

Conductivity as a function of conjugation length: Theory and experiment for conducting polymer complexes

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The dependence of electronic conductivity upon the length (L) of conjugated segments is calculated for conducting polymers for which (1) interruptions in conjugation on neighboring chains are uncorrelated, (2) all chains are equivalent, and (3) intersegment hopping controls chain-direction conductivity. If interchain carrier hopping dominates, the calculated ratio of conductivities parallel (σ_1) and perpendicular (σ_2) to the chain is $\sigma_1/\sigma_2 = L^2/6d^2F$, where d is the interchain separation in the hopping direction and F is a geometric factor which is near unity for directions in which σ_2 is maximum. If intrachain hopping between conjugated segments dominates transport, then this calculated anisotropy ratio is linearly proportional to conjugation length. Derived temperature, pressure, dopant level, and electric field dependencies for the anisotropy ratio are generally near zero only for the case where interchain hopping dominates both σ_1 and σ_2 . The calculated dependence of conductivity on conjugation length is in good agreement with observations for iodine-doped polyacetylene, potassium-doped poly(*p*-phenylene), and iodine-doped polythiophene. Relationships are derived between the conjugation length and the temperature dependencies of conductivity components, which are also supported by experimental results. For conducting polymers having short conjugation lengths, conductivity is predicted to be approximately proportional to $\exp[-(T/T_0)]^{-1/3}$, where T_0 is inversely proportional to conjugation length. This expression, which can also be obtained for variable-range hopping, is here derived for nearest-neighbor hopping with a distribution of activation energies stemming from a distribution of conjugation lengths.

I. INTRODUCTION

From the viewpoint of charge transport, two extreme situations exist for highly conducting organic polymers.¹ In the first extreme is a polymer where charge carriers are localized on short conjugation lengths and carrier transport in all directions is limited by interchain hopping. This extreme is analogous to the case of molecular charge-transfer complexes where intermolecular charge transport is responsible for conductivity in all directions. In the second extreme is a polymer with effectively infinite conjugation lengths [such as an idealized crystal of poly(*p*-phenylene) or polyacetylene], where the chain-direction conductivity is limited by intramolecular carrier mobility and orthogonal conductivities are limited by intermolecular hopping rates.

We can go between these extremes for a polymer such as poly(*p*-phenylene) or polyacetylene by increasing chain conjugation length from short lengths to effectively infinite lengths. Two time scales are relevant here. The first is t_r , the time required for relaxation of the charge-carrier distribution within a particular conjugation length after a carrier hop. The second is the time between hops involving this particular chain segment, t_h . In the long-conjugation-length limit $t_r \gg t_h$, which is a requirement for conductivities to be independent of conjugation length. In the short-conjugation-length limit, $t_r \ll t_h$, and transport is strongly dependent upon conjugation length. An additional requirement for the long-conjugation-length limit is that the overall energy change resulting from an electron hop is much less than $k_B T$.

This requirement means that the conjugation length is sufficiently long that the ionization potential (or electron affinity) varies by less than $k_B T$ in going from this conjugation length to an infinite conjugation length.

The available experimental data for highly conducting doped complexes of polyacetylene, poly(*p*-phenylene), and polythiophene²⁻¹⁶ indicate that limited conjugation lengths can dramatically reduce conductivities. There are uncertainties in the interpretation of these data, especially for polyacetylene, because of possible nonrandom introduction of breaks in conjugation length and the difficulty of reliably establishing the average conjugation length.^{11,17-24} Nevertheless, the experimentally observed conductivities at fixed dopant levels and fixed temperature for unoriented conducting polymers are consistent with $\sigma = AL^m$, where A and m are constants and L is the average conjugation length.^{2-5,9,10,16} For doped polyacetylene and doped poly(*p*-phenylene), experimentally determined values of m range from about 3.2 to 3.5.²⁻⁴

We will here derive the effect of conjugation length upon electrical conductivity and its anisotropy for conducting polymers consisting of parallel polymer chains. The conjugated chain length may extend over the entire chain or only over segments of the chain. The defects separating coaxial conjugated segments are herein referred to as chain blocks. Section II considers the case where these chain blocks provide sufficiently high barriers for carrier transport that macroscopic conductivity is determined by the interchain hopping rate. Section III considers the case where the chain blocks provide barriers which are transmissive, so that interchain charge

transport need not limit macroscopic carrier motion in the chain direction. Section IV analyzes the dependence of carrier hopping rates on conjugation length. Section V derives relationships between the dependence of conductivity on conjugation length and on temperature, which are a consequence of conclusions from Sec. IV. Section VI generalizes the theoretical results to polymers containing chain blocks (defects) which interrupt conjugation to different degrees. Finally, Sec. VII compares experimental results with the predictions of this theory.

The chain blocks can be either composed of the region between chain ends or defects which limit conjugation within a long polymer chain. The relationship between blocking elements on neighboring chains is expected to be random for polymers which have sufficiently high molecular weight and/or dispersion in molecular weight. If the polymer molecules have very low molecular weight and are monodispersed in molecular weight, the chain ends can be segregated into layers. The present analysis is restricted to the opposite case where the relative location of chain blocks on neighboring chains is random. The case where the locations of chain blocks on neighboring chains are ordered is dealt with elsewhere.²⁵ Also, except for differences in conjugation length (dealt with in Sec. IV) and differences in the chain-direction position of neighboring conjugated segments, all conjugated segments are assumed to be in structurally equivalent environments. This means that the analysis must be modified in order to deal with phases having low dopant concentration, for which all chains are not equivalent.

The effect of conjugation length on hopping frequency depends upon the effect of conjugation length on the ionization potential and electron affinity of the polymer. In fact, one convenient definition of conjugation length is the length of defect-free oligomer which reproduces the weight-average first ionization potential and electron affinity of the polymer. Complications due to the existence of defects which interrupt conjugation less efficiently than chain ends are analyzed in Sec. VI.

The present calculations directly pertain to compositions for which interfacial resistances (interfibril, intercrystallite, or intergrain resistances) are negligible. Whether or not this is true, the predicted properties of chain-oriented domains are key for predicting the properties of the bulk material. As long as there is a unique chain-axis direction in microdomains, the applicability of the theory does not require that these microdomains be three-dimensionally-ordered crystallites.

II. ELECTRICAL ANISOTROPY FOR POLYMER CHAINS WITH NONTRANSMISSIVE BLOCKS

The electrical conductivity is given by

$$\sigma_i = qf_2 D_i / E_i, \quad (1)$$

where the subscript i defines the direction ($i = 1$ for parallel to the chain and $i = 2$ for perpendicular to the chain), q is the charge per carrier, f_2 is the number of interchain carrier hops per unit volume and per unit time, and D_i is the average distance a carrier moves in the i th direction as a result of a hop under the influence of the applied

electric field (E_i) in the i th direction. Interchain hops can be approximated to be perpendicular to the chain-axis direction. Nevertheless, D_1 (the average chain-direction displacement per hop) is nonzero if E_1 (the chain-direction electric field) is nonzero. This is because charge redistribution on the "hopped-from" and the "hopped-to" segments after an interchain hop results in a net carrier displacement corresponding to the center-to-center displacement of these segments.

The polymer chain is modeled by alternating conjugated segments (length L) and conjugation blocking elements (length B), where $B \ll L$. In the finite-chain limit the potential drop is approximated to be entirely across the chain blocks, so that each chain segment is equipotential. Consequently, the potential difference between hopped-to and hopped-from segments as a result of the chain-direction applied field (E_1) depends upon the relative displacement of these segments in the chain-axis direction (Z). If the hopped-to segment is down-field of the hopped-from segment (i.e., $Z > 0$), then this potential difference can be taken to be $E_1 L$. On the other hand, if the hopped-to segment is up-field of the hopped-from segment (i.e., $Z < 0$), then this potential difference can be taken to be zero. Although the difference in potential of hopped-from and hopped-to chains depends upon boundary conditions in a chain, the critical point for the analysis is that the difference in potential of up-field and down-field hopped-to segments in a chain is $E_1 L$.

Using these potential differences, the average distance that a carrier moves in the chain-axis direction per interchain hop is as follows:

$$D_1 = \frac{\int_{Z=-L}^{Z=L} \int_{X=\epsilon(Z)}^{X=L-\epsilon(-Z)} Z e^{E_1 q L \epsilon(Z) / 2Z k_B T} dX dZ}{\int_{Z=-L}^{Z=L} \int_{X=\epsilon(Z)}^{X=L-\epsilon(-Z)} e^{E_1 q L \epsilon(Z) / 2Z k_B T} dX dZ}, \quad (2)$$

where q is the charge per carrier, ϵ is a function equal to its argument for positive argument and zero otherwise, and Z is the chain-axis displacement in the electric-field direction of the hopped-to chain segment with respect to the hopped-from chain segment. The factor in the exponential is just the electric-field-dependent component of the activation energy for interchain hopping, normalized by the Boltzmann factor $k_B T$ (i.e., $E_1 q L / 2k_B T$ for positive Z and 0 otherwise). The integral over dX which is present in both numerator and denominator is proportional to the probability that the field-direction carrier displacement will be Z (corresponding to the phase shift between hopped-from and hopped-to chains, which varies between $-L$ and $+L$). D_1 in Eq. (2) is then just the average value of Z , weighted according to this probability. Equation (2) is approximate in that this average corresponds to replacing the statistically variable phase shifts of possible hopped-to chains surrounding a hopped-from chain by an infinite ensemble of hopped-to chains having all of the possible phase shifts. Evaluating Eq. (2), we obtain

$$D_1 = (L/3) \tanh(E_1 q L / 4k_B T). \quad (3)$$

Using this result and Eq. (1), the calculated conductivity

parallel to the chain-axis direction is

$$\sigma_1 = qf_2L \tanh(E_1qL/4k_B T)/3E_1. \quad (4)$$

For $E_1qL/4k_B T \ll 1$, this becomes

$$\sigma_1 = q^2f_2L^2/12k_B T. \quad (5)$$

We will see in Sec. IV that f_2 depends upon L , so σ_1 depends more strongly upon conjugation length than the above L^2 dependence.

