The Source of the Charge Transport Activation Energy in Molecularly Doped Polymers

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Abstract

Energetic disorder plays a central role in many of the theories of charge transport in molecularly doped polymers, MDP. This assumption can be tested experimentally. A review of experimentally characterized MDP systems reveals that there is almost no experimental evidence to support the prediction that the experimentally observed activation energy is due to energetic disorder. Instead, the data appear to suggest that the activation energy is primarily intramolecular in origin.

Introduction

Energetic disorder plays a central role in many of the theories of charge transport in molecularly doped polymers, MDP. In these theories energetic disorder determines the energy width of the hopping site manifold. It is generally assumed that the disorder created energy width σ arises from interactions between the charge on a dopant molecule and its environment, including the dipole moments of neighboring dopant molecules, σ_d, the dipole moments of the molecules of the polymer matrix σ_p, and van der Waals interactions due to the polarization of the medium, σ_{vdw}. Bassler's formulation of the Gaussian Disorder Model (GDM) predicts that σ can be obtained from the temperature dependence of the mobility: it appears as a temperature dependent activation energy [1, 2].

The full expression for the mobility μ [1, 2], obtained by simulation, is

$$\mu = \mu_0 \exp[-(2\sigma/3kT)^2]\exp\{CE^{1/2}[(\sigma/kT)^2 - \Sigma^2]\} \qquad (1)$$

with Σ^2 replaced with 2.5 when $\Sigma<1.5$ for E, the electric field, greater than approximately $4\text{x}10^5$ V/cm. k is the Boltzmann's constant, T is absolute temperature, Σ is a measure of positional disorder (as compared to the energetic disorder, symbolized by σ, which is the focus of this paper), and C is a constant. It is assumed that the various contributions to disorder add quadratically

$$\sigma^2 = \sigma_d^2 + \sigma_p^2 + \sigma_{vdw}^2. \qquad (2)$$

In this paper and in many of Borsenberger's papers, Young's expression [3] is used to characterize σ_d

$$\sigma_d = 7.04c^{0.5}p/(\delta^2\varepsilon) \qquad (3)$$

where σ_d is in eV, c is the fraction of sites occupied by randomly oriented dipoles with dipole moment p (in Debye), δ is the minimum intersite distance (in angstroms) between molecules in the material, and ε is the relative dielectric constant. As far as the authors know no theoretical analysis of σ_p, the charge-dipole interaction with the molecules of the polymer matrix, exists. We suggest using Eq. 3 with a simple change: replacing c with (1-c) to keep the identity of c as the concentration of dopant molecule.

$$\sigma_p = 7.04(1-c)^{0.5}p/(\delta^2\varepsilon) \qquad (4)$$

This allows a quantitative estimate of σ_p.

It is the purpose of this paper to test experimentally the assumption that energetic disorder determines the activation energy in charge transport in molecularly doped polymers. Our procedure is to examine the trends apparent in the data of all of the characterized MDP systems, instead of analyzing one MDP system at a time.

The experiments in which disorder has been systematically varied include experiments in which (1) the concentration of dopant is changed, (2) the polymer matrix is changed, (3) the dipole moment of the dopant molecule is changed at fixed concentration (4) the effect of low concentration of polar additives in MDP is studied, and (5) glasses made from typical dopant molecules are characterized.

Experiments

Probably the most unambiguous experimental tests of the dependence of σ on disorder are experiments in which the polymer matrix and the dopant molecule are held fixed and the only experimental variable changed is the distance between dopant molecules, ρ, by changing the dopant concentration. If ρ of the dopant molecules with a dipole moment is changed, then the charge-dipole interaction is surely changed without changing other potentially important transport parameters, such as the shape or size of the dopant molecule.

There are 26 published experiments [4] in which σ has been found to be independent of ρ. An example is shown in Fig. 1, DTNA:PC (di-p-tolyl-p-nitrophenylamine doped polycarbonate). These data are analyzed in the GDM as follows (and shown in the figure): the dipolar component of σ, σ_d, is calculated based on a Eq. 3 which decreases as ρ increases. The polymer matrix component is assumed zero, which is a reasonable approximation. The remainder is attributed to σ_{vdw} which therefore must increase as ρ increases. This analysis creates a dilemma for the reader. There are no theoretical discussions of σ_{vdw} in the MDP literature which would allow one to judge whether the experimentally determined values of σ_{vdw} and their dependence on ρ are reasonable. Indeed, in the authors' judgment, it is very difficult to understand how such a short range interaction as the polarization of the medium, which is supposed to be the source of σ_{vdw}, can vary over such a large range of ρ as derived from the experiments.

