

Charge Transport in Molecularly Doped Polymers: Tests of the Correlated Disorder Model

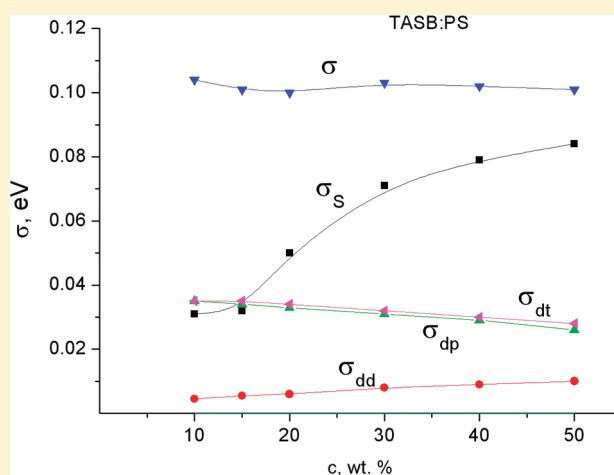
L. B. Schein*

Independent Consultant, 7026 Calcaterra Drive, San Jose, California 95120, United States

Andrey Tyutnev

Moscow State Institute of Electronics and Mathematics, Bol. Trechsvyatitel. per., 3, Moscow, Russia

ABSTRACT: The correlated disorder model (CDM) has been proposed as a theory of charge transport in molecularly doped polymers (MDPs). Recently a test of the CDM was proposed: it was predicted that the dipolar disorder energy can be obtained from the slope of the log of the mobility versus square root of the electric field (the Poole-Frenkel or PF slope). We find that the dipolar disorder energy obtained from the experimental PF slopes are almost always larger than the theoretical predictions, especially for MDPs made from dopants with low dipole moments. In addition, the theory relates the dipolar disorder energy to the temperature T_0 at which the electric field dependence of the mobility vanishes. We find that the observed T_0 does appear to increase as the dipolar disorder increases but is in quantitative agreement (within 25 K) with the theoretical predictions for only a limited set of the measurements. We conclude that it appears that the CDM needs further development to be consistent with charge transport in organic materials.



1. INTRODUCTION

Molecularly doped polymers (MDPs) are amorphous two-component films made from small molecules doped into a polymer matrix. The small dopant molecules are strong electron donors or acceptors. In charge transport, the electron transfer process is believed to occur as a field-assisted, thermally activated hopping mechanism.

The most comprehensive description of our theoretical and experimental understanding of the charge mobility in these materials may be found in ref 1. In this model, the Gaussian Disorder Model (GDM), it is assumed that the charge carriers hop in a Gaussian distribution of states. The correlated disorder models (CDMs)^{2–6} including the polaron correlated disorder model (PCDM)⁷ appeared just at or after publication of this book. In the CDMs, it is recognized that the long-range nature of the multipole interactions that are responsible for molecular site disorder lead to molecules close to one another having similar site energies, rather than having independent energies as is assumed in the GDM. A recent paper⁸ extends the arguments given earlier^{2–7} that the CDMs are better suited for interpretation of mobility data in MDPs than both the Gaussian disorder models (GDM) in the original formulation⁹ or modified¹⁰ (also known as GDM/Σ¹¹). The primary improvement offered by the CDMs (over the GDM) is that it is able to predict better the

linear dependence of the experimentally observed dependence of the log of the mobility on the square root of the electric field, which resembles the Poole-Frenkel (PF) effect. This has been derived analytically in one-dimension,^{3,7} demonstrated by simulations in three dimensions and can be seen in several papers.^{2,3,6,7}

In a recent discussion⁸ of the CDM of ref 6, it was shown explicitly how the slope of the log mobility versus square root of the electric field (PF plots) could be used to obtain the dipolar disorder energy, which could then be compared to accepted theoretical expressions that have been derived earlier.¹² This is a test of the CDM. In addition, the theory also relates the dipolar disorder energy to the temperature T_0 at which the electric field dependence of the mobility vanishes. It is the purpose of this paper to apply these tests of the CDM to experimental values obtained from publications characterizing as many materials as possible. In Section 2, we present enough of the theory so that the reader can understand the tests. In Section 3, a comparison is made between the theoretical values of the dipolar disorder energy and experimental values obtained from published PF plots. In Section 4, we compare the theory of T_0 to published experimental observations. We draw our conclusions in Section 5.

Received: December 27, 2010

Revised: January 30, 2011

Published: March 08, 2011

2. BASIC THEORY

The CDM as a general approach was motivated by the dipolar glass model and is similar in spirit to the original GDM with one important change. The Gaussian energy distribution of the GDM with prescribed rms disorder energy σ is replaced with the electrostatic potential distribution created by the dipoles of the dopant molecules. In the version of the CDM implemented in ref 6, the hopping sites are randomly oriented static dipoles with a constant dipole moment p forming a cubic lattice with a lattice spacing a . It happens to be near Gaussian as well with rms σ_d , but the site energies instead of being random are now spatially correlated. Monte Carlo simulations performed at only one value a and γ ($a = 10 \text{ \AA}$, with $2\gamma a = 10$, see below) have shown that the best overall description of the dependence of the mobility on the electric field F , temperature T , and lattice spacing a is provided by the following empirical formula covering at least 2 decades of the field (F) variation⁶

$$\mu = \mu_c \exp(-2\gamma a) \exp\left[-\frac{9}{25} \left(\frac{\sigma_d}{kT}\right)^2\right] + C_1 F^{1/2} \left[\left(\frac{\sigma_d}{kT}\right)^{3/2} - \Gamma \right] (ea/\sigma_d)^{1/2} \quad (1)$$

Here μ_c is a prefactor, γ^{-1} is the decay radius of a spherical wave function of the electron on the dipolar hopping center, k is the Boltzmann's constant, e is an elementary electric charge, $C_1 \approx 0.78$ and $\Gamma = 2.0$.

