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Effect of Molecular Weight and Orientation on the Conductivity of Conjugated Polymers

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ABSTRACT: A method for calculating the effect of molecular weight and orientation on the conductivity of polymers has been developed. The conductivity in the isotropic state is found to depend on the charge carrier density, the polymers persistence length, the mean lifetime of the charge on a polymer, τ_c, and the time for a charge to diffuse the length of a single polymer, τ_i. We describe a method for estimating these time constants individually by a combination of ac and dc measurements. Our prediction for the enhancement of conductivity when the polymer is stretched is in good agreement with existing experimental data. We conclude with a discussion of how the macroscopic conductivity is affected by chain stiffness, by molecular weight distribution, and by defects that can block charge diffusion along a polymer chain.

Introduction

Doping a conjugated polymer increases the conductivity (σ) by adding electrons to or, more typically, by removing them from the chain. This process creates the carriers needed for conduction and further delocalizes the charge along the polymer backbone. However, macroscopic conductivity is determined not only by charge transport along the polymer chain (intrachain transport) but also by charge hopping from polymer to polymer (interchain transport).

If interchain transport occurs less readily than motion along the polymer chain, it is expected that macroscopic conductivity would be limited by the size of the polymer and, therefore, be dependent on molecular weight. Similar reasoning suggests that if interchain transport occurs more readily than intrachain transport, the conductivity would be independent of molecular weight.

The competition between these two mechanisms has been discussed using scaling arguments by de Gennes[1] and by Heeger and Smith.[2] They describe conductivity in terms of τ_c, the mean lifetime of the charge carrier on the polymer chain, and τ_i, the time required for a charge carrier to completely explore the polymer chain. When τ_c is much greater than τ_i, conductivity is limited by interchain hopping and, for randomly coiled polymers, will increase linearly with molecular weight as given by the following relationship

$$\sigma \propto \frac{ne^2}{kT}\frac{aL}{\tau_c} \tag{1}$$

Here L is the length of the polymer and is proportional to the molecular weight, a is the persistence length of the chain, n is the charge density, and e is the charge per carrier.

However, if τ_i is greater then τ_c, as would be expected for high molecular weight polymers, the conductivity reaches a maximum value independent of molecular weight, and σ is given by

$$\sigma \propto \frac{ne^2}{kT}a\sqrt{\frac{D_i}{\tau_c}} \tag{2}$$

where $D_i \propto L^2/\tau_i$ is the diffusion coefficient for the charge carriers along the chain and is independent of L.

In the discussion which follows, we provide a quantitative derivation of eqs 1 and 2 including a complete formula that includes both regimes. The usefulness of high-frequency ac conductivity measurements is shown. We also present new results on the effects of orienting the sample by stretching along the direction of the conduction axis. For this case, we compare our findings with the considerable amount of experimental data that has been obtained on this subject.[3–5] We conclude with a discussion of other effects that should play an important role in determining conductivity: molecular weight distribution, the presence of defects on the polymer chain, and changes in the polymers persistence length induced by doping or by stretching. Our model is intended to describe the behavior of amorphous melts and solids. Although we are aware of cases where a small change in the amount of crystallinity has a large effect on the conductivity,[6] we believe that the enhancement of conductivity by stretching will be similar for amorphous and semicrystalline polymers.

Discussion

Conductivity for Polymers in the Isotropic State. Let $p(s',t;s'')$ be the probability density that the diffusing charge is between s' and $s' + ds'$ at time t given that it was at s'' at $t = 0$. The function p is the solution of the one-dimensional diffusion equation with reflecting boundary conditions:[7]

$$p(s',t;s'') = \frac{1}{L}\left[1 + 2\sum_{j=1}^{\infty}\cos\frac{j\pi s'}{L}\cos\frac{j\pi s''}{L}\exp\left(\frac{-j^2 t}{\tau_i}\right)\right] \tag{3}$$

Here L is the length of the polymer chain, $\tau_i = L^2/\pi^2 D_i$, and D_i is the diffusion coefficient along the chain. If the charge hops onto the chain at a random position, then the average value of $|s' - s''|$ which we call $\langle s(t)\rangle$ is

$$\langle s(t)\rangle = \frac{1}{L}\int_0^L ds''\int_0^L ds'\,|s' - s''|p(s',t;s'') = \frac{L}{3}\left[1 - \frac{6}{\pi^2}\sum_{j=1}^{\infty}\frac{1}{j^2}\exp\left(\frac{-j^2 t}{\tau_i}\right)\right] \tag{4}$$