In addition, it is not reasonable (to the authors) that the calculated σ_{vdw} is almost zero at small ρ when the dopant molecules are with high probability in contact with each other. The authors would expect σ_{vdw} to be large due to interactions with the neighboring dopant molecules. And there is an assumed coincidence: the van der Waals component and the dopant dipolar component exactly add to give σ independent of ρ. And this coincidence must occur for all 26 experimentally characterized MDP systems in which σ is experimentally observed to be independent of ρ for GDM to account for the data [4].

A simpler explanation of the independence of σ on ρ is that σ (or the activation energy) is not determined by the external environment of the dopant molecule, i.e. the activation energy is intramolecular in origin.

There are 17 additional experimentally [4] characterized MDP systems in which it is observed that σ increases as ρ increases by about 30% (see Fig. 2 for an example). In the GDM it is argued that the rising σ with increasing ρ can be accounted for by assuming σ is due entirely to σ_{vdw}, i.e. the dopant dipolar contribution can be ignored, which is a reasonable approximation because the dipole moment of many of these dopants is small. For TTA it is 0.8 Debye. But it does not address the question of whether these properties of σ_{vdw} are reasonable. In particular it does not address whether it is reasonable for σ_{vdw} to increase as ρ increases given the short range of its interaction. One might argue that a rising σ_{vdw} with increasing ρ is due to the environment around the charged site changing due to "structural randomness" or the ratio of the dopant and polymer molecules changing [4]. But then is it reasonable that σ_{vdw} always increases as ρ increases? Wouldn't one expect that for some reasonable fraction of the MDP systems σ_{vdw} would decrease as ρ increases?

A simpler explanation is that in these 17 MDP systems the activation energy is primarily intramolecular in origin by which we mean that the intramolecular activation energy is reduced by at most 30% by an interaction energy that has properties similar to a transfer integral, i.e. it decreases as the ρ increases [4].

Other charge transport experiments in MDP systems that have been interpreted in terms of the GDM include experiments in which the polymer matrix is changed (see Fig. 2). However, the change does not appear to be related to the dipole moment of the polymer matrix: the change from PS-1 to PC is independent of the polymer concentration as can be seen in the data, inconsistent with Eq. 4, and is the same for two polymers with very different dipole moments (PS-3 and PC) also inconsistent with Eq. 4. Estimates based on Eq. 4 predict much smaller changes than are observed in Fig. 2 [4].

Polar additives have been added to MDP in an attempt to change the dipolar disorder. In the two case in which σ_{exp} is obtained by deconvoluting the data (in which the additives concentration was 2 and 20%) σ is observed to not change; instead the prefactor changed, inconsistent with GDM [4].

Detailed analysis of experiments in which the dopant molecule is changed at constant dopant concentration and experiments on glasses made from typical dopant molecules reveal that the data do not lend support to the GDM [4]. The problem with the interpretation of these experiments is that it is virtually impossible to plot σ vs. p and hold everything else constant, such as the shape and size of the molecule, and the van der Waals component of σ. In addition, the curves obtained depend on the arbitrary choice of molecules used by the particular author. The present authors suggest that this type of data analysis is not helpful in determining the role of energetic disorder in σ.

It is well-known that the GDM cannot explain the electric field dependence of the charge carrier mobility in MDP. Correlated Disorder Models (CDM) have been suggested which take into account long range correlations in the charge-dipole interactions. It is found that much better agreement between the CDM theories and the electric field E dependence of the mobility is achieved, i.e. the ubiquitous dependence of the mobility on the exponential of the square root of E can be accounted for. Unfortunately, these models also predict activation energies that depend entirely or primarily on disorder and therefore are also inconsistent with the experimental observations of the lack of an effect of changing disorder on the activation energy [4].

Conclusion

A review of experimentally characterized MDP systems reveals that there is almost no experimental evidence to support the prediction that the experimentally observed activation energy is due to energetic disorder. Instead, the data appear to suggest that the activation energy is primarily intramolecular in origin [4].

