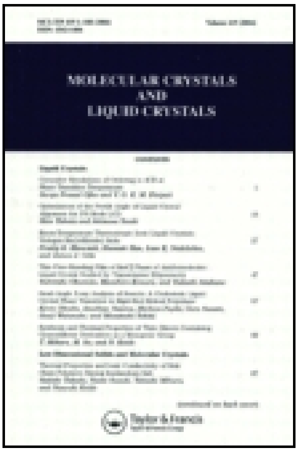

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Anomalous Charge Transport in Molecularly Doped Polymers

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Abstract It is shown that the relative widths of photoconductive current transients, obtained in molecularly doped polymers, are independent of the electric field and sample thickness, even when the current before the transit time is nearly time independent. Such a result has been termed universality in the Scher-Montroll theory of dispersive transport. The implications of these results for the field and temperature dependence of the mobility are considered.

In recent years, transient photoconductivity experiments in molecularly doped polymers have been focused largely on the determination of charge carrier mobilities, in an attempt to elucidate the hopping mechanism. Among the results obtained,[1] perhaps the most challenging to account for theoretically are the dependence of the activation energy on dopant concentration and the dependence of the mobilities μ on the electric field E. It is usually observed that (1) ln μ is approximately[2,3] linear in $\sqrt{E}$ and (2) there exists a temperature[4,5] above which μ becomes a decreasing function of E.

The above results are based on an analysis of the mobility obtained from the transit time, which is only one point on the current-time I(t) curve. It may be possible to obtain further insight into the hopping mechanism and its temperature and field dependence from an analysis of the complete I(t) curve. In fact, several studies[6-12] have addressed this subject. We report the result that the I(t) curve, normalized at the transit time, is independent of the electric field and sample thickness, *even when the current before the transit time is nearly time independent.* This is demonstrated by comparing normalized I(t) curves and quantified by showing that the relative width w of this curve is independent of E from 5 to 140 V/μm and sample thickness from 3.8 to 42 μm in a molecularly doped polymer. Here w is defined as $(t_{1/2} - t_0)/t_{1/2}$ where t_0 is the usual transit time, obtained from the intersection of

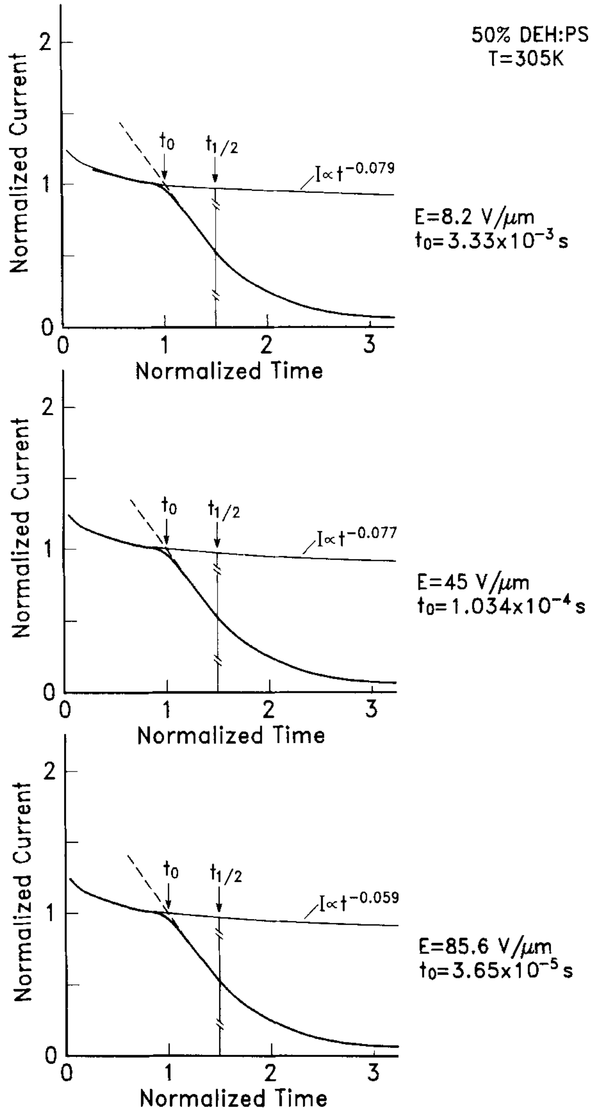

FIGURE 1 Current transients observed in DEH:PS.

