Hole Mobilities in Photochemically Modified DEH-Doped Polycarbonate*

J. W. Stasiak† and T. J. Storch

Lexmark International, Inc., Boulder, Colorado 80301

The hole mobilities of molecularly doped polymer films containing *p*-diethylaminobenzaldehyde diphenylhydrazone (DEH) are measured before and after systematic UV irradiation. Ultraviolet exposure has been shown to induce a photochemical reaction of the DEH molecule. This reaction is known to reduce dramatically the molecule's capability to transport charge. Presumably the reduction in mobility is associated with the substantial increase (about 1 eV) in the ionization potential of the DEH molecule after photocyclization. We demonstrate that systematic UV irradiation of molecularly doped polymer films containing DEH provides a novel approach for diluting the dopant concentration and effectively increasing the intersite separation between "active" dopant molecules in situ. This photochemical process is exploited to study charge transport in DEH-doped polycarbonate films parametric in UV irradiation time. Transport parameters are determined from transient photocurrent measurements over a range of electric fields and temperatures. Our principal observations are: (1) UV irradiation of DEH-doped polycarbonate films results in a corresponding decrease in the effective hole mobility, and (2) despite the systematic drop in mobility, a consequence of the elimination of active hopping sites, the activation energy for hopping, Δ, and the energetic disorder parameter, σ, remain constant.

Journal of Imaging Science and Technology 40: 299–303 (1996)

Introduction

Recently there has been considerable theoretical[1,3] and experimental[2,3] effort focused on developing a unified description of charge transport in molecularly doped polymer systems. This effort has been largely driven by the practical demands for improved performance in electrophotographic applications; however, these systems also provide a unique "laboratory" for studying the fundamental physics of charge transport in highly disordered molecular solids. A molecularly doped polymer consists of a polymer host that contains a randomly dispersed dopant. Typically, the dopant is a small molecule with an attached acceptor or donor functionality. At this time there is general agreement that charge transport in molecularly doped polymers can be described as an activated hopping process in which electrons or holes hop between neighboring dopant sites in response to an externally applied electric field. The mobilities and transport properties of these charges have been shown to be dependent on the electric field, temperature, dopant molecule structure, dopant concentration, and the structure of the polymer host. Most experimental observations of this process are obtained from measurements of the charge drift mobility using the standard time-of-flight technique.

Currently, two predominant theoretical models have been proposed for interpreting the experimental results. Whereas both of these models have some success in predicting specific experimental features, neither one provides a complete description. The first model, developed by Bässler[4] and largely based on Monte-Carlo simulations, suggests that charge transport occurs within a 3-D array of localized sites characterized by superimposed energetic and spatial disorder. Within the context of this model, the charge mobility, μ, is a function of the energetic disorder, the spatial disorder and the electric field,

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

In Eq. 1, σ is the energy width of the hopping site manifold, which provides a measure of the energetic disorder, Σ is a parameter that describes the degree of spatial disorder, μ_0 is a prefactor mobility, C is an empirical constant, and the other symbols have their usual meanings. Recent studies have focused on identifying the specific energetic contributions that determine both the energetic and spatial disorder. These contributions include dipolar interactions between neighboring dopant molecules and interactions between the dopant molecules and the polymer host.[5–13] Contributions arising from Van der Waals interactions have also been discussed.[14,15] The second model[16–18] suggests that hopping transport is determined by the interaction of the charge carrier with molecular vibrations of the host dopant molecule. These interactions "self-trap" the charge carrier and form a new particle called a *polaron*. The polaron model predicts that the mobility is proportional to the product of two probability factors: a jump probability and a Boltzmann probability that determines the energy coincidence between the host and target hopping sites,

$$\mu \propto \frac{e\rho^2}{kT} P \frac{\omega}{2\pi}\exp\left[-\frac{1/2\Delta_P - J}{kT}\right]. \quad (2)$$

In Eq. 2, P is the jump probability, ω is the attempt-to-jump frequency, and ρ is the intersite distance between host and target sites. The argument in the brackets is the Boltzmann probability of an energy coincidence. The term Δ_P is the polaron binding energy and J is the transfer integral. The electric field dependence is usually described as

$$\mu \propto \frac{1}{E}\sinh\frac{eE\rho}{2kT}. \quad (3)$$

Original manuscript received February 2, 1996. Revised May 1, 1996.