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Author Biography

Lawrence B. Schein *received his Ph.D. in solid state experimental physics from the University of Illinois in 1970. He worked at the Xerox Corporation from 1970 to 1983 and at the IBM Corporation from 1983 to 1994. He is now an independent consultant. He has helped implement development systems in IBM laser printers, has proposed theories of most of the known electrophotographic development systems, and has contributed to our understanding of toner charging, toner adhesion, and charge transport mechanisms in photoreceptors. He is the author of "Electrophotography and Development Physics," a Fellow of the American Physical Society, a Fellow of the Society of Imaging Science and Technology, recipient of the Carlson Memorial Award in 1993, a Senior Member of the IEEE, and a member of the Electrostatics Society of America.*

Andrey P. Tyutnev *received his Master's Degree in Radiation Chemistry from the Institute of Electrochemistry in 1977 and Ph.D. in Electrophysics and Physical Chemistry from the Institute of Chemical Physics in 1987 (both institutes of the Russian Academy of Sciences, Moscow). He worked at the Moscow Institute of Electromechanics from 1969 until now and at the Moscow Institute of Electronics and Mathematics (part time) from 1997. He spent his career working on radiation effects in polymer and ceramic insulators studying the radiation-induced conductivity and bulk charging in them. The last 10 years he studied charge carrier transport in molecularly doped polymers using a novel radiation-induced variety of the time of flight method. He is the co-author of 4 books on the subject (all in Russian).*

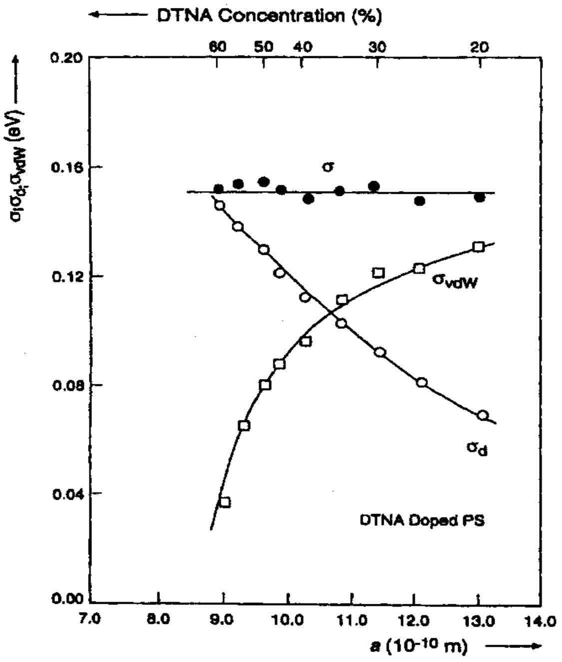

Figure 1. Data and analysis of σ vs. ρ (labeled a) in DTNA:PC (di-p-tolyl-p-nitrophenylamine doped polycarbonate). The data is the constant line labeled σ. The dipolar contribution σ_d is calculated from Eq. 3. The polymer component is assumed to be zero. The rest is assigned to σ_{vdw} using Eq. 2. (From P. M. Borsenberger, W.T.Gruenbaum, J.E. Kaeding, E.H. Magin, Hole Transport in Di-p-Tolyl-p-Nitrophenylamine Doped Poly(styrene), Phys. Status Solidi, 1995, Vol. 191, p. 171, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

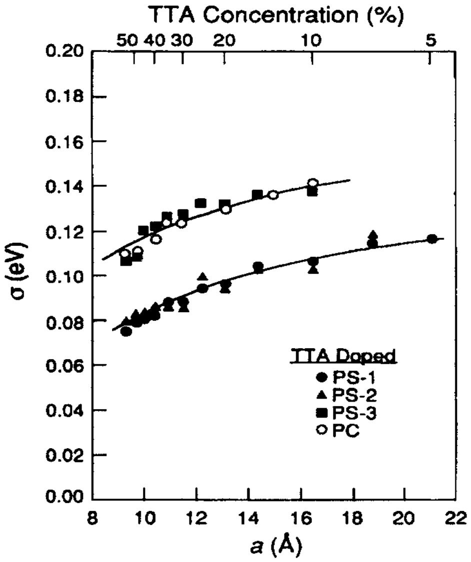

Figure 2. σ vs. concentration of TTA (tri-p-tolylamine) in various types of PC (polycarbonate) and PS (polystyrene) polymers. a is the same as ρ. The dipole moment of PS-1 (polystyrene) is 0.4, PS-2 (a variant of PS) is 0.4 Debye, PS-3 is 1.7 Debye, and PC is 1.0 Debye. (Reprinted from Chem. Phys., Vol 195, P.M. Borsenberger, W.T.Gruenbaum, E.H. Magin, Hole Transport in tri-p-Tolylamine Doped Polymers: the Role of the Polymer Dipole Moment, p. 435, 1995, with permission from Elsevier.)