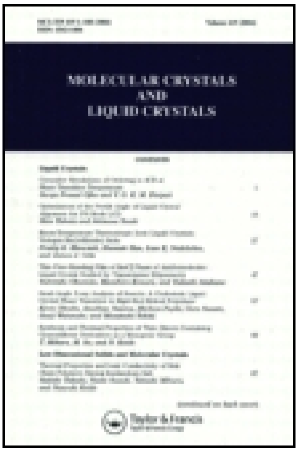


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Comparison of Hole Hopping Diffusion and Migration in a Triarylamine Containing Polymer

John S. Facci [a], Martin A. Abkowitz [a], William W. Limburg [a], Dale S. Renfer [a] & John F. Yanus [a]

[a] Xerox Corporation, 800 Phillips Road, Webster, NY, 14580

To cite this article: John S. Facci , Martin A. Abkowitz , William W. Limburg , Dale S. Renfer & John F. Yanus (1991): Comparison of Hole Hopping Diffusion and Migration in a Triarylamine Containing Polymer, Molecular Crystals and Liquid Crystals, 194:1, 55-63

To link to this article: http://dx.doi.org/10.1080/00268949108041150

Mol. Cryst. Liq. Cryst., 1991, vol. 194, pp. 55–63
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

COMPARISON OF HOLE HOPPING DIFFUSION AND MIGRATION IN A TRIARYLAMINE CONTAINING POLYMER

JOHN S. FACCI, MARTIN A. ABKOWITZ, WILLIAM W. LIMBURG, DALE S. RENFER AND JOHN F. YANUS
Xerox Corporation, 800 Phillips Road, Webster, NY 14580

Abstract Electron hopping charge transport rates in a triarylamine containing polymer were investigated electrochemically in the presence of a contacting electrolyte and in the solid state (absence of liquid electrolyte). Electron hopping diffusion coefficients were measured by steady state voltammetry in thin polymer films on Au microelectrode interdigitated arrays. In addition, zero-field extrapolated electron hopping mobilities and zero-field mobility activation energies are obtained from time-of-flight (TOF) measurements. Electron hopping diffusion coefficients (D_h, cm^2/s) and diffusion activation energies obtained in solid state electrochemical experiments can be correlated with zero-field hole mobilities ($cm^2/V\text{-}s$) and activation energies via the Einstein relationship.

Keywords: Charge transport, hole diffusion, mobility, triarylamine polymer, electron hopping

INTRODUCTION

Charge transport among a network of discrete hopping sites in condensed media is of theoretical and practical interest, being central to many applications including electrophotographic imaging[1], electrocatalysis[2], and molecular electronic devices[3]. Gaining a molecular level understanding of the factors governing charge transport is particularly important if progress in these areas is to be made.

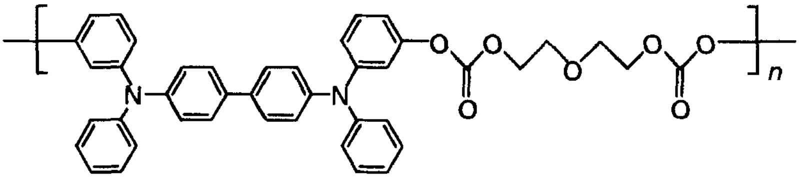
We have been interested in the molecular basis of electric field driven transport in electroactive arylamine polymers in the solid state. Time of flight techniques (TOF)[4] are especially suited to mechanistic studies of electric field driven discrete hopping transport in redox polymers. In TOF experiments, photoinduced charge transport occurs in a constant externally applied electric field. Charge mobility is determined from the transit time of the charge packet, the value of the electric field and the sample thickness. Experimental hopping mobilities in a polymer matrix containing a molecularly dispersed arylamine redox molecule were successfully modeled as an electric field perturbation of an electron self-exchange reaction [5], as shown in eq. 1. Here

$$\mathrm{Ox}^{+} + \mathrm{Red} \overset{k_{ex}}{\rightleftarrows} \mathrm{Red} + \mathrm{Ox}^{+} \tag{1}$$

Ox and Red are the oxidized and reduced forms of the electroactive species. The field induced barrier lowering for hopping in the direction of the electric field was modeled as a fraction of the electric field driving force. This treatment is essentially a bimolecular extension of heterogeneous electrode reaction rate theory[6].

