Charge transfer in polypyrrrole

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Experimental electrical conductivity and optical absorption data are presented for fully oxidized polypyrrole. A charge transfer theory is described which gives an excellent account of the temperature dependence, carrier density dependence, and magnitude of electrical conductivity. The reorganization energy calculated from the temperature dependence of conductivity, 0.23 eV, is in good agreement with the value obtained from the near IR dielectric loss spectrum, ~0.25 eV. Self-consistent hopping distances of about 5–10 Å are obtained from the reorganization energy, conductivity preexponential factor, and carrier density. Hopping between localized sites associated with the counterion is indicated.

I. INTRODUCTION

Polypyrrole is a stable conducting polymer usually prepared by electrophysical oxidation of pyrrole in solution. Its electrical conductivity typically lies in the range 10–100 Ω⁻¹ cm⁻¹. The conduction mechanism in polypyrrole has proven difficult to establish because of structural disorder and because the electrical properties exhibit both metallic and semiconductor behavior. In this paper we present experimental conductivity and optical data on oxidized polypyrrole, and describe a charge-transfer model which gives a self-consistent account of both.

As prepared electrophysically, about one third of the pyrrole rings are oxidized. Recent data on poly(dimethylpyrrole) suggest a degree of polymerization of 100–1000. Electron diffraction patterns have been observed in neutral polypyrrole, prepared by electrophysical reduction of the oxidized polymer. These indicate a sheet structure similar to that of graphite. The ordered regions which produce the diffraction pattern are estimated to be about 20–50 Å in size.

There is good agreement in the literature on the optical spectra of oxidized polypyrrole. Kanazawa, Diaz, Krounbi, and Street reported absorptivity peaks at 1.2 and 2.9 eV. Yakushi, Lauchlan, Clarke, and Street reported absorptivity peaks at 1.0 and 2.7 eV and a shoulder at 3.6 eV. Kronig–Kramers transformation yielded broad peaks at 0.5 and 2.7 eV in the conductivity and 0.25 and 2.7 eV in the dielectric loss. The shift in the low energy band between the absorption and conductivity spectra is due to the dispersion in refractive index, and that between the conductivity and dielectric loss is due to the frequency factor relating them. These shifts are greater at lower frequencies. Arwin, Aspnes, Bjorkland, and Lundstrom obtained spectroscopic ellipsometry data which showed an absorption peak at about 3 eV and a rising absorption at the experimental low frequency limit of 1.5 eV, which they attributed to dc conductivity. However, the real part of the permittivity exhibited a positive frequency dependence at low energy, indicating a resonance absorption rather than a relaxation (dc conductivity) origin for the low frequency rise in absorptivity. This would then be consistent with the conductivity maxima (i.e., resonance absorption) at 1.0 and 1.2 eV observed by Yakushi et al. Sharp absorption peaks at energies below about 0.25 eV are observed in the Raman and IR spectra.

There is less agreement on the temperature dependence of the conductivity of oxidized polypyrrole. Kanazawa et al. reported a maximum in the conductivity of polypyrrole tetrafluoroborate at about 420 K, with reversible behavior below the maximum and irreversible behavior above it. On the other hand, a reversible temperature dependence below 300 K has been reported by others to follow the form

\[ \sigma = \sigma_0 \exp[-(T_0/T)^{1/4}], \]

associated with variable range hopping between localized states in a semiconductor. The thermoelectric power is positive, indicative of hole carriers, and numerically small with a linear temperature dependence below 300 K, characteristic of a metal.

Our conductivity data confirm the temperature dependence reported by Kanazawa et al. We believe the conductivity leveling off at high temperature is a characteristic feature of the conductivity mechanism, and propose a charge transfer model which is consistent with this feature. The model also provides an estimate of hopping distance.

II. EXPERIMENTAL

A. Sample preparation

Films were deposited on tin oxide coated glass at room temperature by electropolymerization from propylene carbonate solutions 0.4 M in pyrrole and 0.1 M in tetrabutylammonium bisulfate or tetrafluoroborate. Current densities of about 2 mA cm⁻² yielded 0.02–0.03 cm thick films in about 3 h; thicker films up to 0.06 cm thick were formed over corresponding longer times. Samples about 4 cm long and 0.5 cm wide were cut from these films, and washed with acetone/toluene and dried at 390 K for 45 min in an air circulating oven. This preconditioning was important for good reproducibility. Bulk density of the films was 1.4 g cm⁻².