tangents to the I(t) curve plotted on linear axes, and $t_{1/2}$ is the time at which the current has decreased to half the value extrapolated from times before t_0 (see Fig. 1).

The observation that normalized I(t) curves are independent of E has been termed "universality" and accounted for by the Scher-Montroll theory of "dispersive transport."[6,7] Universality has usually been associated with a current that decreases rapidly before the transit time[6-9] and demonstrated with log current-log time plots. In contrast, our observations are made on materials in which the current is almost independent of time, i.e., $I \propto t^{-(1-\alpha)}$, $\alpha \approx 0.9$ and linear axes are used because of the weak dependence of current on time. This implies that the average velocity of the carriers is also almost constant. Under the condition in which the current becomes time independent, it is predicted[7] that a transition to "Gaussian" transport should occur with $w \propto E^{-1/2}$ (see Eq. 1). We see no evidence for a transition to Gaussian transport.

Prior reports of this universality in molecularly doped polymers are limited.[6-10] This may reflect a reluctance of some workers to report in detail the shape of I(t) curves because of evidence that the width is sensitive to extrinsic effects, i.e., impurities or contacts. Compare, for example, the pulse shapes in Refs. 13 and 14. We will argue below that in our samples intrinsic effects are being observed by establishing reproducibility among different samples. We know of no other reports of universality with respect to sample thickness in a molecularly doped polymer. Other observations[9,15] of universality have had α considerably less than 1, in contrast to our observations with $\alpha \approx 0.9$. Still other observations[9,10] have been limited to narrow field ranges. Universal behavior in electric field also has been reported in another amorphous organic material, polysilylene.[16]

Typical transients are shown in Fig. 1 on linear time-linear current axes normalized in magnitude and time at t_0. The slowly decreasing current before the transit time varies as $\approx t^{-.07}$ or $\alpha = 0.93$ at T = 305K. α decreases with decreasing temperature to approximately 0.8 at 254K. These normalized I(t) plots (Fig. 1) overlap, as can be demonstrated by the reader by overlapping transparent copies. We have found it useful to quantify the shape of the post t_0 tail by calculating w. We find that w is independent of E over a wide field range, as shown in Fig. 2. Plotted are w vs. E for 50% p-diethyaminobenzaldehyde-diphenyl hydrazone doped polycarbonate (DEH:PC) at 235K, 30% tri-p-tolylamine doped polycarbonate (TTA:PC) at 325K, and 30% DEH:polystyrene (DEH:PS) at 295K. w is independent of E from 5 to 140 V/μm in 30% DEH:PS, 7 − 90 V/μm in 30% TTA:PC, and 20 − 125 V/μm in 50% DEH:PC. We have observed similar results over the experimentally accessible range of temperatures and dopant concentrations in these materials. This includes 10 − 50% TTA in PC (240 − 360K) and 10 − 50% DEH in PS (240 − 320K). Only the 10% DEH:PS data shows a slight 10% rise in w observed across the full field range.