Reference 8 emphasizes the point made earlier⁶ that the disorder energy appearing in the first term in square brackets and the disorder energy appearing in the electric field dependence are not the same. The disorder energy associated with the temperature dependence σ_T is the total disorder energy, which includes the disorder energy associated with, for example, the van der Waals interaction. The disorder energy associated with the electric field dependence is the disorder energy that falls off with distance slowest, which is the dipolar disorder energy σ_S . Taking this into account gives a revised empirical formula for the CDM

$$\mu = \mu_c \exp(-2\gamma\rho) \exp\left[-\frac{9}{25} \left(\frac{\sigma_T}{kT}\right)^2\right] + C_1 F^{1/2} \left[\left(\frac{\sigma_S}{kT}\right)^{3/2} - \Gamma \right] (e\rho/\sigma_S)^{1/2} \quad (2)$$

where a is replaced with the average separation between dopant molecules ρ , traditionally estimated in MDPs on the basis of the lattice gas model

$$\rho = \left(\frac{M}{Aq}\right)^{1/3} \quad (3)$$

where c is the relative weight concentration of the dopant, M is the molecular weight, A is Avogadro's number, and q is the density of the MDP. In eq 2, we have two σ 's (σ_T and σ_S) instead of one as in eq 1. The former defines the temperature dependence of the zero-field mobility in a traditional way¹ whereas the latter is predicted to equal the disorder energy associated with dipoles^{6,8,12}

$$\sigma_{dd} = 0.0707 \frac{p}{\epsilon a^2} c^{0.5} \quad (4)$$

In eq 4, σ_{dd} is in electronvolts; p , the dipole moment, is in debyes; a is in nanometers; and ϵ is the relative dielectric constant. This formula was originally derived by Young¹² (and verified later by Novikov et al.⁶). Equation 4 comes from eq 59 in ref 12 by assuming a simple cubic lattice ($f = 1.0$) and noting that c is the fraction of the sites of this cubic lattice occupied by dopant molecules, which is approximated by the relative weight concentration of the dopant. Equation 4 assumes that the lattice constant a is the actual lattice constant of the material in the limit $c \rightarrow 1.0$ (the pure dopant) and the lattice sites are filled with probability c by dipoles randomly. For example, assuming $a = 1.0 \text{ nm}$, $c = 1$, $p = 3.0 \text{ D}$, and $\epsilon = 2.5$ leads to $\sigma_{dd} = 0.085 \text{ eV}$.

In a given MDP, we define σ_{dd} as the dipolar disorder energy due to the dopant and σ_{dp} as the dipolar disorder due to the polymer. We will assume that the polymer repeat units are point dipoles with their respective average distance ρ defined by eq 3 determined by the concentration $(1 - c)$ of the polymer and M the molecular weight of the polymer repeat unit. It is useful to introduce the dipolar disorder specifically for a dopant glass $\hat{\sigma}_{dd}$ (100% concentration, $c = 1.0$) and a pure polymer $\hat{\sigma}_{dp}$ to be treated as material constants

$$\hat{\sigma}_{dd} = 0.0707 \frac{p}{\epsilon} \left(\frac{Aq_d}{M_d}\right)^{2/3} \quad (5)$$

For DEH, $\hat{\sigma}_{dd}$ is 0.115 eV, and $\hat{\sigma}_{dp}$ is 0.037 eV for polystyrene (PS) and 0.047 eV for polycarbonate (PC). (The meanings of the initials used in this paper can be found in the Appendix and a list of materials constants can be found under Table 2.) Using eq 3 to eliminate the a 's ($a = \rho$ at $c = 1$) and assuming that these two dipole disorder energies add quadratically to give the square of the total dipolar disorder σ_{dt}

$$\sigma_{dt}^2 = (1 - c)\hat{\sigma}_{dp}^2 + c\hat{\sigma}_{dd}^2 \quad (6)$$

According to ref 8, σ_S should equal σ_{dt} . To find σ_S from the PF slope $S = d \ln \mu / d \ln F^{1/2}$ in eq 2, we use a dimensionless equation as in ref 13

$$\frac{x^{3/2}}{(\hat{T})^{3/2}} - 0.016\hat{S} \sqrt{\frac{x}{\hat{\rho}}} - 0.0079 = 0 \quad (7)$$

with $x = \sigma_S/1 \text{ eV}$, $\hat{T} = T/290 \text{ K}$, $\hat{S} = S/10^{-3} \text{ (cm/V)}^{1/2}$ and $\hat{\rho} = \rho/1 \text{ nm}$.

σ_T should equal the total disorder that includes the van der Waals disorder σ_{vdW} . This adds quadratically to σ_{dt} and is given by

$$\sigma_T^2 = \sigma_{vdW}^2 + \sigma_{dt}^2 \quad (8)$$

The comparison of σ_S to σ_d undertaken in ref 8 neglected to take into account the contribution to the dipolar disorder of the polymer matrix, which we will include. In what follows, we reserve the symbol σ for the values obtained by applying the GDM (GDM/ Σ) to experimental data, which is usually reported in papers that analyze data with the GDM. It is related to σ_T by $\sigma_T \approx 1.11\sigma$ (because of the slight difference in the constants in front of σ_T in the CDM in eq 2 ($-9/25$) and the GDM ($-4/9$)).

Note that the CDM, as represented by eq 2, predicts that the electric field dependence of the mobility goes to zero (or the PF slope changes sign). This occurs when

$$\left(\frac{\sigma_S}{kT}\right)^{3/2} = \Gamma = 2 \quad (9)$$

Table 1. List of the PF Slopes S (Obtained from the Literature) and Calculated σ_s (Obtained by Using Equation 7)^a

MDP	T (K)	c (%)	S (10^{-3} (cm/V) ^{1/2})	σ_s (eV)	ref
glasses					
DEH	298	100	5.48	0.125	17
	222		8.55	0.117	
DEASP	316		4.25	0.110	18
	293		5.46	0.117	
TMP-D	287		3.59	0.087	16
	247		5.61	0.096	
	187		10.78	0.109	
TTB	362		0.94	0.065	37
	296		1.57	0.060	
	247		2.89	0.063	
	204		4.52	0.063	
TPD	297		2.19	0.069	14
	213		4.05	0.062	
TAPC	295		0.41	0.045	15
MDPs					
DEH:PS	294	7	1.52	0.054	19
		10	2.47	0.063	
		20	3.86	0.078	
		30	4.00	0.083	
		40	4.14	0.094	
		50	4.56	0.096	
		65	5.37	0.115	
	317		4.38	0.109	
	217		9.58	0.117	
DEASP:PC	295	10	2.27	0.063	20
		20	3.96	0.081	
		30	4.10	0.087	
		40	4.64	0.095	
		50	5.21	0.105	
		70	5.83	0.119	
		90	6.32	0.129	21,22
	385	10	−0.36	0.048	30
	375		−0.084	0.050	
	365		0.14	0.051	
	355		0.64	0.055	
	335		0.84	0.054	
DEH:PC	293	50	4.77	0.102	21,22
DTNA:PS	327	40	1.84	0.070	23
	290		2.73	0.072	
	265		3.69	0.076	
TASB:PS	296	10	−1.35	0.031	24
		15	−0.59	0.032	
		20	1.06	0.050	
		30	3.00	0.071	
		50	3.77	0.084	
	337		3.23	0.090	
	197		9.70	0.091	
ENA-D:PS	294	10	−1.26	0.031	25
		15	−0.44	0.036	
		20	0	0.040	
		25	0.68	0.047	

