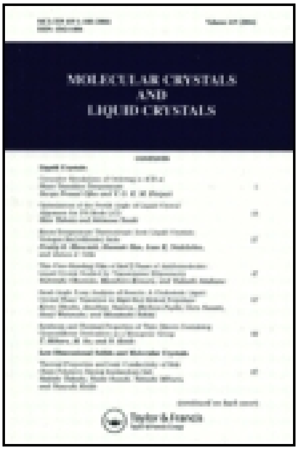

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Defect Generation and Charge Transport in Polyaniline

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Defect Generation and Charge Transport in Polyaniline

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Through analogy with the behavior of polyaniline dimers in solution, it is suggested that the doping of polyaniline by protonic acids is an equilibrium process. The expected equilibrium relation for this reaction successfully predicts the variation of composition of polyaniline as a function of the pH of the doping solution. It is further proposed that in the latter stage of doping the equilibrium population of the insulating undoped chain segments are randomly distributed along chains of the conductive salt form of polyaniline. A model for the conductivity of polyaniline based on these assumptions successfully predicts the temperature dependence of conductivity for both the polymer and the octomer. The model also successfully predicts the variation of conductivity with doping level and fixes a lower limit on the molecular weight of conventionally prepared polyaniline (6,000).

INTRODUCTION

Conducting polymers can be generally characterized as polymeric charge-transfer complexes. These charge-transfer complexes are most often produced via an electron-transfer reaction with an oxidant (p-doping) or a reductant (n-doping) or else via an electrochemical redox process which may be anodic (p-doping) or cathodic (n-doping). A third type of doping process which has only more recently been studied in depth is doping through protonation by non-oxidizing Brønsted acids. Whether doping occurs via charge transfer or via protonation, a conducting polymer results only when the transferred charge can be delocalized along the backbone chain. The conductivity is in fact a sensitive function of the degree of delocalization. In highly conjugated polymers, the spacial extent of delocalization is determined by chain ends or by other defects which interrupt conjugation.

Although protonic acid doping of polyaniline has been the most widely studied,[1–4] most other conjugated polymers are also capable of being doped by strong acids.[5–7] In every case, a proton becomes attached to the chain. When the positive charge becomes delocalized along the chain, the proton remnant is an additional hydrogen atom bonded to the chain. Hence, protonic acid doping invariably affects the chemical structure of the polymer. In polyacetylene, the additional hydrogen will introduce an sp^3 defect which will interrupt conjugation. In poly(2,5-dimethoxyphenylene vinylene), it has been shown that the hydrogen bonds at the 3- or 6-position on the phenyl ring.[5] In this instance, delocalization decreases but conjugation is not completely interrupted, and indeed a relatively high conductivity is observed when this polymer is doped with a Brønsted acid. In polyaniline, the proton attaches at the imine nitrogens, and thereby converts imine backbone segments in polyaniline base to amine segments. When protonation is complete the backbone is fully converted to poly(phenylene amine)[8] which is isomorphic, as a neutral polymer, with poly(phenylene sulfide) and poly(phenylene oxide).[9] All three polymers are characterized by a relatively large band gap which is due in part to the fact that the plane of the phenyl rings is rotated by as much as 45° alternately above and below the plane defined by the 1 and 4 carbons and the heteroatom. A detailed structural study of an oligomer of polyaniline has, however, offered strong evidence that charge transfer to the backbone results in a significant decrease in the angular deviation of the phenyl rings.[8,10] Hence protonation of polyaniline base leads to a backbone structure in which the degree of conjugation is actually increased.

In this paper we will develop a model for the behavior of the conductivity of polyaniline as a function of the degree of protonation starting from the base form, poly(p-phenyleneamineimine), which is also called polyemeraldine (PEM) base. As previously noted, protonic acid doping will affect both the population of charge carriers and the average conjugation length of the resulting polymer. The charge carrier density can be inferred from a previously established equilibrium relation between doping level and pH.[1a,4] The effect of doping induced conjugation length changes can be treated with our recently developed model for the behavior of conductivity as a function of average conjugation length and conjugation length distribution.[11]

DOPING OF POLYANILINE

The base form of polyaniline consists of diamine (A) and diimine (I) units as illustrated below:

$$\{[-(C_6H_4)-NH-(C_6H_4)-NH-]_{1-x}[-(C_6H_4)-N=(C_6H_4)=N-]_x\}_n \quad (1)$$

Studies with solid-state ^{13}C NMR,[12,13] with electron energy loss spectroscopy,[14] and with infrared spectroscopy[10] have previously indicated that this polymer is essentially a regular copolymer of such diamine and diimine units. Although partial reduction in the presence of protons will increase the amount of amine units and partial oxidation of the base form by exposure to air may increase the relative amount of imine units,[15] the polymer as synthesized in acidic media and neutralized by ammonium hydroxide, nevertheless, has a stoichiometry essentially equal to that given in (1) with $x = 0.5$. This particular form of polyaniline is often called polyemeraldine (PEM) base. We will therefore proceed with the assumption that the typical experimental sample of polyaniline base has the structure and stoichiometry of PEM base.

Besides transferring charge to the backbone, protonic acid doping will increase the relative population of amine segments, i.e., decrease x. If we denote the doping level per monomer unit (or per nitrogen) as y, then the new sample-average value of x becomes 0.5-y. Varying degrees of doping are generally produced by allowing the polymer to reach an equilibrium in a doping solution of a given pH. The fact that the doping process is governed by an equilibrium relation has several important consequences.[1a,3,4] The first of which is that it is possible to generate a predictive relationship between pH and doping level.

In a previous work with phenyl-end-capped "dimers" of polyaniline in solution,[4] we demonstrated that a highly reversible relation exists between the concentrations of the amine form (A), N,N′-diphenyl-p-phenylenediamine, the imine form, [I], N,N′-diphenyl-p-phenylenediimine, and the radical cationic form, [CR], as a function of pH, [H⁺]. For the reaction,

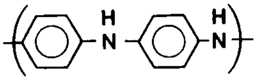
$$A + I + 2H^+ \overset{K_a}{\rightleftharpoons} 2CR \tag{2a}$$

we determined an equilibrium constant $K_a = 10^5\ l^2\ mol^{-2}$ where K_a is given by

$$K_a = [CR]^2/[A][I][H^+]^2. \tag{2b}$$

If we wish to apply these results to polyaniline, we may associate [A], [I], and [CR] with the concentrations of amine, imine, and protonated (polaron containing) polymer chain units, respectively. These structures are illustrated below:

A:



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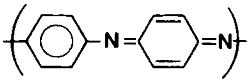

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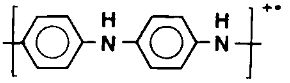

