Temperature and field-dependence of electron currents in films of *trans*-polyphenylacetylene

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Current–voltage–temperature (i–V–T) measurements were made between 22°C and 100°C and at electric fields of 4×10^3 to 1.2×10^5 V cm^{-1} on 5 μm thick films of undoped, amorphous *trans*-polyphenylacetylene supported between a metal and an SnO_2 electrode. With a negative bias on the metal cathode, electron currents dominate; they are exponential in $V^{3/2}$ and show an activation energy, E_A, that decreases toward $E_A \leqslant 0.1$ eV at the higher temperatures. At fields greater than 2×10^4 V cm^{-1} the magnitude of the current is independent of the work function of the metal over the range of 2.6 to 5.2 eV. The conductivity, and particularly its temperature coefficient, are concluded to be controlled by bulk. The temperature dependence of the conductivity is consistent with the presence of a narrow energy band containing poorly conducting states with the Fermi level lying slightly below it in a quasi-bandgap.

(Keywords: electrical conductivity; polyphenylacetylene; electroactive polymer)

INTRODUCTION

Polyphenylacetylene (PPA) is a very poor semiconductor, but when doped with electron acceptors, particularly AsF_5, it shows a large enhancement of its electrical conductivity[1]. The *trans*-form shows a significant photoconductivity in the far visible and the near infra-red when undoped and when doped with some inorganic and organic electron-accepting compounds and with certain dyes[2,3]. There is strong evidence that the dark conductivity of films of undoped *trans*-PPA at electric fields sufficiently large to minimize the electrode–sample potential barrier, as well as the photoconductivity of the doped and undoped polymers, are predominantly n-type and that, in all these cases, charge transport proceeds through states that are characteristic of the polymer. Shallow electron traps, whose concentration can be measured from the trapped charge accumulated in a steady-state photoconductivity experiment, sometimes diminish and sometimes enhance the steady photocurrent, while holes are deeply trapped[4]. Previous work on the dark conductivity and photoconductivity of PPA has been reviewed elsewhere[5].

There are some significant similarities between the behaviour of the dark current and the photocurrent of undoped films of *trans*-PPA at room temperature; when measured in sandwich cells between a metal and an SnO_2 electrode, a negative bias on the metal electrode yields currents that are superlinear in the applied voltage. At sufficiently high electric fields these currents exceed substantially the more Ohmic currents obtained at positive bias[4]. This situation is the opposite of that observed in undoped polyvinylcarbazole[6], which is a p-type photoconductor. This and other considerations indicate that in asymmetric-sandwich cells of the type described, negative bias on the metal electrode leads predominantly to electron currents in undoped PPA[5].

This paper deals with current–voltage measurements in approximately 5 μm thick films of *trans*-PPA between room temperature and 100°C. The films were amorphous and revealed no structure under the electron microscope at a resolution of 500 Å. Under negative bias on the metal electrode, currents reach a steady value quickly and show essentially reversible behaviour with respect to temperature (see below), whereas, under similar conditions, *cis*-PPA undergoes irreversible isomerization reactions[7] that are reflected in its electrical conductivity[8]. After the isomeric structure has become stabilized, the d.c. conductivity of undoped *cis*-PPA, in pellet as well as film form, shows activation energies of about 1.5 to 2.1 eV from room temperature to well above 100°C[8,9]. These values are not far below the band gap (2.3 eV) of crystalline *cis*-PPA, as measured by reflectance spectroscopy[10].