Table 1. Continued

MDP	T (K)	c (%)	S (10^{-3} (cm/V) ^{1/2})	σ_s (eV)	ref
		40	1.02	0.051	
		65	1.41	0.057	
	327		1.31	0.063	
	296		1.67	0.061	
	247		2.81	0.061	
	217		3.78	0.061	
TPM-A:PS	296	45	1.53	0.058	26
TPM-B:PS			2.00	0.063	
TPM-C:PS			2.38	0.067	
TPM-D:PS			2.64	0.072	
TPM-E:PS			3.51	0.082	
TPM-F:PS			4.43	0.094	
TTA:PS	294	4.2	−1.82	0.029	11
	211	10	2.63	0.044	
	209	20	2.59	0.045	
	293	30	0.57	0.047	
	213		2.49	0.046	
	206	50	3.45	0.054	
	296	30	0.75	0.049	38
	245		1.67	0.047	
	205		3.39	0.051	
TAPC:PC	297	65	1.72	0.060	27
	336	60	−0.37	0.042	39
	297		0.78	0.049	
	233		4.00	0.065	
TTA:PC	294	6	3.43	0.071	40
		10	3.05	0.070	
		15	2.46	0.066	
		20	2.01	0.062	
		30	1.64	0.059	
		40	1.64	0.060	
		50	1.46	0.059	
polar additives					
30% TTA:	236	+0%TAP	1.73	0.046	28
PS	230	+2%TAP	5.75	0.081	
	231	+4%TAP	7.47	0.098	
75%	295	+0	1.13	0.053	29
TAPC:PC		+2%p-DNB	−0.19	0.038	
		+2%m-DNB	−0.74	0.033	
		+2%o-DNB	0.86	0.050	

^aThere are more materials listed in this table than are discussed in the text.

The experimentally observed temperature at which this occurs is designated by T_0 . As pointed out above, according to ref 8, σ_s should equal σ_{dt} . This predicts a theoretical value for T_0 which we will call T_0^*

$$T_0^* = 0.63 \frac{\sigma_{dt}}{k} \quad (10)$$

where σ_{dt} can be obtained from eq 6.

3. ELECTRIC FIELD DEPENDENCE OF THE MOBILITY

We are going to test whether the CDM, as represented by eq 2, can describe the electric field dependence of the mobility in

Table 2. Comparison of T_0 (Experimentally Observed) and T_0^* (Calculated Using Equation 10) in Some MDPs^a

MDP	$p(D)$ of dopant	T_0 (K)	T_0^* (K)	ref
10%DEH:PC	3.16	375	421	30,31
20%DEH:PC		375	486	31
30%DEH:PC		400	543	
40%DEH:PC		453	595	
50%DEH:PC		475	642	
70%DEH:PC		475	728	
90%DEH:PC		510	805	
10%DEASP:PC	4.34	360	436	32
20%DEASP:PC		450	511	
50%DEASP:PC		540	691	
90%DEASP:PC		570	873	
20%TTB:PS	1.56	300	285	33
20%TPD:PS	1.52	300	285	
10%TTA:PS	0.9	293	340	
17%TASB:PS	0.54	296	249	24
20%ENA-D:PS	0.38	296	248	25
11%TAPC:PS	1.4	215	272	11
22%TAPC:PS		245	273	
33%TAPC:PS		295	375	
60%TAPC:PC		323	310	39

^a Some of the values of T_0 were obtained by extrapolation (see original references). For these calculations we have taken $\hat{\sigma}$ (for pure materials, polymer binders and dopants) to be 0.047 eV for PC, 0.037 eV for PS, 0.115 eV for DEH, 0.125 eV for DEASP, 0.014 eV for TASB, 0.046 eV for TTB, 0.046 eV for TPD, 0.016 eV for ENA-D, 0.041 eV for TTA, 0.039 eV for TAPC, 0.048 for TPM-A, 0.053 for TPM-B, 0.055 for TPM-C, 0.063 for TPM-D, 0.069 for TPM-E, and 0.101 for TPM-F.

organic materials including glasses, MDPs, and inert polar additives in MDPs. It is predicted⁸ that σ_S should equal σ_{dt} which is the dipolar disorder energy as given by eq 6. To test this, we have processed plots (solved eq 7 from the measured slope) of the field dependence of the mobility (PF plots) that appeared in almost every MDP characterization paper from 1993 on. To assist theorists who may be interested in testing their theories of charge transport, all of the data in this section is tabulated in Table 1.

3a. Glasses. As the assumptions of the CDM of ref 6 and 8 most closely resemble those that characterize a pure dipolar glass, we start our consideration with molecular glasses (100% dopant).^{14–18} The published PF plots are all of high quality with some irregularities at small fields reported in refs 14 and 15.

The extracted σ_S , using eq 7, shows systematic variations with temperature, inconsistent with eq 4 or 6. For example, in DEH glass¹⁷ it is 0.125 eV ($\pm 3\%$ are usual error bars for these measurements) at 298 K and 0.117 eV at 222 K while in TMP-D glass these figures are 0.087 eV at 287 K, 0.096 eV at 247 K, and 0.109 eV at 187 K. Below, we report data only at room temperature unless otherwise mentioned.

The extracted σ_S using eq 7 from glasses at room temperature also does not equal σ_{dt} (which equals $\hat{\sigma}_{dd}$ for a glass) and sometimes exceeds it, inconsistent with the predictions of the CDM. For example in DEH glass ($p = 3.16$ D), $\hat{\sigma}_{dd}$ and σ_S are

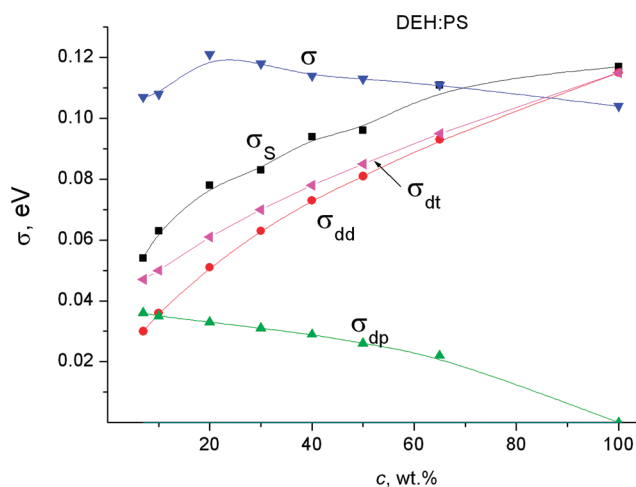


Figure 1. An analysis of DEH–PS as a function of weight percentage. σ_S is disorder determined from experimental data of the electric field dependence of the mobility. σ is disorder determined from experimental data of the temperature dependence of the mobility. σ_{dp} is the theoretical dipolar disorder due to the polymer. σ_{dd} is the theoretical dipolar disorder due to the polar dopants. σ_{dt} is the total dipolar disorder due to both the polymer and the polar dopants. Data taken from refs 17 and 19.