In order to check the thickness dependence of w, samples from 3.8 to 42 μm thick of 30% DEH:PS were prepared. All samples had room temperature mobilities of $1.6 \pm 0.2 \times 10^{-6}$ cm^{2}Vs at E = 20 V/μm. w for all the samples was 0.4 within 5%

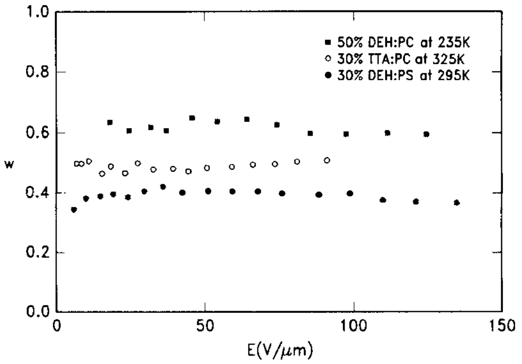

FIGURE 2 w, the relative width of the transient is independent of electric field within experimental error.

indicating that w is independent of the sample thickness. We have found a similar result in 50% DEH:PC over a thickness range of 9.9 – 29 μm. These results should be contrasted with results published by Yuh and Stolka[10] on another molecularly doped polymer N,N′-diphenyl-N,N′-bis (3-methylphenyl)-(1,1′biphenyl)-4,4′-diamine TPD:PC in which it was shown that $w \propto L^{-1/2}$.

As is usually observed, w decreases as T increases, i.e., the photocurrent transient becomes more rectangular at higher temperatures. Shown in Fig. 3 are the temperature dependence of w (averaged over the complete field range at each T) for several concentrations of DEH in PS. Above 30% DEH in PS or 30% TTA in PC (not shown), w appears to be independent of concentration. However, in both materials, at 10% dopant concentration, w is about 10% larger at each temperature.

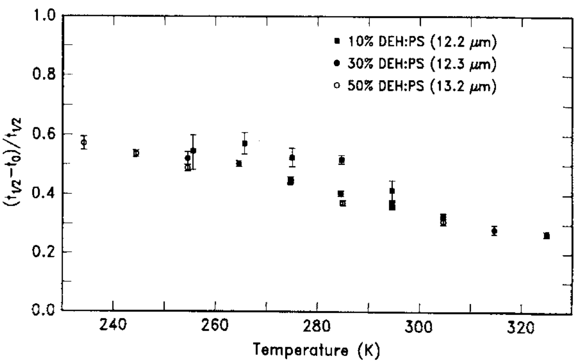

FIGURE 3 The temperature dependence of w

In order to check whether the behavior of w reported here is an intrinsic effect, films of DEH:PS were made from several batches of DEH recrystallized from various solvents (ethanol and methanol/toluene) and from two sources of polystyrene (Scientific Polymer Products and Saint Clair-Koppors). In addition, we investigated both commercial DEH normally used in IBM photoreceptors and DEH synthesized in our lab from 1,1-diphenylhydrazine-hydrochloride and 4-(diethylamino)benzaldehyde. Films were cast from both tetrahydrofuran and dichloromethane. Identical values of the room temperature mobility and w were always obtained within ± 15%. Impurities could be influencing w only if they were present in all samples at identical levels, which seems unlikely. At low electric fields, we sometimes have observed a weak dependence of w on E which varies from sample to sample. The irreproducibility suggests extrinsic causes, e.g., residual impurities. This suspicion was confirmed by eliminating the variability by further purification. Furthermore, these results cannot be attributed to contact effects since identical results were obtained in DEH:PS using UV photogeneration near an Al contact and injection from an amorphous Se photogenerator layer.

In order to understand the implications of these results, we compare them with several microscopic models. Two macroscopic effects are easily shown to be inconsistent with the data. Film thickness variations would broaden the transients, but with a field dependent w because μ depends strongly on E. Dopant concentration variations would produce a temperature independent zero-field extrapolated w because the zero-field mobility has the same temperature dependence at all concentrations of DEH:PS. Both predictions are inconsistent with our data.