* Presented in part at IS&T"s 11th International Congress on Advances in Non-Impact Printing Technologies, October 29–November 3, 1995, Hilton Head, SC.

† IS&T Member

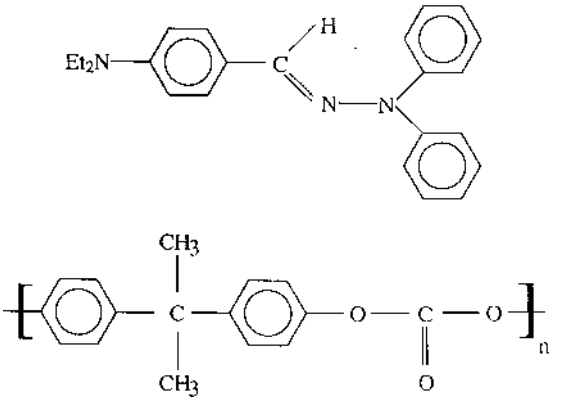

Figure 1. The molecular structures of (a) DEH and (b) polycarbonate.

Experimentally distinguishing between the two models has proved to be difficult. Furthermore, a deficiency common to both models is a satisfactory explanation of the origin of the activation energy. For a detailed discussion of the comparisons and limitations of each model, the reader is directed to the review article by Schein[19] and to Borsenberger and Weiss[3] and references therein.

Experimental approaches designed to distinguish between the two models and clarify the origin of the disorder in molecularly doped polymer systems have been described in the literature. The most promising approaches include transport measurements parametric in dopant concentration[5,20] and measurements that deliberately introduce different levels of "disorder" into the samples.[21–24]

In this study, we describe the results of an experiment that provides an alternate approach to distinguishing between Bässler's model and models based on polaron formation. In contrast to experiments that deliberately control the dopant concentration during sample preparation and coating, we systematically "dilute" the dopant concentration in situ by exploiting a well-characterized photochemical reaction of the hole transport molecule *p*-diethylaminobenzaldehyde diphenylhydrazone (DEH).[25–28] Ultraviolet irradiation of thin solid films of DEH dispersed in bisphenol-A-polycarbonate results in the irreversible conversion of DEH to the photocyclization product, 1-phenyl-3-(4-diethylamino-1-phenyl)-1,3-indazole (IND). Optical absorption spectra, which show an isosbestic point at 300 nm, indicate that IND is the only photoproduct produced during this reaction. Detailed spectroscopic and electrochemical measurements by Pacansky et al.[25–28] further indicate that the reaction proceeds with a moderately high quantum efficiency ($\phi \approx 0.4$) and that the ionization potentials of DEH and IND are 4.3 and 5.3 eV, respectively.

The crucial assumption in our work is that the large difference in ionization potentials between the DEH and IND molecules will split the charge transport manifold and effectively remove the IND molecules from the charge transport process. In the following section, we present spectroscopic and chromatographic evidence of photochemical conversion of DEH to IND. These experiments demonstrate that systematic UV irradiation of doped polymer films containing the hole transport molecule DEH results in a corresponding dilution of active dopant sites. Finally, we present measurements of charge transport parameters over a range of electric fields and temperatures and as a function of UV exposure times.