Here $\langle ... \rangle$ implies an average over all possible starting points on the chain. We also have need for the quantity

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$\langle s^2(t)\rangle$ which is given by

$$\langle s^2(t)\rangle = \frac{1}{L}\int_0^L ds''\int_0^L ds'\,(s'-s'')^2 p(s',t;s'') = \frac{L^2}{6}\left[1-\frac{90}{\pi^4}\sum_{j=1}^{\infty}\frac{1}{j^4}\exp\left(\frac{-j^2t}{\tau_i}\right)\right] \quad (5)$$

Let $m(t)$ be the probability density that the charge leaves the polymer chain at time t. We choose for $m(t)$

$$m(t) = \frac{1}{\tau_c}\exp\left(-\frac{t}{\tau_c}\right) \quad (6)$$

such that the lifetime of the charge on a chain is $\int_0^\infty dt\, t m(t) = \tau_c$.[8]

Under these conditions, the average distance that the charge diffuses along the chain between hopping on and off is equal to $\langle L(\tau_c)\rangle$ and is given by

$$\langle L(\tau_c)\rangle = \int_0^\infty dt\, m(t)\langle s(t)\rangle = L\frac{2}{\pi^2}\sum_{j=1}^{\infty}\frac{\tau_c}{\tau_i + j^2\tau_c} = L\left[\frac{1}{\alpha}\coth\alpha - \frac{1}{\alpha^2}\right] \quad (7)$$

where $\alpha = \pi\sqrt{\tau_i/\tau_c}$ and the brackets on $L(\tau_c)$ indicate averaging with the function $m(t)$. $\langle L^2(\tau_c)\rangle$ was calculated in a similar fashion and is given by

$$\langle L^2(\tau_c)\rangle = \frac{5L^2}{2}\left[\frac{1}{\alpha^2}-\frac{3}{\alpha^3}\coth\alpha+\frac{3}{\alpha^4}\right] \quad (8)$$

The macroscopic dc conductivity, σ, can now be determined using the relation[9]

$$\sigma = ne\mu \quad (9)$$

Here μ is the charge mobility and is obtained from the usual Nernst formula,[9]

$$\mu = eD_c/kT \quad (10)$$

where D_c represents the interchain diffusion coefficient. Using random walk arguments, D_c can be estimated from the square of the displacement divided by the time between hops

$$D_c = \frac{\langle X^2(\tau_c)\rangle_\parallel}{2\tau_c} \quad (11)$$

where $\langle X^2(\tau_c)\rangle_\parallel$ is the mean square step length along the conduction direction.

For an isotropic polymer coil $\langle X^2(\tau_c)\rangle_\parallel$ is given by[10]

$$\langle X^2(\tau_c)\rangle_\parallel = \frac{a\langle L(\tau_c)\rangle}{3} \quad (12)$$

Combining eqs 9–12, we arrive at

$$\sigma = \frac{ne^2}{6kT}\frac{a\langle L(\tau_c)\rangle}{\tau_c} \quad (13)$$

When the time between interchain hops is much greater than the time to explore the polymer chain, i.e. $\tau_c \gg \tau_i$, expansion of eq 5 gives $\langle L(\tau_c)\rangle = L/3$, and

$$\sigma = \frac{ne^2}{18kT}\frac{aL}{\tau_c} \quad (14)$$

In this regime, σ increases linearly with the molecular weight as described above.[1,2]

In the opposite limit where the charge hops from polymer to polymer much faster than it explores a single polymer, the conductivity is determined from the large α limit of eq 7 and is given by