We must next obtain the average value of the down-field displacement per interchain hop when the electric field (E_2) is normal to the chain direction. Consider for the present that E_2 is parallel to the interchain vector for a fraction F of the nearest-neighbor chains which would be equivalent with respect to interchain hopping in the absence of an electric field. For simplification, E_2 is assumed to be orthogonal to the interchain vector for the remaining nearest-neighbor chains. Let d be the interchain separation, which is the same as the interchain hopping distance. Assessing the probabilities of forward and backward hops, the average distance a carrier moves per interchain hop orthogonal to the chain under the influence of a transverse electric field E_2 is

$$D_2 = Fd \tanh(E_2qd/2k_B T). \quad (6)$$

Consequently, using Eqs. (1) and (6) we obtain

$$\sigma_2 = qf_2Fd \tanh(E_2qd/2k_B T)/E_2. \quad (7)$$

For $E_2qd/2k_B T \ll 1$, this becomes

$$\sigma_2 = q^2f_2Fd^2/2k_B T. \quad (8)$$

The electrical-field-dependent anisotropy obtained from Eqs. (4) and (7) is

$$\begin{aligned} \sigma_1/\sigma_2 &= (LE_2/3FE_1d) \\ &\quad \times \tanh(E_1qL/4k_B T)/\tanh(E_2qd/2k_B T). \end{aligned} \quad (9)$$

This equation is valid only when σ_1 and σ_2 are measured under identical electric field conditions, since f_2 will generally depend upon electric field.

For electric fields that are normally of interest ($E_1qL/4k_B T$ and $E_2qL/2k_B T \ll 1$) Eq. (9) reduces to

$$\sigma_1/\sigma_2 = L^2/6Fd^2. \quad (10)$$

As long as the structural relationship between polymer chains is independent of dopant level and we are in the short-conjugation-length limit, an electrical anisotropy proportional to L^2 and largely independent of dopant level, temperature, and pressure is predicted. However, as a caution, it should be recognized that (1) doping typically proceeds throughout much of the accessible dopant concentration range as a two-phase process which does not preserve interchain packing relationships^{26,27} and (2) doping processes can change the effective conjugation length via introduction of structural or chemical disorder.

The geometrical factor F [in Eqs. (6)–(10)] can be easily generalized from the above-described case where the

electric field component perpendicular to the chain-axis direction (E_2) is parallel to the interchain vector for a fraction F of the nearest-neighbor chains which would be equivalent with respect to interchain hopping in the absence of an electric field. In the general case, assuming that all possible hopped-to chains are equivalent in the absence of an electric field and that $E_2qd/2k_B T \ll 1$, F is the average value of $\cos^2\theta_k$, where θ_k is the angle between E_2 and the interchain vector from the hopped-from chain to the k th possible hopped-to chain.

In the low-field limit, the equations derived here are identical to those previously derived making the opposite assumption that the potential drop is largely across the conjugated segments.¹ Even the electric field dependency obtained in the present calculation for electrical anisotropy is little changed from the previously derived result. However, since depolarization fields are ignored in the previous calculations, the present arguments appear to be more appropriate.

Kahlert²⁸ has used a resistor-network model to predict an L^2 dependence for electrical anisotropy in the regime where interchain transport limits both σ_1 and σ_2 . We have used a generalized resistor-network model to obtain, in more-general form, all of the equations which we have derived herein, except for those involving the conjugation-length dependence of hopping frequency.²⁵ Furthermore, using the generalized resistor-network model, we have derived a general relationship between $\sigma_1/\sigma_1(\infty)$ and $[\sigma_2/\sigma_1(\infty)]^{1/2}(L/d)F^{-1/2}$ which is valid outside the short-conjugation-length limit. In this analysis $\sigma_1(\infty)$ is the conductivity in the chain-axis direction for a polymer with effectively infinite conjugation length and all other terms are as defined herein. Finally, it should be noted that Ovchinnikov *et al.* and Balagurov *et al.*²⁹ have used effective-medium theory to predict an L^2 dependence for σ_1/σ_2 in the short-conjugation-length limit.

As discussed in Sec. VI, the case in which chain defects (i.e., chain blocks) do not fully interrupt conjugation poses special problems for the analysis of the dependence of σ_1 and σ_2 upon defect concentration, since the average intrachain, interdefect separation does not directly correspond to average conjugation length. The "conjugation" length referred to in the analyses of Secs. II and III is an average interdefect separation, which corresponds to conjugation length only in the case where the defects effectively terminate conjugation (i.e., have the same effect as chain ends).

III. ANISOTROPY FOR POLYMER CHAINS CONTAINING TRANSMISSIVE BLOCKS

In order for transport directly across chain blocks to be negligible, the total number of interchain hops must be much larger than the total across-block transport of carriers in the same time period. This will certainly be the case for very long conjugation lengths, since the ratio of interchain hops to across-block hops is proportional to L . On the other hand, if the only blocking elements on the chains are readily traversed by carriers (e.g., tunneling across low height or short barriers) then the conjugation

length at which the rate of interchain transport dominates can be so long that the time constant for charge-carrier relaxation after an interchain jump can be much longer than the time between interchain jumps for a conjugated segment. In that case, there would not exist a conjugation-length range where interchain hopping contributes to chain-direction conductivity.

The conjugation dependence of chain-direction conductivity can be readily examined for the case where across-block hopping is much more significant than interchain hopping. We again assume that the length of the blocking segment (break in chain conjugation or separation of chain ends) is much shorter than the length of the conjugated segments. If conjugation lengths are reasonably long, this assumption is, in fact, a necessary requirement for across-block hopping to be significant. The average distance a carrier moves in the chain-axis direction as a consequence of an across-block hop is then

$$D_1 = \frac{e^{E_1 qL/2k_B T} - e^{-E_1 qL/2k_B T}}{e^{E_1 qL/2k_B T} + e^{-E_1 qL/2k_B T}} L$$

$$= L \tanh(qE_1 L/2k_B T). \quad (11)$$

After normalization by the denominator, the two terms in the above numerator correspond to the fraction of total jumps which are down-field, decreased by the fraction of total jumps which are up-field. The linear dependency on L results since the down-field and up-field jump distances are $+L$ and $-L$, respectively. For $qE_1 L/2k_B T \ll 1$, Eq. (11) reduces to

$$D_1 = qE_1 L^2/2k_B T. \quad (12)$$

We now obtain for the case where interchain hopping is negligible compared with across-block hopping

$$\sigma_1 = qf_c D_1/E_1 = q^2 f_c L^2/2k_B T, \quad (13)$$

where f_c is the number of across-block hops per unit time and unit volume. However, since the number of chain blocks per unit volume depends inversely upon conjugation length, we can write that

$$f_c = S f_1/L, \quad (14)$$

where f_1 is the frequency of across-block hopping per conjugated segment and S is the total length of the conjugated segments per unit volume of the conductor. Hence, Eq. (13) becomes

$$\sigma_1 = q^2 f_1 S L/2k_B T. \quad (15)$$

Combining this equation with Eq. (8), we obtain for this case an electrical anisotropy which depends linearly upon L :

$$\sigma_1/\sigma_2 = f_1 S L/f_2 F d^2. \quad (16)$$

For reasons which will be apparent in the next sections, we will generally replace L and L^2 in Eqs. (5), (10), (15), and (16) by L_w and L_w^2 , respectively, where L_w is the weight-average conjugation length. Such replacement is not precise, but is adequate for most analyses—especially since conjugation-length distribution is not generally available as a basis for more accurate evaluations. In the

following work it will often be convenient to replace conjugation length or conjugation-length averages by a constant (chain length per monomer unit) times the number of monomer units in a conjugation length (u) or the corresponding weight average (u_w) or number average (u_n) for the polymer.

IV. CONJUGATION LENGTH DEPENDENCE OF ELECTRON HOPPING FREQUENCIES

In order to obtain the dependence of electronic conductivity upon conjugation length, we must now evaluate the effect of conjugation length on carrier hopping frequencies. The same dependence upon conjugation length will be obtained for both f_2 (the interchain hopping frequency) and f_1 (the across-block hopping frequency). Correspondingly, the numerical subscripts on f_1 and f_2 will be eliminated in the discussions of this section.