Consider the prediction of w from elementary diffusion theory. The Einstein relationship gives a diffusion constant $D = \mu kT/e$ where k is Boltzmann's constant and e is the electron charge. During the time $t_0 = L/\mu E$ in which the charge carriers drift across the film, the charges diffuse relative to their centroid a distance $\sqrt{2Dt_0}$. Therefore

$$w \sim \frac{\sqrt{2Dt_0}}{L} = \sqrt{\frac{2kT}{eLE}}\,, \tag{1}$$

as is well known.[11] Our data are inconsistent with the predicted E and T dependence. Furthermore, using $L = 10\ \mu m$, $E = 10\ V/\mu m$, at $T = 300K$ one obtains $w \approx 0.02$, more than an order of magnitude smaller than the experimental result. Clearly simple diffusion does not account for the value of w, as has been recognized for some time.[10,11] The predicted L dependence is inconsistent with our results but appears to be followed in the system examined by Yuh and Stolka.[10]

Next consider the prediction for hopping modulated by shallow intrinsic traps at a single energy.[17] If the trapping time τ_t is considerably smaller than both the release time and the trap-free transit time $L/(\mu_0 E)$, then $w \sim N^{-1/2}$. N is the mean number of traps visited and μ_0 is the microscopic (trap-free) mobility. N is the given by the ratio of τ_t and $L/(\mu_0 E)$,

$$w = \frac{1}{\sqrt{N}} = \sqrt{\frac{\mu_0 E}{L}\tau_t} \,. \tag{2}$$

Hence, w can be independent of E only if the trapping rate τ_t^{-1} is proportional to the drift velocity $\mu_0 E$. Such might be true at high fields, if most hops are in the direction of the field. At low fields, however, carrier motion should be essentially diffusive, τ_t should be independent of E, and w should increase as $\sqrt{E}$. For hopping sites a distance $a = 1$ nm apart, the low field case should apply if $eaE \leq kT$, e.g., $E \leq 25$ V/μm at $T = 300$K. Our data extend well into this range, but w remains independent of E. Furthermore, the predicted L dependence is inconsistent with our data.

Bässler and coworkers[18] have investigated the consequences of a hopping model in which individual hopping sites have random energies within a Gaussian distribution, the randomness originating in variations of the environment of individual sites, with a standard deviation of about 0.1 eV. They also allow for a distribution in the intersite electron-transfer matrix elements. Their simulations yield a predicted width of

$$w \sim \sqrt{\frac{f(E)}{E}\frac{\pi kT}{eL}} \tag{3}$$

which resembles Eq. 1 except for the enhancement factor f(E). As shown in Fig. 5 of Ref. 18 for a particular set of parameters, f(E) is approximately proportional to E^2 for $E < 45$ V/μm, has a maximum near 150 V/μm, and decreases at higher fields. Near its peak, f(E) has a weaker, approximately linear field dependence that leads to an approximately constant w over a modest field range (45 to 150 V/μm). (These field values should be reduced by a factor of ≈ 1.6 to compensate for the smaller intersite distance used in the simulations.) The E^2 dependence gives $w \propto \sqrt{E}$ at low fields, inconsistent with the data shown in Fig. 2.

There is one known theory which accounts for w being independent of E over a wide field range. As pointed out above, this is the Scher-Montroll theory of "dispersive transport"[6,7] which was constructed specifically to account for such data. It typically assumes a power law distribution ($t^{-(1+\alpha)}$) of hopping times coupled with a random walk formulation. This theory has been applied to materials such as As_2Se_3 and trinitrofluorenone:poly(N-vinylcarbazole)[7] and oxadiazole:polyester.[8] Our observation of the curve shape (Fig. 1) or w (Fig. 2) being independent of E and