For the polymer, PEM, we should set [A] = [I], i.e., x = 0.5 in Equation (1). We can then calculate the ratio,

$$R = [CR]/[A] = [CR]/[I] = 10^{(0.5\ \mathrm{Log}K_a\text{-}pH} = 10^{(2.5\text{-}pH)}, \tag{3}$$

from which the average doping level per monomer unit is

$$y = R/(2R + 4). \tag{4a}$$

and the sample-average stoichiometry is specified for the doped polymer, in reference to Equation (1), by

$$x = 1/(R + 2). \tag{4b}$$

The predicted doping level for PEM as a function of the pH of the doping solution is shown in Figure 1, and is compared with data taken for PEM doped with HCl.[16] The equilibrium constant, K_a, for the polymer may, of course, be somewhat different from that determined for the oligomer. There has in fact been one previous work which has suggested a considerably different value for the K_a of the polymer.[2] A more recent study[17] of the titration of a suspension of polyaniline powder with NaOH has indicated two inflection points in the titration curve corresponding to pK_a values near 2.5 and 5.5. This study gives evidence of the coexistence of two separate sites in the doped polymer having different acidities. The pK_a values were respectively assigned to protonated amine sites ($-NH^+{}_2-$) and protonated imine sites ($-NH^+-$). Since protonation of the pure amine form of polyaniline ($x = 0$) does not lead to an electronically conductive material, the proportion of the polymer which is conductive is controlled by the equilibrium constant associated with the pK_a value of 5.5, i.e., $K_a = 10^{5.5}\ l^2\ mol^{-2}$ for the doping process defined by Equation (2). This value for K_a is very close to that measured for the dimers in solution. The expected populations of the two types of protonated sites has been calculated by Ray *et al.*[1b] They find that the population, [CR], of protonated imine sites predominate, especially for pH = 2 or less.

Instead of using the value of K_a determined for the dimer as the most representative value for the polymer, one can retain the assumption of an equilibrium doping process and treat K_a as an adjustable parameter to achieve the best fit with the experimental data. In Figure 1, however, the curve calculated for $K_a = 10^5\ l^2\ mol^{-2}$ already produces a good fit to the data for doping level vs. pH, even though this analysis does not incorporate the contribution from protonated amine sites. We can also extend the treatment to some recent Raman spectroscopy results on polyaniline as a function of pH.[18] In this study a line at 1196 cm^{-1} was assigned to the CH bending mode of benzenoid rings and a line at 1169 cm^{-1} was assigned to the same mode for quinoid rings. The intensity of these lines, I_{1196} and I_{1169}, can be related to the concentrations of the various species present at any particular doping level in the polymer. Referring to the formulas for A, I, and CR, one can see that the intensities of the two lines are individually proportional to the repeat unit concentrations as follows: $I_{1169} \sim [I]$ and $I_{1196} \sim 2[A] + [I] + 2[CR]$. The ratio of Raman line intensities can then be given by

$$I_{1169}/I_{1196} \sim 1/(2R + 3). \tag{5}$$

The smooth curve in Figure 2 represents a fit of this equation to the experimental

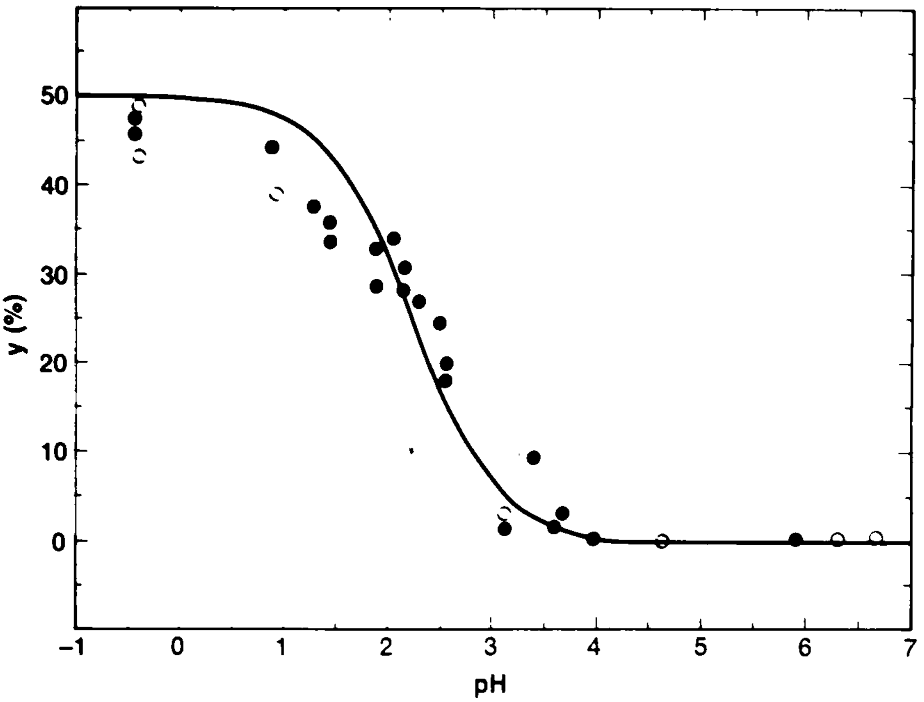

FIGURE 1 Prediction of Equation 4a (solid curve) with $pK_a = 5.0$ compared with the data of reference 16, where two points later determined to be inaccurate in the early data (open circles) have been omitted. (See reference 3b.)

Raman data. This fit was obtained with a value of the equilibrium constant taken to be $K_a = 10^{5.8} = 6.3 \times 10^5\ l^2\ mol^{-2}$. Additional data is also available from electron energy loss spectra taken on the emeraldine salt (PEM chloride).[14] In this case, the ratio of Cl 2p to C 1s absorption edges was plotted as a function of pH of the doping solution. Although there is a great deal of scatter in this data, there is, nevertheless, support for an equilibrium constant near $K_a = 10^5\ l^2\ mol^{-2}$. The value of K_a which appears to best represent all of the data taken for the polymer is $K_a = 10^{5.4}\ l^2\ mol^{-2} = 2.5 \times 10^5\ l^2\ mol^{-2}$.

CONDUCTIVITY IN POLYANILINE

Conductivity is in general a function of the product of charge carrier density and charge carrier mobility. In conductive polymers the charge carrier density is determined by the degree of doping. At low doping levels, the carrier density in most polymers is expected to be roughly equal to the doping level. An exception to the general rule would occur if a significant proportion of the carriers created by the doping were trapped at impurity sites or at any other site in the polymer whose wave functions do not overlap those of the pi-electron system. An example of such an exception would include the protonation of the amine nitrogens in polyaniline.