The key idea in this analysis is also of major importance for metallic conductivity in molecular charge-transfer complexes. Metallic conductivity in molecular charge-transfer complexes requires the existence of donor or acceptor stacks in which the degree of ground-state charge transfer is incomplete. For example, if all acceptor molecules (A) in a linear array have gained one electron as a result of charge transfer, then electron motion requires the transfer of an electron from an A^- molecule to another identical ion, thereby creating an A^0 molecule and an A^{--} ion. The net energy change for this process is the solid-state electron affinity of A^- decreased by the solid-state electron affinity of A^0 . Since the energy change on adding a first electron to a molecule is much more favorable than the energy change on adding a second electron, this net energy change is a prohibitively large positive number for small molecules (i.e., for molecules having short effective conjugation lengths). Such poorly conducting molecular charge-transfer complexes are referred to as Mott insulators.³⁰

There are several differences between the above process in molecular charge-transfer crystals and in conjugated polymers. First, as conjugation length increases, the energy difference between the j th ionization energy and the $(j+1)$ th ionization energy (or the companion electron affinities) decreases to zero. Second, polydispersity in conjugation length results in differences in the ground-state degree of ionization for different conjugated segments in a polymer.

Both of these differences can be addressed by evaluating the conjugation-length dependence of the total energy change, $\Delta E(j, u)$, on going from $j-1$ charges to j charges on a conjugated segment containing u monomer units. The approximation which we use is that

$$\Delta E(j, u) = (K_2 j/u) + K_1 \delta(j) + K_0, \quad (17)$$

where $\delta(j)$ is a function which is unity for j odd and 0 for j even and where K_0 , K_1 , and K_2 are constants for a specified polymer and a specified concentration of a dopant. The motivation for this approximation is as follows: (1) experimental and theoretical³¹ results indicate that the first ionization potential and the first reduction potential (i.e., $j=1$) are proportional to u^{-1} ; (2) the

linear dependence on j/u in the first term of Eq. (17) provides equally favorable energetics for adding an additional charge to different segments having different conjugation lengths as long as this addition leads to the same average charge density on the segments; (3) when j/u is small, the term in $\delta(j)$ in Eq. (17) can provide favorable energetics for adding an electron to a polaron to form a bipolaron versus the formation of a new polaron; and (4) Eq. (17) is consistent with the limited available data^{32(a)} on the relative energies of first and second reduction potentials in solution. The available data pertaining to Eq. (17) are the first reduction potentials of biphenyl, *p*-terphenyl, and *p*-quaterphenyl and the second reduction potentials of *p*-terphenyl and *p*-quaterphenyl.^{32(a)} Using the data on first and second reduction potentials, K_2 for poly(*p*-phenylene) is predicted to be 1.56 and 1.44 eV/electron, respectively. In other words, the slope of $\Delta E(2, u)$ versus inverse conjugation length (u^{-1}) is nearly twice that of the same plot for $\Delta E(1, u)$ —as predicted by Eq. (17).

In the present comparison with experimental data, we will be concerned with heavily doped materials. Since the system is highly degenerate, the differentiation between even and odd electron ionization potentials (or reduction potentials) can be ignored and we can focus on electron transfer processes which involve only one electron. Hence, $K_1\delta(j) + K_0$ in Eq. (17) becomes one constant independent of whether or not the electron transfer results in an even number or an odd number of total charges. Also, since only the total energy change for an electron transfer is relevant, this constant drops out of the calculations. The only key constant remaining is K_2 , which is assigned the value 3.96 eV/electron for polyacetylene with monomer unit C_2H_2 , 1.56 eV/electron for poly(*p*-phenylene) with monomer unit C_6H_4 , and 2.26 eV for polythiophene with monomer unit C_4H_2S —based on theoretical and experimental values³¹ of first oxidation potential, first reduction potential, and band gap as a function of conjugation length.

In order to use these results to obtain the conjugation-length dependence of the hopping frequency f , we must first calculate the shortest conjugated segment which is charged. This is a function of the dopant concentration y , which is defined as the average number of charges transferred per monomer unit in conjugated segments. If $W(u)$ is the weight fraction of conjugated segments containing u monomer units and v is the shortest conjugation length which could be charged, then

$$y = \sum_{u=1}^{\infty} I(u/v)W(u)/u, \quad (18)$$

where I is a function which is equal to the largest integer which does not exceed the argument of this function. Each term in this equation is just the number of charges per monomer unit [$I(u/v)/u$] in a conjugated segment containing a specified number of monomer units (u) times the weight fraction of conjugated segments having this number of monomer units [$W(u)$]. This equation places charge on each conjugated segment in a way which minimizes total energy (at 0 K) according to Eq. (17). Deviation from uniformity in charge per conjugated segment

length results only because the charges added to a segment must be an integer. For a given distribution function of conjugated segments and a given dopant level, iterative solution of Eq. (18) by computer yields v , the shortest conjugated monomer segment which could be charged at 0 K. Note that v need not be an integer, since the function of this parameter is just to define the degree of oxidation or reduction in a way that translates to the number of charges per conjugated segment.

We next approximate the distribution of charge on various conjugated segments at temperature T by the distribution at 0 K. We then calculate the average value of the Arrhenius exponential for the energy change on removal of an electron (or hole) from a hopped-from conjugated segment (A_1) as well as the average value of the Arrhenius exponential for the energy change upon the addition of this carrier to the hopped-to segment (A_2). If C is a constant independent of conjugation length, then

$$f = CA_1A_2. \quad (19)$$

The number of charges at equilibrium ($T=0$) on a conjugated segment of length u is $I(u/v)$. Ignoring the terms in Eq. (17) which are independent of conjugation length (since they cancel in the calculation for a degenerate system), the energy change on removing a charge from this segment varies as $-K_2I(u/v)/u$ and the energy change on adding a charge to this segment varies as $K_2[I(u/v)+1]/u$. Hence, using Eq. (17), the exponentials in energy changes are $\exp[K_2I(u/v)/uk_B T]$ for the A_1 factor and $\exp\{-K_2[I(u/v)+1]/uk_B T\}$ for the A_2 factor, where u varies from 1 to ∞ .

The weighting factor for averaging terms corresponding to different conjugation lengths in A_1 is the fraction of total charges which are on each conjugation-length segment, which is $I(u/v)W(u)/uy$. According to Eq. (18), the sum of these weighting factors is unity. The weighting factor for averaging terms corresponding to different conjugation lengths (u) in the A_2 terms is just the probability that the hopped-to segment has this conjugation length, which is $W(u)$. Hence, A_1 and A_2 are as follows:

$$A_1 = \sum_{u=1}^{\infty} [I(u/v)W(u)/uy] \exp[K_2I(u/v)/uk_B T], \quad (20)$$

$$A_2 = \sum_{u=1}^{\infty} W(u) \exp\{-K_2[I(u/v)+1]/uk_B T\}. \quad (21)$$

Once the hopping frequency per unit time and per unit volume is calculated from Eqs. (18)–(21), then the conductivity in the chain direction can be calculated from Eq. (5), which gives $\sigma_1 \propto L^2 f$. In these equations we have assumed that the total number of mobile charges is related to the doping level y . Whether the appropriate carrier density should depend simply on the doping level or on the total population of π electrons depends on the detailed band structure which best describes the doped polymer. For polyacetylene, where recent calculations have suggested a virtual closing of the band gap at high doping levels, it is appropriate to consider the carrier density to

be close to the π -electron density;^{32(b)} however, in a polymer such as poly(*p*-phenylene) where the gap apparently does not close, the carrier density should have a direct dependence on doping level. Nevertheless, since the present calculations only predict the conjugation-length dependence of the conductivity and not its absolute values, the estimation of carrier density has negligible effect on the present results. More specifically, if carrier density corresponded more closely to the total π -electron density rather than to the amount of donated charge, the only effect would be to change the weighting factor in Eq. (20) from $I(u/v)W(u)/y$ to $W(u)$. Except at very short average conjugation lengths, this change has no significant effect on the results of the calculation.

The dependence of the hopping frequency f on conjugation length will be evaluated for a variety of conjugation-length distributions. We will first consider the random distribution. The random distribution provides a broad dispersion in lengths and is widely used to represent polymer chain-length distributions. This distribution probably best represents the distribution of conjugation lengths in crystalline regions of high polymers such as polyacetylene. For this distribution

$$W(u) = (1-p)^2 u p^{u-1}, \quad (22)$$

which yields

$$u_n = (1-p)^{-1} \quad (23)$$

and

$$u_w = (1+p)/(1-p), \quad (24)$$

where p is a probability which defines the distribution and u_n and u_w are number-average and weight-average conjugation lengths, respectively. Other distributions used to evaluate the dependence of f on conjugation length are the coupling distribution and the Poisson distribution.³³ The coupling distribution, which corresponds in polymerization to chain termination by coupling of growing radicals, provides

$$W(u) = u^2 p^{u-1} (1-p)^3 / (1+p), \quad (25)$$

where

$$u_n = (1+p)/(1-p) \quad (26)$$

and

$$u_w = (1+4p+p^2)/(1-p^2). \quad (27)$$

The Poisson distribution, which comes closest to a monodispersed distribution, results from polymerization in the absence of chain termination. If m is the number of monomer units reacted per initiator, then

$$W(u) = \frac{m}{m+1} u e^{-m} \frac{m^{u-2}}{(u-1)!}, \quad (28)$$

$$u_n = m + 1, \quad (29)$$

and

$$u_w = m + 1 + [m/(m+1)]. \quad (30)$$

The major differences in weight fraction as a function

of conjugation length for these three different distributions are indicated in Fig. 1. For the case where the number-average conjugation length for each distribution is 50 monomer units, the heterogeneity index (u_w/u_n), which is a measure of the broadness of the length distribution, dramatically increases in going from the Poisson distribution to the coupling distribution, and to the random distribution. For example, a number-average length of 100 monomer units yields heterogeneity indices of 1.0099, 1.4999, and 1.9900, respectively, for these distributions, as compared with an index of unity for a monodispersed distribution.