B. Conductivity

Four terminal ac conductivities were measured with a GenRad Digibridge impedance bridge (model 1688) in the frequency range 250 Hz–20 kHz. Separate experiments established that the frequency independent ac conductivity at
room temperature agreed with four terminal dc measurements. Films were mounted on a mica support strip and clamped between copper blocks with narrow (about 1 mm) copper foil wrapped around the mica and film at two points between the blocks for the four terminal potential probes. The experimental jig was placed in a grounded aluminum cylinder heated by cartridge heaters in conjunction with an in-house temperature controller. For subambient temperatures the aluminum block was packed in dry ice and dry nitrogen passed through the sample compartment. Measurements were made under near isothermal conditions, from about 200 to 540 K. Temperature drift during conductivity measurements was less than 0.1 K min⁻¹. During heating between thermal equilibration points the sample was short circuited to minimize any long time ionic polarization developing from the thermo-emf. A two minute equilibration time following open circuit switching was programmed before conductivity data were collected. The entire experimental protocol was controlled by a Hewlett-Packard 83 computer.

C. Optical spectra

Optical measurements were made on deposited films of estimated thickness (1000 Å), with tin oxide coated glass as reference. The UV-visible spectrum (12 500 to 30 000 cm⁻¹) was measured with a Hewlett-Packard 8450A diode array spectrophotometer, and the near IR with a Beckman 5270 dual beam spectrophotometer. The absorbances from each instrument were adjusted for best overlap to give a composite spectrum.

III. THEORY

We describe a charge-transfer multiphonon hopping model which gives a good account of our conductivity data. This formalism was developed in a general form by Kubo and Toyazawa and Holstein, and has been successfully applied to polaron conductivity in semiconductors, inorganic redox reactions in solution, electron transfer in low temperature glasses, electron exchange reactions in organo-metallic systems, charge transfer in molecular doped polymers, and electron transfer in biological systems.

The transition probability W for charge carrier transfer between donor-acceptor ions (or localized states) can be expressed in the nonadiabatic approximation (weak electronic interaction) as the product of the square of the charge-exchange integral V and thermally averaged Franck-Condon (FC) factors F(ω_n), S_n, T, ΔE):

\[ W = (2\pi/\hbar) V^2 F. \]  

(2)

The charge exchange interaction V decreases exponentially with distance R as:

\[ V = V_0 \exp(-\alpha R), \]

(3)

where \( \alpha = 1 \, \text{Å}^{-1} \) and \( V_0 = 12.5 \, \text{eV} \) are found from analysis of nearest-neighbor interactions between aromatic molecules such as naphthalene and anthracene. It has recently been shown that the electron transfer integral between redox sites connected by rigid polymer links is characterized by \( \alpha = 0.98 \, \text{Å}^{-1} \) (through the bonds) and \( \alpha = 1.3 \, \text{Å}^{-1} \) (through space). The FC factors depend on the electronic energy difference between donor-acceptor centers (redox potential, ΔE), the frequencies \( \omega_n \) of vibrational modes \( \{\omega_n\} \), and the corresponding electron-phonon coupling factors \( S_n \), and temperature T. As shown by several investigators, in the harmonic approximation the FC factors for electron transfer between isoelectronic states (ΔE = 0) assume the form:

\[ F = \left[ 2\pi \sum S_n \left( \frac{\omega_n}{2kT} \right)^2 \cosh \left( \frac{\hbar \omega_n}{2kT} \right) \right]^{-1/2} \times \exp \left[ -\sum S_n \tan \left( \frac{\hbar \omega_n}{4kT} \right) \right]. \]

(4)

In the high temperature limit \( \hbar \omega_n < kT \), valid for polymer electronic transport, where low frequency torsional/backbone modes are involved, Franck-Condon factors assume the form:

\[ F = (4\pi \hbar \omega_n kT)^{-1/2} \exp \left[ -\frac{E_r}{4kT} \right], \]