0.115 eV, 0.125 eV ($\pm 3\%$), respectively, and in TTB ($p = 1.56$ D)³⁷ the numbers are 0.046 eV, 0.060 eV. σ_S exceeds $\hat{\sigma}_{dd}$ in both materials. In DEASP¹⁸ ($p = 4.34$ D) the values are 0.125 eV, 0.117 eV. In this case, σ_S is less than $\hat{\sigma}_{dd}$. In these calculations, it has been assumed that ε is equal to 3.0 (DEH), 3.1 (DEASP), and 2.8 (TTB).

3b. Molecularly Doped Polymers. DEH ($p = 3.16$ D) and DEASP ($p = 4.34$ D) doped PS ($p = 0.4$ D) or PC ($p = 1.0$ D) are systems with a highly polar dopant and relatively nonpolar polymer binder. According to the CDM, this may be regarded as a dispersion of dipoles serving as hopping centers in an inert medium with intersite distance being varied in a controlled manner. There are two main papers presenting PF plots on the subject.^{19,31} Of special significance are results reported in ref 19 because special precautions concerning sample purity were taken. The range of concentrations used is extraordinary large and detailed (7 to 65 wt % with 17 data points). This data was analyzed in ref 8 but the authors of the cited paper restricted themselves to studying only 4 systems and σ_S was compared to σ , not σ_{dt} . We provide a complete analysis, including the data σ_S (obtained from applying eq 7 to published PF plots), σ_{dd} , σ_{dp} , σ_{dt} (calculated from eqs 4 and 6) and σ (usually given in the papers and readily convertible to σ_T since $\sigma_T \approx 1.11\sigma$), as shown in the figures.

Figure 1 presents the concentration dependence of all quantities for DEH–PS. The general trends are quite clear. As c rises, both σ_{dt} and σ_S increase with a tendency to approach each other, and to coincide at 100%. At 7%, σ_S is 0.054 eV with $\sigma_{dt} = 0.047$ eV. Thus σ_S only slightly exceeds σ_{dt} and this difference decreases as c increases (until 100%). Even better agreement between σ_S and σ_{dt} has been found in DEASP–PC (c varied in 10–90% range) as can be seen in Figure 2.²⁰ For DEASP, at $c = 10\%$ σ_S is 0.063 eV with $\sigma_{dt} = 0.062$ eV. The agreement of the data and theory for these two materials is within the error bars of the known value of ε . It is assumed that that $\varepsilon = 3.0$ for DEH and $\varepsilon = 3.1$ for DEASP and $\varepsilon = 3.0$ for PC. An increase of ε (DEASP)

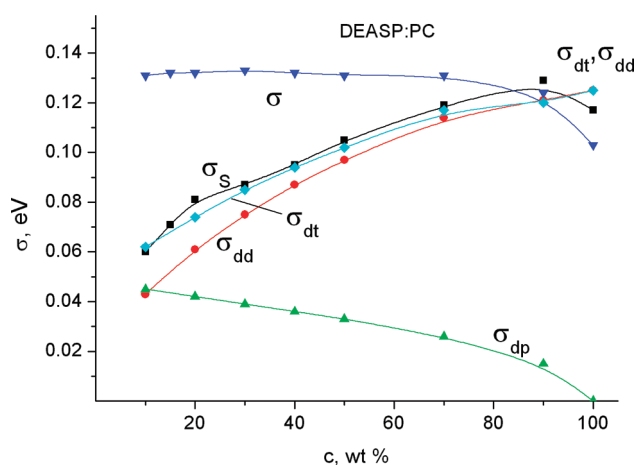


Figure 2. An analysis of DEASP–PC as a function of weight percentage. σ_S is disorder determined from experimental data of the electric field dependence of the mobility. σ is disorder determined from experimental data of the temperature dependence of the mobility. σ_{dp} is the theoretical dipolar disorder due to the polymer. σ_{dd} is the theoretical dipolar disorder due to the polar dopants. σ_{dt} is the total dipolar disorder due to both the polymer and the polar dopants. Data taken from refs 18 and 20.

by 0.1 would shift the DEASP theory curve into disagreement with experiment over most of the data, similar to the disagreement of theory and experiment of DEH:PC data of Figure 1. However at high c , ε is bound to increase because we suspect $\varepsilon(\text{DEASP})$ is greater than 3.1 and this agreement will be compromised. Unfortunately $\varepsilon(c)$ data for DEASP are not available.

It has been shown that in 50% DEH:PC^{21,22} at room temperature that the PF field dependence exists over the widest electric field range yet measured, from 0.82 to 206 V/ μm (covering more than 2 decades) with a correlation coefficient of 0.999. The reported value of the PF slope is $4.77 \times 10^{-3} (\text{cm/V})^{1/2}$, giving $\sigma_S = 0.102 \text{ eV}$. Computations show that $\sigma_{dd} = 0.074 \text{ eV}$ and $\sigma_{dp} = 0.028 \text{ eV}$, which quadratically add up to $\sigma_{dt} = 0.090 \text{ eV}$, which is appreciably smaller than σ_S .

A material that has the highest dipole moment yet studied is DTNA:PS²³ ($p = 5.78 \text{ D}$) in a wide range of concentration from 20 to 60%. (The fraction used in the temperature dependence of the theory was $-1/4$ instead of the usual $-4/9$; we have converted the sigmas in the paper to the $-4/9$ factor so that they can be compared to other materials.) σ was found to be almost constant, irrespective of c ($0.113 \pm 0.003 \text{ eV}$; originally 0.15V). Unfortunately, PF plots exist for only one concentration (40%) but at several temperatures. Again, σ_S drops as T increases (inconsistent with eq 4 and 6) ($\sigma_S = 0.076, 0.072$, and 0.070 eV at $T = 265, 290$, and 327 K , respectively). At room temperature, σ_S is 0.072 eV . The estimated σ_{dd} for 40% DTNA:PS is 0.135 eV , which is almost equal to σ_{dt} (0.137 eV) because of the large dipole moment. This discrepancy presents a clear challenge to the CDM as represented by eq 2.

