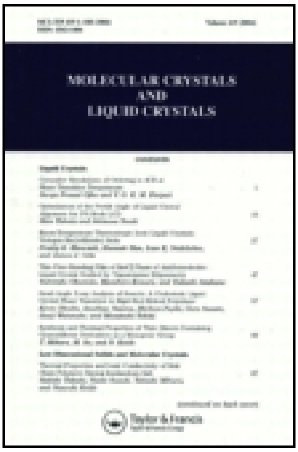

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Electronic Transport in a Model Tetraphenylbenzidine Main Chain Polymer. Direct Comparison of Time-of-Flight Hole Drift Mobility and Electrochemical Determinations of Hole Diffusion

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ELECTRONIC TRANSPORT IN A MODEL TETRAPHENYLBENZIDINE MAIN CHAIN POLYMER. DIRECT COMPARISON OF TIME-OF-FLIGHT HOLE DRIFT MOBILITY AND ELECTROCHEMICAL DETERMINATIONS OF HOLE DIFFUSION

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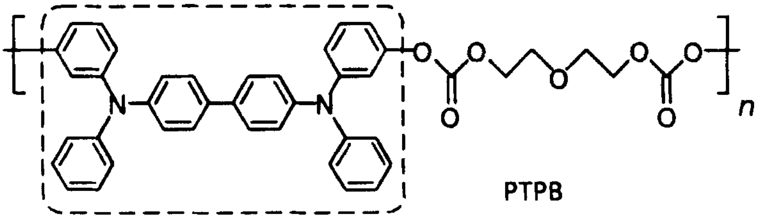
Abstract The first direct comparison of time of flight (TOF) hole drift mobilities with a novel dry film electrochemical determination of hole diffusivity is reported in a polytetraphenylbenzidene (PTPB) main chain polymer. In conjunction with the Einstein relation, electrochemical diffusivity measurements provide a means for determining the zero field hole mobility and its apparent activation. It is demonstrated that TOF drift mobility vs. field data extrapolated to zero field (from ln μ vs. $E^{1/2}$ plots made over the range 10^3-10^6 V/cm) and electrochemical data are fully convergent over a range of temperatures. The zero field activation for holes in PTPB is 0.53eV from both measurements.

INTRODUCTION

On the basis of recently compiled time of flight (TOF) drift mobility data it has become evident that a wide assortment of disordered molecular materials share a common pattern of features in their transport behavior[1]. A canonical example of this behavior is observed in the hole drift mobility data for polytetraphenylbenzidine (PTPB). This polymer, the structure of which is illustrated below, serves as the venue for the present comparative study of



PTPB

hole diffusivity and mobility. The tetraphenylbenzidine (TPB) moiety, which is the active site among which holes hop, is highlighted by the dashed rectangle.

Figure 1A exhibits the essential features provided by (small signal, current mode) TOF measurements on PTPB carried out within the usual field range for this technique, 10^3-10^6 V/cm. The TOF hole drift mobilty is field dependent, varying exponentially with the square root of the applied field. The slopes of a family of such curves decrease progressively with increasing temperature. Zero field mobilities (shaded circles) parametric in temperature can be estimated by extrapolating to zero field along each of the lnμ vs. $E^{1/2}$ plots. These results are depicted in the Arrhenius plot in Figure 1B. The estimated zero field activation is 0.53eV. The temperature dependence of the hole drift mobility parametric in field can also be represented as Arrhenius activated, as shown in Figure 1C. The plot demonstrates that the activation energy scales with the square root of the applied field. Extrapolation of the