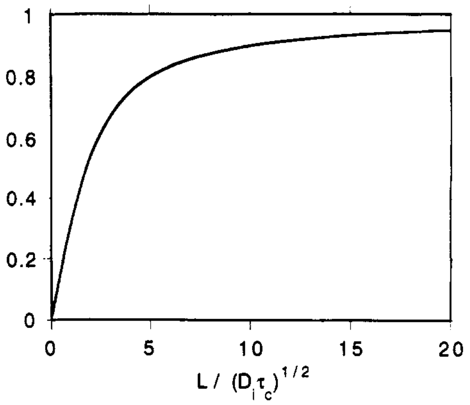

Figure 1. Conductivity of a Gaussian coil as a function of the length of the polymer. The conductivity has been made dimensionless by the conductivity of an infinitely long chain, eq 15, and the length has been made dimensionless by the distance, $\sqrt{D_i\tau_c}$, charge would diffuse on an infinitely long chain in a time τ_c.

$$\sigma = \frac{ne^2}{6kT}a\sqrt{\frac{D_i}{\tau_c}} \quad (15)$$

This quantity is independent of molecular weight, in agreement with results cited above.[1,2] The crossover between the two regimes is smooth. The quantity $\langle L(\tau_c)\rangle$ first grows in proportion to the square root of τ_c and then becomes constant as is expected for diffusion in a bounded region. When eq 14 is set equal to eq 15, it can be seen that the transition between the molecular weight dependent regime and the constant conductivity regime occurs when the ratio of τ_i/τ_c is approximately 1 (actually $9/\pi^2$). The full eq 13 normalized by the conductivity of an infinite molecular weight polymer is

$$\frac{\sigma(\alpha)}{\sigma(\infty)} = \coth\alpha - \frac{1}{\alpha} = \mathcal{L}(\alpha) \quad (16)$$

where $\mathcal{L}(\alpha)$ is the Langevin function.[11] The right-hand side of eq 14 is shown in Figure 1 as a function of the ordinate α. The value of α has a simple physical interpretation. It is equal to the length of a polymer chain divided by the distance a charge would diffuse in a time τ_c on a chain of infinite length, $\alpha = L/\sqrt{D_i\tau_c}$. This figure looks very similar to recent data obtained by Osawa et al.[12] on electrochemically polymerized poly(3-hexylthiophene).

Equation 13 depends on four parameters: n, a, τ_i, and τ_c. Although under some conditions it is possible to directly measure n, a lack of information about a in the doped state means that an experimental determination of σ can only be used to determine the ratio of τ_i and τ_c. However, we show in the following discussion that measuring the ac conductivity at a frequency, ω, where $\omega\tau_c > \omega\tau_i \gg 1$ should allow a direct measurement of τ_i.

If the individual charge carriers move independently of each other, a measurement of the frequency-dependent conductivity is equivalent to a measurement of the frequency-dependent diffusion coefficient, which are given by

$$\sigma(\omega) = ne\mu(\omega) = \frac{ne^2}{kT}D(\omega) \quad (17)$$

The value of $D(\omega)$ can be obtained from the cosine transform of the velocity correlation function[9]

$$D(\omega) = \frac{1}{3}\int_0^{\infty} \mathrm{d}t \cos \omega t \langle v(0)v(t)\rangle$$
$$= \frac{1}{6}\int_0^{\infty} \mathrm{d}t \cos \omega t \frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle \Delta r^2(t)\rangle \qquad (18)$$

where $\Delta r^2(t)$ is the mean square displacement of a charge carrier during a time t. If measurements are made on polymers with a length such that $\tau_c > \tau_i$ and at frequencies such that the charge is confined on a single polymer, then the value of $\langle \Delta r^2(t)\rangle$ will be $a\langle s(t)\rangle$ with $\langle s(t)\rangle$ given by eq 4. Leaving the details to Appendix 1, the dominant contribution to $D(\omega)$ under these conditions is

$$D(\omega) \cong \frac{aL}{\sqrt{2\pi^2}}\sqrt{\frac{\omega}{\tau_i}} \qquad (19)$$

In this way a direct estimate of τ_i is possible which, when combined with dc measurements of σ, leads to an estimate of τ_c.