Even more striking results that are inconsistent with the CDM have been obtained for the low dipole moment material ($p = 0.54 \text{ D}$) TASB–PS (Figure 3) for a wide c range (10 to 50%) in ref 24. At the highest concentration measured (50%) σ_S (0.084 eV) far exceeds $\sigma_{dt} = 0.025 \text{ eV}$ ($\sigma_{dd} = 0.009 \text{ eV}$ and $\sigma_{dp} = 0.023 \text{ eV}$). At about 17%, the PF slope changes sign (see Section 4). At 15%, σ_S is 0.032 eV , which is about 10 times σ_{dd} . As σ_{dp} is close to

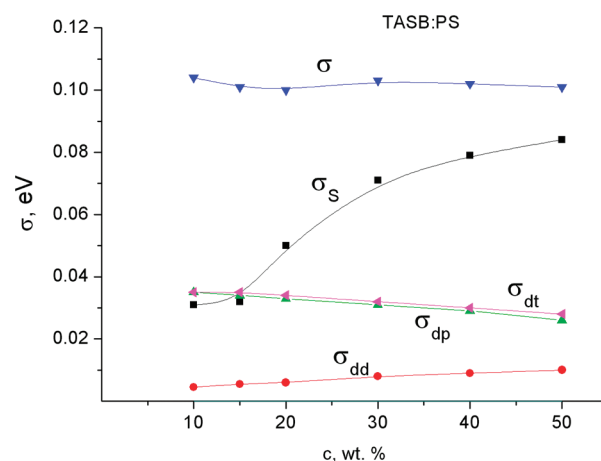


Figure 3. An analysis of TASB–PS as a function of weight percentage. σ_S is disorder determined from experimental data of the electric field dependence of the mobility. σ is disorder determined from experimental data of the temperature dependence of the mobility. σ_{dp} is the theoretical dipolar disorder due to the polymer. σ_{dd} is the theoretical dipolar disorder due to the polar dopants. σ_{dt} is the total dipolar disorder due to both the polymer and the polar dopants. Data taken from ref 24.

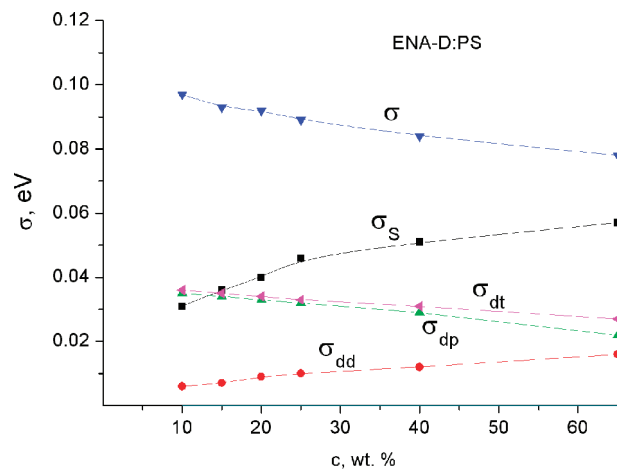


Figure 4. An analysis of ENA-D–PS as a function of weight percentage. σ_S is disorder determined from experimental data of the electric field dependence of the mobility. σ is disorder determined from experimental data of the temperature dependence of the mobility. σ_{dp} is the theoretical dipolar disorder due to the polymer. σ_{dd} is the theoretical dipolar disorder due to the polar dopants. σ_{dt} is the total dipolar disorder due to both the polymer and the polar dopants. Data taken from ref 25.

0.033 eV , we find that in this case σ_S almost coincides with $\sigma_{dt} = 0.033 \text{ eV}$. As can be seen in Figure 3, σ_S increases with c , while σ_{dt} decreases with c . (σ_{dt} decreases with c because the dipole moment of the polymer exceeds the dipole moment of the dopant, see eq 6.)

The same type of behavior can be observed in ENA-D (Figure 4)²⁵ another low dipole moment material ($p = 0.38 \text{ D}$). As can be seen in Figure 4, σ_S increases with c , while σ_{dt} decreases with c .

The same type of data is encountered in 45% TPM:PS,²⁶ as could be seen on Figure 5, which plots TPM type on the x -axis (TPM-A, B,...F). The dipole moments are 1.33, 1.51, 1.7, 1.81, 2.1, 3.2 D for TPM-A through F, respectively. The large discrepancy between σ_S and σ_{dt} occurs for all TPMs. At the

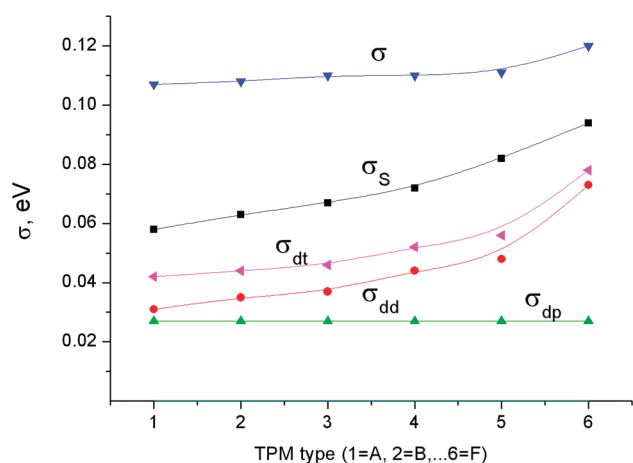


Figure 5. An analysis of TPM:PS as a function of TPM-type from TPM-A through TPM-F. σ_s is disorder determined from experimental data of the electric field dependence of the mobility. σ is disorder determined from experimental data of the temperature dependence of the mobility. σ_{dp} is the theoretical dipolar disorder due to the polymer. σ_{dd} is the theoretical dipolar disorder due to the polar dopants. σ_{dt} is the total dipolar disorder due to both the polymer and the polar dopants. Data taken from ref 26.

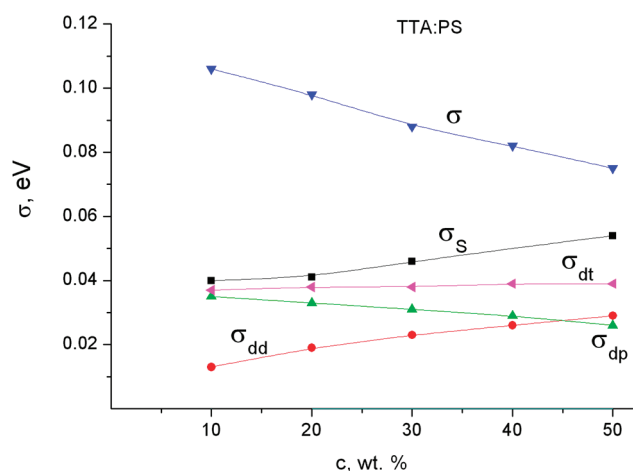


Figure 6. An analysis of TTA:PS as a function of weight percentage. σ_s is disorder determined from experimental data of the electric field dependence of the mobility. σ is disorder determined from experimental data of the temperature dependence of the mobility. σ_{dp} is the theoretical dipolar disorder due to the polymer. σ_{dd} is the theoretical dipolar disorder due to the polar dopants. σ_{dt} is the total dipolar disorder due to both the polymer and the polar dopants. Data taken from refs 11 and 38.

highest dipole moment, TPM-F-PS ($p = 3.20$ D) we have $\sigma_s = 0.094$ eV, $\sigma_{dd} = 0.073$ eV and $\sigma_{dt} = 0.078$ eV.