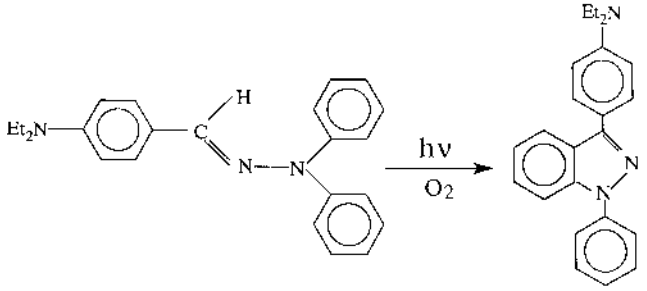

Figure 2. Photochemical conversion of DEH to IND.

Materials and Experimental Details

The molecular structures of DEH and bisphenol-A-polycarbonate (PC) are shown in Fig. 1, and the photocyclization reaction[25] of DEH to IND is shown in Fig. 2. Coating solutions were prepared by dissolving the appropriate ratio of DEH and PC in HPLC-grade tetrahydrofuran. All measurements discussed in this work were made using 40% (wt) concentrations of DEH. Samples were prepared by solvent coating the solutions onto semitransparent aluminized Mylar substrates. The coated substrates were oven dried, in air, at 100°C for 1 h to reduce residual solvent content. With the exception of the control samples, which received no irradiation, films were uniformly exposed to UV light using a 15-W Phillips BLB fluorescent lamp. The peak spectral output of this lamp is between 350 and 390 nm. The incident exposure power was measured by a United Detector Technology Model 351 optical power meter. The incident energy was determined to be 0.13 J/cm^2 per minute of exposure. The exposure times ranged from 30 to 960 min. Counterelectrodes were deposited onto the free surfaces of the films using an electron beam evaporation process. The electrodes were 1 cm in diameter and consisted of 2000 Å of aluminum. Finally, all samples were annealed well above the glass transition temperature of the film (100°C) for 3 h to homogeneously redistribute the DEH and IND molecules and eliminate damage caused by the metal deposition step. The thickness of each sample was determined by capacitance and precision step height measurements. Typical film thicknesses were between 10 and 10.5 μm.

Figures 3 and 4 show the optical absorption spectra and chromatographic data obtained from DEH-doped polycarbonate film samples before and after systematic UV irradiation. As discussed above, all samples were prepared using 40% (wt) concentration of DEH in PC. With the exception of the counterelectrode deposition and postdeposition annealing steps, the samples used in the spectroscopic and chromatographic measurements were prepared identically to those used in the transport measurements.

In Fig. 3, two features are apparent in the spectra. First, the peak at 365 nm attributed to DEH decreases systematically with increasing exposure time. Second, a new peak at ≈265 nm develops with increasing exposure time. This new peak is attributed to the IND photoproduct and provides evidence that the photoreaction discussed here has occurred. Note that the curves in this figure were normalized to a known isosbestic point at 300 nm to correct for minor coat weight differences. The HPLC data provides further evidence of photoconversion. Figure 4 shows peaks at two well-separated retention times. The peak at 6.75 min. is attributed to DEH and decreases with increasing UV exposure. A new peak at 8.75 min. begins to grow systematically with UV exposure, as shown in the inset. Although an authentic IND reference sample was

