Nematic Order Imposes Molecular Weight Effect on Charge Transport in Conjugated Polymers

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ABSTRACT: Nematic order, in the bulk or at interfaces, is ubiquitous for semiflexible conjugated polymers. Nevertheless, the effect of liquid crystalline order on charge transport remains unclear. Using an analytical model, we demonstrate that nematic order leads to an enhancement in charge mobilities when compared to isotropic chains. Furthermore, we predict a quadratic dependence of the charge mobility on molecular weight of the chains. Analysis of the probability of forming hairpin defects also shows how the persistence length affects charge transport in conjugated polymers. We speculate that the prevalence of nematic order in conjugated polymers explains the reported increase in charge mobilities with molecular weight.

INTRODUCTION

Conjugated polymers are promising materials for many flexible electronic applications, including displays and stretchable transistors.1–3 Despite recent progress in the development of these soft semiconductors, charge transfer in conjugated polymers is still not fully understood. Indeed, models have been proposed based on experimental trends to qualitatively capture the dependence of charge mobility on morphological parameters, such as crystallinity and intercrystalline connectivity for semicrystalline conjugated polymers.4,5 Still, the lack of mechanistic models inhibits quantitative predictions of charge transport behaviors based on molecular properties for conjugated polymers, such as the drastic molecular weight dependence of the charge mobility.6

Because many high-performance conjugated polymers are semicrystalline, or even nearly amorphous,7,8 charge transport on amorphous chains plays an important role in overall electronic properties of conjugated polymers. Amorphous chains may orient isotropically or exhibit some degree of liquid crystalline order, depending on processing conditions and their abilities to access a liquid crystalline phase. Even for strongly crystalline polymers, accessing a liquid crystalline phase prior to macroscopic transport is likely limited by intercrystallite connectivity for amorphous tie chains that connect adjacent crystals. For amorphous conjugated polymers, chain conformations can significantly affect electronic properties of samples. Using density functional theory (DFT) calculations, previous work has shown that distortion of backbone dihedral angles can localize charge carriers, and, in turn, hinder intrachain charge transfer in amorphous chains.9,10 Under the assumption that chains are isotropic, Pearson et al. have predicted that charge mobilities scale linearly with molecular weights before leveling out at a high molecular weight.11 In the model based on Marcus theory12 and kinetic Monte Carlo (KMC) simulations developed by Spakowitz and co-workers, field-dependent charge mobilities increase with molecular weight for short isotropic chains as a result of reduction of chain ends that bound the length scale of fast intrachain charge transport.13–16 When the chain length is greater than the Kuhn length, polymer backbones can bend noticeably, creating conformational traps for charge carriers, and, in turn, leading to constant charge mobilities at high molecular weights.

The local alignment of polymer backbones, such as in nematic order, can also be crucial for charge transport in amorphous chains. Uniaxially aligned polymer backbones can act as straight pathways for charge transfer and lead to enhanced charge mobility in the aligned direction. The anisotropic shapes of the nematic chains may also affect statistics of charge trajectories, which then leads to a dependence of charge transport on material properties, such as molecular weight and persistence length.

In fact, conjugated polymers can spontaneously exhibit nematic order in the bulk and at interfaces. In the bulk, the semiflexible backbones of conjugated polymers may be regarded as sequences of rod-like segments with length of about a Kuhn length, LK, dispersed either in a real solvent or in “bound solvent” composed of alkyl side chains. When the polymer concentration is high enough, randomly placing rod-like segments with a random orientation in the system is no longer entropically viable.17–19 The system then undergoes a first-order transition from an isotropic phase to a nematic phase, in which chain segments align uniaxially. Experimental evidence for liquid crystalline phases abounds for many
polythiophenes and donor—acceptor conjugated polymers.

Near impenetrable surfaces, such as gate dielectric layers in field-effect transistors (FET), conjugated polymers can exhibit surface-induced nematic order. Instead of bending chain trajectories sharply to avoid collisions with the walls, semiflexible polymers tend to align parallel to impenetrable interfaces, creating alignment layers of thickness of about a persistence length, \( l_p \). Nematic interactions between backbone segments can further enhance surface-induced alignment. For chains that are near the isotropic-to-nematic phase boundary, surface-induced alignment is uniaxial, with the nematic director parallel to the interface.