EXPERIMENTAL

Current–voltage measurements over the temperature range from room temperature to 100°C were made with the sample as an approximately 5 μm thick film in a sandwich- or diode-like arrangement that consisted of an SnO_2-coated (NESA) glass slide supporting the polymer film on which circular metal electrodes, approximately 1 μm thick and 3 mm in diameter had been evaporated in an Edwards thermal evaporator. Cooling of the sample during evaporation was required to avoid crack formation. Several electrodes were deposited on top of the polymer film to improve the chances of obtaining test areas that did not short, and to study sample and contact uniformity. Adjustable pressure contacts were used (Signatone micropositioner). This method was found to be more dependable than that making use of silver paste to anchor the leads on the electrodes; it also avoided any

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possible problems due to diffusion of the silver paste into the sample. A 70 V d.c. power supply (Hewlett Packard Model 6206 B) and a Keithley 610 C electrometer, used in the current mode, were put in series with the sample, which was supported on a hot plate, heated by resistance heaters operated from a d.c. power supply to avoid the interference of any a.c. noise with the current measurements. Temperature was measured with a thermocouple in contact with the top surface of the glass slide.

An examination of the effect of sample thickness on the conductivity behaviour could not be made because the sample thickness could not be varied over a sufficient range: samples less than about 4 μm thick shorted too frequently and were too irregular in thickness, while those thicker than 7 or 8 μm tended to crack during a heating and cooling cycle because of good adhesion to the electrodes combined with insufficient flexibility. We attribute this to the semi-rigid nature of the polymer and, perhaps, inadequate molecular weight.

PPA films were prepared by first dissolving the polymer at about 15 wt% in chloroform and pouring the resulting solution over the glass slide. This led to films that were reasonably uniform in thickness judging from the good agreement between measurements made on different electrodes (circular spots) deposited on the same film. The film thickness was determined gravimetrically. The solvent was first allowed to evaporate in air and the samples were then placed into the evaporator for deposition of the top electrode. The electrical measurements were made in air.

Upon imposing an electric field across the sample, with the metal electrode under negative bias (predominantly electron currents), currents stabilized after several minutes. Under positive bias (hole currents), currents had not stabilized over a period of 5 h and showed a progressive increase, or decrease, depending on the applied potential. In view of this instability, and of the fact that our previous interest was centred on currents obtained with the metal electrode under negative bias, only the latter type of data will be reported. Currents obtained under such conditions will be referred to as electron currents without further proof[5].

Current densities, J, at different voltages, V, and temperatures, T, were obtained under conditions of very slow heating such that the temperature of the hot plate and the sample had stabilized at a fixed value determined by the voltage applied to the heaters. The entire voltage of the power supply for the measuring circuit, V, appeared across the sample. The electric field across the electrodes ranged from about 3×10^3 to 1.2×10^5 V cm^{-1}. It took 5 to 8 h to obtain readings from room temperature to 100°C. The hot plate and sample were then allowed to cool overnight. A second heating sequence was followed on the next day. Rapid cooling of the sample tended to lead to crack formation.

The PPA samples were prepared from *trans*-rich PPA, obtained either in the presence of $W(CO)_6$ activated by light and polymerized in carbon tetrachloride, according to the method of Masuda *et al.* (samples A to D)[11], or in the presence of WCl_6 and tetraphenyl-tin in dioxane (sample E: a gift of Professor Higashimura, Kyoto University). These samples have not yet been well characterized with respect to *trans*-content or molecular weight. There is still some question as to the best method of measuring the *trans*-content, whereas molecular weight measurements are rendered difficult by the polymer's tendency to either degrade with respect to molecular weight or lose conjugation in solution in the presence of air, judged from a drop in solution viscosity[12]. Percec has estimated the *trans*-content of PPA samples prepared by a method similar to that used for sample E to be 87% (ref. 13*). Masuda *et al.* report molecular weights approaching 100 000 for samples polymerized under conditions similar to our samples A–C[11]. A measurement of $\bar{M}_n$ for one of our samples (sample A) made on a membrane osmometer (courtesy Aero Laboratories, Joliet, Illinois) yielded a value of 27 500, but some degradation may have affected the results. While our efforts to stabilize these samples in solution and to characterize the *trans*-contents are in progress, we can refer to these samples at this time only as *trans*-rich PPA of molecular weight at least 25 000 and possibly as high as 100 000 (samples A–C), with a lower molecular weight assignable to sample E (10 000). Most measurements were made on sample A. *Table 1* summarizes data relating to the preparation and characterization of these samples.