The last case to be considered is where all conjugated segments have the same length (monodispersed distribution in which each conjugated segment contains u monomer units) and the same number of charges at 0 K (u/v charges per conjugated segment). Evaluation of Eqs. (18)–(21) for this case provides

$$f = C \exp(-K_2/uk_B T). \quad (31)$$

Figure 2 shows the calculated dependence of hopping frequency f (normalized with respect to the infinite-chain hopping frequency) upon number-average conjugation length (u_n) for polyacetylene at 300 K. These curves for the random, coupling, and Poisson distributions result from numerical evaluation of Eqs. (18)–(21) using the appropriate distribution function of Eqs. (22)–(30). The curve for the monodispersed distribution is generated by Eq. (31). Although the polydispersed distributions provide similar dependencies of hopping frequency on number-average conjugation length, the calculated hopping frequency for low average conjugation lengths is much higher for the polydispersed distributions than for the monodispersed distribution. The hopping frequency at fixed number-average conjugation length increases with increasing polydispersity in going from the Poisson, to the coupling, and to the random distribution. However, as long as the dopant concentration per monomer unit

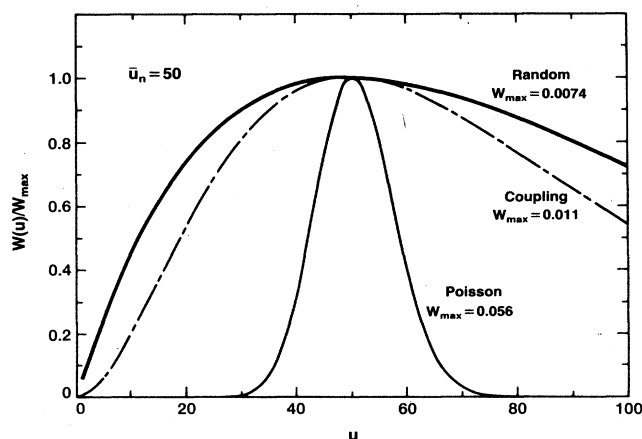


FIG. 1. Weight fraction of conjugation length u , normalized with respect to the maximum weight fraction (W_{\max}), for the random, coupling, and Poisson distributions. In all cases the number average conjugation length (u_n) is 50.

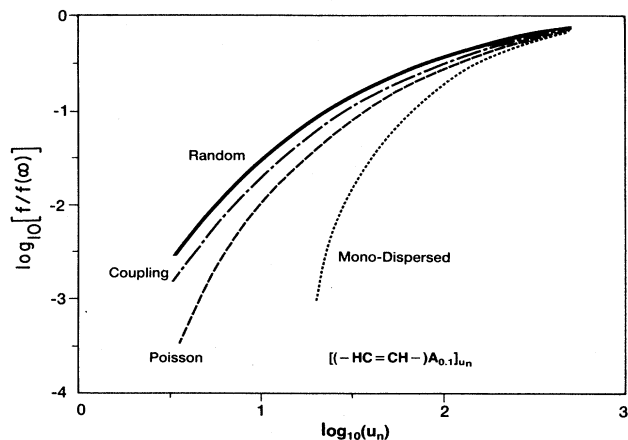


FIG. 2. The calculated dependence of hopping frequency (f), normalized with respect to the infinite-chain value $f(\infty)$, upon number-average conjugation length (u_n) for various molecular-weight distributions of 10% doped polyacetylene. The results for the monodispersed distribution are for equally ionized chains.

is much less than unity, the calculated frequencies for these polydispersed distributions essentially coincide if plotted as a function of weight-average conjugation length rather than number-average conjugation length. This is shown in Fig. 3, which is a plot of the calculated frequencies as a function of weight-average conjugation length for the random and Poisson distributions. Note that for each of these polydispersed distributions, limited conjugation lengths reduce hopping frequency relative to $f(\infty)$ by less than 30% for weight-average conjugation lengths above 200 polyacetylene double bonds.

One must also consider to what extent variations in dopant level affect the hopping frequency for a polymer having polydispersity in conjugation lengths. The results

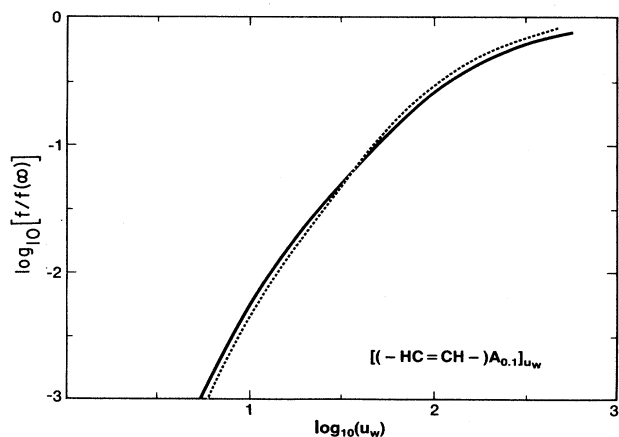


FIG. 3. The calculated dependence of hopping frequency (f), normalized with respect to the infinite-chain value $[f(\infty)]$, upon weight-average conjugation length (u_w) for 10% doped polyacetylene having a random distribution (solid line) and a Poisson distribution (dashed line) of conjugation lengths.

shown in Fig. 2 are for polyacetylene at a dopant level (charge per C_2H_2) of 0.10. Figure 4 compares results for dopant levels of 0.01 and 0.10. Decreased dopant levels result in slightly increased normalized hopping frequencies (relative to the infinite-chain hopping frequencies). However, the general form of the chain-length dependence of hopping frequency is basically unchanged. Also, note from Eqs. (17)–(21) that $f/f(\infty)$ depends upon K_2 only through the ratio K_2/T . Thus, a decrease in temperature has an effect indistinguishable from an increase in K_2 .

Figure 5 shows the calculated change in effective activation energy for electronic conductivity in polyacetylene upon going from a finite number-average conjugation length (u_n) to an infinite conjugation length. Note that the actual temperature dependence of hopping frequency (or conductivity) is not obtained, but the change in temperature dependence for samples having different average conjugation lengths can be predicted using this theory. We find that an Arrhenius expression approximates reasonably well the ratio of finite-chain and infinite-chain hopping frequencies (and conductivities) over a fairly broad temperature range (100–500 K) for polyacetylene. Consistent with observations,^{9–11} the effect of decreasing conjugation length is to increase the ratio of high-temperature to low-temperature conductivities. We will later provide a more precise representation for the temperature dependence of calculated hopping frequency.

V. DERIVATION OF RELATIONSHIPS BETWEEN THE DEPENDENCE OF CONDUCTIVITY ON CONJUGATION LENGTH AND TEMPERATURE

Since $f/f(\infty)$ at constant u_w is insensitive to the particular conjugation-length distribution for a polydispersed polymer having $y \ll 1$, a number of interesting relationships can be derived between various func-

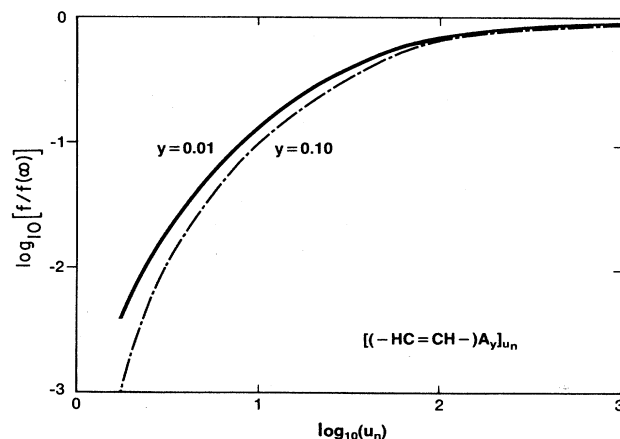


FIG. 4. The calculated effect of charge transfer (y) per monomer unit (C_2H_2) upon the normalized interchain hopping frequency as a function of number-average conjugation length for polyacetylene having a random distribution of conjugation lengths.