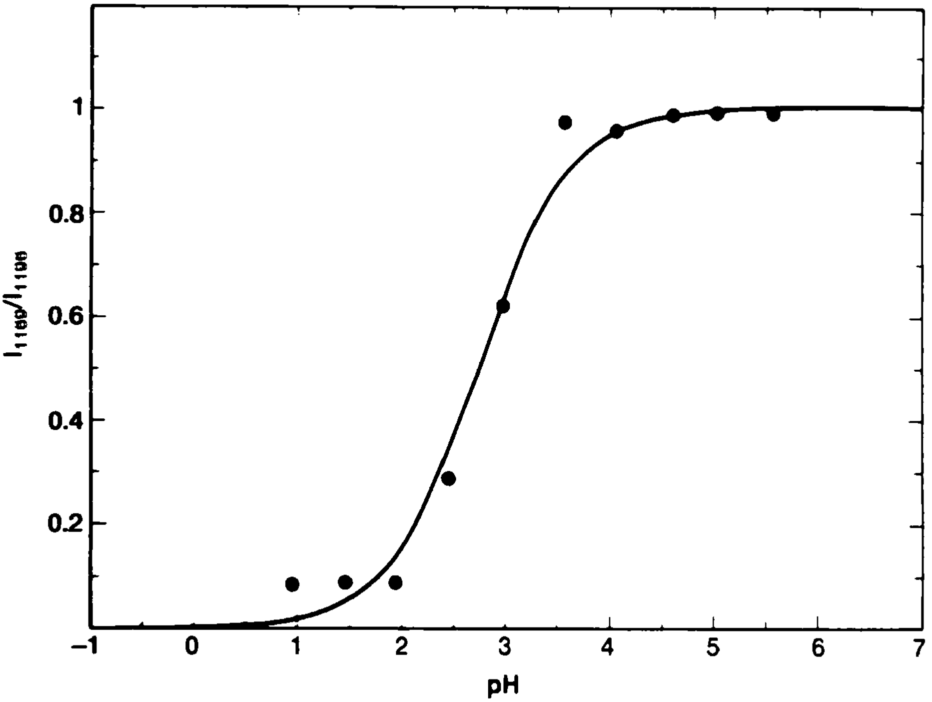

FIGURE 2 Prediction of Equation 5 (solid curve) with $pK_a = 5.8$ compared with the data of reference 18.

At high doping levels the carrier density can depend on the details of the doping-induced changes in the band structure. If the defect bands originally created in the gap overlap with the valence band, or if the gap actually closes, then the carrier density can become essentially equal to the density of pi electrons in the polymer. In the present analysis, we will assume that the carrier population can be represented by the doping level, y.

The actual electronic conductivity obtainable with any real polymer is most strongly dependent on the carrier mobility. Although the observed mobility of charge carriers can be influenced by the one-dimensional electronic band structure of the polymer, the average mobility in real polymeric systems is most heavily influenced by structural defects, disorder, and morphology. Defects which interrupt conjugation length are a particularly important factor in real polymeric materials. Within a particular conjugated segment, conductivity is determined by band structure considerations as outlined above; however, the bulk conductivity of space-filled polymer samples will be predominantly determined by the necessity of hopping between conjugated segments along a chain or between chains.

We have previously developed a model for hopping conductivity in conjugated polymers.[11] In the infinite-conjugation-length limit, carrier mobility will be determined by a combination of band structure (effective mass), electron-phonon scattering, and morphology. Our previous work addresses the behavior of the conductivity in the short-conjugation-length limit,[11a] as well as in the region of transition from short to long conjugation lengths.[11b] With the possible exception of the "new" polyacetylene,[19] conjugated polymers synthesized by the current state of the art fall within the short-conjugation-length limit. Defects which limit conjugation length include chemical defects, conformational defects and chain ends. The model which we have developed and will here apply to polyaniline assumes that chain defects are randomly distributed and that they are short in comparison to the average dimension of uninterrupted conjugated segments. For this work, we will also assume that the conjugation defects represent an infinite barrier to chain-direction transport. Thus, chain-direction transport can only be effected via transverse hopping. Conductivity in the chain direction then depends on the carrier density, the transverse hopping frequency (f), and the average distance that a carrier travels in the chain-axis direction per interchain hop (D_l). The conductivity in the chain direction (σ_l) in the low-field limit can be expressed as

$$\sigma_l = nQfD_l/E_l \sim yfu_zu_w/T, \tag{6}$$

where n is the carrier density, Q is the charge per carrier, E_l is the electric field applied in the chain direction, u_z is the z-average conjugation length, u_w is the weight-average conjugation length, and T is absolute temperature.[11] In the following analysis, we will assume that the conductivity normal to the chain direction is negligible and approximate the average conductivity of unoriented samples by the chain-direction conductivity described above.

The calculation of the hopping frequency assumes that at equilibrium charge is placed on each conjugated segment in a manner which maintains the charge per monomer unit (q/u) as uniform as possible (i.e., as close to the average doping level (y) as possible). A hop of an electron from the ith segment (length, u_i and positive charge, q_i) to the jth segment (length, u_j and charge, q_j) results in a change of energy (E_{ij}) equal to the sum of the ionization potential ($IP(q_i, u_i)$) for the ith segment and the electron affinity ($-IP(q_j - 1, u_j)$) of the jth segment, where IP(q,u) is the ionization potential of a conjugated segment of length, u, containing a positive charge, q. Thus, a distribution of conjugation lengths gives rise to a distribution of hopping energies. The change in energy of a given conjugated segment of length u monomer units in going from j-1 to j charges is given by

$$E = K_2j/u + K_0 \tag{7}$$

This semiemperically derived relation requires that the energy change for the given segment be proportional to the final charge density on that segment (j/u). The constant, K_0, drops out of subsequent calculations, since only the total energy change for electron transfer is relevant. Thus, K_2 is left as the only important experimentally or theoretically derived parameter which relates to the chemical structure of the polymer. The value of K_2 can be estimated from experimental or theoretical data on the variation of band gap, reduction potential, or oxidation potential with conjugation length. Finally, the conjugation length dependence of the hopping frequency can be calculated from the average value of the Arrhenius exponential for the energy change for a hop, where the average value is weighted by using the conjugation length distribution appropriate for the given polymer sample.

Before applying this conductivity model to polyaniline, we must first consider the unusual chemistry of polyaniline doping. As we have seen in the preceding section, the doping of PEM not only generates charge carriers but also produces an alteration of the chemical structure of the backbone. During the latter stages of protonic acid doping, the population of diimine segments (I) will be in a minority in comparison with the population of conjugated polaron containing segments (CR). It is possible to explore the consequences of this dual change in charge level and backbone structure with the conductivity model outlined above, if assumptions can be made that the A + I units are doubly protonated at random and that unprotonated segments represent strong scattering centers for charge carriers.