Investigating the effect of uniaxial nematic alignment on charge mobility for amorphous conjugated polymers is, therefore, important for understanding overall charge transport in electronic devices. For example, regardless of whether it is nematic in the bulk or not, conjugated polymers near interfaces may be uniaxially ordered. In FETs, charge carriers are localized within 5 nm thick layers at the dielectric surface. Because the value of \( l_p \) of high-performance conjugated polymers usually exceeds 3 nm, we expect that amorphous chains align uniaxially in the conductive channel. Thus, modeling of charge mobilities of conjugated polymers requires a description of the role of nematic alignment on charge transport.

In this work, we use an analytical model to investigate charge transport for uniaxially aligned conjugated polymers. We show that nematic order may lead to the observed molecular weight dependence of charge mobility in conjugated polymers. We predict that charge mobilities are enhanced by nematic order and increase quadratically with molecular weight. The bending stiffness of chain backbones, characterized by the persistence length, governs formations of hairpin defects, which in turn alter the shapes of intrachain trajectories and the macroscopic charge mobility of nematic chains.

### RESULTS

**Charge Transfer in Isotropic Chains.** In our model for charge transport, intrachain charge motion is regarded as a one-dimensional diffusion of charge carriers with reflecting boundaries at the chain ends. In the absence of applied electric fields, charge carriers diffuse randomly along polymer backbones. The probability density for a charge carrier that is injected at time 0 into monomer \( s \) to be found at monomer \( s' \) at time \( t \) is

\[
p(s, s', t) = \frac{1}{N} \left(1 + 2 \sum_{j=1}^{N} \cos \left( \frac{j \pi s}{N} \right) \cos \left( \frac{j \pi s'}{N} \right) \exp \left( - \frac{j^2 t}{\tau_i} \right) \right)
\]

(1)

where \( N \) is the chain length and \( \tau_i \) is the characteristic time for a charge to diffusively spread along a chain of length \( N \), defined as \( \tau_i = N^2 \pi^2 k_B T \). The parameter \( k_B \) is the mean local intrachain charge transfer rate. The effect of local distortions of backbone dihedral angles is not explicitly included in the model; rather, we assume that disorder in dihedral angles leads to a smaller \( k_B \).

On average, the relative distance (measured in number of monomers) between the location of a charge carrier at \( t \) and its initial position is

\[
\langle \Delta N(t) \rangle = \frac{1}{N} \int_0^N ds' \int_0^N ds \delta(s - s' \mid p(s, s', t))
\]

\[
= \frac{N}{3} \left(1 + \frac{6}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp \left( - \frac{j^2 t}{\tau_i} \right) \right)
\]

(2)

After diffusing on the same chain for a while, the charge carrier can hop to another chain. We assume that the time required for interchain hopping follows an exponential distribution:

\[
h(t) = \frac{1}{\tau_h} \exp \left( - \frac{t}{\tau_h} \right)
\]

(3)

so that the mean lifetime for intrachain charge transfer is \( \tau_h = \int_0^\infty dt \ h(t) \). The value of \( \tau_h \) is inversely proportional to the interchain charge transfer rate, \( k_h \).

Between two interchain hopping events, the trajectory of charge motion is governed by the conformation of a semiflexible chain segment with length \( \langle \Delta N(\tau_h) \rangle \):

\[
\langle \Delta N(\tau_h) \rangle = \int_0^{\infty} dt h(t) \langle \Delta N(t) \rangle = \frac{N}{\gamma} \left( \coth \left( \frac{\pi \gamma}{2} \right) - 1 \right)
\]

(4)

where \( \gamma = \pi(\tau_h/\tau_i)^{1/2} = N(k_B/k)\). \( \gamma \) is a measure of the characteristic time for intra- and interchain charge transport. If chains are long enough and hopping between chains is frequent enough, then \( \gamma \) is large, and \( \langle \Delta N(t) \rangle \) is much shorter than (and independent of) the total chain length \( N \).

Using eq 4, we can obtain the mean square displacement per hopping time \( \tau_h \) for charge carriers in the conducting direction as the chain dimension \( \langle R_0^2(\tau_h) \rangle \). By regarding the long-time scale charge transfer as a one-dimensional random walk of step length \( \langle R_0^2(\tau_h) \rangle^{1/2} \), we obtain the charge mobility from the diffusion coefficient of charge carriers using the Einstein relation:

\[
\mu_\parallel = \frac{eD}{kT} = \frac{e(R_0^2(\tau_h))}{2kT\tau_h}
\]

(5)

For chains in the isotropic phase, Pearson et al. obtained the charge mobility by treating conjugated polymers as random walks of Kuhn segments:

\[
\mu_\parallel = \frac{e(\Delta N(\tau_h))a l_p}{6kT\tau_h}
\]

(6)

in which \( a \) is the length of a monomer and \( l_p \) is the persistence length. The charge mobility scales linearly with persistence length, which governs the straightness of the intrachain charge trajectories for isotropic chains.

