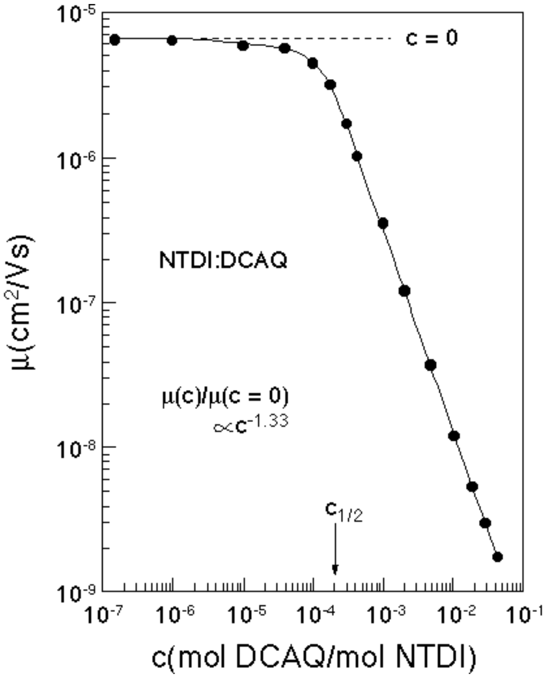

Figure 6. The mobility versus DCAQ concentration. The field was 3.6×10^5 V/cm. The dashed line is the mobility in the absence of DCAQ. The arrow indicates the trap concentration for which the trap-free mobility is decreased by a factor of two.

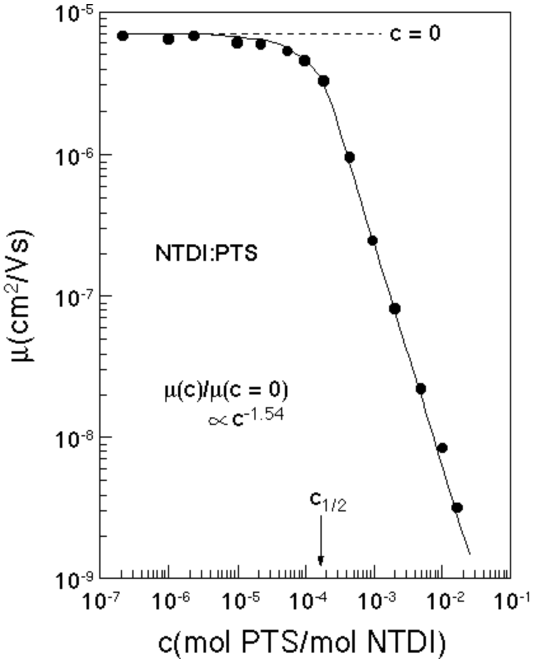

Figure 7. The mobility versus PTS concentration. The field was 3.6×10^5 V/cm. The dashed line is the mobility in the absence of PTS. The arrow indicates the trap concentration for which the trap-free mobility is decreased by a factor of two.

Table 2. NTDI Electron Trapping Parameters

Trap molecule	Et(eV)	$c_{1/2EXP}$	$c_{1/2CAL}$	n
MNQ	0.19	3.0×10^{-3}	5.5×10^{-4}	0.89
DPQ	0.19	2.5×10^{-3}	5.5×10^{-4}	0.91
TBS	0.20	3.5×10^{-3}	3.6×10^{-4}	0.96
DCAQ	0.35	2.0×10^{-5}	1.2×10^{-6}	1.33
PTS	0.40	1.5×10^{-4}	1.6×10^{-7}	1.54

The parameter n is derived from the relationship $\mu(c) \propto \mu(c = 0)c^{-n}$.