L is an additional observation of universality. But our transients are characterized by a particularly large α, namely $\alpha \approx 0.9$, i.e., the current is almost time independent before the transit time. The familiar characteristics of "dispersive" transport should still persist, given a power law waiting time distribution, for all values of α up to 1. However, as α approaches 1 it takes increasingly longer to reach the long time limiting behavior characteristic of "dispersive transport." For example, Fig. 5 of Ref. 19 shows that it takes 5 orders of magnitude in time longer for $\alpha = 0.9$ as compared to $\alpha = 0.5$ to reach the power law behavior of the current. Hence it is unclear whether our experimental time scale is long enough that Scher-Montroll theory would actually predict universality for $\alpha = 0.9$ in a power law distribution of hopping times. Another possibility is that the waiting time distribution function is not power law: there are other waiting time distribution functions that produce universality over a finite time range. For example, Montroll and Scher[20] have given an example of a different function, their ψ_4 which has a finite mean (unlike the power law distribution) and gives universality over a substantial but finite range of times. Hence with either distribution, consistency with our observations of universality hinges on determining an absolute time scale for the theory.

Within the Scher-Montroll theory, the "dispersion," determining the width of the current pulse, and the mean position of the carrier packet both depend on the electric field only through $\bar{l}(E)$, the mean displacement for a Single hop. *But*, the ratio of these factors is independent of $\bar{l}$ and therefore E. In fact the ratio, which is an estimate of our w, only depends on α through the relation (Eq. 33 of Ref. 6)

$$w \sim \left\{ \frac{2\Gamma^2(1+\alpha)}{\Gamma(1+2\alpha)} - 1 \right\}^{1/2} \tag{4}$$

where Γ is the gamma function. Therefore, the observation of universality does not by itself provide direct information about the field dependence of $\bar{l}$ and therefore does not shed light on the microscopic mechanism of the field dependence of the mobility. Physically, the field dependence of the mobility merely determines the mean displacement per hop, but does not affect the distribution of carrier positions in the sample. However, an additional consistency check between our data and the Scher-Montroll theory is provided by Eq. 4 since both α and w have been measured. The results (Fig. 4) are in qualitative agreement.

In the Scher-Montroll theory, the electric field sets the distance scale over which the mean of the packet of charge carriers is displaced as a function of time, whereas the shape of the packet is field independent. It follows that if universality

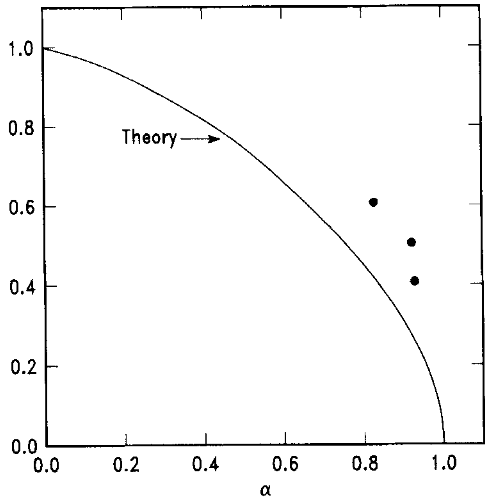

FIGURE 4 w vs. α from the Scher-Montroll theory and our data.

with respect to E is observed at a given thickness, universality with respect to L should also be observed. We have observed both forms of universality for 30% DEH:PS and 50% DEH:PC. For a different molecularly doped polymer, Yuh and Stolka[10] found approximate universality with respect to E (at least at two fields differing by a factor of 6 as can be seen in their Fig. 4), but not L, inconsistent with the theory. Perhaps their α is closer to 1 and a transition to a new behavior is observed. Or, there may be another physical mechanism for field universality.

The observed temperature dependencies of w and α clearly suggest that the waiting time distribution function depends on temperature. The original Scher-Montroll theory was generalized to account for such dependencies by Marshall,[21] Schmidlin,[22] Pollak,[23] Noolandi,[24] Rudenko and Arkhipov,[25] Tiedje and Rose,[26] and others who pointed out that traps with a distribution of energy levels could also produce the characteristics of "dispersive transport." Some of these treatments yield instructive analytical formulas for both dispersive transport characteristics and the behavior of the mobility. For example, the basic equations governing carrier transport are solved in closed form by Rudenko and Arkhipov for an arbitrary energy distribution of traps and the results are applied to particular models of trap distributions. One model which predicts dispersive transport characteristics, traps distributed uniformly in energy, predicts several features of the mobility which are clearly inconsistent with our data, e.g., a mobility that increases with increasing sample thickness. Dispersive transport is also predicted for traps distributed exponentially in energy.[7, 26] For α near 1 the mobility is almost independent of thickness and any field dependence of μ arises almost entirely from the microscopic trap free mobility. The field dependence of the microscopic mobility and trapping parameters are not considered. A model in which multiple trapping with a narrow Gaussian energy distribution does not appear to give field universality, as can be seen in Fig. 13 of Ref. 27.