Orientation Induced by Stretching. We now consider how conductivity is affected by orientation in the sample. If the polymer is stretched so that the distance between the ends of each molecule is increased by a factor of λ along the conduction direction, $\langle X^2(\tau_c)\rangle_{\parallel}$ will given by[13-15]

$$\langle X^2(\tau_c)\rangle_{\parallel} = \frac{a}{3}\langle L(\tau_c)\rangle + \frac{a}{2L}\langle L^2(\tau_c)\rangle(\lambda^2 - 1) \qquad (20)$$

For $\tau_c \gg \tau_i$, expansion of eq 20 and combination with eqs 9–11 leads to the prediction that the conductivity will increase to

$$\sigma = \frac{ne^2}{kT}\frac{aL}{18\tau_c}\left[1 + \frac{3}{4}(\lambda^2 - 1)\right] \qquad (21)$$

If the stretching ratio λ is large, its effect can be substantial. A stretch ratio of only 3.6 is enough to produce a 1 order of magnitude increase in σ. The maximum stretch ratio for Gaussian coils is expected to be on the order of $\sqrt{L/a}$.[16] Near this point the conductivity would increase with the square of the molecular weight in a manner similar to rigid rods (see below).[2]

In the opposite limit where $\tau_i \gg \tau_c$, σ can still be enhanced by stretching. The large α limit of eqs 7, 8, and 20 leads to

$$\sigma = \frac{ne^2}{6kT}a\sqrt{\frac{D_i}{\tau_c}}\left[1 + \frac{15}{4}\frac{\sqrt{D_i\tau_c}}{L}(\lambda^2 - 1)\right] \qquad (22)$$

Again, when λ nears its maximum value of $\approx \sqrt{L/a}$, it can be shown that the conductivity of coils and rods are essentially the same.

If conductivity is determined as a function of $\lambda^2 - 1$, the first regime (eq 21) has an intercept that is linear in molecular weight and a slope that is independent of it. The second regime (eq 22) has an intercept that is independent of molecular weight, but the slope is inversely dependent on it. Because of this, when the time to explore a polymer chain is approximately equal to the lifetime on the charge on a polymer ($\tau_i \approx \tau_c$), stretching has its greatest effect on conductivity. This leads to a maximum in σ as a function of α for certain values of λ, which is shown in Figure 2. Figure 3 gives σ as a function of λ for different values of α.

Experiments on the effect of stretching on different conducting polymers have been done by Moulton and Smith,[3] by Tokito, Smith, and Heeger,[4] and by Cao, Smith, and Heeger.[5] Our result that the conductivity should increase with λ^2 agrees well with their findings (see Figure 4a–c).

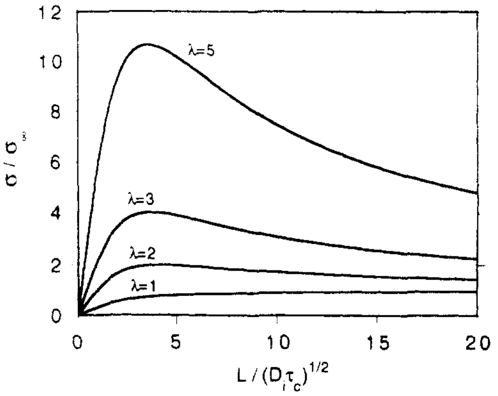

Figure 2. Conductivity of stretched Gaussian coils versus length of the polymer for various values of the stretch ratio, λ. For definitions see the caption of Figure 1.

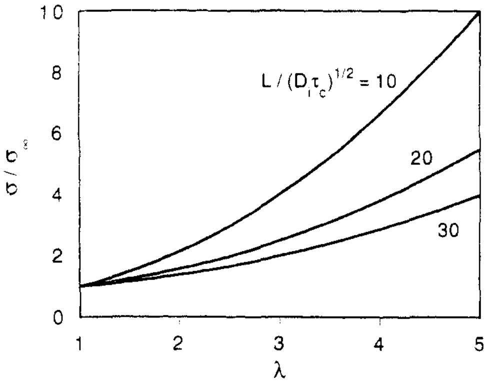

Figure 3. Conductivity of stretched Gaussian coils versus the stretch ratio, λ, for various values of the polymer length. For definitions see the caption of Figure 1.

The anisotropy of conductivity can be determined from the ratio of conductivity measured parallel to the direction of stretching to that measured perpendicular to stretching. Figure 5 gives a theoretical prediction for this ratio at different values of the chain length. Experimental measurements have been carried out by Cao, Smith, and Heeger,[5] and again our results agree well with their observations (see Figure 6).