Discussion

First, we discuss the temporal features of the photocurrent transients. Provided the trapping lifetime is well in excess of the transit time, a carrier does not interact with trapping centers during its transit and the transients remain unaffected. As the trap concentration is further increased, the trapping lifetime eventually becomes comparable to the transit time. Consider the case where the number of traps is within a factor of two of the number of jumps a carrier makes upon traversing the sample and the trap depth is such that it takes several multiples of the trap-free transit time to escape thermally. For these conditions, some of the carriers will traverse the thickness without trapping, some will have single trapping events, and some will have multiple trapping events. This regime is usually described as trap-perturbed and characterized by a wide dispersion of transit times. As the concentration is further increased, all carriers experience multiple trapping events during their transit. Under these conditions, the dispersion of transit times is considerably reduced and the transients more closely resemble those in the absence of traps, although featuring transit times that are substantially longer. This regime is usually described as trap-controlled. At very high trap concentrations, trap-to-trap hopping occurs with the result that the mobility increases with trap concentration. Depending on the trap depth, the trap-to-trap regime may or may not be observed. The results observed with NTDI containing MNQ, DPQ, TBS, DCAQ, and PTS are in accord with these arguments. The results clearly show that the trap depth and concentration play a major role in the temporal features of the transients.

Next, we discuss the Hoesterey-Letson formalism. This is perhaps the simplest approach to trapping. It is based on a multiple trapping argument and premised on the early work of Shockley and Read[29] and Bube.[30] The model assumes a discrete trap depth and does not include effects related to disorder. The model leads to two basic predictions. First, the concentration at which the mobility is decreased by a factor of two is

$$c_{1/2} = exp(-E_t/kT) \qquad (3)$$

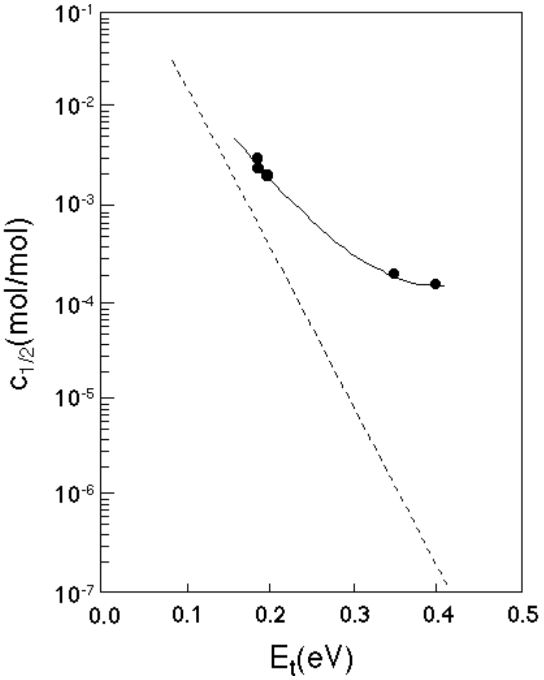

Figure 8. The concentration $c_{1/2}$ at which the mobility is decreased by a factor of two from its trap-free value versus trap depth. The dashed line was calculated from Eq. (3).

Figure 8 shows results derived from Figs. 3 to 7. The results are clearly not in accord with Eq. (3). The formalism underestimates the onset of the trap-controlled regime, particularly for deep traps. For MNQ, DPQ, and TBS, traps with depths of 0.19, 0.19, and 0.20 eV, the discrepancies are approximately a factor of five. For PTS, a 0.40 eV trap, the discrepancy is a factor of 103. The second prediction is that for $c[exp(E_t/kT)] >> 1$, the mobility scales with trap concentration as c-1. Figure 9 shows the results obtained from the data in Figs. 3 to 7. Contrary to predictions, the dependence of the mobility on trap concentration is clearly dependent on trap depth. While the multiple trapping assumption must eventually break down with increasing trap depth, this cannot account for coefficients of less than unity. The most likely explanation is related to the width of the intrinsic and trap manifolds. The Hoesterey-Letson formalism is based on a discrete trap depth, an assumption which is likely unrealistic for disordered molecular solids. Physically, this assumption neglects the opening of new relaxation pathways for an ensemble of carriers due to the additional states at the tail of the DOS. This causes the trapping factor in Eq. (1) to deviate from a product of the trap concentration and an exponential term that contains the trap depth.