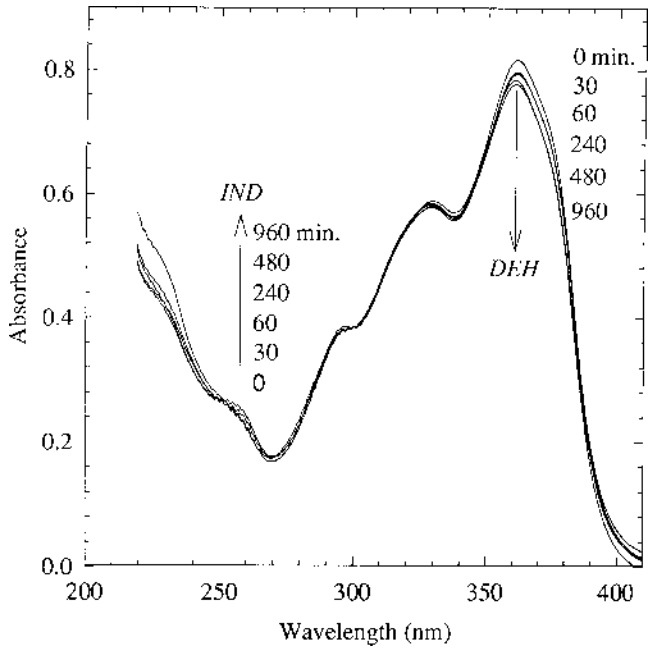

Figure 3. Optical absorption spectra of 40% DEH in polycarbonate as a function of UV exposure time. (Note that the curves have been normalized to the isobestic point at 300 nm to correct for minor coat weight differences.)

unavailable during this work, prior chromatographic studies of this photoreaction indicate that this peak is associated with the indazole photoproduct.[29] Without an authentic reference, accurate estimates for the conversion efficiencies and reactant concentrations could not be made. A simple estimate that takes into consideration the quantum efficiency for this reaction,[25] the incident exposure intensities, and the extinction coefficient of DEH, suggests that the longest irradiation time (16 h) reduced the effective dopant concentration from 40% to about 30%. Prior concentration dependence studies in which the amount of DEH was determined during sample preparation agree with this estimate.

Photocurrent transients were measured, using the conventional time-of-flight technique.[30] In this technique, the film sample acts as a parallel plate capacitor. Under a constant voltage bias, a 337-nm, 10-ns light pulse is delivered through the bottom electrode. The strongly absorbed light pulse photogenerates a narrow distribution of free charge carriers that drift across the sample in response to the electric field. In this experiment, the majority of charge carriers were holes. The light pulse was generated by a Laser Photonics UV24 nitrogen laser. Samples were mounted in an Oxford Instruments DN1704 variable temperature cryostat, which provided temperature control (± 0.5 K) and optical access to the sample. Photocurrent transients were acquired by an HP 54502A digitizing oscilloscope. To maintain small signal measurement conditions and avoid space-charge effects within the sample, the laser intensity was attenuated by appropriate neutral density filters. Throughout the measurement process, the sample capacitance was checked for drift. Samples that exhibited drift were rejected. The drift mobilities were determined from the digitized photocurrent transients, using the conventional relationship:

$$\mu = \frac{L}{\tau_T E} = \frac{L^2}{\tau_T V}, \tag{4}$$

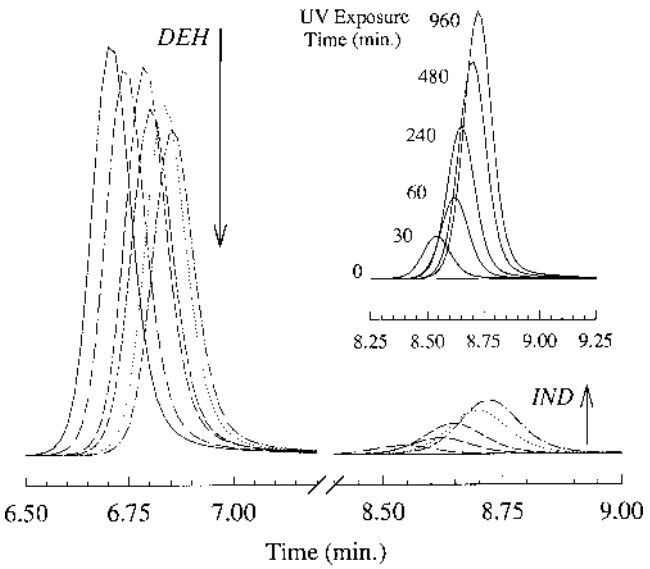

Figure 4. HPLC of 40% DEH in polycarbonate parametric in UV exposure time.