Charge transport in electroactive polymer films on electrodes in a contacting liquid electrolyte[7] can be electroanalytically characterized by an electron (D_e) or hole (D_h) hopping diffusion coefficient. In addition, a new solid state voltammetric technique was recently used[8] to measure D_e in a liquid electrolyte free redox polymer. Given the underlying importance of the electron self exchange reaction in such diverse manifestations of hopping transport, it was appealing to undertake a comparison of hopping mobility and diffusion in the same transport polymer. Such studies, not heretofore reported, are shown to result in wider understanding of hopping in solid state redox polymers.

Polymer I, shown below, containing an electroactive tetraphenylbenzidine group, was selected as model system for these initial comparisons of hole hopping mobility and diffusion.



Polymer I

Measurements of D_h are done by steady state voltammetric determination of limiting currents at polymer coated microelectrode interdigitated arrays (IDA's) as previously described by Murray[9] and Wrighton[10-13]. Such determinations circumvent shortcomings associated with transient determinations of D_h such as counterion transport limiting of electron hopping[14]. We show rigorously below that counterion transport limitation are absent in our steady state voltammetry measurements of D_h.

EXPERIMENTAL

Electrochemical hole diffusion coefficient measurements employed polymer coated microelectrode interdigitated arrays (IDA's) as schematically shown in Figure 1. The IDA's contain 101 closely spaced microelectrodes 5 µm wide, 1000 µm long and 0.1 µm thick on 10 µm centers. Adjacent microelectrodes are separated by 5 µm on an electrically insulating base of 500 nm SiO_2. Films of polymer I were solvent cast over both the microelectrodes and the insulating gap between microelectrodes from microliter aliquots of 1-5 mg/ml solutions of the polymer in chlorobenzene. The active area of the IDA was masked after solvent casting by overcoating the Au lead-in lines with a silicone adhesive (Dow Silastic) with the aid of a translation stage and a stereomicroscope. The 50 inner and 51 outer microelectrodes form the two terminals of the IDA, denoted W_1 and W_2, respectively. W_1 and W_2 are employed as a hole (oxidized species) generator and collector, respectively. A Pine Instruments Model RDE-4X bipotentiostat was used to independently control the potentials of W_1 and W_2 versus a SCE reference electrode.

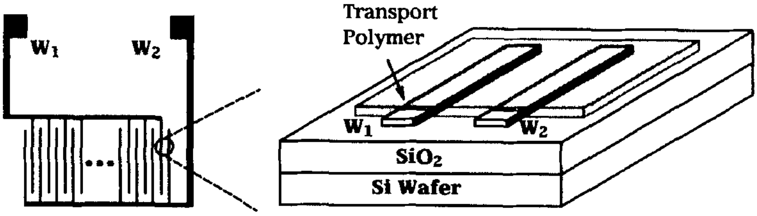


Figure 1. Schematic of the microelectrode interdigitated array

An Al-polymer-Au sandwich cell was used in time-of-flight drift mobility measurements. A 10-15 µm polymer film is cast onto an evaporated Au coated Si wafer (ground plane). The polymer is then overcoated with a 150Å evaporated Al film. A potential difference of 50-900V (3×10^4 - 6×10^5 V/cm) is applied with the ground plane charged negative. An attenuated nanosecond laser pulse of 337 nm light is impinged on the sample so that a small fraction of the polymer near the Al-polymer interface is photo-oxidized by the UV radiation. The packet of photogenerated holes (oxidized triarylamine) then migrates to the Au electrode under the influence of the electric field.