RESULTS

Exploratory measurements of the d.c. resistivity of *trans*-PPA made between room temperature and 100°C at an applied potential of 1 V across a 4 μm thick sample yielded essentially identical results in a heating and cooling cycle, and steady currents were attained quickly after application of the potential when the metal electrode was biased negatively[14]. This behaviour contrast with that of many insulating polymers, which show substantial polarization currents[15] and/or a history-dependent d.c. conductivity[16]; *cis*-PPA, as well, can show a history-dependent conductivity due to progressive isomerization[8]. The reversible conductivity behaviour observed with *trans*-PPA at low fields[14] (2.5×10^3 V cm^{-1}), suggested that a similarly history-independent i–V–T behaviour might be obtainable. *Figure 1* shows the results for sample A in an Al/PPA/SnO_2 sandwich, with negative bias on the metal, during the first heating cycle. Currents obtained during the second heating cycle were within experimental error of the first, except for the room-temperature values which were rather lower. This was true for some, but not all, samples. There remains, therefore, some question as to whether truly reversible behaviour exists below about 40°C. *Trans*-PPA degrades in solution, and there is some question as to its long-term stability even at room temperature[17]. We have, therefore, chosen to report data obtained on the fresh samples in the first heating cycle. While absolute values of the

* We cannot as yet report the *trans*-content of PPA prepared in the presence of $W(CO)_6$ (samples A–D), but it should be comparable to that of sample E

Table 1 Preparation and estimated properties of *trans*-polyphenylacetylene

Sample	Catalyst	Solvent	*Trans*-content	$\bar{M}_n$
A–C	$W(CO)_6$ + light	CCl_4	≥80%	≥27 500
D	$W(CO)_6$ + light	CCl_4	≥80%	–[a]
E	$WCl_6/SnPh_4$	Dioxane	≥80%	≃10 000

[a] Prepared at low catalyst concentration. Masuda *et al.* report a reduced molecular weight under these conditions[11]

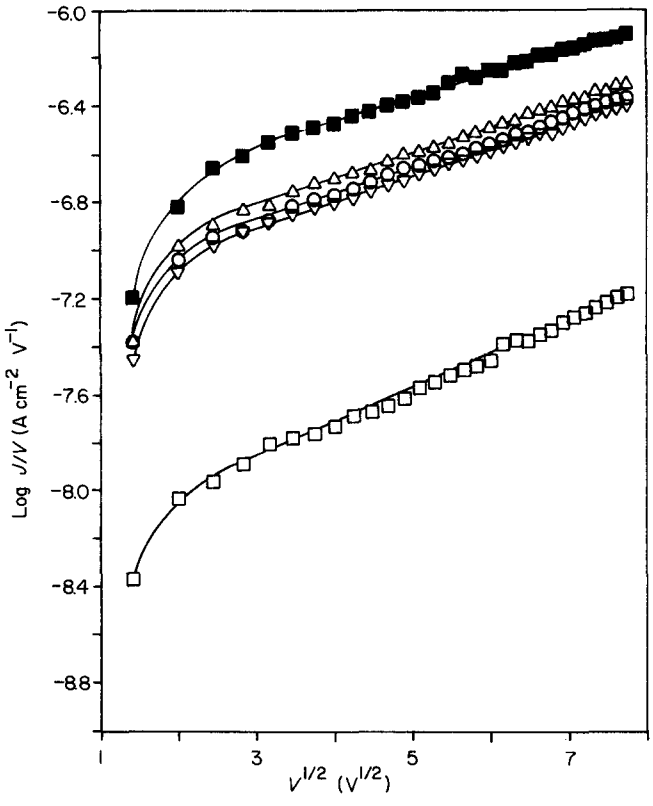

Figure 1 Logarithm of (current-density/voltage) *versus* (voltage)$^{1/2}$ plot for an aluminium cathode: □, 22°C; ▽, 60°C; ○, 70°C; △, 80°C; ■, 100°C

conductivity obtained in the two cycles often differ somewhat, as indicated, the form of the temperature-dependence in the two cycles is closely similar[18].