where L is the sample thickness, τ_T is the mean transit time of the charge packet, E is the electric field, and V is the applied voltage. The mean transit times were determined by fitting the photocurrent transients, using the procedure developed by Scott, Pautmeier, and Schein.[31]

Results

Figure 5 is a plot of the log of the mobility versus $E^{1/2}$ for two measurement temperatures, parametric in UV exposure time. A common feature of each curve shown in this figure is the linear relationship between log μ and $E^{1/2}$ over a moderately wide range of electric fields. This dependence, which can be expressed as

$$\mu \propto \exp(\beta E^{1/2}), \tag{5}$$

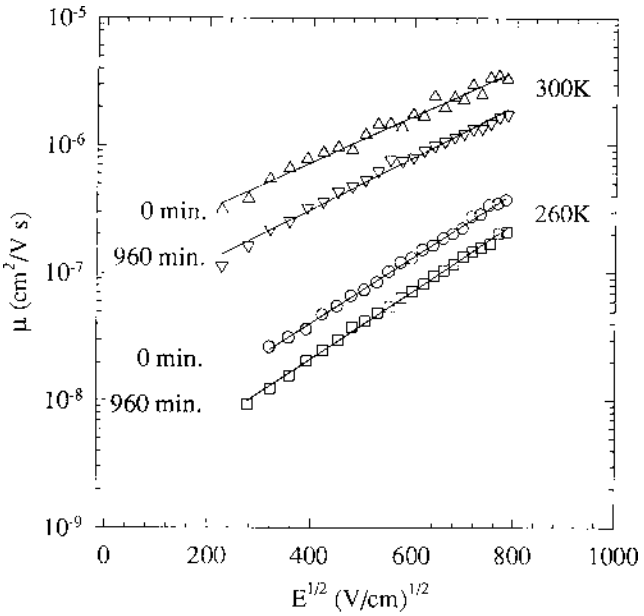

Figure 5. The log of the mobility versus $E^{1/2}$ for 40% DEH in polycarbonate at 260 and 300 K parametric in UV exposure time.

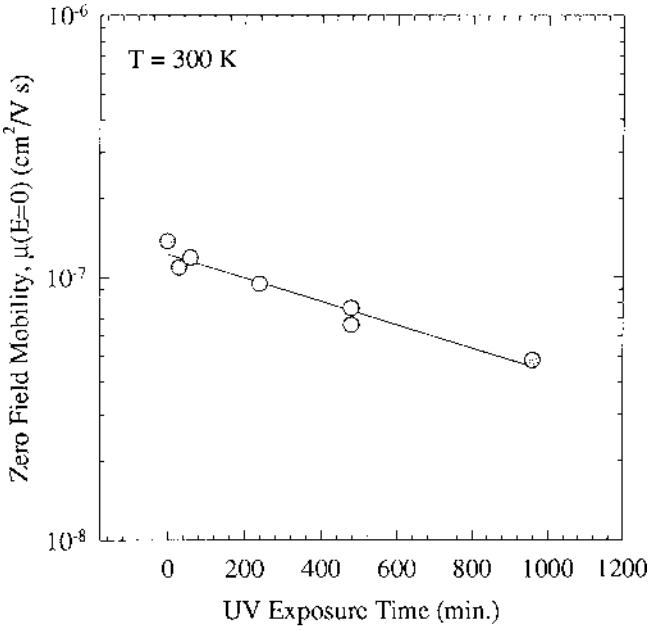

Figure 6. The zero-field mobility at 300 K parametric in UV exposure time.