RESULTS AND DISCUSSION

Cyclic Voltammetry of Films of I

Films of I were solvent cast onto vitreous carbon electrodes from a 1 µl aliquot of a 1-5 mg/ml chlorobenzene solution of the polymer by slow evaporation in a chlorobenzene saturated atmosphere. A 50 mV/s cyclic voltammogram of a *ca.*

500Å film of I on vitreous carbon (A=0.07cm^2) in 0.3M $LiClO_4/CH_3CN$ is shown in Figure 2. Polymer I undergoes two overlapping one electron oxidations in 0.3M $LiClO_4/CH_3CN$. The first and second formal oxidation potentials are $E^{\circ\prime}_1=0.80$ and $E^{\circ\prime}_2=0.86$ V *vs.* SCE, respectively. The charge under the anodic waves, using the dashed integration baseline, corresponds to a tetraphenylbenzidine (TPB) coverage $\Gamma_{TPB}=6.8\times10^{-9}$ mole/cm^2. The formal potential difference $E^{\circ\prime}_1 - E^{\circ\prime}_2=60$ mV results from electronic delocalization over the two triarylamine halves of the TPB moiety.

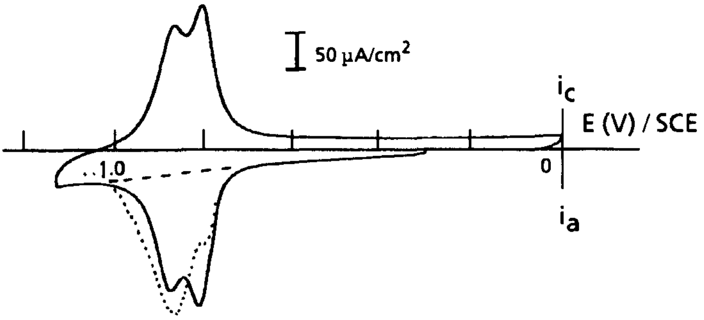


Figure 2. Cyclic voltammogram of a film of I in 0.3M $LiClO_4/CH_3CN$.

The dotted line in the figure shows the anodic cyclic voltammetry resulting from extended potential cycling (7 cycles) of a film of I in 0.3 M $LiClO_4/CH_3CN$. The anodic branch of the voltammogram is characterized by a single anodic wave at $E^{\circ\prime}_2$ (the cathodic branch remains unchanged); thus we treat the oxidation of I as the independent oxidation of triarylamine moieties. Extended potential cycling results in crosslinking of I: a cyclic voltammetric assay of the polymer coverage (in 0.3M $LiClO_4/CH_3CN$ electrolyte) following a 25 min immersion in chlorobenzene showed no dissolution of the polymer film. Based on the electropolymerization of analogs of I[15] and the known dimerization reaction of the triphenylamine radical cation[16], films of I appear to crosslink through unsubstituted TPB para positions.

Hole Diffusion Rates in Films of I in a Contacting Electrolyte

Figure 3A shows a pair of sigmoidal steady state voltammograms for a polymer coated IDA when E_1 (applied to W_1) is slowly swept from 0.5V to 1.1V while a fixed $E_2=0.5$V is applied to W_2, a potential where the polymer is reduced. Equation 2 relates the hole diffusion coefficient to the limiting

$$i_{lim} = nFAD_hC_I/d \qquad (2)$$

current i_{lim} in Figure 3. In the equation, A is the active electrode area of the IDA (10^{-4} cm^2), C_I is the concentration of electroactive sites, and d is the gap width (5 μm). From the limiting current $i_{lim} = 1.6$ μA and the estimated TPB concentration $C_I = 1.05 \times 10^{-3}$ mole/cm^2, one finds $D_h = 3.7X10^{-8}$ cm^2/s. Extended potential cycling of a film of I results in crosslinking via the electroactive sites and enhancement in D_h as shown in Figure 4, Panel B. Curves a-f of the inset show a series of consecutive steady voltammetric plots for a 2000Å film of polymer I. The hole diffusion coefficient increases dramatically with time spent in the oxidized state though the absolute crosslinking density is not quantitatively known. To the best of our knowledge such charge transport behavior has not been seen before. When crosslinking is complete, D_h attains a maximum value of $D_h = 8.2X10^{-7}$ cm^2/s, a *factor of 26* increase over the uncrosslinked sample.