When interchain charge hopping is slow or molecular weight is low (\( \tau_i \ll \tau_h \)), the charge carrier can explore the whole chain between two hopping events so that \( \langle \Delta N(\tau_h) \rangle \sim N \). In this case, the charge mobility scales linearly with the molecular weight. When interchain charge transfer is fast or molecular weight is high (\( \tau_i \gg \tau_h \)), a charge carrier will hop to another chain before it realizes how long the polymer is. For this case, the overall charge mobility is independent of molecular weight.

As a consequence, the charge mobility for isotropic chains increases linearly with molecular weight and reaches a plateau at high molecular weight. By normalizing the charge mobility...
with respect to the plateau value, one can obtain the molecular weight dependence of charge mobility:

\[
\frac{\mu_\|^{(N)}}{\mu_\|^{(\infty)}} = \coth(N\sqrt{k_c/k_i}) - \frac{1}{N\sqrt{k_c/k_i}} \tag{7}
\]

Depending on the ratio of intra and interchain charge transfer rates \(k_i/k_h\), the molecular weight dependence may be significant for isotropic polymers.

**Effect of Nematic Order on Charge Mobility.** We now consider charge transport in semiflexible chains with uniaxial alignment. Assuming the intrachain charge transfer rate, \(k_i\), is not affected by uniaxial alignment, we can combine the chain dimension in the alignment direction with eq 4 to predict the anisotropic charge mobility for conjugated polymers.

For conjugated polymers with nematic order, chain backbones align along the nematic director \(x\). The degree of alignment can be described using a quadrupolar order parameter \(q\):

\[
q = \frac{3}{2} \left( \langle \cos \theta \rangle^2 - \frac{1}{2} \right) \tag{8}
\]

where \(\theta\) is the deflection angle between a backbone tangent and the nematic director.

Thermal fluctuations can lead to deviations of chain paths from the aligning direction \(x\). The nematic field, however, can constrain transverse fluctuations of chain paths \(\Delta r_\perp^2\). We can define a deflection length \(\lambda\) below which the transverse fluctuations of nematic chains are governed by the bending stiffness of semiflexible chains and are unaffected by the nematic field. The average transverse fluctuation of the ends of the deflection segments (of length \(\lambda\)) is

\[
\Delta r_\perp^2 \approx \frac{2\lambda^2}{l_p} \tag{9}
\]

Effectively, the uniaxial alignment field acts as a cylindrical confinement of radius \(\Delta r_\perp\) and axis in the \(x\) direction.33–36

When \(l_p\) is greater than \(\lambda\), the deflection segments are rather straight, and the nematic order in the system can be approximated as

\[
q = \frac{3}{2} \left( \langle \cos \theta \rangle^2 - \frac{1}{2} \right) \approx 1 - \frac{3}{2} \left( \frac{\Delta r_\perp}{\lambda} \right)^2 \tag{10}
\]

where \(\theta_l\) is the angle between the deflection segment and the nematic director \(x\).

Combining eqs 9 and 10, one can also write the deflection length, \(\lambda\), as a function of the nematic order, \(q\), and the chain persistence length, \(l_p\):

\[
\lambda = \frac{1}{3} (1 - q) l_p \tag{11}
\]

In the uniaxial alignment direction, charge carriers travel along some rod-like paths with sequences of length, \(\lambda \langle \cos \theta_l \rangle\). As a consequence, the intrachain charge trajectory between two interchain hopping events follows the statistics of rod-like chains:

\[
\langle R_\|^2(t_\|) \rangle_n = \langle \Delta N(t_\|) \rangle_n^2 a^2 \langle \cos \theta \rangle^2 \\
\approx \langle \Delta N(t_\|) \rangle_n^2 a^2 (2 + q)^2 \tag{12}
\]

By treating long-time charge transfer as a one-dimensional random walk in the alignment direction, we predict the charge mobility in the aligning direction for uniaxially ordered chains:

\[
\mu_\| = \frac{e\langle R_\|^2(t_\|) \rangle_n}{2\pi kT} = \frac{e\langle \Delta N(t_\|) \rangle_n^2 a^2 (2 + q)^2}{18\pi kT} \tag{13}
\]

The charge mobility of uniaxially ordered \((q > 0)\) chains can be about 3 orders of magnitude higher than the charge mobility of isotropic chains (Figure 1a). The rod-like intrachain charge transfer