The polymers shown in Figures 4 and 6 are semicrystalline materials. We expect that the orientation of the chains between the crystalline regions should produce an enhancement of conductivity in the same way as ordering chains in an amorphous system. However, if additional crystallinity is produced by stretching, the enhancement of conductivity might be larger than our predictions.

Our comparison with experimental data has assumed that the polymer chain is stretched by the same ratio λ as the macroscopic dimensions of the sample. This may not always be the case if the chains partially relax before being quenched into the solid state. However, the conductivity can also be related to the order parameter, $S = (3\langle \cos^2\theta\rangle - 1)/2$, where $\langle \cos^2\theta\rangle$ is the mean square orientation of a repeat unit relative to the stretching direction. Methods of relating λ to S have been given by Ullman[16] and measurements of σ as a function of S have been reported by Gagnon, Karasz, Thomas, and Lenz.[17]

Changes in the Persistence Length Caused by Stretching. Stretching might also produce a feedback effect on the conductivity. If pulling the polymer aligns the π-conjugated orbitals in a way that enhances the charge-transfer integrals,[18-20] there will be further delo-

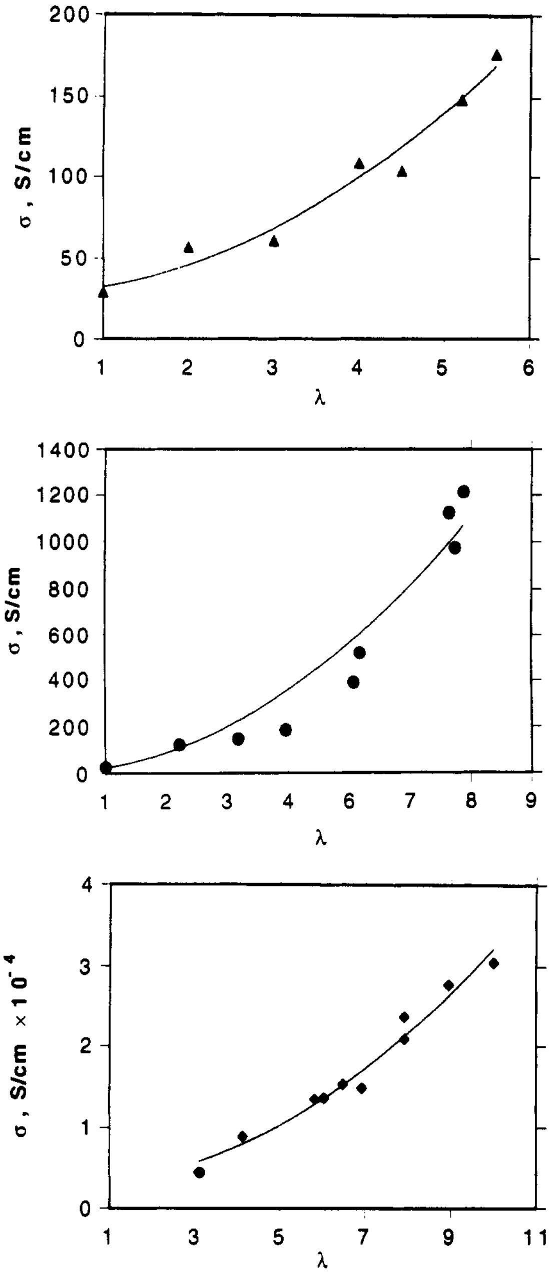

Figure 4. (a, Top) Conductivity of poly(3-octylthiophene) vs stretch ratio, λ (data from ref 3). (b, Middle) Conductivity of poly(2,5-dimethoxy-*p*-phenylenevinylene) vs stretch ratio, λ (data from ref 4). (c, Bottom) Conductivity of polyacetylene vs stretch ratio, λ (data from ref 6). All curves have the form $\sigma(\lambda) = \sigma(0)[1 + k(\lambda^2 - 1)]$ with $\sigma(0)$ equal to 32.2, 26, and 3280 and k equal to 0.14, 0.68, and 0.09 for Figure 4a–c.

calization of electrons and an increase in the persistence length a. Such effects might be detected by examining the stress dependence of the polymers birefringence—the usual linear law obtained by assuming that the polarizability of a chain repeat unit is independent of the stress would not be found under these conditions.[21] Stretching the polymer and the subsequent alignment of neighboring bonds along the chain should also increase the rate that charge diffuses. Under these conditions, D_i should be given by $D_i = l^2 \exp(-\Delta t)/\tau_0$ where l is the length of a dimer of conjugated bonds, τ_0 is the hopping time when the bonds are fully aligned, and Δt is the difference in transfer integrals measured in units of kT between the fully aligned and actual positions of the bonds. Reducing Δt is like removing defects that slow diffusion of charge along the polymer chain. The greatest increase in conductivity should occur in the molecular weight independent regime where σ is proportional to $\sqrt{D_i}$.