A satisfactory theory of charge transport in molecularly doped polymers must be able to account simultaneously for universality of I(t) even when α approaches 1—the new result in this paper—and the characteristic field and temperature dependencies of the mobility. Suitable multiple trapping theories can probably account for the former but have offered no explanation of the latter perhaps because they generally ignore any field dependence of the microscopic parameters such as trapping and release times. The approach of Rudenko and Arkhipov and the work of Bässler show promise in this area in that both the problems are addressed in a tractable manner. It could be hoped that these approaches will be able to explain both features of the data in a cogent manner.

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REFERENCES

1. L. B. Schein, Phil. Mag. B, 65, (1992) to be published.
2. L. B. Schein, A. Peled and D. Glatz, J. Appl. Phys., 66, 686 (1989).
3. J. C. Scott, L. Th. Pautmeier and L. B. Schein, submitted.
4. A. Peled and L. B. Schein, Chem. Phys. Lett., **153**, 422 (1988).
5. P. M. Borsenberger, J. Appl. Phys., 68, 5682 (1990).
6. H. Scher and E. W. Montroll, Phys. Rev. B, 12, 2455 (1975).
7. G. Pfister and H. Scher, Adv. Phys., 27, 747 (1978).
8. N. Crisa, Phys. Stat. Sol. B, 116, 269 (1983).
9. H. Seki, Proceedings of the 5th International Conference on Amorphous and Liquid Semiconductor Conference, Garmish-Parlenkirchen, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974), p. 1015.
10. H. J. Yuh and M. Stolka, Phil. Mag. B, 58, 539 (1988).
11. R. Richert, L. Pautmeier and H. Bässler, Phys. Rev. Lett, 63, 547 (1989).
12. P.M. Borsenberger, L. Pautmeier, R. Richert and H. Bässler, J. Chem. Phys., 94, 8276 (1991)
13. G. Pfister, Phys. Rev. B, 16, 3676 (1977).
14. P. M. Borsenberger, W. Mey and A. Chowdry, J. Appl. Phys., 49, 273 (1978).

15. L. B. Schein, Mol. Cryst. Liq. Cryst., 183, 41 (1990).
16. M. A. Abkowitz, M. J. Rice and M. Stolka, Phil. Mag. B, 61, 25 (1990).
17. W. E. Tefft, J. Appl. Phys., 38, 5265 (1967).
18. L. Pautmeier, R. Richert and H. Bässler, Phil. Mag. B, 63, 587 (1991).
19. H. Schnörer, D. Haarer and A. Blumen, Phys. Rev. B, 38, 8097 (1988).
20. E. Montroll and H. Scher, J. Stat. Phys., 9, 101 (1973).
21. J. M. Marshall, Phil. Mag., 36, 959 (1977).
22. F. Schmidlin, Phys. Rev. B, 16, 2362 (1977).
23. M. Pollak, Phil. Mag., 36, 1157 (1977).
24. J. Noolandi, Phys. Rev. B, 16, 4466 (1977); 4474 (1977).
25. A.I. Rudenko and V.I. Arkhipov, J. Non-Cryst. Solids, 30, 163 (1978)
26. T. Tiedje and A. Rose, Solid State Commun., 37, 49 (1980)
27. A. Blumen and H. Schnörer, Angewandte Chemie, 29, 113 (1990)