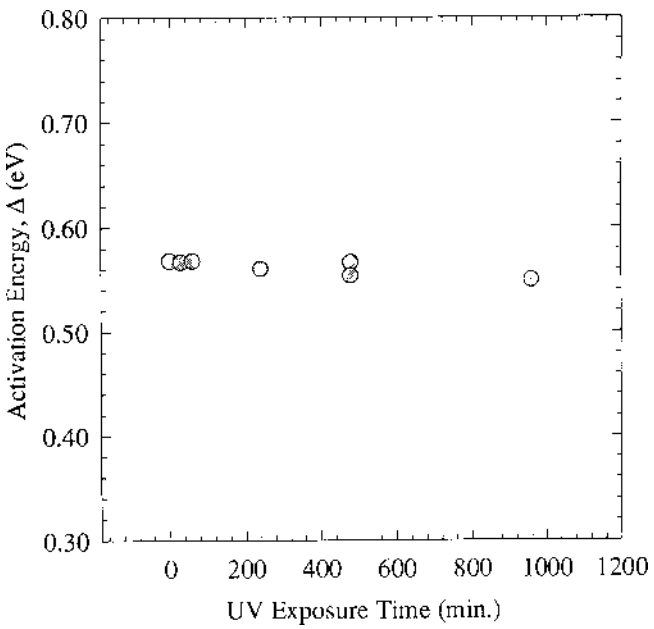

Figure 8. The activation energy, Δ, parametric in UV exposure time.

was a ubiquitous characteristic of all the electric field measurements discussed in this study. Although we have selected data obtained at 260 and 300 K to show in this figure, the universal characteristic of the log μ-versus-$E^{1/2}$ data obtained after irradiation is a uniform depression of the effective mobility at all electric fields.

Figure 6 is a semilogarithmic plot of the zero-field mobilities obtained at 300 K, parametric in UV exposure time. The zero-field mobilities were obtained by extrapolating each of the log μ-versus-$E^{1/2}$ curves to zero electric field. Note that with increasing exposure times the zero-field mobilities decrease correspondingly. The behavior shown in Fig. 6 is observed at all measurement temperatures. This dependence, which has been observed in previous concentration dependence studies of DEH-doped polymer systems,[5] provides experimental evidence that the effective separation between active hopping sites can be controlled photochemically.

In the disorder model framework, the slopes obtained by plotting the zero-field mobilities versus $1/T^2$ give the energetic disorder parameter, σ. In Fig. 7, we plot σ as a function of UV exposure time. Within experimental error, σ is independent of exposure time and is approximately 0.124 eV.

In the polaron model, the slopes obtained by plotting the zero-field mobilities versus $1/T$, give the activation energy, Δ. If we plot Δ as a function of UV exposure time, as shown in Fig. 8, we see that Δ is also independent of exposure time and is approximately 0.562 eV.

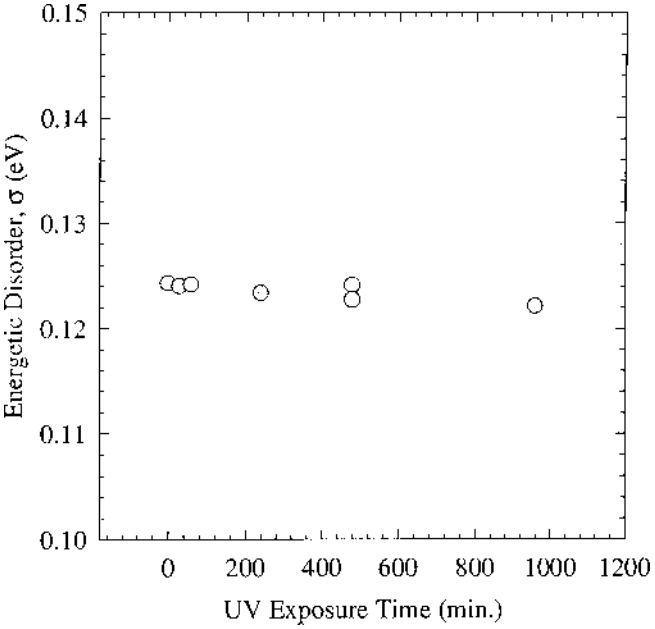

Figure 7. The energetic disorder parameter, σ, parametric in UV exposure time.