The question of imine segments functioning as charge scattering centers is readily addressable. Even though such imine segments may be considered conjugated in the sense of having alternating single and double bonds, they represent a very different electronic environment for the delocalization of charge than do reduced segments (A) or protonated segments (CR). Kaplan *et al.*[13] have commented that ^{13}C NMR studies of PEM indicate "that extensive electron delocalization along the backbone does not occur." This point of view is further supported by the observation that photoinduced charged excitations in PEM are "localized and not highly mobile."[20] When PEM is protonated the opportunity arises for producing long, nearly planar[8] conjugated segments with the polaron lattice structure (CR). These structures can be interrupted by diimine segments ($-N = Ph = N-$) or protonated amine segments ($-Ph - NH_2^+$). The abruptly different electronic structure of the diimine segments and the electrostatic interaction of the charge carriers with the localized charge on protonated amine segments will likely make both such defects strongly scattering.

The question of the distribution of conductive segments after protonic acid doping is complicated and to some degree controversial. It has historically been frequently assumed that dopants in conducting polymers are randomly distributed. More recently it has been shown for particular dopants and polymers that doping typically proceeds as a first order process in which phase segregation occurs. The evidence for such phase segregation is particularly compelling for polyacetylene doped with alkali metals.[21] In the case of polyaniline, a tendency toward phase segregation has also been observed for electron-transfer doping (specifically, for electrochemical doping).[10] The lack of a clear isosbestic point, however, suggested that phase segregation was incomplete in this considerably less crystalline polymer. More convincing evidence exists which is consistent with phase segregation of PEM during protonic acid doping, where clear isosbestic points have been observed in UV-Vis optical absorption spectra for pH > ~3.[22,18b] These observations, however, are also consistent with our present assumption that the elimination of transport-blocking diimine segments occurs randomly. A doping reaction for the polymer analogous to reaction 2 for the dimers in solution will produce segments of the conductive protonated form (CR) which are a minimum of 4 or 6 monomer units long, where the value of 6 assumes that once an diimine unit (I) is doubly protonated the conjugation extends into the adjacent diamine unit (A) to provide a $(C_6H_4NH)_6$

sequence. At low doping levels (high pH) and for a random distribution of doped conjugated segments, one expects to observe one or more clear isosbestic points just as for the oligomers in solution.[10] When the pH becomes low enough for the production of a significant population of conjugated segments longer than 6, a shift in the absorption spectra away from the previously established isosbestic point(s) will occur only if the longer conjugated segments are spectroscopically distinguishable from the 6-unit conjugated segments. Such a shift is in fact observed in the data cited above[22,18b] when the pH of the doping solution is less than about 2. Another more subtle point is that the size of any proposed metallic islands in a segregated-phase polymer is limited by the fact that the doping process illustrated in Figures 1 and 2 is evidently well described by an equilibrium relation (as in reaction 2). The establishment of such an equilibrium requires a co-mingling of the components, A, I, and CR, on a molecular scale.

A proposal for a granular-metal model for polyaniline[23] has been made on the basis of magnetic susceptibility data. The observation of a steadily increasing Pauli susceptibility with increasing protonation starting at very low levels of protonation suggests the appearance of a phase which contains unpaired spins (e.g., polarons) at the very beginning of the doping process. This conductive phase then grows at the expense of the insulating phase in rough proportion to the doping level. As with the appearance of isosbestic points in the optical spectra of polyaniline, the observation of Pauli spin does not necessarily imply the segregation of the polymer into a discrete domain structure. The observation requires the creation of conjugated segments which are large enough to allow the disassociation of bipolarons into polarons. Studies of oligomers have shown that while a tetramer of polyaniline supports only bipolarons,[10] an octomer does support polarons and produces a magnetic susceptibility similar to that of the polymer.[24] Thus, the observation of a Pauli susceptibility rigorously implies only the formation of charged conjugated backbone segments having a conjugation length equal to or longer than 6 or 8 monomer repeat units. These conjugated segments may or may not be preferentially segregated into metallic domains. Moreover, Nechtschein *et al.* have concluded from the spin dynamics behavior of polyaniline that the "metallic islands" in polyaniline consist of fully protonated *single* chains.[25] This idea is, of course, completely consistent with our hypothesis.

The difference in the proposed models is largely one of scale, that is, whether metallic regions are segregated within single chains or within domains consisting of many metallic chains. Although it is difficult to fully determine the scale of the discrete metallic phase, it is reasonable to proceed with the application of the present conductivity model and judge its applicability by the quality of fit to the experimental data. We must first determine the appropriate value of K_2 for polyaniline. The available data consists of estimates of the variation of band gap with molecular length for oligomers of polyaniline taken from theoretical calculations[26] and optical measurements on the dimer[4] and the octomer.[25b] The calculations for a dimer and a trimer of polyaniline suggest $K_2 = 1.5$ eV, while the optical band gap data suggest $K_2 = 1.26$ eV neglecting delocalization into end groups and $K_2 = 1.9$ eV including end groups. These data suggest that an appropriate value for polyaniline would be $K_2 = 1.54$ eV, although there is considerable uncertainty in this estimate. This value of K_2 and the assumption of a random distribution of protonated A + I units can be used to calculate the appropriate hopping frequency for polyaniline.

Central to the proposed model is the idea that conjugation length is a function of doping level and pH. We define u_n as the number-average conjugation length measured in terms of A + I repeat units which are doubly protonated. The probability which governs this random distribution is $p = 1 - 1/u_n$, where the random distribution function is given by

$$W(u) = (1 - p)^2 u p^{u-1}. \tag{8}$$

The probability, p, is related to the doping level, y, according to $p = 2y$ and to the ratio, R, through Equation (4a). We must also consider an upper limit of conjugation length, which will be determined either by finite chain length or by an inherent defect concentration. We can generalize the concept of defects to include chain ends and other defects, in addition to diimine groups, which interrupt conjugation. If we define the relative concentration of such defects to be $d = [D]/([A] + [I] + [CR])$, then the probability can be written as

$$p = 2y(1 - d). \tag{9}$$

The number-average conjugation length in terms of doubly protonated A + I units is then given by:

$$u_n = 1/(1 - 2y + 2yd), \tag{10}$$

from which it follows that the maximum average conjugation length equals $1/d$ when $y = 0.5$. We consider herein two different measures of conjugation length: conjugation length measured in terms of the number of doubly protonated A + I units (u), which provides the basis for the probability analysis, and conjugation lengths measured in terms of the number of monomer ($-$Ph $-$ NH$-$) units in an uninterrupted sequence (L), which is the relevant length for the analysis of hopping energy and average chain-direction translation per hop. If we employ the assumption that charge will be delocalized over all directly coupled amine units ($-$Ph $-$ NH$-$) in any particular chain segment, then the number of monomer repeat units will become, $L = 4u + 2$, where u is the number of doubly protonated A + I units in that segment. The average conjugation lengths can be computed in terms of the number of monomer units for a random distribution of A + I units from the relations:

$$L = \left(\sum_{u=1}^{\infty} (4u + 2)^a W(u)\right) \Big/ \left(\sum_{u=1}^{\infty} (4u + 2)^{a-1} W(u)\right), \tag{11}$$

where $L = L_n$ (number average) when $a = 0$, $L = L_w$ (weight average) when $a = 1$, and $L = L_z$ (z average) when $a = 2$. These conjugation lengths are a function of the doping level and ultimately of the pH of the doping solution in which the PEM base was equilibrated. Taking the pK_a for the formation of doped chain segments as 5.4, one obtains

$$pH = 2.7 - \log(R), \tag{12}$$

where from Equation (4a), $R = 4y/(1 - 2y)$.

There is a minimum doping level below which the polymer will be either phase segregated or the charged conjugated segments will be widely separated by long conjugation interrupting segments. This minimum doping level relates to the doping concentration necessary for there to be a sufficient probability for neighboring conductive chain segments to overlap to an extent necessary for the existence of a critical percolation path through the sample. In either case above, the assumptions of the present model will begin to break down as the doping level declines below about 0.25.

In order to predict the conductivity of polyaniline as a function of doping level and temperature from Equation (6), we must finally calculate the carrier hopping frequency relative to the infinite conjugation length limit, $f/f(\infty)$. The interchain hopping frequency for a carrier hop between conjugated segments containing u and u′ A + I units, respectively, is reduced from the infinite-conjugation-length value by a factor of $\exp(-E_h/k_BT)$, where E_h is the net energy change of the hop. The monomer lengths corresponding to u and u′ are $4u + 2$ and $4u' + 2$, respectively, and the $T = 0$ values of charge on respective segments are 2u and 2u′. From Equation (7), E_h is $K_2/(4u + 2)$. Since the fraction of the total charge, F(u), on conjugation lengths containing u doubly protonated A + I units is

$$F(u) = (2u/(4u + 2))W(u)/\sum_{u=1}^{\infty} (2u/(4u + 2))W(u),$$

the relative hopping frequency at finite conjugation length is given by

$$f/f(\infty) = \sum_{u=1}^{\infty} F(u)\exp[-K_2/(4u + 2)k_BT]. \tag{13}$$

This equation uses the $T = 0$ distribution of charge to evaluate the hopping energy E_h. The weighting factor, F(u), for a given conjugation length, u, is the fraction of charges on that conjugation length at $T = 0$.

If we assume that, once the doping level has exceeded about 0.25, the major factor in determining the conductivity is the conjugation length, then the variation of conductivity with pH of the doping solution can be found from Equations (4a), (6), (8), (9), (11), (12) and (13), where L_w and L_z are appropriately used in place of u_w and u_z in Equation (6). The present model is fitted to the available conductivity data as a function of pH in Figure 3. The model predicts the variation of conductivity to within a constant multiplicative factor; thus, the theoretical curve (dashed line) is displaced by a constant value along the vertical axis representing the log of

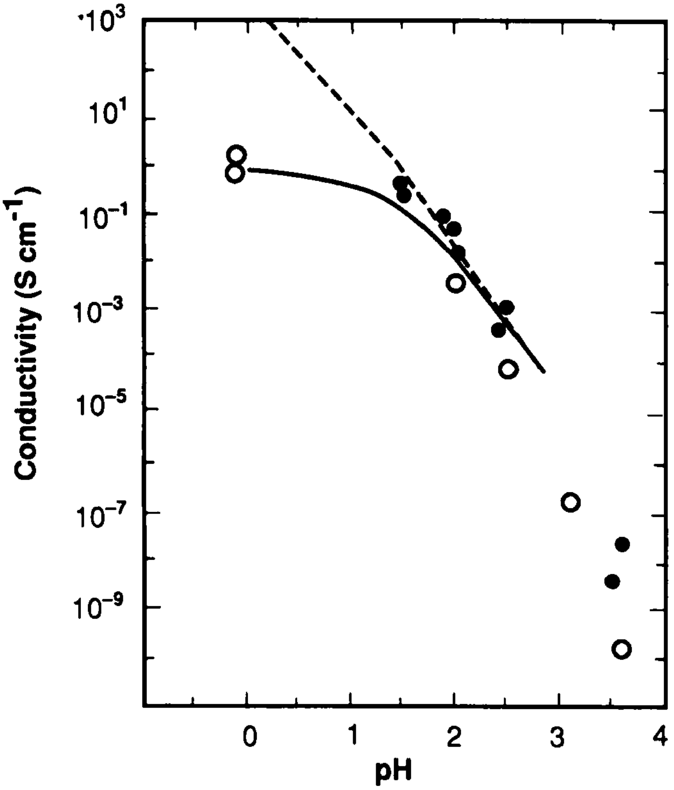

FIGURE 3 Conductivity as a function of pH is predicted (dotted curve) for a polyaniline sample in which conjugation length is limited by a random distribution of diimine segments only. The solid curve assumes a population of inherent defects (d = 0.125) to obtain a best fit to the data of references 1a (open circles) and 1b (filled circles).

conductivity. The theoretical curve extends from a number average conjugation length (L_n) of about 8 to about 600. When this model was previously applied to the doped conducting polymers, polyacetylene and poly(p-phenylene),[11] it was found that the available experimental data fit the theoretical curve well over the entire range of the data. The region of fit suggested that the experimental polymer samples were all well within the short chain limit, and thus significant further increases in conductivity could be expected from further increases in average conjugation length. A similar expectation would also apply to polyaniline. The model curve (dashed line) illustrates the increases which are possible if the sole conjugation limiting defect is determined by the doping level alone. Since the experimental data saturate prematurely, there evidently exists a source of inherent defects which limit conjugation length. An estimate of the concentration of these inherent defects (d) can be made by adjusting the value of d in Equation (9) to obtain a good fit over the entire range of experimental data. The solid curve in Figure 3 illustrates the fit obtained when d = 0.125 (i.e., when $(u_n)_{max} = 8$ or $L_n = 36$).