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** (a) Charge mobility for isotropic chains and nematic chains with different order \(q\). (b) Charge mobility for nematic chains and nematic chains with hairpin defects. Reference mobility is \(\mu_\|^{*} = \frac{ea k_T}{6h^2}\) and \(a\) is the monomer size. Relative charge transfer rate is \(k_i/k_h = 10^5\) and persistence length is \(N_p = 5\). (c) Normalized charge mobility for isotropic chains, nematic chains, and nematic chains with hairpin defects. Relative charge transfer rate is \(k_i/k_h = 10^5\). \(N_p = 5\) (green) and 10 (purple).
trajectories lead to the drastic enhancement of charge transport. Indeed, the nematic order, \(q\), may also depend on chain length, \(N\), because longer chains have fewer chain ends and may interact more effectively with the aligning field. Once chains transition into the nematic phase and become uniaxially aligned, however, further increases in the degree of alignment, \(q\), result only in a slight enhancement of charge mobility, about a factor of 2. As such, we expect that our model, in which \(q\) is independent of \(N\), can capture the molecular weight dependence of charge mobility for nematic conjugated polymers.

We also obtained the molecular weight dependence of charge mobility for uniaxially aligned semiflexible chains. When \(\tau_i \ll \tau_0\), the charge mobility in the alignment direction scales with \(N^2\). This molecular weight dependence is the same as the prediction by Pearson and co-workers for charge transport on nematic rod-like chains.\(^2\) When interchain charge transfer is very fast or the molecular weight is high (\(\tau_i \gg \tau_0\)), the charge mobility of aligned polymers is independent of molecular weight. We write the normalized charge mobility in the alignment direction as

\[
\mu_{\|}^{\infty}(N) = \left( \coth(N\sqrt{k_h/k_i}) - \frac{1}{N\sqrt{k_h/k_i}} \right)^2
\]

(14)

The molecular weight dependence is more significant for the uniaxially aligned polymers than for the isotropic chains (Figure 1c).

In the direction perpendicular to the aligning field, the intrachain charge trajectory is governed by the random transverse fluctuations of the deflection segments:

\[
\langle R_s^2(\tau_i) \rangle_n = \frac{\langle \Delta N(\tau_i) \rangle}{\lambda/a} \Delta_l^2 = \frac{2\langle \Delta N(\tau_i) \rangle a_p (1 - q)^2}{9}
\]

(15)

The resulting charge mobility is

\[
\mu_{\perp}^{\infty} = \frac{e\langle R_s^2(\tau_i) \rangle_n}{2\pi kT} = \frac{e\langle \Delta N(\tau_i) \rangle a_p (1 - q)^2}{9\tau_i kT}
\]

(16)

The molecular weight dependence of the charge mobility of nematic chains in the perpendicular direction is the same as that of isotropic chains. The value of \(\mu_{\perp}^{\infty}\) also decreases as the nematic order, \(q\), increases. We expect that the charge mobility in the aligning direction is much higher than the mobility in the perpendicular direction.

**Role of Hairpin Defects on Charge Transport.** In the above analysis, we assume that every segment of the aligned chains uniaxially points in the alignment direction. The assumption is true when the chain contour length, \(l_c\), is comparable to the persistence length, \(l_p\). For short semiflexible chains, forming a hairpin defect involves sharply bending the stiff polymer backbone against the nematic field. As a consequence, the energy penalty for forming short hairpins is large and the probability for finding those defects is negligible. When chains are long enough, however, semiflexible polymers can form hairpin defects by bending the chain trajectory more smoothly over a length greater than \(l_p\). In this way, the elastic energy penalty for bending a chain is smaller and the probability for forming hairpins is higher.

The existence of these “U-turns” can affect the statistics of charge trajectories. If intrachain charge transport occurs on a length scale shorter than the mean distance between two hairpin defects, \(N_h\) (Figure 2a), the charge trajectory is rod-like

(eq 12). When the contour length of the intrachain charge trajectory is much longer than \(N_h\) intrachain charge motions are essentially one-dimensional random walks with step length \(N_h\).

To reveal the effect of hairpin defects on charge transport for polymer nematics, we construct a simple model to estimate the bending energy cost of a hairpin, \(E_{bh}\), and the mean chain length, \(N_h\), between two defects. In the model, we align semiflexible chains using an external aligning field, \(A\), and write the single chain Hamiltonian as

\[
\beta H[u(s)] = \int_0^N ds \left[ \frac{N_p}{2} \left| \frac{du(s)}{ds} \right|^2 + U(u_s) \right]
\]

(17)

in which \(N_p\) is the persistence length measured in a number of monomers \((N_p = l_p/a)\), and \(u(s)\) is the normalized chain path, in which each segment is a unit vector. The interaction of a chain segment, \(u_s\) with the external aligning field is

\[
U(u_s) = -AB^2 (\cos \theta)
\]

(18)

where \(\theta\) is the angle between the \(s^{th}\) chain segment and the aligning axis, and \(P_2\) is the second order Legendre polynomial.