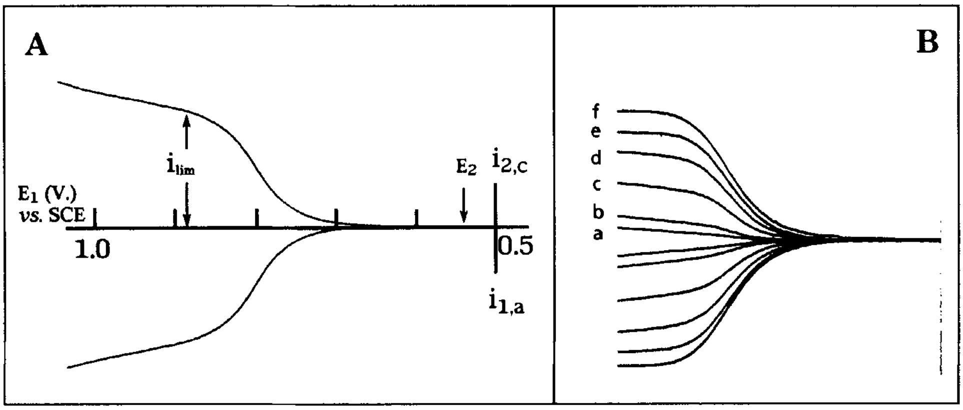
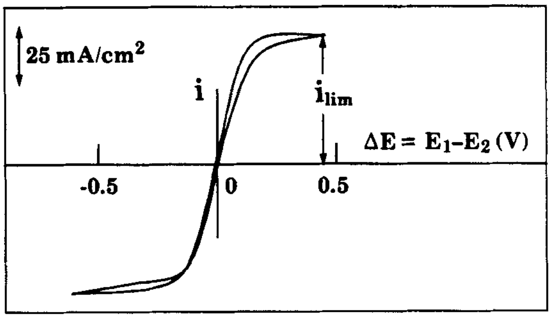


Figure 3. Steady state voltammetry of I coated on an IDA.

Solid State Voltammetry: Hole Diffusion in the Absence of Liquid Electrolyte

The hole diffusion coefficient in the absence of electrolyte $D_{h,ss}$ was measured *via* solid state voltammetry. A film of I (solvent cast onto an IDA which is attached to a heat sink) is pre-electrolyzed at 0.83 V so that it is half oxidized. It is then rinsed in CH_3CN to remove excess electrolyte and returned to a cell containing CH_3CN vapor. A 20 mV/s potential scan of $\Delta E = E_1 - E_2$ is initiated and the current-voltage results shown in Figure 4. From $i_{lim} = 2.3$ μA at room temperature, one finds $D_{h,ss} = 4.8 \times 10^{-8}$ cm^2/s. Figure 5A and 5B show, respectively, Arrhenius plots of the temperature dependence of D_h and $D_{h,ss}$. The figure shows that the hole diffusion (hopping) activation energy in the solid state (12.6 kcal/mole) is significantly higher than the hole diffusion activation energy in I exposed to a contacting electrolyte (7.1 kcal/mole).

Presumably the higher activation energy is a result of the coupling of the microscopic molecular motions to the electron self-exchange reaction. Exposure of the film to a liquid electrolyte has the effect of plasticizing the polymer chains resulting in a more facile approach to the transition state.



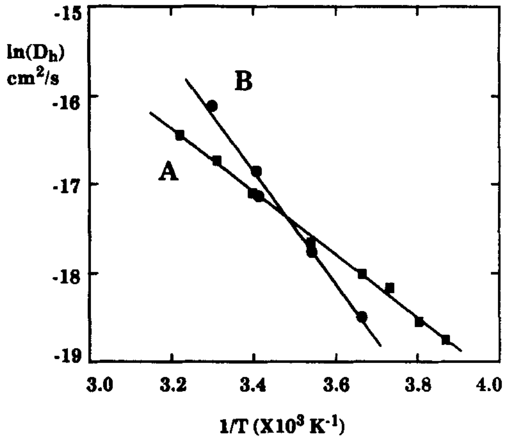


Figure 4. Solid state voltammetry of I on an IDA.