The *i–V–T* behaviour of the electron currents in sample A with Al electrodes (*Figure 1*) thus yields, first of all, a linear log J/V *versus* $V^{1/2}$ plot above a fixed electric field, about 2×10^4 V cm^{-1}, in this particular case. Richardson–Schottky plots ($\log J \propto V^{1/2}$) give a poorer fit. Secondly, there is a clear decrease in activation energy with increasing temperature. These two qualitative features, with the metal electrode under negative bias, were found in all samples, regardless of the identity of the metal cathode. We may note that the d.c. conductivity at 100°C and at the highest field (1.2×10^5 V cm^{-1}) corresponds to a value of about 10^{-10} S cm^{-1}.

As indicated earlier, currents obtained with the electrode under positive bias (hole currents) did not stabilize over a period of several hours, and no further attempts were made to follow their course with time. All subsequent results to be cited refer to currents obtained with the metal electrode under negative bias.

Data for Ytterbium and Palladium electrodes are shown in *Figures 2* and *3*, respectively. These data are qualitatively similar to one another, and to *Figure 1*, with respect to the voltage in the linear range of the plot and with respect to the temperature-dependence, although neither the absolute magnitudes of the currents nor of the slope of the log J/V *versus* $V^{1/2}$ plot are identical. Data obtained with an indium electrode were again qualitatively similar. Noting that the work functions of Pd (5.2 eV) and of Yb (2.6 eV) represent the highest and lowest values, respectively, amongst the metals used for the top contacts, and the substantial sample variability, we conclude that the nature of the metal electrode does not exert a major control over the magnitude of the current along the linear portion of the plot. The nonlinear part in the low-field region of the log J/V *versus* $V^{1/2}$ plot is missing when a Pd electrode is used. This might be associated with the fact that Pd matches most closely the low-field work function of PPA (see Discussion).

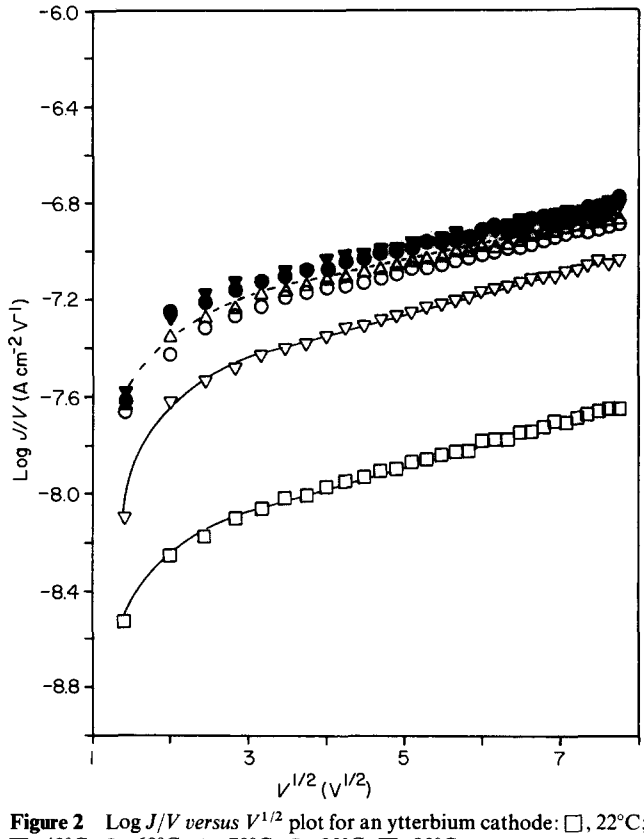

Figure 2 Log J/V *versus* $V^{1/2}$ plot for an ytterbium cathode: □, 22°C; ▽, 40°C; ○, 60°C; △, 70°C; ●, 80°C; ▼, 90°C