For nematic polymers, we expect that the energy cost for forming a hairpin defect is expensive, of at least several \(kT\). As a consequence, the conformation of the hairpin must be dominated by a classical chain path that possesses the lowest free energy. Assuming the fluctuations around the most favorable chain path are negligible, we obtain the hairpin conformation by minimizing the free energy:
0 = \frac{\delta F[u(s)]}{\delta u(s)}
= \delta \frac{\delta}{\delta u(s)} \int_0^N ds \left( \frac{N_b}{2} \left| \frac{\partial u(s)}{\partial s} \right|^2 + U(u) \right)
= -N_b \frac{\partial^2 u(s)}{\partial s^2} + \frac{\partial U}{\partial u(s)} \tag{19}

Because the alignment is uniaxial, we are only interested in the deflection angle $\theta$ of the chain path from the alignment axis:

$$\frac{\partial^2 \theta(s)}{\partial s^2} - \frac{3}{2} \omega \sin 2\theta(s) = 0$$ \tag{20}

in which $\omega = \frac{A}{N_b}$. Using eq 20, we can solve the most favorable conformation of a hairpin by constraining the orientation of the chain ends so that $\theta(0) = 0$ and $\theta(N) = \pi$.

In absence of the aligning field, $A (\omega = 0)$, the solution of the above equation is evidently $\theta(s) = \pi s / N$. The hairpin is a semicircle so that the deflection angle $\theta$ linearly varies over the chain length (Figure 2b). The stiff polymer backbone bends uniformly to reduce the elastic energy cost.

For systems with uniaxial alignment (so that $A$ and $\omega$ are greater than zero), we analytically solve eq 20 by realizing the differential equation is essentially the equation of motion for a particle subjected to a force given by $-\omega \sin 2\theta(s)$:

$$\theta(s) = 2\arccot(\exp[(3\omega)^{1/2}N/2 - s])] \tag{21}$$

When the strength of the uniaxial aligning field, $A$, increases (and so $\omega = A/N_b$ also increases), the radius of the hairpin decreases (Figure 2b). Although the bending energy is higher for smaller hairpins, the cost of alignment against the field, $A$, is lower.

Using the most favorable chain path, $\theta(s)$ (eq 21), we can obtain the characteristic size of the hairpin elbow, $N_b$ (see Figure 2a):

$$N_b = (3\omega)^{-1/2} = (3N_p/A)^{1/2} \tag{22}$$

We can also compute the bending energy cost per hairpin defect for long nematic chains:

$$\beta E_b = \lim_{N \to \infty} \frac{N_b}{N} \frac{N_p}{2} \left( \frac{\partial \theta(s)}{\partial s} \right)^2 = (3AN_p)^{1/2} \tag{23}$$

The value of $E_b$ arises from the optimal size of the hairpin elbow ($N_b$) and increases with both the aligning field, $A$, and the chain stiffness, $N_p$.

Because the bending energy of a hairpin can be as large as several $kT$, the probability for finding these defects is low. We may consider the hairpin defects as a one-dimensional ideal gas, distributed randomly on the uniaxially aligned chains. The “volume fraction” of the hairpin defects can be approximated as

$$\phi = \frac{N_b}{N_a} \tag{24}$$

and we can write the free energy for the “hairpin gas molecules” as

$$F = \frac{N}{N_b} \ln \phi + \frac{N}{N_a} E_b \tag{25}$$

By minimizing the free energy with respect to $N_a$, we obtain the mean chain length between two defects:

$$N_a = 3^{1/2} e^{1/(3AN_p)^{1/2}} \left( \frac{N_p}{A} \right)^{1/2} \tag{26}$$