(5)

where

\[ E_r = \sum S_n \left( \frac{\omega_n}{kT} \right). \]

(6)

\( E_r \) is the reorganization energy which in the continuum approximation yields:

\[ E_r = e^2(1/\epsilon_{op} - 1/\epsilon_{a}) (1/\alpha - 1/R), \]

(7a)

where \( \epsilon_{op} = \epsilon_2 \) and \( \epsilon_{a} \) are the limiting high and low frequency relative permittivities, respectively (relative to the hopping frequency), \( \alpha \) is the radius of a redox center, and \( R \) is the distance between the redox centers (elementary jump distance). For \( R = 2\alpha \), Eq. (7a) becomes:

\[ E_r = e^2(1/\epsilon_{op} - 1/\epsilon_{a}) (1/R). \]

(7b)

The appearance of the relative permittivities in Eqs. (7) reflects the polaron nature of the hopping event.

The electrical conductivity \( \sigma \) of a p-type conductor is given in its simplest form by:

\[ \sigma = \rho \mu, \]

(8)

where \( \rho \) is the hole concentration and \( \mu \) is the mobility related to the diffusion coefficient \( D \) through the Einstein relation:

\[ \mu = eD/kT. \]

(9)

The diffusion coefficient of the carrier is related to the transition probability W and hopping distance R by:

\[ D = R^2 W/6. \]

(10)

The metal-like behavior of the thermo-emf of fully oxidized polypyrrole indicates that the hole concentration is independent of temperature. Thus the temperature dependence of electrical conductivity is determined by the hole mobility. For charge transfer between localized states which are coupled to lattice vibrational modes, we obtain the relation:

\[ \sigma = (e^2/6)(2\pi/\hbar)pV^2R^2 \exp(-2\alpha R/(16\pi E_a))^{-1/2} \times (kT)^{-3/2} \exp(-E_a/kT), \]

(11)

where \( p \) is the hole concentration and the activation energy \( E_a = E_r/4. \)

(12)

Equation (11) predicts a maximum in conductivity vs temperature at \( T = 2E_a/3k. \)

The optical transition probability I(Ω) which is photon assisted by a photon \( h\Omega \) charge carrier transfer between local-
in ZBLA glasses.\textsuperscript{11} Mohnihan’s foray into polymer relaxation was restricted to poly(vinyl acetate),\textsuperscript{22} which, however, has parameters more like those for inorganics rather than those for PVC. Hence, it turned out to be extremely fortunate that I worked at a company that manufactured the very polymer for which sub-\(T_g\) endotherms are by far the easiest to generate.

The sub-\(T_g\) endotherms indicate, of course, that the enthalpy lost during annealing is entirely recovered in the glassy state (the shape of the glass transition is essentially unaltered if the endotherms occur far enough below \(T_g\)). This reveals an important feature of the TNM handling of nonlinearity. During scanning after the anneal, the shortest time components of \(g(t)\) allow partial recovery of enthalpy to occur deep in the glassy state. The subsequent increase in \(T_r\) then moves the entire distribution to shorter times, allowing slightly longer time components of \(g(t)\) to contribute to enthalpy recovery. This occurs because each component in \(1_g\) of \(g(t)\) is determined by the global \(T_h\) and not by the corresponding \(T_r\) component. Thus, the recovery accelerates during scanning and can be completed before the glass transition temperature range is entered. The WW function seems uniquely suited to describing both the short-time components of the \(g(t)\), responsible for the endotherms, as well as the long-time components that dominate the glass transition behavior. The cryptic message from Nature, that WW is good for a wide range of relaxation processes in a wide range of materials, remains to be deciphered.

### III. Data Fitting

Berens and I were obligated, of course, to present our NSF results to BFGO research staff. After one of my talks, an exceptionally bright chemical engineer named Gary Hayward approached me and said that the mathematical structure of the TNM intrigued him, and that the parameters could probably be determined using optimization algorithms that were routinely used by chemical engineers to design commercial-scale chemical processes (Marquardt, for example). Gary and I successfully applied his idea to polystyrene,\textsuperscript{23} and was easily extended to other polymers shortly thereafter.\textsuperscript{24}

The TNM method is computationally much faster than the essentially equivalent KAHR phenomenology\textsuperscript{25} used by the polymer community up to then. Thus, Mohnihan has also had a major influence on annealing studies in polymers.