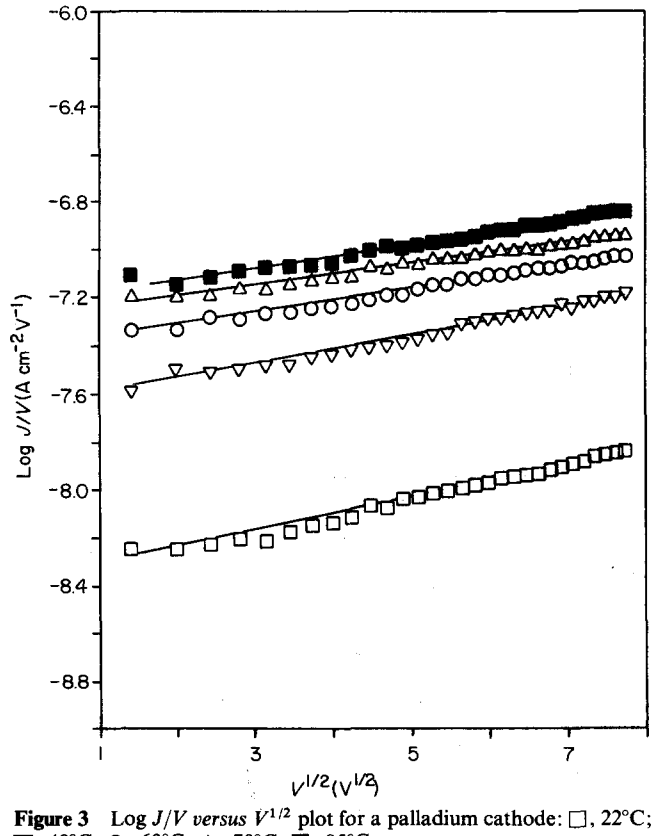

Figure 3 Log J/V *versus* $V^{1/2}$ plot for a palladium cathode: □, 22°C; ▽, 40°C; ○, 60°C; △, 70°C; ■, 85°C

In further support of the statement that the nature of the electrode had no demonstrable effect on the current in the linear portion of the log J/V *versus* $V^{1/2}$ plot, we offer our finding that the standard deviation in current values measured at 22°C and 30 V did not exceed significantly the standard deviation of about ±40% obtained in casting different films from the same polymer sample (sample A)[18]*. Results obtained with Al electrodes from samples B and C, polymerized under conditions identical to those for sample A, were the same as those for A within experimental error. However, the conductivities obtained for Sample D, obtained with the same catalyst as samples A, B and C, but at a lower concentration, and for sample E, obtained with a different catalyst, were significantly lower than those of samples A, B and C. We can only conclude at this time that molecular weight and/or microstructure may have an effect on the conductivity, without attributing this to any particular factor, in view of the very incomplete characterization of the polymer. *Table 2* lists several selected values of the conductivity of samples A, D and E, as well as the slope, β, of the log J/V *versus* $V^{1/2}$ plot. Whereas this slope has a theoretical significance in the Richardson–Schottky–Simmons, as well as Poole–Frenkel models (see Discussion section), the error is too large to derive any theoretical significance from it.

* The standard deviation at 90°C was less (±25%). The difference may indicate non-equilibrium trapping at room temperature.

Finally, we must consider the temperature coefficient of the d.c. conductivity, σ. *Figures 4* and *5* show a plot of log σ *versus* T^{-1} for sample A at two values of the electric field using the metals of lowest (Yb) and highest (Pd) work function as cathodes. All plots are qualitatively similar, and so the activation energy is neither cathode nor field dependent, but shows a strong decrease with increasing temperature. It is difficult to tell from these data whether σ tends toward a maximum or whether E_A tends toward a finite non-zero value. In *cis*-PPA, E_A is approximately constant between room temperature and 100°C and equal to about 1.5 to 2.1 eV. The data of *Figures 4* and *5* indicate that $E_A \leqslant 0.1$ eV above 60°C.