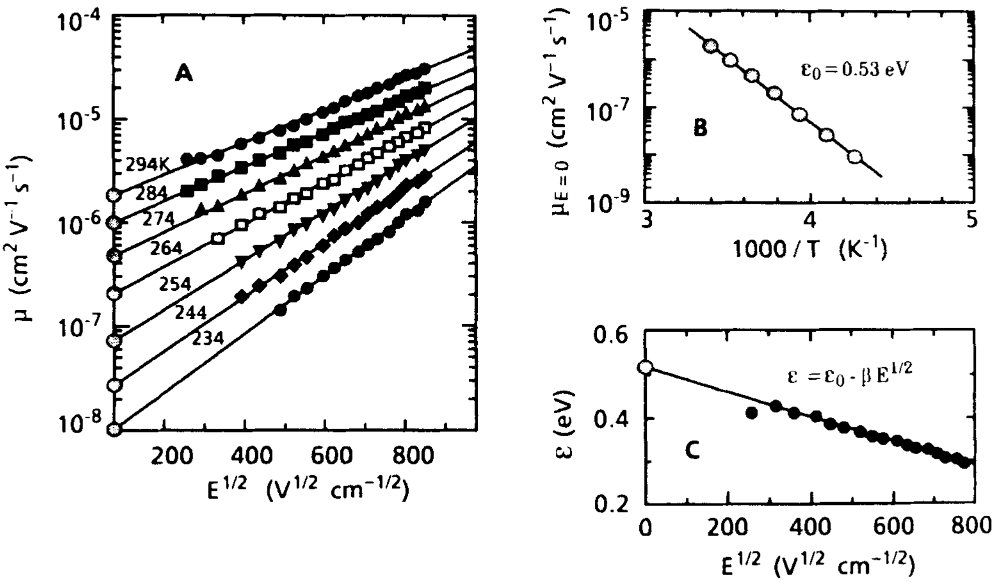


FIGURE 1. (A) Log mobility vs. E1/2 parametric in temperature for PTPB. extrapolated zero mobilities are highlighted (shaded circle; (B) Arrhenius diagram of zero field mobilities; (C) Hole mobility activation energy vs $E^{1/2}$. Zero field activation determined in (B) is given by the shaded circle.

latter results to zero field is clearly consistent with the previous estimate 0.53eV. Although the indicated extrapolations to zero field appear to provide a self-consistent phenomenological picture, the validity of such a procedure is called into question by conventional theoretical models including the most recent work which is based on numerical simulation of hopping transport in a disordered broadened manifold of localized states[2]. These models, in fact, all predict the possibility of a fairly significant deviation from the square root scaling of ln μ at fields below those readily accessed by the TOF technique. The present study was motivated by the need to resolve this issue. The approach was to employ an alternative experimental means for examining transport behavior in the zero field limit.

DRY FILM ELECTROCHEMICAL DIFFUSION MEASUREMENTS

Thin (*ca.* 200nm) PTPB films for electrochemical diffusion measurements were prepared by solvent casting a dilute solution (1-5 mg/ml) of the polymer in chlorobenzene onto a microelectrode interdigitated array (IDA) with an interdigital distance of 5 µm (see Figure 2A). Prior to measurement, the PTPB film was converted to the half oxidized state as follows. The specimen was immersed into an electrochemical cell containing a permeating solution of $LiClO_4$ electrolyte in high purity acetonitrile. The cell also contains a reference (SCE) and a counterelectrode. The IDA is incorporated into a conventional electrochemical circuit with both terminals W_1 and W_2 of the IDA configured as a common working electrode. In this configuration and with information available from cyclic voltametry of PTPB[3], any desired degree of oxidative conversion of the redox active TPB sites on the polymer molecule can be achieved by application of the appropriate potential to the interdigitated array relative to the reference electrode. Application of 0.83V *vs.* the SCE oxidizes precisely half of the triarylamine groups to the radical cation, i.e., the film is composed on average of TPB^{+1} moieties. The specimen film is removed from the electrolyte under potentiostatic control and washed in acetonitrile to remove all excess electrolyte. The specimen, once removed from electrolyte, is fixed with respect to its total ion content. Note that each of the oxidized TPB^+ sites is compensated by a perchlorate anion (ClO_4^-). The spatial distribution of ion pairs is uniform throughout the film. The two sides of the interdigitated array W_1 and W_2 are then disconnected from each other

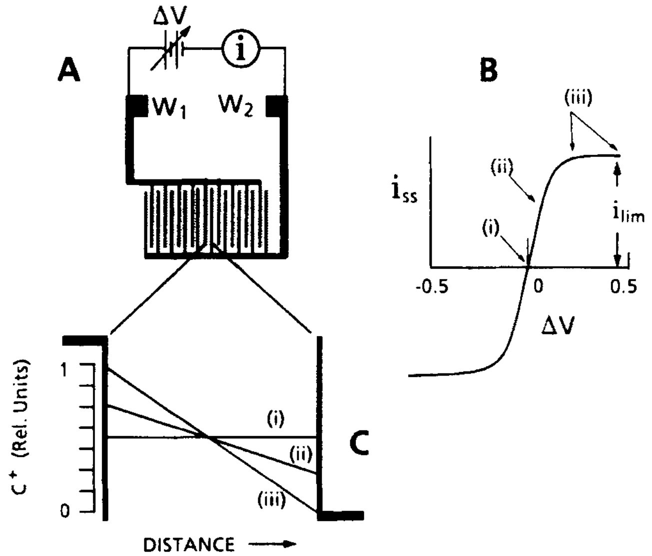


FIGURE 2. (A) Schematic of interdigitated array and measurement. (B) Steady state diffusion current, i_{ss}, vs. interelectrode potential ΔV. Saturation of i_{ss} occurs in region designated 'C'; (C) Concentration gradient profiles between adjacent microelectrode pairs: A, B, C correspond to potentials and iss in (B).