A similar situation appears in TTA:PS.¹¹ At 30% TTA (see Figure 6), we find that $\sigma_s = 0.047$ eV, which is larger than $\sigma_{dt} = 0.038$ (and $\sigma = 0.088$ eV, $\sigma_{dd} = 0.023$ eV, $\sigma_{dp} = 0.031$ eV). In this MDP, σ_{dt} is approximately independent of c while σ_s increases with c .

In 65% TAPC:PC,²⁷ σ_s cannot be accounted for by the dipolar disorder. The numbers are as follow ($T = 297$ K): $\sigma_s = 0.060$ eV and $\sigma_{dt} = 0.040$ eV (and $\sigma = 0.11$ eV, $\sigma_{dd} = 0.029$ eV, $\sigma_{dp} = 0.028$ eV).

We see that there are numerous occasions when σ_s almost coincides with the theoretical total dipolar disorder σ_{dt} as the CDM would predict. This happens for DEH:PS and

DEASP:PC at all concentrations (Figures 1 and 2) and for TASB:PS, ENA-D:PS, and TTA:PS at small concentrations (Figures 3, 4, and 6). Also this near coincidence occurs in 45% TPM-F:PS (Figure 5), which has the highest dipole moment of the TPMs. These observations are evidence in favor of the CDM. However, as the concentration of TASB:PS, ENA-D:PS, or TTA-PS rises (Figures 3, 4, and 6) the difference between σ_s and σ_{dt} increases. Also, the values of σ_{dt} are appreciably smaller than σ_s for 40% DTNA:PS, 50% DEH:PC, and 45% TPM-F:PS. These are experimental evidence contrary to the predictions of the CDM.

3c. Inert Polar Additives. A special system to test the CDM is provided by studies of the effects of small amounts of inert polar additives on the mobility of a MDP. As these additives should increase the dipolar disorder, they should affect σ_s , if the CDM is a valid description of the data. In ref 2, data from ref 28 was analyzed, which used the polar additive TAP ($p = 6.6$ D) in 30% TTA-PS. The PF plots were published²⁸ for 0, 2, and 4% TAP. For this range of additive concentration, σ_s increased from 0.046 to 0.081 to 0.098 eV. This effect must be attributed in the CDM to the additional dipolar disorder due to TAP molecules. At 4%, the calculated contributed σ_{da} (the dipolar disorder due to additives) amounts to only 0.065 eV and σ_{dt} is predicted to be 0.075 eV, falling short of what is required to account properly for the observed rise. The missing dipolar contribution is not small (0.066 eV). The same discrepancy reveals itself in the temperature dependence (σ). At room temperature, σ (0.088 eV) increases to 0.118 eV when for 4% TAP is added to the MDP. Within the context of the CDM this change should be ascribed to σ_{da} only since other sources of disorder do not appear to be changed. The estimation shows that there is a deficit of 0.079 eV. Note that two missing disorder energies are close despite the fact that they enter two different effects, σ_s and σ . It is remarkable that zero-field mobility at room temperature drops 450 times with a 4% TAP addition, an effect strongly reminiscent of trapping, which is not included in the CDMs.

Similar studies have been reported for 75% TAPC:PC in the presence of 2% p-, m-, and o-DNB additives with dipole moments of 0.5, 4.0, and 6.0 D respectively.²⁹ The original σ was 0.095 eV but after DNB addition it rose to 0.117 ± 0.002 eV irrespective of the isomer type used (measurements were done at the electric field of 4×10^4 V/cm). σ_{da} is calculated to increase from 0 to 0.017 to 0.026 eV for p-, m-, and o-DNB respectively. Even for o-DNB, the missing total disorder energy constitutes 0.063 eV. Very unusual results emerged for the behavior of σ_s . In the presence of additives, it fell from 0.053 eV in original MDP to 0.050 eV in case of o-DNB and even more for p- or m-isomers (approximately to 0.035 eV). This last effect is opposite to the predictions of the CDM! Again, 2% of o-DNB decreases the magnitude of the mobility by almost 50 times, which suggests a trapping mechanism may be responsible for the observed anomaly.

4. TEMPERATURE AT WHICH THE ELECTRIC FIELD DEPENDENCE VANISHES

As pointed out in Section 2, the CDM predicts that the electric field dependence of the mobility should go to zero at a specific temperature related to the dipolar disorder. A comparison of the experimentally observed T_0 and the theoretical values T_0^* of this temperature is a second test of the CDM. The theoretically predicted value is given in eq 10. The first direct observation of a

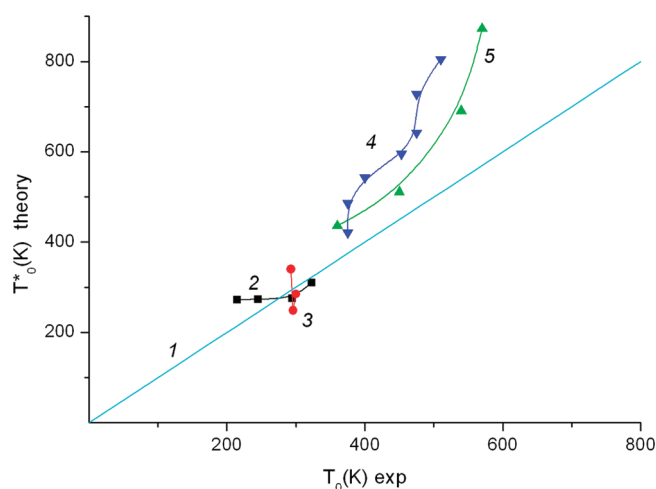


Figure 7. T_0 , the experimentally observed temperature at which the electric field dependence of the mobility goes to zero, vs the theoretical predictions, eq 10, for DEH:PC (curve 4) DEASP:PC (curve 5), TAPC (PS and PC) (curve 2), and various MDP's at $c = 20\%$ (curve 3). Exact agreement is shown in curve 1. Numerical values of the data are shown in Table 2.

mobility that was electric field independent was reported in ref 30 for 10% DEASP:PC. It occurred at a temperature of approximately 360 K. Equation 10 predicts 436 K.

T_0 has been determined as a function of concentration in DEH:PC,³¹ DEASP:PC,³² and TAPC:PS.¹¹ The experiment and theory are compared for these materials in Table 2 and in Figure 7. Only a few values of T_0 are in quantitative agreement with theory (within 25 K): 20% TTB:PS, 20% TPD:PS, 33% TAPC:PS, and 60% TAPC:PC. Also, the trend with concentration change (see Figure 7) does not seem to be captured by the theory. On the other hand, it is encouraging that the theory does predict the existence of T_0 , which is at least within the right order of magnitude.

T_0 has also been determined at one concentration in several polymers near 20% concentration. (Note that if T is fixed and the concentration of dopant is varied, then when the concentration reaches the value given by eq 10 an electric field dependence of the mobility will vanish at a specific value of the concentration.) These are listed in the middle of Table 2 and as the red dots and lines on Figure 7. T_0 appears to be independent of the MDP, but the theory predicts a variation from about 250 to 340 K.