It is perhaps more pertinent to examine the behavior of the conductivity directly as a function of doping level. There have been reports of the observation of hysteresis in y as a function of pH between doping and undoping,[25] which may place limitations on the use of Equation (12) and suggests that it is important to determine y directly. In Figure 4, we present data for the conductivity of polyaniline samples fabricated from powders equilibrated in various concentrations of HCl. The open circles are data of Travers *et al.*[27] which were obtained by directly measuring y by chemical analysis. The filled circles are the conductivity vs. pH data of reference 1a which we have adjusted to fit the data of Travers *et al.* by introducing an assumed constant deviation of pH below that of the doping solution. This deviation is actually very small (-0.2) for this data which was obtained for doping rather than undoping. The actual doping level was estimated from Equation (4) and the relation $R = 10^{(2.7\text{-pH-}0.2)}$. We should note that this correction is equivalent to assuming a $pK_a = 5.0$, which in fact is the conclusion of Figure 1. Superimposed on the data points in Figure 4 are the theoretical behavior of the conductivity for inherent defect concentrations of $d = 0, 0.125$, and 0.25. The correspondence between theory and experiment is again the best for an assumed defect concentration of $d = 0.125$ (middle curve in Figure 4). The theory predicts that the conductivity of samples having a low inherent defect concentration should grow rapidly as the concentration of extrinsic defects (unprotonated diimine units) decreases to zero at a doping level

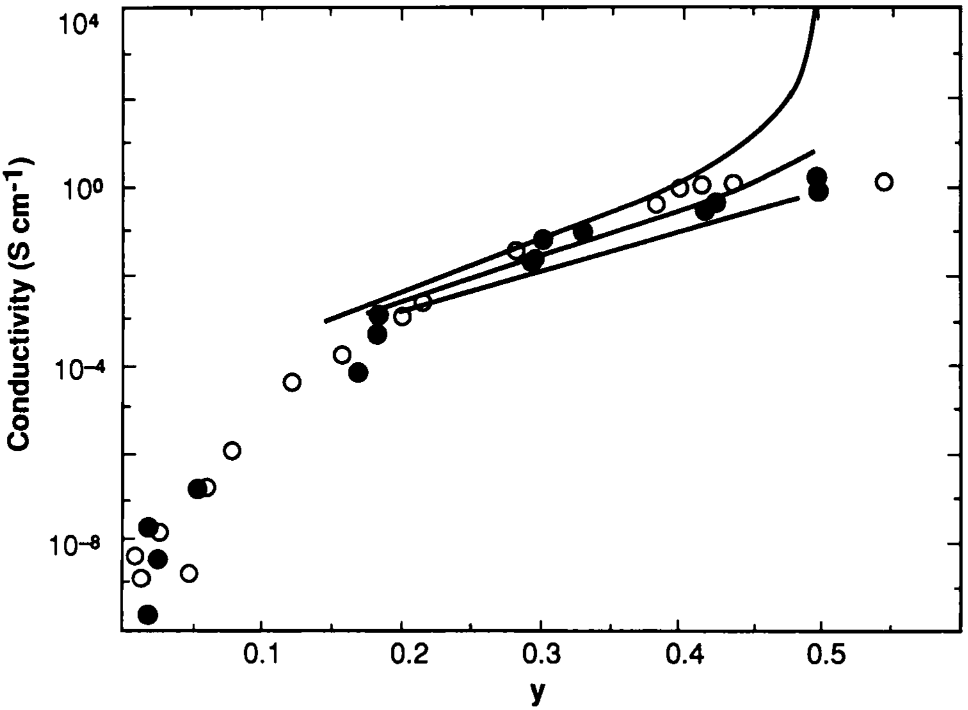

FIGURE 4 Conductivity as a function of y is predicted for polyaniline with assumed inherent defect concentrations of $d = 0$ (top curve), $d = 0.125$ (middle curve), and $d = 0.25$ (bottom curve). Comparison is made to the experimental data of references 1 (filled circles) and 27 (open circles).

of $y = 0.5$. The fact that the experimental data do not reflect this divergence in the conductivity suggests either a rather high inherent defect concentration or a difficulty in actually achieving a doping level close to 0.5.

If the inherent defect concentration is taken to be solely due to chain ends, then the number-average chain length is about 36 monomer units, and the weight-average is 62 units (Equation (11)). With this assumption, the weight-average molecular weight for the polyaniline used in the referenced studies would be about 6000. This projected minimum molecular weight compares favorably with those obtained from a study of the viscosity of polyaniline solutions in sulfuric acid: 12,000 for a rigid chain limit and 40,000 for a flexible chain limit.[28] The present model then predicts that a significant increase in conductivity following the dotted-line theoretical curve in Figure 3 or the upper line of Figure 4 could be obtained with linear polymer of enhanced molecular weight doped at low pH. Some additional concern would exist, however, over the environmental stability of this lower pH composition.

The next important aspect of the model which we will consider is its predictions for the variation of conductivity with temperature. The temperature dependence of the conductivity comes through the temperature dependence of the hopping frequency. We have previously shown[11] that the relative hopping frequency, $f/f(\infty)$ where $f(\infty)$ is the frequency in the infinite chain limit, could be expressed for polydispersed conjugation length distributions and fixed dopant level as a universal function of K_2/k_BTu_w, where k_B is Boltzmann's constant and T is absolute temperature. This function has the approximate form,

$$f/f(\infty) \sim \exp(-(T_o/T)^a) \qquad (14)$$

with $T_o = K_2/k_Bu_w$. For the present study, we found that the result obtained with varying L more closely follows that with varying T if we used $K_2/kT(L_wL_z)^{1/2}$ as the independent variable. In this case we find that $a = 0.71$ when the calculated data are plotted for fixed T and varying L_w and L_z. The temperature dependence of the conductivity which arises predominantly from that of $f/f(\infty)$, can be expressed as

$$\sigma = \sigma_o\exp(-(T_o/T)^a) \qquad (15)$$

where

$$T_o \sim K_2/k_B(L_wL_z)^{1/2}$$

and

$$\sigma_o \sim f(\infty)L_wL_z/T$$

This expression for the present theory which allows nearest neighbor hopping between states having a distribution of energies is very similar to Mott's expression for variable-range-hopping (VRH). When Mott assumes a constant density of states within k_BT of the Fermi level, he obtains an exponent of ⅓ for two dimensional VRH and an exponent of ¼ for three dimensional VRH. There is also a temperature dependence in the prefactor, σ_o, which is not well established by either Mott's theory or the present one. Calculation with Mott's theory leads to a prefactor which varies as $T^{-1/2}$, but alternate treatments of VRH lead to other prefactors.[29] The present theory appears to indicate $\sigma_o \sim T^{-1}$, but there is a hidden and unspecified temperature dependence in $f(\infty)$. In the following we will assume the temperature dependence in the prefactor to be dominated by that in the exponential.