DISCUSSION

We will attempt to account qualitatively for the limited, but significant, dark d.c. conductivity, σ, found in what appear to be homogeneous films of undoped, amorphous, *trans*-polyphenylacetylene, which, in these measurements, ranges from about 1×10^{-13} to 3×10^{-10} S cm^{-1}. These conductivities are several orders of magnitude greater than those observed in truly insulating polymer

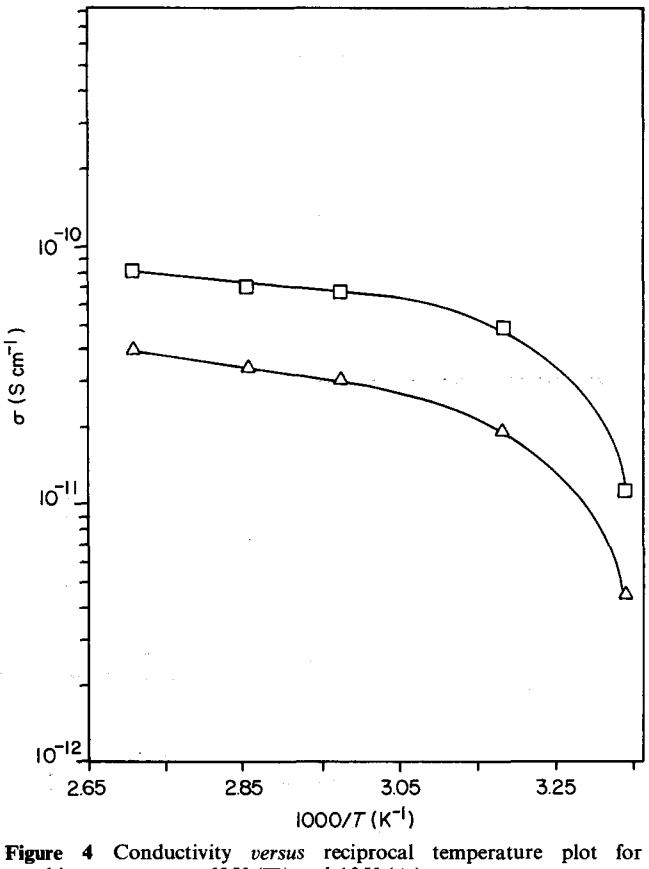

Figure 4 Conductivity *versus* reciprocal temperature plot for ytterbium contacts at 60 V (□) and 10 V (△)

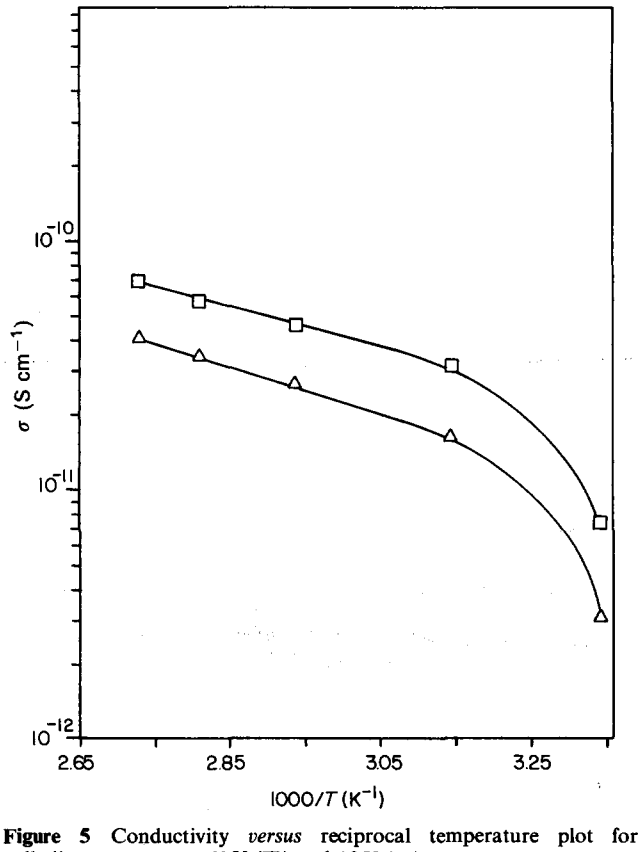

Figure 5 Conductivity *versus* reciprocal temperature plot for palladium contacts at 60 V (□) and 10 V (△)