and reconnected across a two electrode potentiostat in which a voltage is applied and a current is simultaneously measured as indicated schematically in Figure 2A. The solid state diffusivity measurement is carried out following a procedure initiated by Murray and co-workers[4]. The film coated IDA is reinserted in a cell which contains an argon atmosphere saturated with acetonitrile vapor. In the presence of this acetonitrile vapor the perchlorate anions become free to move and are therefore capable of rapidly readjusting their spatial distribution in response to an applied field (i.e., the field will be immediately screened from the film bulk).

Upon application of a potential between W_1 and W_2, a rapid displacement of a small but finite quantity of ClO_4^- ions against the fixed distribution TPB^+ is all that is required to cause the applied potential to be completely dropped across the contact-polymer interfaces (i.e., the Helmholtz layer) thereby converting W_1 and W_2 into electrochemically working electrodes. Oxidation of TPB to TPB+ and reduction of TPB+ to TPB occurs at adjacent microelectrodes. As the applied potential difference ΔV is varied, indicated by the arrows (i), (ii) and (iii) in Figure 2B, the distribution of TPB+ sites and their charge compensating by ClO_4^- ions will be altered. A voltage dependent steady state concentration gradient of TPB+ is established as illustrated in the lower left of Figure 2C. As a consequence, a steady state diffusion of holes is sustained between adjacent microelectrodes (e.g., W_1 and W_2) giving rise to the diffusion currents i_{ss}, as indicated in Figure 2B. The maximum concentration gradient is achieved under conditions when all the TPB sites are oxidized to TPB+ at one IDA terminal and all the TPB sites are reduced at the other ($C_{TPB} = 2.5 \times 10^{-3}$ mole/cm^3). This gradient is achieved at the ΔV indicated schematically as the plateau voltage in region (iii) of the steady state voltammogram. Any further increase in ΔV should have no additional effect on i_{ss}. This is, in fact, experimentally observed. Diffusion measurements following the procedure described have been carried out as a function of temperature in PTPB. Under these conditions, the diffusion coefficient D_h of holes through a sample of thickness L is related to the limiting value of the diffusion current density J_D by Fick's first law,

$$J_D = n\,F\,D_h\,C_{TPB} / L. \qquad (1)$$

In equation 1, F is the Faraday and n the number of electrons hopping per hopping event.

At each temperature an effective zero field mobility is computed from the diffusivity by using the Einstein relation

$$\mu = (e / kT) D_h. \qquad (2)$$

In Figure 3, results of these dry film electrochemical measurements on PTPB are compared to the hole drift mobility data extrapolated as indicated in Figure 1A. The agreement is excellent to within experimental resolution. While the legitimacy of the square root extrapolation in PTPB is supported by the present results the origin of this field dependence and indeed of the entire pervasive pattern of field and temperature dependent transport in disordered molecular materials remains an unresolved issue of central

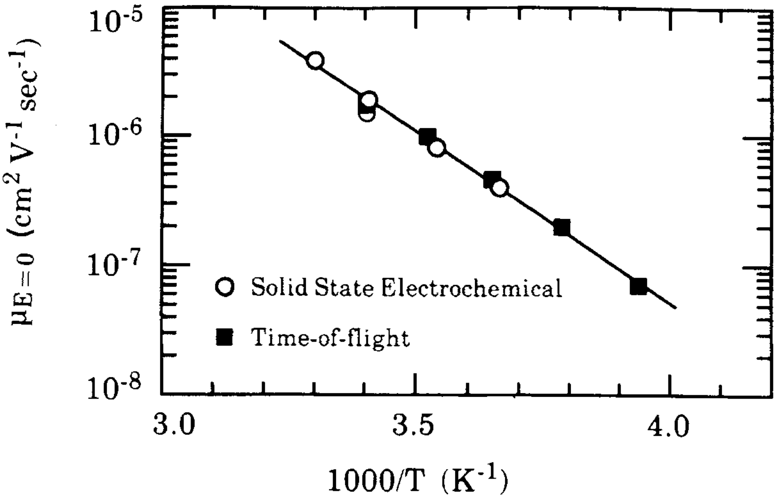


FIGURE 3. Arrhenius diagram comparing zero feld hole mobilities extrapolated from TOF measurement and mobilities determined from solid state electrochemical measurements and the Einstein relation.

importance. It appears increasingly probable that the field dependence of tl drift mobility arises at the level of the individual intersite hop and a more realistic model description of this process is therefore required.

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