The TNM phenomenology computes \(T_r\) as a function of time and temperature during rate cooling and heating, and the TNM heat capacity is computed as \(dT_r/dT\). From Eq. (9), this is given by\textsuperscript{7}

\[
\frac{dT_r}{dT} = \left[\frac{(C_p - C_p^a)}{C_p}\right]_{T_r}
\]

(15)

where \(C_p\) is the observed heat capacity and \(C_p^a\) is the equilibrium heat capacity (rubbery \(C_p^a\) for polymers and liquid \(C_p^a\) for other materials). The right-hand side of Eq. (15) is similar to but not identical to, the normalized heat capacity

\[
C_p^N = \left[\frac{(C_p - C_p^a)}{(C_p - C_p^a)}\right]_{T_r}
\]

(16)

Mohnihan has stressed (personal communication), and Sindic Simon has confirmed (personal communication), that the difference between \(dT_r/dT\) and \(C_p^N\) can be significant. I have always ignored this, because it was my belief that the differences were small compared with other systematic errors, such as those due to heat transfer and sample temperature gradient effects, for example. Given the speed and ease of present computation and data collection, however, this position can no longer be justified.

Another valuable contribution by Mohnihan and colleagues\textsuperscript{5} was the algebraic prediction that when the heating rate is changed under the constraint that the ratio of heating to cooling rates is held constant, the heat capacity function is simply shifted along the temperature axis without any change in shape. This feature of the TNM model has been used by Hutchinson,\textsuperscript{26} and Hodge\textsuperscript{27} in their assessments of thermal lag, about which more is said below.

It is now known that TNM is imperfect, especially for rapidly quenched glasses, but the source of the problem remains unclear. Mohnihan has described some of the modifications to the distribution function that he tried in order to improve matters,\textsuperscript{28} and other modifications as well that were unpublished but have been cited in a 1994 review (with Connie’s permission of course),\textsuperscript{29} all without success. My personal motivation for continuing TNM analyses is analogous to that given by Heisenberg for the development of early versions of quantum electrodynamics.\textsuperscript{30} “In order to find the direction in which we should depart from what prevails, we must know the consequences of the prevailing formalism much better than we do.” It is my opinion that if we cannot reproduce such a global property as heat capacity, then we cannot possibly hope to understand the myriad details of the glass transition phenomenon. Mohnihan has set us on the path.

### IV. Nonlinear Adam–Gibbs

In 1983, I was invited by Mohnihan to give a presentation at a Gordon Research Conference that he was chairing. George Scherer was there and reported his extension of the Adam–Gibbs model into the nonlinear glass transition region, by assuming that the configurational entropy was determined by \(T_r\) rather than \(T^\text{conf}\).

\[
S_r(T_r) = \int_{T_r}^{T_r} \frac{\Delta C_p}{T} \, dT
\]

(17)

Scherer used the expression \(\Delta C_p = \varepsilon - B T\) and found improved fits to some inorganic glasses. He and I discussed his results at length, and in 1987\textsuperscript{31} I inserted a slightly modified form of Eq. (1) into Scherer’s formalism:

\[
\Delta C_p = \frac{C T_2}{T} \quad (18)
\]

where \(C\) is now the (extrapolated) value of \(\Delta C_p\) at \(T = T_2\). The parameter \(T_2\) is in principle equal to the Fulcher \(T_0\) and Kauzman temperature \(T_k\), but is given a different symbol to emphasize that the putative equivalences need to be established experimentally. The resulting expression for the relaxation time is

\[
\tau(T, T_r) = A \exp \left[ \frac{B}{T(1 - T/T_r)} \right]
\]

(19)

\[
B = \frac{N s^a \Delta \mu}{k_B C}
\]