Table 2 Summary of d.c. conductivity measurements (aluminium electrodes)

Sample	σ_{22}^{10} [a] (S cm^{-1})	σ_{22}^{50} (S cm^{-1})	σ_{90}^{10} (S cm^{-1})	σ_{90}^{50} (S cm^{-1})	β_{22} (V$^{-\frac{1}{2}}$)	β_{90} (V$^{-\frac{1}{2}}$)
A	7×10^{-12}	3.0×10^{-11}	1.1×10^{-10}	2.3×10^{-10}	0.15	0.10
D	6×10^{-13}	1.2×10^{-12}	1.7×10^{-11}	3.0×10^{-11}	0.08	0.06
E	1.35×10^{-13}	3.7×10^{-13}	8.6×10^{-13}	1.5×10^{-12}	0.12	0.10

[a] Subscript refers to temperature, superscript to voltage

films[6,15]. Despite very significant differences in the values reported for preparations with different isomeric content and in sample geometry (film cf. pellet)[8,9], all measurements fall within a limited range of orders of magnitude of σ, distinctly higher than observed in good insulators, and so suggest that the major component of σ is intrinsic to the polymer[5].

Although the I–V characteristics of insulating polymer films have sometimes been analysed in terms of the Richardson–Schottky equation for emission-limited currents[19,20] ($\log J \propto \beta V^{1/2}$), this equation does not, in general, provide a good fit for the data. Indeed, it was shown by Simmons[21] that, in a low-mobility material, the bulk properties, as specified by the mobility, μ, often exert the major control over the magnitude of the current, and that a clear distinction between electrode and bulk-limited processes could ordinarily not be made. The Simmons equation, with $\ln J$ proportional to $V^{3/2}$, may be written as

$$J/V = (\sigma_0/d)[\exp(\beta V^{\frac{1}{2}})][\exp(-\phi/K\,T)] \qquad (1)$$

where σ_0, which has the dimension of electrical conductivity, and β are constants calculable from the Simmons-modified Richardson–Schottky theory, with β representing the rate of lowering of the surface potential by the applied field. The symbol ϕ represents the interfacial barrier and d the sample thickness. The Poole–Frenkel effect, associated with potential barriers arising from bulk traps results in a very similar equation.

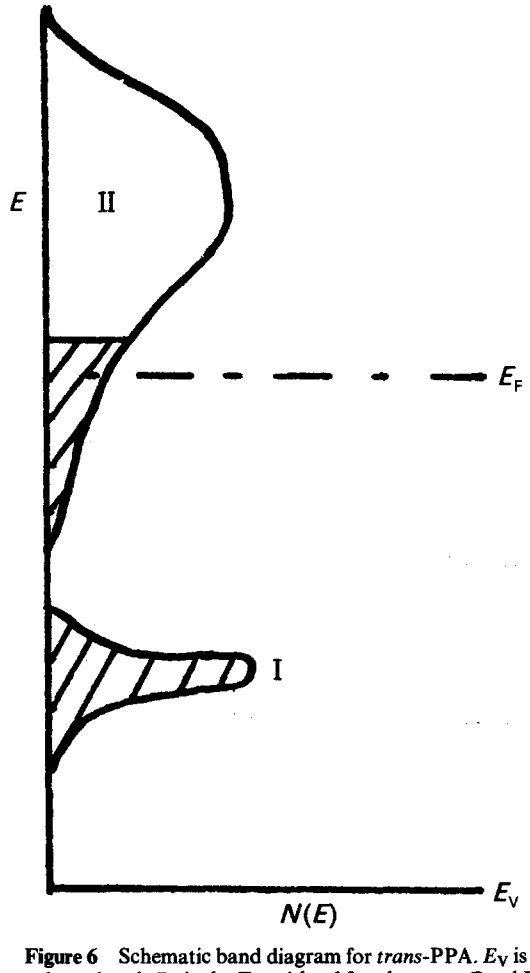

Figure 6 Schematic band diagram for *trans*-PPA. E_V is the edge of the valence band. E_F is the Fermi-level for electrons. Band I contains deep traps for holes, and Band II is the conduction band (shallow electron traps are indistinguishable from low-lying energy states within the band)