A correlation between theory and experimental results (of all of the Table 2 entries) gives a correlation coefficient of about 0.81, which is generally considered to be a poor correlation.

5. DISCUSSION

We have analyzed many materials from three organic systems, all of which experimentally have the characteristic that the log of the mobility is linear in the square root of the electric field. The systems are glasses, molecularly doped polymers, and inert polar dopants in molecularly doped polymers. The goals of our analysis are (1) to test a prediction⁸ of the CDM model of ref 6 that the dipolar disorder energy can be obtained directly from the slopes of these curves and (2) to test whether the temperature at which the electric field dependence of the mobility vanishes is related to the dipolar disorder. The first attempt to do such an analysis was undertaken in ref 8 on the basis of four materials. It was shown that σ_S increases as c of the polar dopant or a polar additive

increases for three of the four materials analyzed. Comparisons are drawn between σ_S and σ rather than σ_{dt} . So it was not determined whether σ_S equals σ_{dt} as predicted.

In our analysis, (1) we included all possible sources of dipolar disorder (dopant, polymer matrix, inert polar dopants, taking into account their concentrations) and directly compared this to the experimentally determined σ_S and (2) the list of materials tested has been greatly enlarged.

To do this analysis, we have made certain assumptions. First, the simulations of the CDM and the resulting empirical equation, eq 2, were only done at one intermolecular separation of 10 Å. We have assumed that this equation is valid over the concentration range of the various experiments used in this analysis. Second, we have assumed that the dipolar disorder of a polymer chain can be obtained from eq 2 using the dipole moment and molecular weight of the repeat unit. Third, we have used an assumption, common in the literature that the square of the total dipolar disorder can be obtained from the sum of the squares of the two contributing dipolar disorders of the dopant and the polymer (eq 6).

In the course of this analysis, we found that σ_S increases as c of the dopant increases and this happens universally, independent of the dipole moment of the dopant or the polymer matrix. Almost always σ_S is larger than σ_{dt} . For some polar dopants (DEH:PS and DEASP:PC), this difference was small and within the error bars of the known value of ϵ . For others (40% DTNA:PS, 50% DEH-PC, 45% TPM-A-F:PS), this difference is quite large. For nonpolar dopants, this difference was largest at high concentrations and tended to vanish at low concentrations. The correlations suggest that for high dipole moment materials, the dipole disorder may be important but for low dipole moment materials, the correlation is negative. This result is reminiscent of the correlation of dipole moment and activation energy shown in Figure 1 of ref 41. Here the correlation is poor except for the highest dipole moment materials.

In some cases, the PF slope was available as a function of temperature. It appears that σ_S has temperature dependence, inconsistent with the predictions of the CDM (eqs 4 and 6).

While the empirical equation (eq 2) of the CDM gives an exact straight line in PF coordinates (log mobility vs square root of electric field), it is not clear that computer simulations will give this linearity over the range of electric fields that have been used experimentally. Recall that there is one measurement,^{21,22} in which electric field was varied from 0.82 to 206 V/micrometer and gave a straight line PF dependence with a correlation coefficient of 0.999. Furthermore any valid theory needs to account for this linearity with reasonable parameters and at the same time predict σ (or σ_T) independent of dopant concentration.³⁴ It is recognized in ref 8 that predicting that σ (or σ_T) is independent of dopant concentration will be problematic for the CDM and it is suggested that either the experimental data had systematic errors or some compensation effect was in play. In addition, it is not clear that the CDM can account for universality (the current vs time curve is independent of electric field), which has now been reported in two independent experiments with MDPs, Figure 5 in ref 35 and Figure 3 in ref 36.

Finally, we have tested the ability of the CDM to account for T_0 , the temperature at which the electric field dependence of the mobility vanishes. It appears to be in agreement (within 25 K) with only a limited set of the measurements and we have found a correlation coefficient of 0.81 between experimental and predicted values of T_0 .

CONCLUSIONS

Unlike the GDM, the CDM explains the linearity of the log mobility versus the square root of the electric field, not in a prescribed fashion, but based on sound physical principles. A recent prediction of the CDM model, that the dipolar disorder energy can be obtained from the slope of the log of the mobility vs square root of the electric field,⁸ has been tested with experimental measurements on many organic materials drawn from three classes: glasses, molecularly doped polymers, and inert polar dopants in molecularly doped polymers. We find that σ_S almost coincides with the predicted dipolar disorder energy for some high dipole moment materials (DEH:PS and DEASP:PC), while it is in disagreement with others (40% DTNA:PS, 50% DEH:PC, 45% TPM-A-F:PS). For low dipole moment materials, the difference between σ_S and the predicted dipolar disorder energy increases as the concentration increase. We also find experimentally that σ_S appears to have some temperature dependence, inconsistent with the predictions of the CDM of ref 6. The predictions of the CDM are not consistent with observed σ_S when inert polar additives are added to MDPs, but this may be because trapping effects are not included in the CDM.

It is quite encouraging that the CDM accounts quite naturally for the existence of T_0 , a temperature at which the electric field dependence of the mobility vanishes, attributing it to the dipolar disorder. The CDM appears to be in agreement (within 25 K) with only a limited set of the measurements, and we have found a correlation coefficient of 0.81 between experimental and predicted values of T_0 .

In view of the above contradictory picture of the successes and shortcomings of the CDM of ref 6 in its ability to describe experimental data through its empirical equation (eq 2) and to interpret correctly the extracted parameters values, we suggest the CDM still needs further development to be consistent with charge transport in organic materials. In particular, (1) the experimental observation that the disorder parameter (or the activation energy) is independent of dopant concentration in 26 MDPs, as discussed in ref 34, needs to be accounted for here; (2) the linearity of the PF slope with a correlation coefficient of 0.999 needs to be accounted for with reasonable parameters; (3) while the agreement of theory and experiment with high dipole moment materials is encouraging, there appears to be a missing contribution for low dipole moment materials; (4) while order of magnitude agreement with experimentally observed T_0 's is encouraging, obtaining detailed quantitative agreement will need further thought on the fundamental reason for the theoretical prediction of T_0 .

AUTHOR INFORMATION

Corresponding Author

*E-mail: schein@prodigy.net. Phone: 408-997-7946.

ACKNOWLEDGMENT

The authors would like to acknowledge comments on the manuscript made by Paul Parris and David Weiss.