To demonstrate the typical value of $N_a$ for uniaxially aligned conjugated polymers, we approximate the aligning field strength, $A$, for long semiflexible chains in the nematic phase. We estimate the aligning field that a chain segment experiences as the product of the average order in the system, $q$, and the nematic coupling parameter, $\alpha$. For nematic chains near the isotropic-to-nematic phase boundary, we expect that $A = \alpha q_{\nu}$ where $\alpha_c$ is the critical nematic coupling constant and $q_{\nu}$ is the critical order parameter for the system to undergo a first order transition from the isotropic phase to the nematic phase. In our previous work, we estimated the values of $\alpha_c$ and $q_{\nu}$ for chains with differing stiffness, $N_p$.36 For long chains ($N \gg N_p$), the critical coupling parameter, $\alpha_c \sim N_p^{-1}$, and $q_{\nu}$ are rather constant for chains with differing stiffness. As a consequence, we estimate the aligning field strength, $A \approx N_p^{-1}$ (a coefficient of order unity is neglected here). The mean chain length between adjacent hairpin defects now depends only on the chain stiffness:

$$N_a \approx 27N_p \tag{27}$$

The linear relation between $N_a$ and $N_p$ agrees with the previous prediction by Vroege and Odijk, which is obtained by applying a Gaussian trial function to approximate the narrow distribution of backbone tangent orientation near $\theta = 0$ and $\pi$ for nematic chains.37 For mildly stiff chains, we expect $N_a$ to be as large as $10^5$ (Figure 3).

Figure 3. Mean distance between two hairpin defects, $N_a$, vs persistence length $N_p$, for chains in the nematic phase.

When the chain length is much longer than the typical distance between two defects ($N \gg N_a$), the intrachain charge trajectory is no longer rod-like. We expect charge motion along the polymer backbone is now a one-dimensional random walk with step length equal to $N_p(2 + q)/3$:

$$\langle R_f^2(q) \rangle_{\text{hairpin}} = (\Delta N(q)) N_p^2 \langle \cos \theta \rangle^2 \approx 3(\Delta N(q)) I_p(2 + q)^2 \tag{28}$$

The resulting charge mobility depends linearly on the persistence length, $I_p$, comparable to the charge mobility for
isotropic chains. For nematic chains without hairpin defects, however, the charge mobility is independent of the persistence length (eq 13).

Our simple model captures the chain dimensions of uniaxially aligned semiflexible polymers in both the ballistic ($R^2_{b} \sim N^2$) and random walk ($R^2_{w} \sim N$) regimes. Our results are consistent with previous calculations by Spakowitz et al. Using self-consistent field theory and the ground state dominance approximation, these authors analytically compute a correlation length, $\xi_{b}^{*}$, that separates the ballistic and random walk regimes for chain conformations in strong aligning fields. The correlation length, $\xi_{b}^{*}$, represents the critical length for hairpin formation. Similar to our $N_{p}$, the value of $\xi_{b}^{*}$ linearly scales with $N_{p}$ at the isotropic-to-nematic phase boundary (assuming the critical value of $AN_{p}$ is a constant for the phase transition).

We write the molecular weight dependence of charge mobility using a piecewise function:

$$
\frac{\mu_{I}^{\text{harm}}(N)}{\mu_{I}^{\text{harm}}(\infty)} = \begin{cases} 
\frac{k_{h}^{1/2}}{k_{b}^{1/2}} \left( \frac{1}{\sqrt{k_{h}/k_{b}}} - \frac{1}{\sqrt{k_{b}/k_{h}}} \right), & \text{if } N \leq N_{c} \\
\coth\left( \frac{1}{\sqrt{k_{h}/k_{b}}} \right) - \frac{1}{\sqrt{k_{h}/k_{b}}}, & \text{if } N > N_{c}
\end{cases}
$$

in which the crossover point, $N_{c}$, can be solved by equating the two portions of eq 29. The value of $N_{c}$ depends on the arm length of hairpin defects, $N_{a}$ and the relative charge transfer rate, $k_{h}/k_{b}$.

To observe the transition of the intrachain charge trajectory from the rod-like scaling regime ($\mu \sim N^{-2}$) to the coil-like regime ($\mu \sim N^{-1}$), the relative charge transfer rate, $k_{h}/k_{b}$ needs to be large enough that

$$
k_{h} > N_{a}^{2}
$$

If $k_{h}/k_{b}$ is small, a charge carrier can hop to another chain before it realizes the existence of hairpin defects.

Nonetheless, the existence of hairpins does not significantly alter the overall molecular weight dependence and the value of charge mobility (Figure 1b). For uniaxially aligned chains with hairpin defects, we expect that the charge mobility increases with $N^2$ when the molecular weight is low, comparable to the mobility of defect-free chains. When the chain length exceeds $N_{c}$, which is much greater than the hairpin arm length, $N_{a}$, the dependence on molecular weight becomes small, similarly to our predictions for isotropic coils. Because $N_{c}$ is rather large, the charge mobility for $N > N_{c}$ can be close to the plateau value and the coil-like behaviors of the charge trajectories may not be obvious. In fact, hairpin defects only reduce the charge mobility of a high molecular weight sample by a factor of about two.