This universal relation is only an approximation and we have found that it is in fact desirable to calculate $f/f(\infty)$ directly as a function of temperature from Equation (13) for a range of doping levels and inherent defect concentrations. The results of such a set of calculations with an assumed defect concentration of $d = 0.125$ is presented in Table I. The predicted temperature dependence as embodied in the calculated values for the exponent (a) and T_o is, as expected, a function of doping level, y. The theoretical value of (a) is obtained from the value which produces a linear plot of Equation (14) as $\ln[f/f(\infty)]$ vs $(1/T)^a$, and the value of T_o is obtained from the slope of this plot. The average value of the exponent for the range of doping levels considered can be approximated as $a = 0.6$.

Zuo *et al.*[23a] have obtained conductivity data for polyaniline films cast from acetic acid solution and doped to various levels of protonation with HCl. They have fit these data to a granular-metal model which assumes charging-energy-limited tunneling between metallic grains,[23] and which predicts a temperature dependence as in Equation (15) with an exponent of ½. In Figure 5, we have fit these same data to our Equation (15) with an exponent of 0.6 as is found above for the assumption of a random distribution of A + I conjugation lengths. The agreement between the data and the predicted temperature dependence is quite good, even for the sample with a doping level of $y = 0.13$, which falls outside the range where the theory is fully applicable. It is also possible to extract the value of T_o from the slopes of the curves in Figure 5. To improve the accuracy of the estimate we have in fact calculated the slope for the conductivity of each sample plotted vs. $(1/T)^a$ with a value of (a) appropriate to the given doping level (Table I). The resulting experimental T_o values are compared with those predicted by the theory in Table

TABLE I

Thermal Behavior of Polyaniline with $d = 0.125$

U_n	L_w	L_z	y	Exponent (a)	To (theory) (K)	To (exp't) (K)
1.294	8.35	9.81	0.13	0.565	9330	11450
1.414	9.31	11.3	0.167	0.569	7460	—
1.626	11	14.0	0.22	0.575	5510	4390
2	14	18.6	0.2857	0.584	3850	—
3	22	30.7	0.381	0.600	1940	2440
4	30	42.8	0.4286	0.614	1260	—
5	38	54.8	0.4571	0.625	920	—
6	46	66.9	0.4762	0.634	730	1830
7	54	78.9	0.4898	0.642	590	—

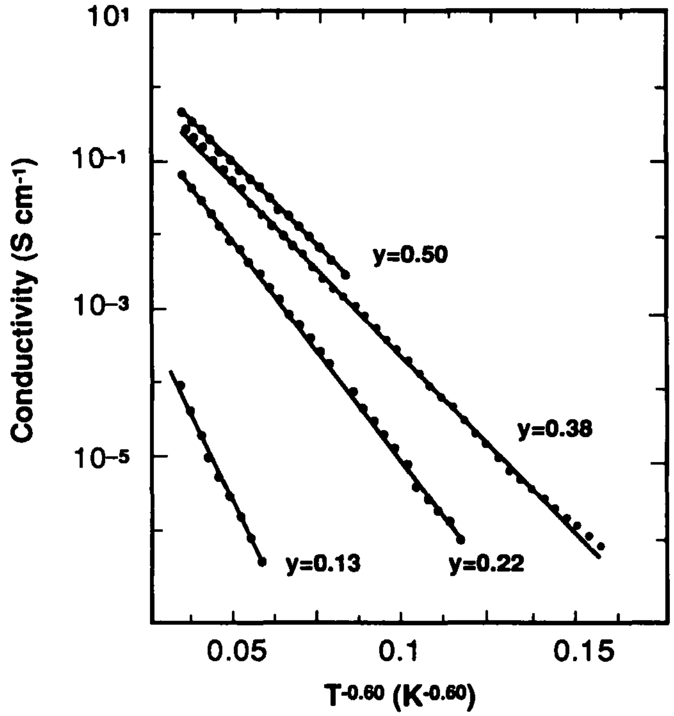

FIGURE 5 Conductivity data of reference 23 are plotted vs $T^{-0.6}$ as suggested by Equation 15 and Table I. The solid lines represent a linear least-squares fit to the data.

I and in Figure 6. Even though no adjustable parameters are employed, the theoretical values of T_0 closely follow the measured values. The experimental values of T_0, however, saturate at a relatively high value as y approaches 0.5, where the theory predicts that T_0 in the absence of inherent defects should approach zero. The experimental value of T_0 for the sample with y near 0.5 is not well described by the theoretical curve which assumes an inherent defect concentration of d = 0.125. This deviation may suggest that the actual defect concentration is higher than we have assumed, but it more likely suggests that the actual doping level is less than we have assumed. Note that in Table I we have already taken the liberty of assuming a slightly lower doping level (0.475) than the nominal value of y = 0.5 specified by Zuo *et al.* It is possible that these polyaniline samples possess a high concentration of inherent defects (e.g., chain ends), since only the lower molecular weight fraction of polyaniline is soluble in the acetic acid from which these films were cast. Finally, the measured conductivities of the Zuo *et al.* samples could be additionally influenced by morphology and intergranular resistances.

The value of (a) found for the temperature exponential in Equation (14) is characteristic of the nature of the distribution of conjugation lengths. The polydispersity of the distribution affects the value of the exponent such that distributions having a lower polydispersity have a higher value and vice versa for distributions

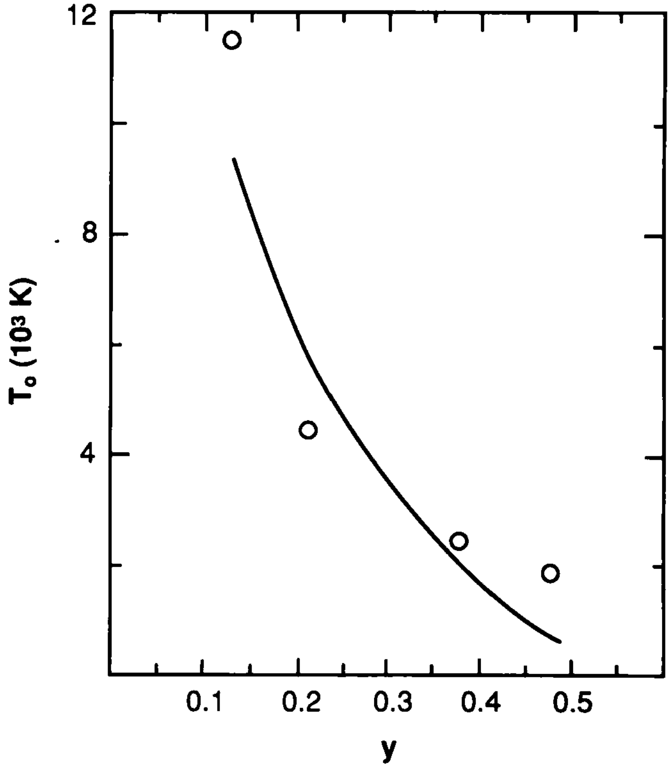

FIGURE 6 Predicted values of T_o for d = 0.125 (smooth curve) are compared with the values obtained for the data of reference 23 plotted according to $(1/T)^a$ with (a) taken from Table I.