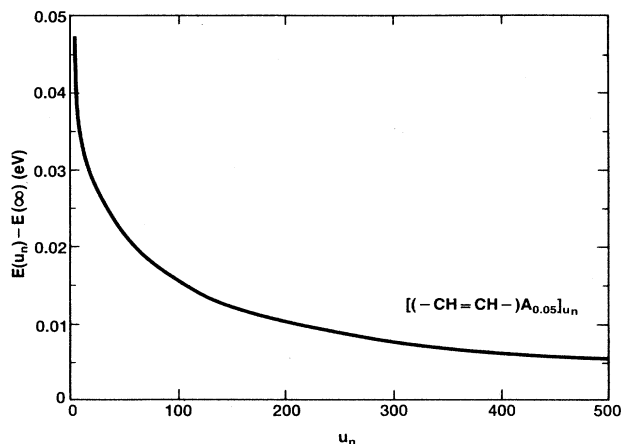


FIG. 5. The calculated activation energy for electronic conductivity in doped polyacetylene, decreased by the same quantity for infinite-conjugation-length polyacetylene, as a function of number-average conjugation length. Results are for $y=0.05$ and a random distribution of conjugation lengths.

tions of conductivity for diverse polymers. To understand the following discussion, first consider the same polymer formed by polymerization of either a monomer or a dimer. The parameter u_w refers to the weight-average number of monomer units in the first case and the weight-average number of dimer units in the second case. Correspondingly, K_2 for the monomer-unit-described polymer is twice the value of K_2 for the dimer-unit-described polymer [which can be seen using Eq. (17)]. The frequency ratio $f/f(\infty)$ is essentially the same for the two polydispersed polymers as long as temperature, u_w/K_2 , and yK_2 are the same. When these conditions are met, the two polymers have the same weight-average number of monomer units per conjugation length and the same dopant concentration per monomer unit. Hence, $f/f(\infty)$ should be nearly the same, aside from any small effect due to differences in the distribution of conjugation lengths for the monomer-derived and the dimer-derived samples. The argument is basically unchanged if the two polymers are chemically different. Most generally, since K_2 enters the equations only as K_2/T , such arguments [based on Eqs. (17)–(21)] predict that $f/f(\infty)$ is essentially the same even for different conjugated polymers as long as $u_w T/K_2$ and yK_2/T are the same and $y \ll 1$.

Figure 6 shows the calculated $f/f(\infty)$ as a function of $k_B u_w T/K_2$ [obtained using Eqs. (18)–(24)] for polymers having K_2 between 1.5 and 4 eV/electron, dopant concentrations between 0.05 and 1.0, and temperatures between 100 and 300 K. Consistent with the above discussion, independent of the specific values of any of these parameters, the derived $f/f(\infty)$ for $y \ll 1$ is largely determined by $u_w T/K_2$. As shown in Fig. 7, the values of $\ln[f/f(\infty)]$ calculated for this range of parameters are well represented as a linear function of $(k_B u_w T/K_2)^{-n}$, where n is approximately $\frac{1}{3}$. For u_w sufficiently large that $f/f(\infty)$ is close to unity, deviations from this dependence are indicated in Fig. 7. In this limit, where

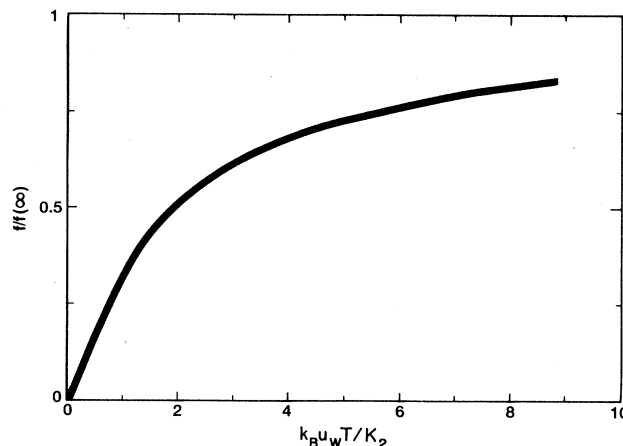


FIG. 6. The calculated dependence of $f/f(\infty)$ upon the composite parameter $k_B u_w T/K_2$. The width of the line denotes the scatter of calculated values dependent upon the specific choice of dopant concentration (between 0.05 and 1.0), temperature (between 100 and 300 K), and K_2 (between 1.5 eV/electron and 4 eV/electron).

$(k_B u_w T/K_2)^{-1} \ll 1$, $f/f(\infty)$ can be approximated by $\exp[-(k_B u_w T/K_2)^{-1}]$. These results will be compared later with conductivity data for conducting polymers.

Using the Sec. II and III results [Eqs. (5), (8), and (15)] for the relationships between conductivity components and both hopping frequency and conjugation length and the above-described dependence of $f/f(\infty)$ upon $u_w T/K_2$, we can make useful generalizations which are valid in the finite-chain limit when $y \ll 1$. Specifically, the plot of $\ln(\sigma_1 T/L^n)$, where $n=1$ for dominant across-block hopping and $n=2$ for dominant interchain hopping, or $\ln(\sigma_2 T)$ as a function of $u_w T/K_2$ should re-

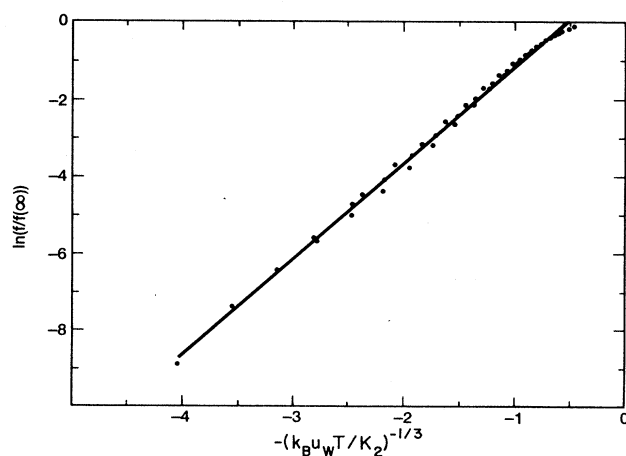


FIG. 7. The calculated $f/f(\infty)$, for the parameter range indicated in Fig. 6, are used to obtain an approximately linear relationship between the natural logarithm of $f/f(\infty)$ and $(k_B u_w T/K_2)^{-1}$, where n is equal to $\frac{1}{3}$. The solid line is a least-squares fit of the calculated data points and corresponds to a slope of 2.47 ± 0.02 .

sult in a family of parallel curves. The relative displacement of these parallel curves in the conductivity-axis direction is predicted to depend upon polymer molecular structure, crystal structure, dopant, dopant concentration, and temperature—but be independent of conjugation length. Using Eqs. (5), (15), and (8), the curve displacement differs for different polymer samples, different conductivity components, different ambient conditions, and different hopping regimes according to changes in $\ln[q^2 f_2(\infty)]$ for plots of $\ln(\sigma_1 T/L^2)$ in the interchain hopping regime; changes in $\ln[q^2 S f_1(\infty)]$ for plots of $\ln(\sigma_1 T/L)$ in the across-block hopping regime; and changes in $\ln[q^2 F d^2 f_2(\infty)]$ for plots of $\ln(\sigma_2 T)$. Note that $\ln(\sigma_i T/L^n)$ versus $u_w T/K_2$ is predicted to be independent of temperature as long as the dominant hopping mechanism is unchanged ($n=1$ or 2 for σ_1 and $n=0$ for σ_2) and the corresponding infinite-chain hopping frequency [$f_1(\infty)$ or $f_2(\infty)$] has a negligible temperature dependence.

Likewise, we can generate universal conductivity plots using the difference between the measured optical band gap (E_0) and the infinite chain gap [$E_0(\infty)$] as the normalization parameter. Based on the application of Eq. (17) to polydispersed systems with $j=1$,

$$\Delta E_0 \equiv E_0 - E_0(\infty) = 2K_2/u_w. \quad (32)$$

Since $\ln(\sigma_i T/L^n)$ versus $u_w T/K_2$ is predicted to provide a series of parallel curves for diverse random-phase polymers (where $n=0$ for $i=2$, $n=1$ for $i=1$ with dominant across-block hopping, and $n=2$ for $i=1$ with dominant interchain hopping), Eq. (32) implies that a similar series of parallel curves should result for a plot of $\ln[\sigma_i T(\Delta E_0)^n]$ versus $T/\Delta E_0$.

VI. GENERALIZATION FOR POLYMERS HAVING COMPLEX DEFECT STRUCTURES

The term conjugation length, as used herein, needs clarification. This is because a variety of different types of chain defects can be present which interrupt electronic interactions within the polymer chain to different degrees.^{21-24,34} If the only significant interruptions in electronic connectivity are essentially complete breaks, such as chain ends, it is useful to define conjugation length as the length of a defect-free oligomer having the same optical band gap (or first ionization potential or electron affinity) as the weight-average optical band gap (or first ionization potential or electron affinity) for the polymer. In this case, the chain length variable in the equations for both σ_1/σ_2 and the hopping frequencies is this conjugation length, which corresponds to the weight-average separation between the defects which provide essentially complete interruption in conjugation. We will see in the following discussion that the situation is much more complicated for the case where there exist diverse types of defects in the polymer chains. The existence of defects which do not completely terminate electronic interactions in the chain can result in differences in the appropriate chain length dimensions for the anisotropy equations and the equations for hopping frequency. The

former length is the "equilibration length" over which charge distribution becomes equilibrated in the time interval between rate-limiting hops (either interchain or intrachain). On the other hand, the characteristic average length appropriate for calculation of the interchain hopping frequency can generally be identified as the above-defined conjugation length. However, we will see that it is sometimes convenient to redefine conjugation length, by referencing polymer properties to the properties of oligomers containing a specified concentration of defects which provide weak disruption in electronic connectivity. By doing this, as well as evaluating K_2 in Eq. (17) using such defect-containing oligomers, the same characteristic lengths can be used more generally in the anisotropy equations and the equations for hopping frequencies.