Figure 5. Arrhenius plot of the temperature dependence of D_h (A) and $D_{h,ss}$ (B)

The hole hopping activation energy in fully crosslinked I (exposed to electrolyte) is found to be 4.5 kcal/mole, considerably lower than that in uncrosslinked I (7.1 kcal/mole, see above). The pre-exponential factors in uncrosslinked and crosslinked I are experimentally equal (factor of 5 difference) and do not account for the 26-fold enhancement in D_h. The crosslink induced D_h enhancement is therefore due mainly to the lower hopping activation energy. From this we conclude that counterion transport does not limit the rate of electron hopping in uncrosslinked I as the counterions are able to keep up with the much higher D_h values in crosslinked I.

Time of Flight Drift Mobility

A sandwich cell containing an 11.3 μm film of I solvent cast on Au was overcoated with a 150Å thick 0.32 cm^2 evaporated Al electrode and capacitively charged so that the Al is positively biased. Figure 6 shows a sample photodischarge curve at 21°C when the cell is capacitively charged to 24.8 nC (dielectric constant = 2.8) with a 350V potential bias (3.0×10^5 V/cm). The sample was exposed to a nanosecond pulse of low intensity 337 nm laser light (165 ergs), photooxidizing a quantity of TPB sites at the Al/polymer interface equivalent to 13% of the capacitive charge. The figure shows the

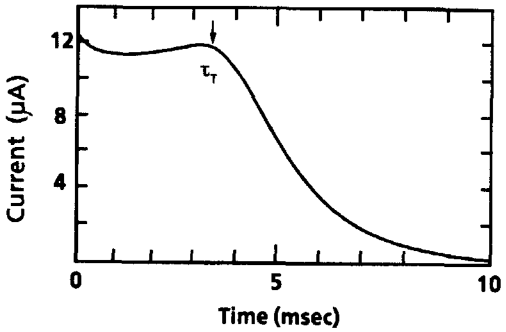


Figure 6. Time of flight photodischarge in polymer I at 3.0×10^5 V/cm.

transit of Q = 3.3 nC, corresponding to 1.1×10^{-13} mole/cm^2 of TPB sites. The transit time t_T, taken from the knee of the curve, is 3.5 msec and is related to the charge mobility by

$$\mu = d^2 / t_T E \tag{3}$$

where d is the film thickness and E is the electric field gradient. Under the above conditions the hole mobility $\mu = 1.04 \times 10^{-6}$ cm^2/V/sec. The hole mobility is strongly dependent on electric field as is generally the case in disordered molecular systems[17]. Because theoretical models predict both a linear[18] and square root[19] dependence of μ on electric field, we extrapolate μ to zero-field (μ_0) using both log μ vs. E and log μ vs. $\sqrt{E}$. At 21°C, the linear field extrapolation yields $\mu_0 = 4.2 \times 10^{-6}$ cm^2/V/sec while the square root of field extrapolation yields $\mu_0' = 1.8 \times 10^{-6}$ cm^2/V/sec at 21°C. An Arrhenius plot of the temperature dependence of μ_0 and μ_0' is shown in Figure 7A and 7B, respectively. The hopping mobility activation energies from curves A and B are 10.4 (linear E) and 12.2 kcal/mole ($\sqrt{E}$), respectively. These values represent the uncertainty in the mobility activation energy due to the uncertainty in the extrapolation.

Zero-field hole mobilities can be related to hole diffusion via the Einstein equation,

$$\mu_0 = D_h (F/RT), \tag{4}$$

where F and R are the Faraday and the gas constant, respectively ($F/R = e/k_B$). The filled circle data of Figure 7 are values of $D_{h,ss}(F/RT)$. These values are quantitatively correlated with experimentally determined μ_0' over the temperature range studied. Overlaid for comparison in Figure 7C is the $D_{h,ss}$ data. Absolute values of $D_h(F/RT)$, not shown, are in fair agreement with μ_0' and μ_0. However, an Arrhenius plot of these values yields an activation energy of 6.5 kcal/mole in poor agreement with the (zero-field) hole mobility activation energy of 10-12 kcal/mole.