having greater polydispersity. In the limit of a monodisperse distribution, the exponent is 1:

$$\sigma = \sigma_0 \exp(-(T_o/T)) \qquad (16)$$

where

$$T_o = K_2/2k_B u$$

$$\sigma_o \sim f(\infty)L^2/T$$

Equation (16) is derived quite easily from Equations (6) and (7) by evaluating $f/f(\infty)$ for the case of a monodisperse distribution in which all conjugated segments have identical charges at $T = 0$. At temperatures such that $K_2/2k_B u \gg T$, the fraction of conjugated segments having one excess charge is $\exp[-K_2/2uk_B T]$, which also equals the fraction of conjugated segments having a charge deficiency. The energy term in the exponential is one half of the total energy change calculated from Equation (7) upon transferring a charge carrier between two conjugated segments originally having an equal number of charges. The dominant modes of carrier transport are hopping from segments containing q charges to segments with q-1 charges and hopping from segments with q + 1 charges to segments with q charges. Since both of these processes are isoenergetic, $f/f(\infty)$ is proportional to the fraction of conjugated segments having a charge excess or deficiency, that is, proportional to $\exp[-K_2/2uk_BT]$. Equation (16) follows from using this result in Equation (6). In a previous paper we assumed a charge distribution equal to that at $T = 0$, an assumption which resulted in a predicted T_o which was double that given here in Equation (16).

The influence of the form of the conjugation length distribution can be tested by reference to data on the conductivity of an octomer of polyaniline,[24] which was composed of 8 amine linkages between 9 phenyl rings in its fully reduced state. In this case the conjugation lengths in a highly doped sample are expected to be nearly monodisperse at the value of $u = 8$ (assuming that end groups partially participate). As can be seen from Figure 7, the data for the octomer well fits the temperature dependence predicted by Equation (16). The data also taken by these authors on polyaniline prepared in the conventional manner would show a curvature in this plot, but does follow a linear relation when plotted as in Figure 5. Even more

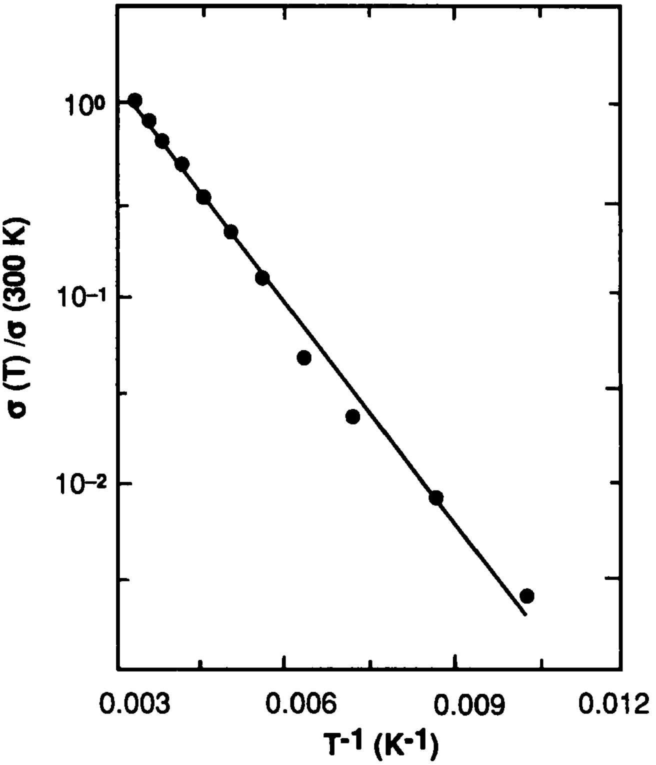

FIGURE 7 Conductivity data of reference 24 for an octomer of polyaniline are plotted according to the relation predicted for a monodisperse distribution of conjugation lengths (Equation (16)).

convincing is the fact that in the case of the octomer, where there is much less uncertainty in the nature of the conjugation length distribution, the predicted value of T_0 (1100 K) agrees quite well with the experimental value from Figure 6 (875 K). If we use the pre-exponential temperature dependence of 1/T suggested by Equation (16), then we obtain an even closer value of 1040 K.

CONCLUSIONS

We have shown that the doping of the emeraldine base form of polyaniline (PEM) by Brønsted acids is largely regulated by an equilibrium relation which requires that at any given pH the concentration of diamine, diimine, and doped (cation radical) segments be a function of the initial composition (x) and the pH. The doping behavior of polyaniline appears to closely follow that of short-chain oligomers in solution. This similarity is expected to hold particularly well for the amorphous sections of the polymer (which are frequently the predominant fraction). More highly crystalline forms may exhibit deviations from this behavior. The observations of hysteresis in the doping[25] may be explained by slow diffusion of the acid or may be the result of first-order doping kinetics for the crystalline regions.

The presently proposed model requires the coexistence of doped and undoped polymer. In contrast to the granular metal model, the present model suggests that the two phases are distributed on a molecular scale. In this case the undoped (diimine) segments are distributed along the polymer chains and constitute conjugation blocking defects. These defects control the conductivity in the bulk of the polymer sample by forcing charge carriers to hop to neighboring chains. Although only nearest neighbor hopping is considered, the assumed distribution of hopping energies (resulting from the distribution of conjugation lengths) produces a predicted temperature dependence of conductivity which is similar to that predicted for variable range hopping. The experimental data for polydisperse and monodisperse conjugation lengths indeed follows the respective predicted temperature dependence for each distribution. Indeed, there is remarkably good agreement between the predicted values for parameters which control the temperature dependence of the conductivity, exponent (a) and T_0, and the experimental values. The model also successfully predicts the variation of room-temperature conductivity with pH and with doping level. The model in combination with the experimental data suggests that the conductivity of polyaniline as prepared in the current state of the art is limited by inherent defects. The analysis suggests that the weight-average molecular weight of polyaniline is greater than about 6,000.

In summary, the present model offers an alternative view of polyaniline which is entirely consistent with the available data. The model does not treat the effects of morphology or of crystalline domain structure, which can make important contributions to the resistivity of bulk samples. Because it is not possible to readily separate the various contributions to the resistivity, we have compared data taken on bulk samples (pressed powders or solution deposited films) to the predictions of the theory. Conductivity measurements on better samples (e.g., space-filled highly oriented fibers) would provide a much better test of the model.

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