**Comparison with Experiments.** Because the ratio of intra- and interchain charge transfer rates, $k_{h}/k_{b}$, can be large, the enhancement in charge mobility can be many orders of magnitude as the molecular weight increases for nematic chains (Figure 1c). For example, by fitting the experimental mobility data, Spakowitz et al. suggest that the ratio, $k_{h}/k_{b}$, can be as large as $10^{4}$ for amorphous poly(spirobifluorene) and $10^{4}$ for poly(3-hexylthiophene) (P3HT) in amorphous regions. Using microwave conductivity measurements, previous authors have found that the intrachain charge transfer can be $10^{7}$ times faster than overall charge transport for fluorene-thiophene copolymers. We expect the ratio, $k_{h}/k_{b}$, to be smaller for high-performance materials, but still much greater than unity.

Our analytical charge transfer model for nematic chains may explain the strong molecular weight dependence of charge mobility for conjugated polymers. Current measurements of charge mobilities rely on thin-film transistors, where the conductive channel is localized to about $5$ nm from the dielectric interface. In the conductive region, the dielectric interface can induce uniaxial order to semiflexible conjugated polymers. Indeed, the nematic order of real conjugated polymers may not be truly long-ranged. Any quenched disorder can disturb long-range uniaxial order, and lead to nematic domains in which the liquid crystalline directors point in different directions. The sizes of nematic domains may affect long-range charge transfer in the sample. For example, using resonant scattering of polarized soft X-rays, Collins et al. showed that charge mobility can be enhanced by an order of magnitude as the nematic domain size, $\xi$, increases for liquid crystalline poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]-thiophene (PBTHT)). When the sizes of ordered regions, $\xi$, are large or charge transfer across domain boundaries is sufficient, we expect that the molecular weight dependence of charge mobility arises from the “short-range” uniaxial order of chains in the nematic domains.

To show the effects of domain sizes and interdomain charge transport on net charge mobilities in nematic conjugated polymer samples, we make a simple argument as follows. In the absence of applied fields, the net charge mobility, $\mu_{\text{net}}$, is proportional to the long time scale diffusion constant of charge carriers, $D_{\text{net}}$. Assuming the orientations of nematic domains are random, we can write the diffusion constant, $D_{\text{net}} \sim \xi_{b}^{2}/\tau_{b}$, in which $\xi_{b}$ is the domain size and $\tau_{b}$ is the time for a charge carrier move from one domain to another. Inside the local nematic domains, the charge motion is a one-dimensional random walk, with diffusion constant $D_{\text{local}}(N) \sim (\Delta N/d)$. For intradomain charge transport, we consider diffusion in the direction parallel to the nematic field because charge transport in the perpendicular direction is much slower. In the direction perpendicular to the nematic field, the intrachain charge trajectory is a random walk with a step size decreasing with the nematic order, $q$. The resulting mobility, $\mu_{\text{I}}$, is much smaller than $\mu_{\text{ff}}$ for long chains. We expect charge carriers move more effectively to the domain boundaries in the aligning direction, followed by interdomain charge transport. In this way, we can write $\tau_{d}$ by summing the time for charges to move across a domain, $\xi_{D}^{2}/D_{\text{local}}(N)$, and an additional time, $\tau_{w}$, for charges to hop across the domain boundaries. Thus, the net charge mobility scales as

$$
\mu_{\text{net}}(N) \sim D_{\text{net}}(N) \sim \frac{D_{\text{local}}(N)}{1 + \tau_{b}D_{\text{local}}(N)/\xi_{D}^{2}}
$$

The value of $\mu_{\text{net}}$ increases as the nematic domain size increases and the interdomain transfer time, $\tau_{d}$, decreases. When $\xi_{D}$ is large or $\tau_{d}$ is small, the net charge mobility is proportional to $(\Delta N/d)^{2}$, the same as our nematic model prediction.