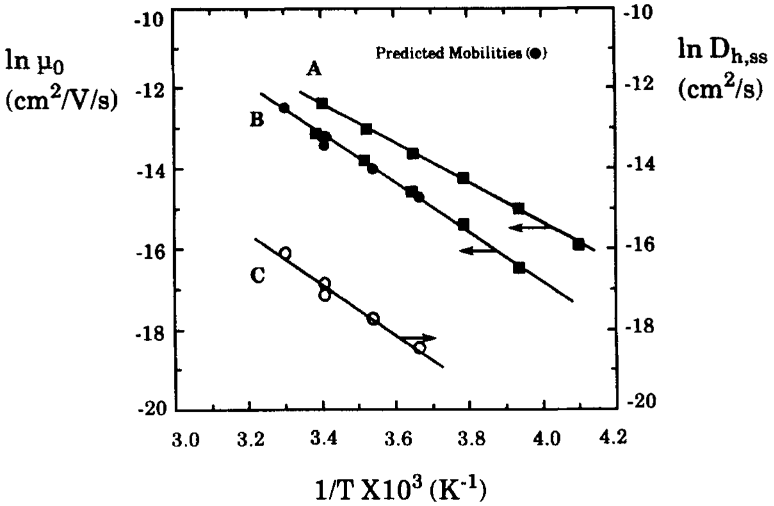


Figure 7. Arrhenius plots of $D_{h,ss}$, μ_0, and μ_0'.

The success of the Einstein correlation in these comparisons lies in the absence of counterion transport limitations on hole hopping in the solid state and on similar coupling of (polymeric) molecular motions with the electron exchange reaction (eq. 1)[15]. That hole mobility and diffusion coefficients in the solid state are related by the Einstein coefficient has implications in terms of the statistics of hopping, namely, that the distribution of hopping times in the solid state is an exponential waiting function (gaussian) and that charge diffusion and migration is the sum of mutually independent electron hops. Details of the implications are discussed in a separate paper[20].

REFERENCES

1. J. Mort, Science, 20, 819 (1980).
2. R.W. Murray, in Electroanalytical Chemistry, A.J. Bard, ed., Marcel Dekker, New York (1984) Vol. 13, 191.
3. C.E.D. Chidsey and R.W. Murray, Science, 231, 25 (1986).
4. M. A. Abkowitz and D. M. Pai, Phil. Mag. B, 53, 193 (1986).
5. J.S. Facci and M. Stolka, Phil. Mag. B, 54 1 (1986).
6. A.J. Bard and L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, John Wiley & Sons, New York, Chapter 3 (1980).
7. P. Daum, J.R. Lenhard, D.R. Rolison, and R.W. Murray, J. Amer. Chem. Soc., 102, 4649 (1980).
8. R.A. Reed, L. Geng, and R.W. Murray, J. Electroanal. Chem., 185, 208 (1986).
9. C. E. D. Chidsey, B. J. Feldman, C. Lundgren, and R. W. Murray, Anal. Chem., 58, 601 (1986).
10. G.P. Kittlesen, H.S. White and M.S. Wrighton, J. Amer. Chem. Soc., 107, 7373 (1985).
11. J.W. Thackery, H.S. White, and M.S. Wrighton, J. Phys. Chem., 89, 5133 (1985).
12. G.P. Kittlesen, H.S. White, and M.S. Wrighton, J. Amer. Chem. Soc., 106, 7389 (1984).
13. E.W. Paul, A.J. Ricco, and M.S. Wrighton, J. Phys. Chem., 89, 1441 (1985).
14. X. Chen, P. He, and L.R. Faulkner, J. Electroanal. Chem. 222, 223 (1987).
15. J. Facci, M. Abkowitz, W. Limburg, to be submitted to J. Phys. Chem.
16. Adams, R.N., Electrochemistry at Solid Electrodes, Marcel Dekker, 1969, Chapter 10.
17. H. Bassler, G. Schonherr, M. Abkowitz, and D.M. Pai, Phys. Rev. B, 26, 3105 (1982).
18. G. Schonherr, H. Bassler, and M. Silver, Phil. Mag. B, 44, 47 (1981).
19. W.D. Gill, J. Appl. Phys., 43, 5088 (1972).
20. M.A. Abkowitz and J.S. Facci, manuscript in preparation.