Discussion

There are two significant observations in this study. First, for DEH-doped polycarbonate films, we observe a systematic decrease in the magnitude of the effective hole mobility with increasing UV exposure time. This observation provides evidence that the photochemical conversion of DEH to IND can be exploited to control the effective "active" dopant concentration (i.e., intersite separation) in situ. Second, the energetic disorder parameter, σ, determined within the framework of the disorder formalism, and the activation energy, Δ, determined within the polaron formalism, are independent of exposure time, within experimental error.

Accepting the premise that UV irradiation provides an approach for diluting the "active" doping concentration in DEH-doped polycarbonate systems, as suggested by our data, we can restate the observations discussed above in the context of dopant concentration. First, we recover the well-established relationship between the mobility and dopant concentration. Second, we observe that the energetic disorder parameter, σ, and the activation energy, Δ, are independent of dopant concentration. This observation is in agreement with the concentration studies reported by Mack, Schein and Peled[5] and Schein and Borsenberger[20] in which the DEH-doping concentration was determined during sample preparation and film coating.

Within the framework of the disorder model,[32] it is proposed that the statistical interactions between the dopant molecules and the randomly oriented dipole moments of the surrounding molecules are largely responsible for energetic disorder. The observation that the energetic disorder is independent of intersite spacing is inconsistent with this picture. Although it has been proposed that this independence could be the result of a delicate balance of coincidences and cancellations between the energetic interactions of the dopant molecules and the surrounding molecular landscape,[14] we suggest that such a balance between the charge–dipole interactions is unlikely. Furthermore, although it is possible to imagine that the DEH:polycarbonate system satisfies these conditions for independence, it seems unreasonable to expect that the same balance would be achieved in systems containing different dopant molecules, such as 1-phenyl-3-*p*-diethylaminostyryl-5-diethylphenyl pyrazoline (DEASP).[10] Finally, consider that the computed dipole moment of the IND photoproduct (2.1 Debye)[33] is considerably smaller than that of the DEH molecule (3.1 Debye).[19] As the density of IND molecules increases with systematic photoconversion and redistribution, the disorder model would predict that σ (and Δ) should systematically *decrease*. Within experimental error, we do not observe this behavior in our data. A simpler explanation for our experimental observations is that charge transport for certain molecular dopants, including DEH and DEASP, is dominated by intramolecular interactions and that the independence of the activation energy on intersite spacing is best explained within the small poloron model in the nonadiabatic regime.[19]

Summary

In this study we have described a novel, photochemical method for modifying the doping concentrations of molecularly doped polymers in situ. Although this method is less efficient than determining the dopant concentration during formulation, it eliminates concerns regarding impurities and differences arising from sample preparation. We have provided spectroscopic and chromatographic evidence that supports the assumption that the dopant density can be controlled photochemically, and we have exploited this method in an attempt to distinguish between the two predominant models of charge transport in molecularly doped polymers. Our results, which are in agreement with previous concentration-dependence studies, clearly show that the energetic disorder, σ, and the activation energy, Δ, are independent of intersite spacing. We conclude that this observation cannot be reconciled within the current framework of the disorder model and suggest that the data are best described by using the small polaron model in the nonadiabatic regime.

Acknowledgments. We are grateful to L. Kierstein, D. Sandbach, and G. Schmitt for sample preparation and thickness measurements and to B. Munson for UV-vis and HPLC measurements. A special thanks to Dr. G. Hinch for critical reading of the manuscript and to Dr. J. C. Scott for useful discussions.