APPENDIX – DEFINITION OF INITIALS USED IN THIS PAPER

DEASP – 1-phenyl-3((diethylamino)styryl)-5-(p-(diethylamino)-phenyl)pyrazoline

DEH – p-diethylaminobenzaldehyde diphenylhydrazone

DNTA – di-p-tolyl-p-nitrophenylamine

DNB – dinitrobenzene

DPQ – 3,3'-dimethyl-5-5'-di-t-butyl-diphenylquinone

ENA-D – N-(2,2-diphenylvinyl)-diphenylamine

PC – bisphenol A polycarbonate

PS – polystyrene

TAP – t-amylphthalonitrile

TAPC – 1,1-bis(di-4-tolylaminophenyl)cyclohexane

TASB – bis(ditolylaminostyryl)benzene

TPM-A – bis(4-N,N-diethylamino-2-methylphenyl)-4-methyl-phenylmethane

TMP-B – bis(4-N,N-diethylamino-2-methylphenyl)(4-propyl-phenyl) methane

TMP-C – bis(4-N,N-diethylamino-2-methylphenyl)(4-phenyl-phenyl) methane

TMP-D – bis(4-N,N-diethylamino-2-methylphenyl)(4-phenyl) methane

TMP-E – bis(4-N,N-diethylamino-2-methylphenyl)(4-methoxy-phenyl) methane

TMP-F – bis(4-N,N-diethylamino-2-methylphenyl)(4-chlorophenyl) methane

TPD – N,N'-diphenyl-N,N-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine

TTA – tri-p-tolylamine

TTB – N,N',N'',N'''-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine

REFERENCES

- (1) Borsenberger, P. M.; Weiss, D. S. *Organic Photoreceptors for Xerography*; Marcel Dekker: New York, 1998.
- (2) Gartstein, Yu N.; Conwell, E. M. *Chem. Phys. Lett.* **1995**, 245, 351.
- (3) Dunlap, D. H.; Parris, P. E.; Kenkre, V. M. *Phys. Rev. Lett.* **1996**, 77, 542.
- (4) Dunlap, H.; Kenkre, V. M.; Parris, P. E. *J. Imaging Sci. Technol.* **1999**, 43, 437.
- (5) Parris, P. E.; Dunlap, D. H.; Kenkre, V. M. *Phys. Status Solidi B* **2000**, 218, 47.
- (6) Novikov, S. V.; Dunlap, D. H.; Kenkre, V. M.; Parris, P. E.; Vannikov, A. V. *Phys. Rev. Lett.* **1998**, 81, 4472.
- (7) Parris, P. E.; Kenkre, V. M.; Dunlap, D. H. *Phys. Rev. Lett.* **2001**, 87, 126601.
- (8) Novikov, S. V.; Vannikov, A. V. *J. Phys. Chem. C* **2009**, 113, 2532.
- (9) Bässler, H. *Phys. Status Solidi B* **1981**, 107, 9.
- (10) Bässler, H. *Phys. Status Solidi B* **1993**, 175, 15.
- (11) Young, R. H. *J. Chem. Phys.* **1995**, 103, 6749.
- (12) Young, R. H. *Philos. Mag. B* **1995**, 72, 435.
- (13) Malliaras, G. G.; Shen, Y.; Dunlap, D. H.; Murata, H.; Kafafi, S. H. *Appl. Phys. Lett.* **2001**, 79, 2582.
- (14) Heun, S.; Borsenberger, P. M. *Chem. Phys.* **1995**, 200, 245.
- (15) Borsenberger, P. M.; Pautmeier, L.; Richert, R.; Bässler, H. *J. Chem. Phys.* **1991**, 94, 8276.
- (16) Borsenberger, P. M.; Gruenbaum, W. T.; Magin, E. H. *Jpn. J. Appl. Phys.* **1996**, 35, 2698.
- (17) Borsenberger, P. *Adv. Mater. Opt. Electron.* **1992**, 1, 73.
- (18) Bässler, H.; Borsenberger, P. *Chem. Phys.* **1993**, 177, 763.
- (19) Borsenberger, P. M.; Magin, E. H.; Sinicropi, J. A.; Lin, L.-B. *Jpn. J. Appl. Phys.* **1998**, 37, 166.
- (20) Borsenberger, P. M.; Schein, L. J. *Phys. Chem.* **1994**, 98, 233.
- (21) Schein, L. B.; Peled, A.; Glatz, D. J. *Appl. Phys.* **1989**, 66, 686.
- (22) Schein, L. B. *Mol. Cryst. Liq. Cryst.* **1990**, 183, 41.
- (23) Borsenberger, P. M.; Gruenbaum, W. T.; Kaeding, J. E.; Magin, E. H. *Phys. Status Solidi B* **1995**, 191, 171.

- (24) Borsenberger, P. M.; Gruenbaum, W. T.; Magin, E. H. *Physica B* **1996**, 228, 233.
- (25) Visser, S. A.; Sinicropi, J. A.; Magin, E. H.; Borsenberger, P. M. *Proc. SPIE* **1997**, 3144, 110.
- (26) Borsenberger, P. M.; Weiss, D. S. *J. Imaging Sci. Technol.* **1997**, 41, 185.
- (27) Borsenberger, P. M. *J. Appl. Phys.* **1992**, 72, 5283.
- (28) Young, R.; Fitzgerald, J. J. *J. Chem. Phys.* **1995**, 102, 6290.
- (29) Borsenberger, P. M.; Bässler, H. *Phys. Status Solidi B* **1992**, 170, 291.
- (30) Peled A.; Schein, L. B. *Chem. Phys. Lett.* **1988**, 153, 422.
- (31) Mack, J. X.; Schein, L. B.; Peled, A. *Phys. Rev. B* **1989**, 39, 7500.
- (32) Peled, A.; Schein, L. B.; Glatz, D. *Phys. Rev. B* **1990**, 31, 10835.
- (33) Heun, S.; Borsenberger, P. M. *Physica B* **1995**, 216, 43.
- (34) Schein, L. B.; Tyutnev, A. J. *J. Phys. Chem. C* **2008**, 112, 7295.
- (35) Schein, L. B.; Saenko, V.; Pozhidaev, E. D.; Tyutnev, A.; Weiss, D. S. *J. Phys. Chem. C* **2009**, 113, 1067.
- (36) Dunlap, D. H.; Schein, L. B.; Tyutnev, A.; Saenko, V.; Pozhidaev, E. D.; Parris, P. E.; Weiss, D. S. *J. Phys. Chem. C* **2010**, 114, 9076.
- (37) Borsenberger, P. M.; Fitzgerald, J. J. *J. Phys. Chem.* **1993**, 97, 4815.
- (38) Borsenberger, P. M.; Gruenbaum, W. T.; Magin, E. H.; Sorriero, L. J. *Chem. Phys.* **1995**, 195, 435.
- (39) Borsenberger, P. M. *J. Appl. Phys.* **1990**, 68, 5682.
- (40) Borsenberger, P. M. *J. Appl. Phys.* **1990**, 68, 6263.
- (41) Schein, L. B.; Weiss, D. S.; Tyutnev, A. *Chem. Phys.* **2009**, 365, 101.