(20)

where the Adam–Gibbs quantities \(s^a\) and \(\Delta \mu\) are, respectively, the minimum entropy required for rearrangement, and the activation energy for a single rearrangement. Equation (19) will be referred to here as nonlinear Adam–Gibbs (NLAG), although it is sometimes referred to as Scherer–Hodge by some researchers. In the equilibrium state above \(T_\infty\), where \(T(t) = T_\infty\), Eq. (19) yields the Fulcher equation with \(T_\infty = T_2\). Equation (19) also generates very simple relations between its parameters \(B\) and \(T_2\) and the TNM parameters \(x\) and \(\Delta S^2\):

\[
x \approx 1 - T_2 / T_\infty
\]

(21)

\[
h / R \approx B / x^2 \approx B / (1 - T_2 / T_\infty)^2
\]

(22)

obtained from Eq. (19) using the approximation \(T \approx T_r \approx T_\infty\) and elementary calculus. Equations (21) and (22) have proven to be reliable. It must be stressed that NLAG is only a modest
1.4 g cm$^{-3}$, and if $p$ is equated to the anion concentration, then $p$ is given by

$$p = \rho N / M.$$  \hspace{1cm} (20)

In Eq. (20), $\rho$ is the density, $N$ is Avagadro's number, and $M$ is the molecular weight of $f$ pyrrole rings and the counteranion, given by

$$M = f M_p + M_a,$$  \hspace{1cm} (21)

where $M_p$ is the molecular weight of the pyrrole repeat unit and $M_a$ is the formula weight of the anion. Equations (20) and (21) give

$$p = 1.3 \times 10^{22} / (f + m),$$  \hspace{1cm} (22)

where $m = M_a/M_p = 1.69$ and 1.34 for the bisulfate and tetrafluoroborate dopants, respectively. For as-prepared films, $f$ is about 3 and $p$ is calculated to be about $3 \times 10^{21}$ cm$^{-3}$ for both materials. This estimate of $p$ is sufficiently accurate for our needs, since $R$ is insensitive to $p$. As noted in the introduction, $\alpha$ typically lies in the range 0.5 to 1.5 Å$^{-1}$ and $V_0$ is generally of the order 5 to 20 eV. Figure 3 shows the relationship between $\alpha$ and $R$ for values of $V_0$ between 5 and 20 eV, obtained by inserting the experimental values of $A$, $E_a$, and $p$ into Eq. (11). For $\alpha$ between 0.5 and 1.5 Å$^{-1}$, $R$ is estimated to lie in the range 4–12 Å.

These estimated hopping distances are comparable with the average anion separation $p^{-1/3} \approx 7$ Å for oxidized pyrrole ($f = 3$), which suggests that hopping occurs between localized sites associated with the counteranion. Assuming this to be true, the carrier density dependence of conductivity can be calculated in terms of the $R$ dependence given by Eq. (11). Putting $R = p^{1/3}$ in Eq. (11) gives

$$\sigma \sim p^{1/3} \exp[-2\alpha p^{-1/3}).$$  \hspace{1cm} (23)

The functional dependence of $\sigma$ on degree of oxidation ($1/f$), calculated from Eqs. (22) and (23), is displayed in Fig. 4 for $m = 1.4$ and $\alpha = 0.5$ Å$^{-1}$. A rapid increase in conductivity with $p$ is seen at low $1/f$, with a leveling off at higher values of $1/f$. Similar behavior has been reported for O$_2$ doped polypyrroles. 12,18

As noted above the transition probability $I(\Omega)$ is directly proportional to the dielectric loss [Eq. (18)]. It has been shown by Buhks' that the first moment of $I(\Omega)$ is proportional to $E_c$, with a proportionality constant close to unity. Since the first moment is numerically equal to the peak frequency for symmetric peaks, a dielectric loss peak is predicted to occur at about $E_c = 4 \times E_a = 4 \times 0.057 = 0.23$ eV, in good agreement with the observed value of about 0.25 eV. 7 For $E_a = 0.25$ eV, $n = 1.5^8$ and estimated permittivity between 2.8 and 3.7, $R$ is calculated to lie between 5 and 10 Å. This range is in good agreement with that calculated from the conductivity preexponential factor.

The physically reasonable and self-consistent estimates of hopping distance obtained from the activation energy and preexponential factor for conductivity lend strong support to our description of charge transfer in polypyrrole.