Charge transport across misaligned domain boundaries may involve charge motion in disordered chains so that $(D(N) \sim (\Delta N/d))$ and the required time $\tau_{w} \sim (\Delta N/d)^{-1}$. When $\tau_{w}$ is much greater than the intradomain charge diffusion time, $\tau_{b}$, we expect the net charge mobility, $\mu_{\text{net}}(N)$, is proportional to $(\Delta N/d)$, comparable to the charge mobility for isotropic chains. When $\tau_{b}$ and $\tau_{d}$ are comparable, we expect an
We compare the nematic model (eq 14) with the experimentally measured charge mobilities for semicrystalline P3HT, obtained by different groups using various processing conditions (Figure 4a). Because the nematic phase has been reported for P3HT, we expect chains in amorphous regions to align uniaxially. The different degrees of crystallinity and the various sizes of nematic domains in the amorphous regions may lead to the rather scattered experimental charge mobilities. Nonetheless, our model can qualitatively capture the molecular weight dependence of charge mobility for P3HT by assuming a relative transfer rate, \( k_c/k_h \), of about \( 10^8 - 10^9 \).

We also compare our model with the experimental mobilities obtained by Chang et al. for P3HT samples with similar degrees of crystallinity. Using eq 14 and the relative transfer rate, \( k_c/k_h \), and the plateau mobility, \( \mu_\parallel(\infty) \), as fitting parameters, the nematic transfer model nicely captures the molecular weight dependence of charge mobility for P3HT. Nematic-like order may be more important than semicrystallinity in P3HT for governing macroscopic charge transport. We propose that the straight backbones of nematic conjugated polymers may give rise to the significant molecular weight dependence of charge mobility.

**DISCUSSION**

We propose an analytical model to describe the effect of uniaxial alignment on charge transport for conjugated polymers. We show that charge mobilities of uniaxially aligned chains depend more significantly on molecular weight than charge mobilities of isotropic chains. When the molecular weight is low, we predict that the charge mobility in the alignment direction, \( \mu_\parallel \), for nematic chains quadratically scales with the chain length (\( \sim N^2 \)). Indeed, nematic conjugated polymer samples are composed of domains with different orientations. Still, when interdomain charge transport is sufficient or the domain size, \( \xi_i \), is large, we expect that the local rod-like charge trajectories lead to a quadratic molecular weight dependence of the overall charge mobility. For isotropic chains, however, \( \mu_\parallel \) in the conducting direction only scales linearly with \( N \). This is because the intrachain charge trajectories are rod-like for nematic chains in the alignment direction and coil-like for isotropic chains. For both nematic and isotropic chains, their charge mobilities reach plateau values when the time for a charge carrier to explore the whole chain is comparable to the interchain hopping time.

The charge mobility, \( \mu_\parallel \), for nematic chains without any defects is expected to be independent of the persistence length, \( l_p \), although \( \mu_\parallel \) of isotropic chains depends linearly on \( l_p \). For isotropic chains, the straightness of local charge trajectories is governed by the bending stiffness of the polymer backbone so that the charge mobility depends on \( l_p \). For nematic chains, however, the rod-like intrachain charge trajectories are controlled by the nematic order, \( q \), instead of \( l_p \). As a consequence, \( \mu_\parallel \) scales with \( (2 + q)^2 \) and is independent of \( l_p \) for nematic chains.

Together with the alignment field, the persistence length, however, governs the probability for forming hairpin defects in polymer nematics, and, in turn, they affect the overall charge mobility. For chains with longer \( l_p \), the bending energy penalty for forming a hairpin is larger, and the concentration of these defects is lower. As a consequence, the distance between two intrachain hairpin defects, \( N_h \), increases with increasing persistence length, \( N_h \). When the chain length, \( N \), is smaller than \( N_h \), the intrachain charge trajectory is not affected by the existence of hairpin defects and is still rod-like. When \( N \) is greater than \( N_h \) the nematic polymer backbones become one-dimensional random walks of rod-like pieces of length about \( N_h \). With a large enough relative charge transfer rate, \( k_c/k_h \), we expect intrachain charge trajectories to also behave like one-dimensional random walks. Because \( N_h \) scales linearly with \( N \) in the nematic phase, we expect the charge mobility of nematic polymers in the high molecular weight limit to also scale linearly with the persistence length.

For many conjugated polymers, however, hairpin defects may not affect the charge mobility, because their relative charge transfer rates, \( k_c/k_h \), are not large enough, only about \( 10^3 - 10^4 \), smaller than the typical value of \( N_h \). A charge carrier can hop to another chain before realizing the existence of hairpin “U-turns”.

Using a nematic charge transfer model, we demonstrate that nematic order and the rather large relative transfer rate, \( k_c/k_h \), may give rise to the significant molecular weight dependence of the charge mobility for semicrystalline P3HT. Unfortunately, the molecular weight dependence of the mobility in other conjugated polymers has not been characterized in the same level of detail. Further efforts are warranted to compare our
model with experimental results from both amorphous and stiff conjugated polymers.

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**Notes**
The authors declare no competing financial interest.

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