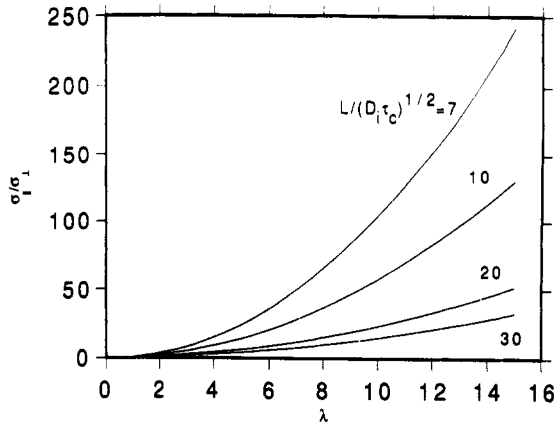

Figure 5. Anisotropy of conductivity vs stretch ratio, λ, for various values of the polymer length.

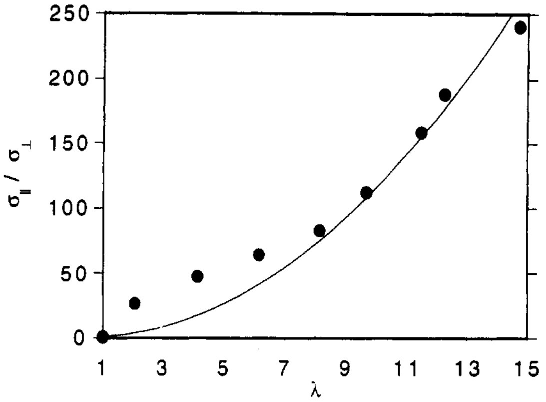

Figure 6. Anisotropy of conductivity of polyacetylene vs stretch ratio, λ (data from ref 6).

Molecular Weight Distribution and Defects. So far we have assumed that all of the polymer chains have the same length. If the sample has a distribution of lengths, the above results can easily be averaged to account for this effect. A finite width to the molecular weight distribution would be most important when $\tau_c \gg \tau_i$.

If, on the other hand, the polymer chains contain defects that actually block the diffusion of charge, all of our results could be changed. When defects are present, the relevant distribution function for averaging the results given above is the distribution of distances between defects. If their density is high, the regimes described above will be independent of the total molecular weight of the polymer and instead depend on the molecular weight between defects.

Figure 7 shows how the conductivity of a polymer is decreased when a fraction, β, of the repeat units contains defects that block the diffusion of charge. Details of this calculation can be found in Appendix 2.

Such blocks might be missing double bonds that were not formed during synthesis or that were lost in subsequent reactions during exposure to the environment. The block might also be due to the local steric arrangement of a dimer that effectively makes the transfer integrals so large that charge diffusion is stopped.[19] Configurations such as these could be the result of large side chain substituents on neighboring repeat units.

Liquid Crystallinity. It is interesting to further discuss the case of rigid rods. If the rods have a preferred orientation axis that corresponds to the conduction axis,

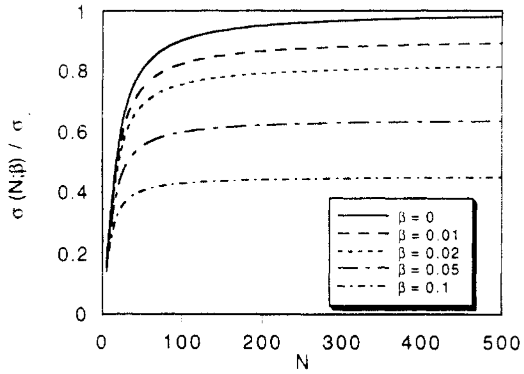

Figure 7. Effect of charge blocking sites on the conductivity. Conductivity of a polymer chain containing *N* repeat units divided by that of an infinite molecular weight polymer with no blocking sites. The fraction of bonds blocked is β. Appendix 2 describes how the calculations were done.