Equation (1) was found to be applicable to polyvinylcarbazole[6], and it fits the PPA data better than a Richardson–Schottky plot. Poor reproducibilities in β, as in the present case, are not uncommon. While we, therefore, refrain from analysing the magnitude of β, which, in the Richardson–Schottky–Simmons and Poole–Frenkel models contains the dielectric constant, the similar magnitudes and temperature-dependencies of σ with cathodes of widely varying work functions call for the inference that potentials associated with bulk traps (Poole–Frenkel effect), rather than with the interface, may dominate the form of the voltage dependence.

While the temperature-dependence of the conductivity also calls for an interpretation as bulk effect, the data on $\sigma(T)$ are insufficient to justify detailed modelling of the band structure and conductivity mechanisms, as was done recently for polyacetylene[22]. However, the decrease in the activation energy with increasing temperature, suggesting an approaching plateau in the conductivity, prompts some general considerations of the band structure. The conductivity of a material with a complex band structure may be written as

$$\sigma(T) = e\int N(E)\mu(E)f(E,T)[1-f(E,T)]\,\mathrm{d}E \qquad (2)$$

where E is the energy, $N(E)$ is the density of states, $\mu(E)$ is the mobility and $f(E, T)$ is the Fermi–Dirac distribution. The product $f(E, T)[1-f(E, T)]\,\mathrm{d}E$ may be taken as the probability of an electron jump or of electron tunnelling between sites and redefined as $P(E, T)\,\mathrm{d}E$.

The overlap between the known function $P(E, T)$ and the unknown function $N(E)\mu(E)$ then determines $\sigma(T)$ at all temperatures, where the latter function is temperature-independent in a rigid-band model, which may be inapplicable here. In fact, any additional lattice motions liberated by temperature in the interval studied are likely to make both $N(E)$ and $\mu(E)$ temperature dependent. The results of this study show that E_A decreases strongly with increasing temperature, suggesting a saturation in σ. While, strictly speaking, this imposes only limits on $\int N(E)\mu(E)\,\mathrm{d}E$, it is difficult to see how equation (2) could be satisfied, unless the band of potentially conducting states $N(E)$ were narrow and close to the Fermi-level*. If, in addition, the band edge is blurred, any distinction between shallow traps and low-lying states in a conduction band is removed. The schematic model of *Figure 6*, therefore, seems preferable to one proposed earlier[5], which allows a wide conduction band. The essence of the model is a narrow conduction band with the Fermi-level lying near its lower diffuse edge. We must note, however, that the conductivity data for *cis*-polyacetylene show a nearly temperature-independent activation energy[8,9]**, which is not much less than the bandgap of crystalline *cis*-PPA[10], and so the revision of the band structure to that shown in *Figure 6* is not called for in the latter case. The significant differences between the electronic structures and dynamics of electron transport in *cis*- and *trans*-PPA suggested by these data

* Since currents under negative bias of the metal electrode dominate currents obtained under positive bias only when the electric field exceeds a certain value[4], the Fermi level rises with increasing field, as shallow traps become filled.

** A similarly high and temperature-independent activation energy was reported by Simionescu *et al.*[23] for samples prepared by thermal polymerization and $(PPh_3)_2PdCl_2$ and referred to as *trans*-cisoid PPA. It is likely that the *trans*-contents and molecular weights of these samples were lower than ours.

and considerations need to be confirmed by other measurements.

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