Consider the case in which two different types of defects are present on the polymer chains. The first type of defect (weak defects) is sufficiently numerous and provides a sufficiently weak interruption in conjugation that two conditions are satisfied. First, the volumetric frequency of interchain hopping is much less than the volumetric frequency of hopping across the weak defects. Second, the time required for charge-carrier redistribution on a segment length L_1 , defined by the average separation of their weak defects, is much shorter than the time interval between carrier hops involving this segment. The second type of defect (strong defects) is less numerous and provides a more complete interruption in chain conjugation, so that the volumetric frequency of carrier hopping across these strong defects is much less than the volumetric frequency of interchain hopping. Whether electrical anisotropy depends upon the weight-average separation of the strong defects (L_2) or the weight-average separation of the weak defects (L_1) depends upon the time required for charge redistribution within L_2 after an interchain hop from within L_2 . If the time required for charge redistribution on L_2 is much longer than the time interval between interchain charge transfer involving L_2 , then σ_1/σ_2 depends linearly upon L_1 and is independent of L_2 [according to Eq. (16), in which L is L_1]. In the opposite extreme where the time required for redistribution of charge carriers between the segments within L_2 is negligible, σ_1/σ_2 depends quadratically upon L_2 [according to Eq. (10) in which L is L_2]. If the concentration of the weak defects is held constant and the concentration of strong defects is progressively decreased, a transition will eventually occur from the second limit to the first limit of time scales, so that σ_1/σ_2 goes from a quadratic dependence on L_2 to a linear dependence on L_1 . If at this point the concentrations of both weak defects and strong defects are progressively decreased, so that the ratio of defect concentrations is held constant, σ_1/σ_2 can go from a linear dependence on L_1 to a quadratic dependence on L_1 . At this point the separation of weak defects is sufficiently long that the volumetric frequency of interchain hopping is much higher than the volumetric frequency of intrachain hopping across the weak defects. Upon further progressive decrease in defect concentration, σ_1/σ_2 will eventually become independent of either L_1 or L_2 . In this final lim-

it, the time required for charge redistribution within L_1 is much longer than the time interval between interchain hops.

The effect on chain-direction conductivity (σ_1) of variations in the concentrations of defects having various strengths is the effect of these variations on σ_1/σ_2 , augmented by the effect of these variations on the hopping frequency which limits σ_1 . Consider the case where there exist numerous weak defects on chain segments whose conjugation is completely terminated by strong defects. The average separation of weak defects (L_1) is much shorter than the average separation of strong defects (L_2). If the time interval between interchain hops is much longer than the time required for charge redistribution on L_2 and the volumetric frequency of interchain hopping is much higher than the volumetric frequency of across-block hops over the complete breaks in conjugation, then σ_1/σ_2 is proportional to L_2^2 [Eq. (10) in which L is L_2] and independent of L_1 . However, the interchain hopping frequency will generally depend upon both L_1 and L_2 . This is because the ionization potential (and electron affinity) of the polymer depends upon both L_1 and L_2 . For the case where the concentration and distribution of weak defects is held constant and only L_2 is variable, it is convenient to incorporate the effect of the weak defects by selecting a K_2 value [Eq. (17)] which is reduced compared with that for conjugated segments which do not contain weak defects. This K_2 is derived empirically or by quantum-chemical calculations so as to reproduce the dependence of ionization potential (and electron affinity) upon oligomer length for oligomer molecules containing fixed concentrations of the same weak defects. The calculation of the dependence of σ_1 and σ_2 on L_2 then proceeds exactly as previously described for the case where the only interruptions in conjugation are complete breaks.

In the above calculation we can still view L_2 as the conjugation length of the polymer. However, the conjugation length of the polymer now denotes the length of an oligomer, containing a specified concentration of weak defects, which has the same optical band gap, first ionization potential, and electron affinity as the weight-average values of these electronic parameters for the polymer. Alternatively, it is sometimes useful to define the conjugation length of a polymer containing various strength defects by comparison of polymer electronic properties with those of defect-free oligomers. If this is done, K_2 remains the same as that determined from the length-dependent electronic properties of the defect-free oligomers. The disadvantage of this approach for the above calculation is that the conjugation length referenced to the defect-free oligomer is not the localization length appropriate as a variable for the anisotropy equation.

The following example is one in which it is convenient to use two different length scales to describe the effective defect separations, one for the anisotropy equation and one for calculation of the defect dependence of hopping frequency. For the purpose of differentiation between these lengths, the former length is referred to as the equilibration length (since this is the length upon which

charge-carrier equilibration occurs in the time interval between rate-controlling carrier hops) and the latter length is designated the conjugation length. This equilibration length will closely correspond with the conjugation length (referenced with respect to the defect-free oligomer) only for the case where the rate-controlling chain defect provides a comparable interruption in electronic structure as a chain end. The present example is one important limit for the case where the polymer contains a variety of different defects having various strengths. This limit is the case where (1) the average separation of such defects is sufficiently long that across-defect intrachain hopping (i.e., across-block hopping) is negligible compared with interchain hopping for effectively all defect pairs which bound polymer chain segments and (2) the time required for charge-carrier redistribution on such a segment is negligible compared with the time between interchain hops. Then σ_1/σ_2 will depend quadratically upon the average separation between defects [corresponding to Eq. (10) in which L is the average separation of defects], independent of the strengths of the individual defects. In this limit, calculation of the effect of defects upon interchain hopping frequency proceeds similar to that described in Sec. IV. However, it is here convenient to identify the average conjugation length in the polymer (containing diverse defect types) as the length of a defect-free oligomer which reproduces the average value of electron affinity, ionization potential, and optical band gap for the polymer.

Complications in the analysis are clearly introduced for a polymer containing diverse defects having different strengths. Furthermore, experimental ability to characterize these defects for a given polymer sample are presently limited to a rudimentary level. Fortunately, as long as the conjugation length relevant for evaluation of $f/f(\infty)$ is appropriately determined, the errors introduced in using the conjugation length as the equilibration length can be unimportant. This will be true if a proportionality exists between the conjugation length and the equilibration length for the samples being analyzed, since the fractional change in σ_1 as a function of conjugation length is independent of the value of the proportionality constant. Also, the calculated anisotropy as a function of equilibration length will be in error only by a constant factor, which is the square of the proportionality constant relating equilibration length and conjugation length. For this reason, and because of the absence of experimental data pertaining to the concentrations of defects having different strengths, the following comparison of theoretical and experimental results will not differentiate between conjugation length and the equilibration length.

VII. COMPARISON OF THEORY AND EXPERIMENT

Using the results of the previous sections, we can directly obtain the conjugation-length dependence of both σ_1 and σ_2 in the limit where either interchain hopping (Secs. II and IV) or across-block hopping (Secs. III and IV) dominates chain-direction conductivity (σ_1).

The conjugation-length dependence of σ_1 is just the conjugation-length dependence of σ_1/σ_2 (proportional to L^2 for interchain hopping and proportional to L for across-block hopping) times the identical conjugation-length dependencies of the interchain hopping frequency (f_2) or the across-block hopping frequency (f_1).

The observed electrical conductivity anisotropies for a variety of doped polymer compositions are largely independent of temperature.^{15,34-37} This independence suggests that these polymers are in the finite-chain limit where interchain hopping determines both σ_1 and σ_2 , since different temperature dependencies would generally be expected for σ_1 and σ_2 if across-block hopping were important or if the polymers were in the infinite-chain limit. Hence, the calculations of this section will assume determination of both σ_1 and σ_2 by interchain hopping.

While the calculated conductivities are for samples which have order in three dimensions, the experimental observations of conjugation length effects are for samples in which structural orientation is randomized on a macroscopic level. An upper bound on conductivity for the randomized sample (i.e., unoriented sample) is directly obtained as an average of calculated conductivities, i.e., $(\sigma_1 + 2\sigma_2)/3$.³⁸ For the range of conjugation lengths of primary interest here, for which $\sigma_1 \gg \sigma_2$, the conductivity in the chain-axis direction dominates this average and, therefore, the conductivities orthogonal to the chain-axis direction have little effect on the calculated results for unoriented samples.