References

1. P. M. Borsenberger, E. H. Magin, M. Van der Auweraer, and F. C. De Schryver, *Phys. Stat. Sol.* (a), **140** (9): 9 (1993) and references therein.
2. M. Van der Auweraer, F. C. De Schryver, P. M. Borsenberger, and H. Bässler, *Adv. Mater.* **6** (3): 199 (1994).
3. P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors For Imaging Systems*, Chaps. 7 and 8, Marcel Dekker Inc., New York, 1993.
4. H. Bässler, *Phys. Stat. Sol.* (b), **175** (15): 15 (1993), and references therein.
5. J. X. Mack, L. B. Schein, and A. Peled, *Phys. Rev. B* **39**: 7500 (1989).
6. M. Stolka, J. F. Yanus, and D. M. Pai, *J. Phys. Chem.* **88**: 4707 (1984).
7. L. B. Schein, D. Glatz, and J. C. Scott, *Phys. Rev. Lett.* **65**: 472 (1990).
8. H.-J. Yuh and D. M. Pai, *Phil. Mag. Lett.* **62**: 61 (1990).
9. L. B. Schein and P. M. Borsenberger, *Chem. Phys.* **177**: 773 (1993).
10. P. M. Borsenberger and L. B. Schein, *J. Phys. Chem.* **98**: 233 (1994).
11. M. Sugiuchi, H. Nishizawa, and T. Uehara, in *Proceedings, IS&T's 6th International Congress on Advances in Non-impact Printing Technologies*, R. J. Nash, Ed., IS&T, Springfield, VA, 1991, p. 298.
12. P. M. Borsenberger and H. Bässler, *J. Chem. Phys.* **95**: 5327 (1991).
13. A. Dieckmann, H. Bässler, and P. M. Borsenberger, *J. Chem. Phys.* **99**: 8136 (1993).
14. P. M. Borsenberger, W. T. Gruenbaum, E. H. Magin, and L. J. Sorriero, *Chem. Phys.* **195**: 435 (1995).
15. P. M. Borsenberger, W. T. Gruenbaum, J. E. Kaeding, and E. H. Magin, *Phys. Stat. Sol. (b)* **191**: 171 (1995).
16. T. Holstein, *Ann. Phys.* (N.Y.) **8**: 325 (1959).
17. D. Emin, *Electronic and Structural Properties of Amorphous Semiconductors*, P. G. LeComber and J. Mort, Eds., Academic Press, New York, Chap. 7.
18. L. B. Schein and J. X. Mack, *Chem. Phys. Lett.* **149**: 109 (1988).
19. L. B. Schein, *Phil. Mag. B* **65**(4): 795 (1992).
20. L. B. Schein and P. M. Borsenberger, *Chem. Phys.* **177**: 773 (1993).
21. G. Pfister, S. Grammatica, and J. Mort, *Phys. Rev. Lett.* **37**: 1360 (1976).
22. H.-J. Yuh, D. Abramsohn, and M. Stolka, *Phil. Mag. Lett.* **55**(6): 277 (1987).
23. Y. Kanemitsu, H. Funada, and Y. Masumoto, *Appl. Phys. Lett.* **59** (6): 697 (1991).
24. Th. Pautmeier, J. C. Scott, and L. B. Schein, *Chem. Phys. Letters* **197** (6): 586 (1992).
25. J. Pacansky, H. C. Coufal, and D. W. Brown, *J. Photochem.* **37**: 293 (1987).
26. J. Pacansky, R. J. Waltman, R. Grygier, and R. Cox, *Chem. Mater.* **3**: 454 (1991).
27. J. Pacansky, R. J. Waltman, and R. Cox, *Chem. Mater.* **3**: 903 (1991).
28. J. Pacansky and R. J. Waltman, *Chem. Mater.* **3**: 912 (1991).
29. C. Butler, unpublished results.
30. F. K. Dolezalek, in *Photoconductivity and Related Phenomena*, J. Mort and D.M. Pai, Eds., Elsevier, New York, 1967, pp 27-69.
31. J. C. Scott, L. Th. Pautmeier, and L. B. Schein, *Phys. Rev. B* **46**: 8603 (1992).
32. H. Bässler, *Adv. Mater.* **5** (9): 662 (1993) and references therein.
33. J. Pacansky, Private Communication.