Equation (7b) predicts that the energy of maximum dielectric loss should red shift by a factor inversely proportional to the hopping distance. Published spectra7 show a shift in absorptivity from 1 eV for an as-prepared sample to 0.7 eV

FIG. 3. Electron transfer parameter $\alpha$ as a function of hopping distance $R$, calculated from the experimental values of the conductivity preexponential factor and activation energy in Eq. (11), for the indicated range in $V_0$. The shading corresponds to the area constrained by physically reasonable values of $\alpha$ and $V_0$ (see the text).

FIG. 4. Conductivity as a function of degree of oxidation according to Eq. (23) with $\alpha = 0.5$ Å$^{-1}$.
for a sample electrochemically reduced for 30 min at a potential of 2 V. If a degree of oxidation of 0.3 is assumed for the as-prepared film and the shift in absorbity assumed to be the same as the dielectric loss, a degree of oxidation of 0.1 is calculated for the reduced film. The corresponding reduction in intensity of the absorption is calculated from Eqs. (13) and (16) to be of the order 10^{-2} for \( \alpha = 1 \text{ Å}^{-1} \). This is consistent with the published qualitative spectra.

An absorption peak is also seen at about 1.4 eV for the most reduced films, and a shoulder at the same energy appears in the spectrum of the most oxidized film. This energy corresponds to a hopping distance of about 3.6 Å, assuming that the permittivity and refractive index are the same as the oxidized polymer. It is speculated that this absorption reflects a localized ring to ring charge transfer process which significantly contributes to the conductivity only at the highest degrees of oxidation. At lower carrier densities this process would still take place but the long-range conductivity and associated charge transfer absorption would be determined by the less probable longer hops. Also, we note that the calculated hopping distances are comparable with the separation of closely packed chains. Since chain packing is expected to be sensitive to solvent type and other preparation details, interchain hopping may explain the extreme sensitivity of conductivity to solvent reported by Diaz and Hall.

Charge mobilities of about 10^{-1} cm^{2}/V·s are estimated from the experimental values of conductivity, assuming \( \rho = 3 \times 10^{11} \text{ cm}^{-1} \) for the fully oxidized polypyrrole. This value, although typical of inorganic semiconductors, is quite close to the upper mobility limit \( \sim 1 \text{ cm}^{2}/V·s \) observed in molecular crystals and polymers.

From the experimental value of the conductivity preexponential factor \( A \) and the estimated hopping distance of 7 Å, the charge–exchange interaction \( V \) is estimated from Eq. (11) to be about 10^{-2} eV. This value is typical of similarly spaced donor–acceptor pairs in inorganic and biological systems.

It is of interest that the electron transfer rate, \( 1/W \), as calculated from Eq. (2) with \( V = 10^{-2} \text{ eV} \) and \( E_r = 0.25 \text{ eV} \), is very fast (of the order 10^{-11} s). Similarly, fast rates have been observed in biological systems and have been described in terms of activationless processes in which the redox potential of an exothermic electron transfer process is matched by the reorganization energy. However, in the case of polypyrrole the reorganization energy \( E_r \) is smaller than in biological systems (because of weaker electron–phonon interactions), and charge transfer occurs by activated hopping between isoelectronic sites.

If it is assumed that \( \alpha \) and \( V_0 \) are similar for all conducting polymers, we predict maximum conductivities of 10^{2} to 10^{3} Ω^{-1} cm^{-1}. This is observed.

In a recent study of the magnetic properties of polypyrrole no correlation was observed between ESR signals and changes in conductivity with oxidation. This has been interpreted as evidence for spinless charge carriers (bipolars). Since our model is quite general and does not depend on the nature of the charge carrier, bipolarons can be readily introduced into it.

VI. SUMMARY

The charge transfer theory presented here accounts for the temperature dependence and magnitude of conductivity and the near IR optical spectrum of highly doped polypyrrole. The energy of maximum dielectric loss and the conductivity activation energy are shown to be determined by the reorganization energy for charge transfer between localized sites. The magnitude of the conductivity and the reorganization energy give self-consistent estimates of the hopping distance which correspond to the distance between anions. The dependence of conductivity on carrier density is qualitatively reproduced.

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