Figures 8, 9, and 10 compare the calculated conjugation-length dependence of conductivity with that observed by Soga and Nakamura² for iodine-doped polyacetylene, by Shacklette⁴ for potassium-doped poly(*p*-phenylene), and by Cao *et al.*⁵ for iodine-doped polythiophene, respectively. The agreement between the theoretical curves and these experimental results is quite good. The conjugation-length dependence within the ex-

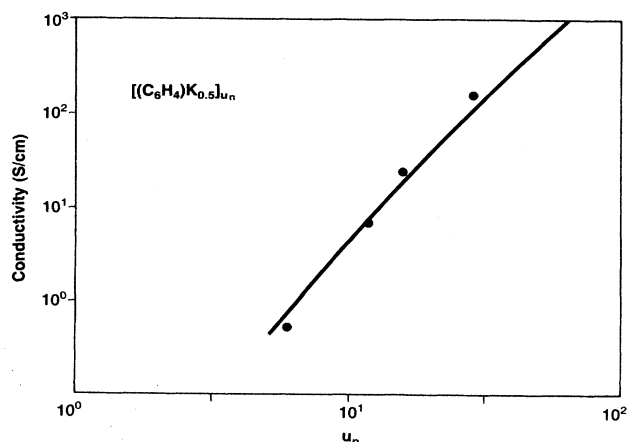


FIG. 9. Comparison of the calculated (random distribution with $y=0.5$) and observed (Ref. 4) dependence of conductivity upon number-average conjugation length for potassium-doped poly(*p*-phenylene). The calculated curve involves a multiplicative constant that is used to place calculated and observed conductivities on the same scale.

perimental range approximates L^3 , but is not strictly L^3 , either theoretically or experimentally. These calculations assume that the distribution of conjugation lengths in the bulk of the polymer sample corresponds to a random distribution. The data of Yaniger *et al.*³ on AsF_5 -doped polyacetylene increase too rapidly at short conjugation lengths to be fit by the theoretical curve for a random distribution of conjugation lengths. This deviation is consistent with recent results^{11,20-23} which suggest that the $-\text{CH}_2-$ defects which limit conjugation are not randomly located. The problem of deviation from random distribution would not necessarily be important if the average conjugation length were known and identical for

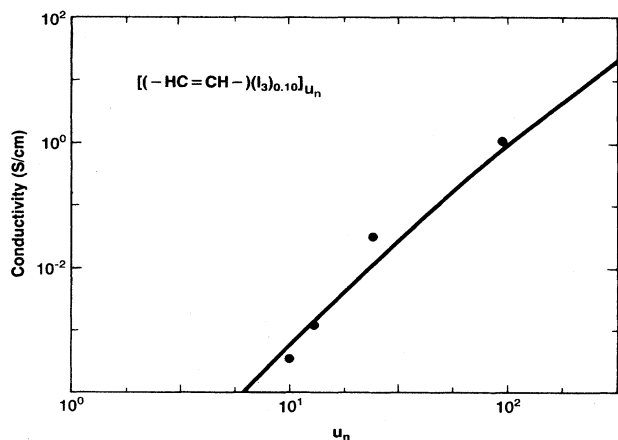


FIG. 8. Comparison of the calculated (random distribution with $y=0.10$) and observed (Ref. 2) dependence of conductivity upon number-average conjugation length for iodine-doped polyacetylene. The calculated curve involves a multiplicative constant that is used to place calculated and observed conductivities on the same scale.

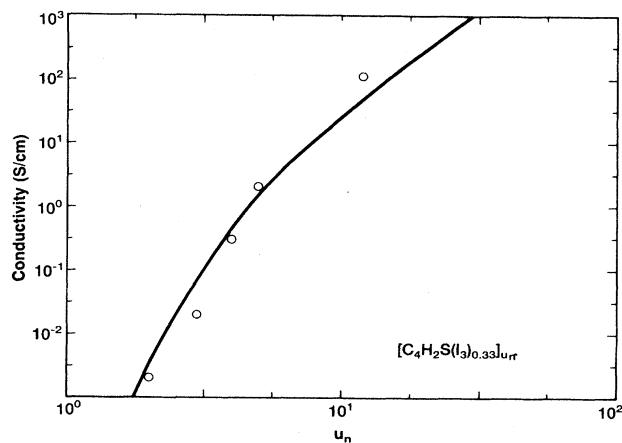


FIG. 10. Comparison of the calculated (random distribution with $y=0.33$) and observed (Ref. 5) dependence of conductivity upon number-average conjugation length for iodine-doped polythiophene. The calculated curve involves a multiplicative constant that is used to place calculated and observed conductivities on the same scale.

all regions of the polymer, but this is not likely the case for the above polyacetylene samples. Aggregation of $-\text{CH}_2-$ defects results in uncertainties in the determination of average conjugation length, and domains containing long conjugation lengths can effectively short-circuit the effect of domains containing much shorter conjugation lengths. The lowest conductivity data point in Fig. 9 for K-doped poly(*p*-phenylene) corresponds to sexiphenyl. The agreement between this data point and the results for the remaining samples, which are polydispersed in conjugation lengths, suggests that a statistical distribution in the degree of charge transfer per chain has a consequence in increasing conductivity similar to that of polydispersity in conjugation length.

An electrical anisotropy as high as 100 was measured by Leising *et al.*³⁹ for highly chain-oriented $(\text{CHI}_{0.09})_x$. This anisotropy is approximately constant from room temperature down to 10 K. Similar results were obtained by Park *et al.*¹⁵ for other polyacetylene complexes. If we neglect any anisotropy in conductivity normal to the chain-axis direction and approximate the geometrical factor F by unity, an average conjugation length of about 40 carbon double bonds is calculated from Eq. (9) using this anisotropy and an interchain jump distance of 4.1 Å (corresponding to the approximate interchain separation in undoped polyacetylene).⁴⁰ While no independent estimate of average conjugation length is available for this doped sample, the above estimate is consistent with estimates (Raman spectroscopy) of conjugation length in polyacetylene prepared using the Shirakawa catalyst.⁴¹ Contrary to our present assumption, the electrical conductivity transverse to the chain-axis direction for iodine-doped polyacetylene might be far from isotropic, as a consequence of layer structure formation.

Anisotropy in conductivity orthogonal to the polymer chain can dramatically affect measured σ_1/σ_2 for chain-oriented samples. More specifically, for samples having fully aligned chains and random orientation on a local scale orthogonal to the alignment direction, the conductivity orthogonal to the chain is the geometric mean of tensor components perpendicular to the chains.⁴² This analysis implies that the electrical conductivity for such chain-aligned samples could reach high levels as a consequence of high anisotropy orthogonal to the chain-axis direction.

The results in Fig. 11 provide important confirmation of both the analysis leading to an L^2 dependence of σ_1/σ_2 and the validity of the approximations leading to the predicted dependence of $f/f(\infty)$ upon the generalized parameter $u_w T/K_2$. According to Eq. (5), in the short-conjugation-length limit, where both σ_1 and σ_2 are controlled by interchain hopping, $\ln(\sigma_1 T/L^2)$ equals $\ln[q^2 f_2(\infty)/12k_B] + \ln[f_2/f_2(\infty)]$. Hence, $\ln(\sigma_1 T/u_w^2)$ [or $\ln(\sigma T/u_w^2)$ for the case of an unoriented polymer] is predicted to differ from $\ln[f_2/f_2(\infty)]$ only by a constant. This constant varies from polymer to polymer, largely according to variation in $f_2(\infty)$, but depends upon temperature and pressure for a particular composition of doped polymer only to the extent these variables affect $f_2(\infty)$. These arguments imply that the

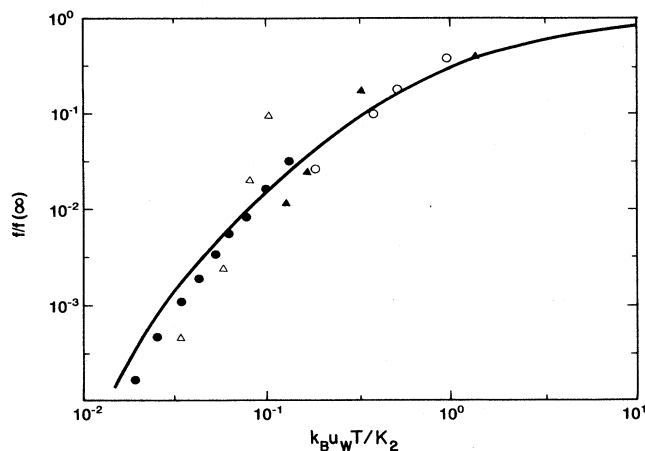


FIG. 11. Comparison of the calculated (solid curve) and experimentally derived dependence of $f/f(\infty)$ upon $k_B u_w T/K_2$. The experimental points correspond to $\sigma T/u_w^2$ multiplied by a constant which is adjusted to minimize the y -axis displacement of the experimental data set from the theoretical curve. Although this adjustable constant is necessary because $f(\infty)$ is unknown for each doped polymer, the comparison of rate of change of $\ln[f/f(\infty)]$ and $\ln(\sigma T/u_w^2)$ as a function of $k_B u_w T/K_2$ involves no fit parameter. Symbols denote polymer compositions as follows for variations of u_w : solid triangles for I-doped polyacetylene, open circles for K-doped poly(*p*-phenylene), open triangles for I-doped polythiophene. For variation of temperature: solid circles denote I-doped polyacetylene with a u_w of about 21 as determined by mass uptake.

experimentally determined plot of $\ln(\sigma T/u_w^2)$ versus $k_B u_w T/K_2$ should superimpose upon the theoretically determined plot of $\ln[f/f(\infty)]$ versus $k_B u_w T/K_2$ after a constant shift in the vertical-axis direction. This comparison is made in Fig. 11, where the experimental results are for iodine-doped polyacetylene,^{2,9,10} potassium-doped poly(*p*-phenylene),⁴ and iodine-doped polythiophene⁵ as a function of u_w and for iodine-doped polyacetylene as a function of temperature.^{9,10} This comparison provides a severe test of the theory, since the major contribution to the conjugation-length dependence of σ (i.e., u_w^2) has been divided out. We see that the theory correctly predicts not only the conjugation-length dependence of conductivity, but also how this dependence varies with temperature.