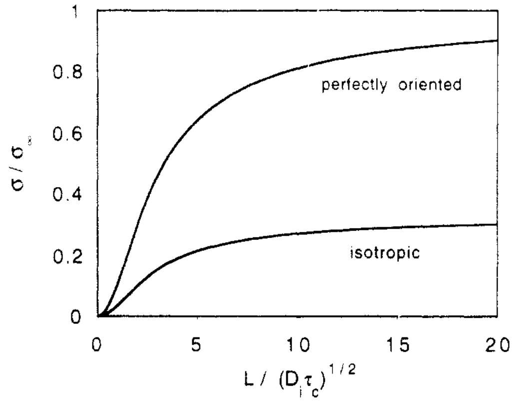

Figure 8. Conductivity of rigid rods as a function of the length of the rod. The upper curve is for perfectly oriented rods, and the lower one for isotropic rods. The conductivity has been made dimensionless by the conductivity of an infinitely long rod that is perfectly oriented along the conduction axis and the length has been made dimensionless by the distance, $\sqrt{D_i\tau_c}$, charge would diffuse on an infinitely long rod in a time τ_c.

the value of $\langle X^2(\tau_c)\rangle_\parallel$ is

$$\langle X^2(\tau_c)\rangle_\parallel = \langle L(\tau_c)\rangle^2\langle\cos^2\theta\rangle \tag{23}$$

where $\langle\cos^2\theta\rangle$ is the mean square projection of L along the direction of conductivity. It varies from $^1/_3$ in the isotropic state to 1 in the fully aligned sample. The conductivity would now be given by

$$\sigma = \frac{ne^2}{kT}\frac{\langle L(\tau_c)\rangle^2\langle\cos^2\theta\rangle}{2\tau_c} = \frac{ne^2}{kT}\frac{L^2\langle\cos^2\theta\rangle}{2\tau_c}\left(\frac{1}{\alpha}\coth\alpha - \frac{1}{\alpha^2}\right)^2 \tag{24}$$

in place of eq 13 for polymer coils. According to eq 20, the conductivity grows as L^2 when $\tau_c \gg \tau_i$, before becoming independent of L when $\tau_i \gg \tau_c$ (see Figure 8).

There is good reason to believe that in the future conjugated polymers will be found that spontaneously form liquid crystalline phases.[21,22] If the axis of the director is along the conduction direction, then $\langle\cos^2\theta\rangle$ will be greater than $^1/_3$ even in the rest state and conductivity will be enhanced. However, liquid crystallinity alone is not enough to enhance conductivity. Many liquid crystalline polymers are highly oriented on a microscopic scale (<1 μm) but on a macroscopic scale are isotropic. They appear to consist of many small domains with the director axis of each domain oriented randomly with respect to the other domains. In this case, conductivity will be depressed by the randomization of θ and possibly by resistance at the domain boundaries. This effect may be minimized by the development of alignment techniques that reduce orientational disorder in liquid crystalline polymers.

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Appendix 1: Calculation of AC Conductivity

The requirements for using a measurement of the ac conductivity to determine the time, τ_i, are that the polymer is of sufficiently short length so that $\tau_i < \tau_c$ and that the diffusion time t is less than τ_i. Under these condition, the charge motion is primarily confined to a single chain and the value of $\langle\Delta r^2(t)\rangle$ is $a\langle s(t)\rangle$. Using $\langle s(t)\rangle$ from eq 4, the velocity correlation function is obtained by differentiating $\langle\Delta r^2(t)\rangle$ to obtain

$$\langle v(0)v(t)\rangle = \frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle\Delta r^2(t)\rangle = \frac{aL}{\pi^2\tau_i}\left[2\delta(t)\sum_{j=1}^{\infty}\exp(-j^2|t|/\tau_i) - \frac{[2H(t)-1]^2}{\tau_i}\sum_{j=1}^{\infty}j^2\exp(-j^2|t|/\tau_i)\right] \tag{A1-1}$$