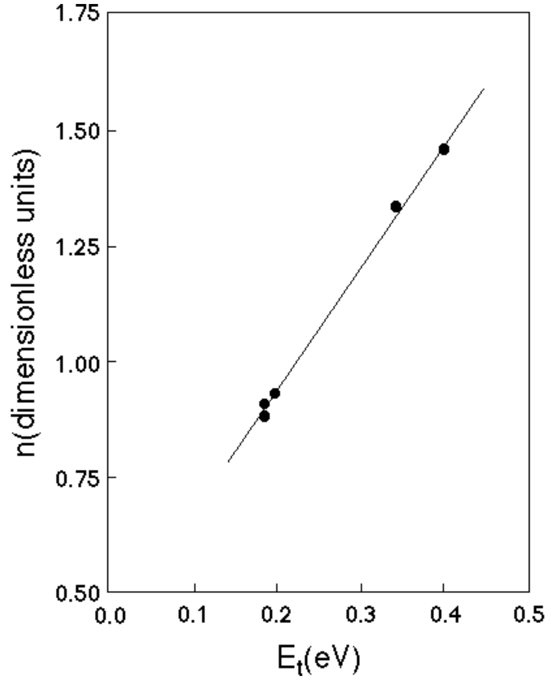

Figure 9. The dependence of the mobility on trap concentration versus trap depth. The parameter n is derived from the relationship $\mu(c) \propto \mu(c = 0)\, c^{-n}$.

Concluding Remarks

The results of this study show that the field dependencies of the mobility for NTDI containing traps with depths between 0.19 and 0.40 eV agree with the simulations of Wolf et al.[20] The characteristic $\ln\mu \propto \beta E^{1/2}$ dependencies were observed for all trap depths and concentrations. There were no evidences of dependencies of the form $\ln\mu \propto \beta E$, as predicted for the deep trapping regime.[21] The use of the Hoesterey-Letson formalism to describe the effects of trap concentration leads to significant discrepancies concerning the onset of the trap-controlled regime and the dependence of the mobility on trap concentration at high concentrations. A similar effect has been previously reported for hole trapping in a series of arylamine doped polymers.[23-26] It is our speculation that the discrepancies are due to the neglect of disorder in the derivation of the trapping factor that describes the time spent by carriers in traps.

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Biographies

Susan A. Visser

Susan A. Visser is a Senior Research Scientist in the Office Imaging Research and Technology Department of Eastman Kodak Company, Rochester, New York. Originally from Huntington Beach, California, she received a B.S. in chemical engineering and a B.S. in biology from the Massachusetts Institute of Technology in 1986. She successfully completed the coursework, doctoral qualifying examinations, and initial research assignments for a Ph.D. in molecular biology at the University of Wisconsin - Madison in 1987. In 1988, she began Ph.D. work in chemical engineering at the University of Wisconsin - Madison, earning her Ph.D. in 1991. Her Ph.D. research in chemical engineering involved elucidation of structure-property relationships in polyurethane ionomers. While at the University of Wisconsin - Madison, she was a National Science Foundation Fellow, a University Fellow, and an American Association of University Women Fellow. In 1991, she joined the Research Laboratories of Eastman Kodak Company. Since that time, her research activities have been in areas related to polymer structure-property relationships, filled polymer systems, plasma polymerized films, and applications of traditional and plasma-deposited polymer systems to imaging. She has published over 30 scientific articles and holds 13 patents.

Paul M. Borsenberger

Paul M. Borsenberger was a Senior Research Associate in the Office Imaging Research and Technology Department of Eastman Kodak Company, Rochester, New York. Originally from St. Louis, Missouri, he received a B.S. in metallurgy from the Missouri School of Mines and Metallurgy in 1960. Following three years service in the U.S. Army, he attended Stanford University where he received a M.S. degree in 1965 and a Ph.D. degree in 1967, both in materials science. His Ph.D. dissertation was concerned with photoconductivity and defect chemistry of compound semiconductors. While at Stanford, he was a Sloan Fellow. In 1967, he joined the Research Laboratories of Eastman Kodak Company. Since that time, his research activities had been in areas related to photoconductivity of disordered solids and the application of these materials to electrophotography. This research involved studies of molecularly doped polymer, amorphous silicon, and the chalcogenide glasses. He published over 100 scientific articles, including the book Organic Photoreceptors for Xerography. He was appointed to the Research Scientific Council of Eastman Kodak Company in 1985 and served as chairman from 1987 to 1989. He passed away at his home in Hilton, New York on July 17, 1998.