Although a simple expression for the variation of conductivity with temperature is not derived by analytic means from the present theory, we have demonstrated that a universal relationship exists for $y \ll 1$ between normalized hopping frequency $f/f(\infty)$ and a parameter involving temperature, $u_w T/K_2$. As depicted in Fig. 7, this relationship is best linearized (linear correlation coefficient closest to 1) for $k_B u_w T/K_2 < 1$ when $\ln[f/f(\infty)]$ is plotted as a function of $-(k_B u_w T/K_2)^{-1/3}$. As discussed earlier, $f/f(\infty)$ corresponds to both $f_1/f_1(\infty)$ and $f_2/f_2(\infty)$. Since by Eq. (5), $\sigma_1 \propto f_2 L^2/T \propto f_2 u_w^2/T$, the linear curve in Fig. 7 predicts

$$\sigma_1 = \sigma_0 \exp[-(T/T_0)^{-1/3}], \quad (33)$$

where (from the slope of Fig. 7),

$$T_0 = 15.1K_2/k_B u_w$$

and

$$\sigma_0 \propto f_2(\infty) u_w^2 / T.$$

According to the present theory, σ_1 depends on carrier concentration (doping level) through the dependence of the infinite-conjugation-length frequency of interchain hopping [$f_2(\infty)$], on this parameter. Since $f_2(\infty)$ is the hopping frequency per unit volume, rather than per carrier, $f_2(\infty)$ will increase in proportion to carrier concentration if the hopping frequency per carrier is a constant. Unless the preexponential factor σ_0 is a strongly varying function of temperature, the temperature dependence of conductivity for a short-conjugation-length polymer is expected to be dominated by the above exponential factor. Such a temperature dependence, $\exp[-(T/T_0)^{-n}]$ where $\frac{1}{4} < n < \frac{1}{2}$, is observed for most conducting polymers.¹⁰ This temperature dependence is generally thought to result from Mott's law of variable-range hopping. However, as seen above, such a temperature dependence can also result from the effect of finite conjugation lengths on the frequency of nearest-neighbor interchain hopping. Consistent with the present results, Bernasconi⁴³ and Zeller⁴⁴ have shown both by theory and experiment (oxide-coated metal particles) that a nearest-neighbor hopping process with a distribution of activation energies can yield the same type of exponential temperature dependence for conductivity as obtained for variable-range hopping.

Equation (33) allows one to predict T_0 as a function of conjugation length u_w . Values of T_0 obtained from fitting curves of published conductivity data⁹ to the exponential dependence in Eq. (33) are compared in Table I with those calculated from our expression for T_0 , which contains no adjustable parameter. The value of K_2 is taken to equal 3.96 eV/electron for polyacetylene, based not on transport data but on the effect of conjugation length on electron affinity, ionization potential, and optical band gap for polyene oligomers. The magnitudes of theoretically and experimentally derived values of T_0 are in general agreement throughout the range of experimentally

investigated defect concentrations.

Although Eq. (33) provides that σ_0 is proportional to u_w^2 , it should be realized that the conjugation-length dependence of σ_0 is not uniquely determined by the present analysis. Since the calculated points can also be fit by an expression which includes a prefactor, the calculated $f/f(\infty)$ can be more generally approximated for small $f/f(\infty)$ as proportional to $(k_B u_w T / K_2)^{-p} \exp[-(C k_B u_w T / K_2)^{-m}]$, where p need not be zero and the constant C need not be unity. Hence p , C , and m are interdependent fit parameters used to describe the theoretically calculated $f/f(\infty)$, with m a slowly varying function of p [$p=0$, $C=1$, and $m=\frac{1}{3}$ for Eq. (33)]. Using this more general representation of the calculated $f/f(\infty)$, σ_0 becomes proportional to u_w^{2-p} . Correspondingly, the temperature dependence of σ_0 is proportional to that for $f(\infty)/T^{p+1}$. However, independent of this generalization, T_0 is predicted to be proportional to K_2/u_w , as in Eq. (33).

A variety of theories based on variable-range hopping (VRH) or tunneling through barriers⁴⁵ have previously been used to derive similar exponentially varying temperature dependence for conductivity. In the case of VRH in two dimensions, which gives a temperature dependence varying as $\exp[-(T/T_0)^{-1/3}]$, $T_0 = 9\alpha^2/\pi k_B N_F$, where α^{-1} is a localization length and N_F is the density of states at the Fermi energy (per unit area and per unit energy). In this VRH model, T_0 may derive a dependence on doping level y through a variation of N_F with y . In our model, the scale upon which states are distributed in energy is related to K_2^{-1} . We have assumed here, in first approximation, a rigid-band model in which K_2 (which is related to the gap energy) does not vary with y .

As shown in Figs. 8–10, the present theory successfully explains the observed conjugation-length dependence of electrical conductivity in iodine-doped polyacetylene, potassium-doped poly(*p*-phenylene), and iodine-doped polythiophene. The theory predicts that hopping frequency depends upon $u_w T / K_2$, which leads to relationships in the short-chain limit between conjugation length, temperature, and pressure derivatives of conductivities. The conjugation-length dependence of conductivity is predicted to be largely independent of dopant level for a polymer which is polydispersed in conjugation length as long as

TABLE I. Variation of the conductivity parameter T_0 with conjugation length for iodine-doped polyacetylene. The theoretically derived values of T_0 assume a negligible temperature dependence for the conductivity of the infinite-conjugation-length polymer.

Weight average conjugation length (u_w)		Experimental ^a T_0 (10^4 K)	Theoretical ^b T_0 (10^4 K)	
u_w derived from mass uptake	u_w derived from Raman spectroscopy		u_w derived from mass uptake	u_w derived from Raman spectroscopy
51.6		0.35	1.34	
20.7	32	1.4	3.35	2.17
12.5	24	6.5	5.55	2.89
8.8	21.5	10	7.89	3.23
6.7	19	21.5	10.3	3.63

^aFrom a fit of Ref. 9 data for segmented polyacetylene to $\sigma \propto \exp[-(T/T_0)^{-1/3}]$.

^bFrom $T_0 = 15.1K_2/k_B u_w$.

$y \ll 1$. This prediction agrees with the experimental results of Schafer-Siebert *et al.*⁹ on the conjugation-length dependence of conductivity for polyacetylene containing different iodine dopant levels ($y=0.035-0.15$) corresponding to an order-of-magnitude difference in conductivity. Experimental results (Fig. 11 and Table I) agree with predictions of the temperature dependence of the variation of conductivity with conjugation length. Also, the conjugation length calculated from the electrical anisotropy of iodine-doped polyacetylene is consistent with expectations. However, several issues should be remembered when applying this theory to experimental data. First, the present theory is applicable only to polymers having a random phase relationship between conjugation termination elements in neighboring chains. Oligomers with a fixed conjugation length (monodispersed distribution) are most likely to deviate from the random-phase approximation. Havinga *et al.*⁷ have pointed out that the electrical conductivity of alkali-metal-doped phenylene oligomers strongly depends upon conjugation length, but this dependence is irregular because of varying structure for the doped oligomers. We will present elsewhere calculations of conjugation-length effects for oligomer and polymer phases having a fixed phase relationship between conjugation terminating elements in neighboring chains.²⁵ Second, doping of conducting polymers typically proceeds heterogeneously over much of the dopant range, so that the partially doped polymer typically consists of two different phases.^{26,27} Changes in the arrangement of polymer chains as a function of dopant level or conjugation length would affect the calcu-

lated conjugation-length dependence of transport. Third, only at relatively high dopant levels (greater than about 12% per double bond in polyacetylene) do all chains have equivalent positions.^{26,27,46} The present theory addresses only the single-phase material in which conductivity is dominated by hopping within or between equivalent chains.

Because solvent-free polyacetylene heavily doped with K, Rb, or Cs has a structure in which all chains are equivalent and conductivity orthogonal to the chain-axis direction is isotropic,²⁷ this material provides the best opportunity for a more detailed comparison of theory and experiment.

Since precise characterization of conjugation length is not presently available for conducting polymers, it is convenient to approximate the conjugation length (L) in the anisotropy equation [Eq. (10)] by L_w , the weight-average conjugation length. However, detailed analysis shows that L is more rigorously specified as $(L_w L_z)^{1/2}$, where L_z is the z-average conjugation length.⁴⁷

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