where $\delta(t)$ is the Dirac delta function and $H(t)$ is the Heaviside function.[11] The cosine transform according to eq 18 is given by

$$D(\omega) = \frac{2aL}{\pi^2\tau_i}\left(\sum_{j=0}^{\infty}\frac{\omega^2\tau_i^{\,2}}{j^4+\omega^2\tau_i^{\,2}} - 1\right) = \frac{2aL}{\pi^2\tau_i}\left(\frac{\nu}{4}\,\frac{\sinh\nu+\sin\nu}{4\cosh\nu-\cos\nu} - \frac{1}{2}\right) \tag{A1-2}$$

where $\nu = \pi\sqrt{2\omega\tau_i}$. Under conditions where $\nu \gg 1$, the dominant term is

$$D(\omega) = \frac{aL}{\sqrt{2\pi^2}}\sqrt{\frac{\omega}{\tau_i}} \tag{A1-3}$$

which is the same as eq 19.

From these results, one finds that the ratio of the ac conductivity at low molecular weight, $\sigma_{L\ll\sqrt{D_i\tau_c}}(\omega)$, to the dc conductivity at high molecular weight, $\sigma_\infty(0)$, produces an expression that involves τ_c alone:

$$\frac{\sigma_{L\ll\sqrt{D_i\tau_c}}(\omega)}{\sigma_\infty(0)} = 3\sqrt{2\omega\tau_c} \tag{A1-4}$$

The ratio of dc conductivities under the same conditions gives

$$\frac{\sigma_{L\ll\sqrt{D_i\tau_c}}(0)}{\sigma_\infty(0)} = \frac{\pi}{3}\sqrt{\frac{\tau_i}{\tau_c}} \tag{A1-5}$$

and hence a means of estimating the two time constants.

Appendix 2: Conductivity of a Polymer Chain with Defects

Determining the effect of charge blocking defects on conductivity requires a knowledge of the distribution function of chain lengths between defects. Let β represent the fraction of repeat units that are defects and let $W_r(\beta)\,dr$ represent the mass fraction of chain segments in which there are r repeat units between defects. If the defects are distributed at random, the following formula gives the relationship between $W_r(\beta)$ and the mass fraction of chain segments having r units between the chain ends and no defects:

$$W_r(\beta) = W_r(0)(1-\beta)^{r-1} + r\beta(1-\beta)^{r-1}\sum_{l=r+1}^{\infty}\frac{W_l(0)}{l}[2+\beta(l-r-1)] \quad \text{(A2-1)}$$

The function $W_r(\beta)$ also describes the length of chains after a fraction β of the units has been fractured. It has been studied extensively by Montroll and Simha.[24,25]

The conductivity of an ensemble of chains all having N repeat units and having a fraction, β, of blocked units implies that $W_r(0) = \delta(N-r)$ and that

$$\begin{aligned}\sigma(N;\beta) &= \sum_{r=1}^{\infty} W_r(\beta)\sigma(r)\\ &= (1-\beta)^{N-1}\sigma(N) + \frac{\beta}{N}\sum_{r=1}^{N-1} r\sigma(r)(1-\beta)^{r-1}[2+\\ &\qquad \beta(N-1-r)] \quad \text{(A2-2)}\end{aligned}$$

The results shown in Figure 7 were obtained from this equation after substituting $\sigma(r) = \sigma_\infty \mathcal{L}(\alpha_r)$ where σ_∞ is the conductivity of an infinite molecular weight polymer, $\mathcal{L}$ is the Langevin function, and $\alpha_r = ar/\sqrt{D_i\tau_c}$ is its argument.

For large values of N, the ordinate of Figure 7 reaches a constant value. Although we have not obtained an analytical result for this, a reasonable estimate can be obtained by approximating the Langevin function, $\mathcal{L}(x)$, as $x/3$ for $x \le 3$ and as 1 for $x \ge 3$. Under these conditions the plateau in Figure 7 is equal to

$$\frac{\gamma}{3}\left(\frac{2-\beta}{\beta}\right)[1-(1-\beta)^{3/\gamma}] - (1-\beta)^{3/\gamma}$$

where γ is equal to $a\sqrt{D_i\tau_c}$.

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