

# Intramolecular Charge Transport along Isolated Chains of Conjugated Polymers: Effect of Torsional Disorder and Polymerization Defects

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Recently, it has become possible to measure the mobility of charges along isolated chains of conjugated polymers. The mobility of holes along poly(phenylenevinylene) and polythiophene backbones were reported to be 0.43 and 0.02 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. The large difference between the mobility of holes on poly(phenylenevinylene) and polythiophene chains can be attributed to deviations from the coplanar alignment of structural units in the polymer backbone. The effect of such torsional disorder on intramolecular hole transport is studied theoretically in this paper using a model based on the tight-binding approximation. The calculated ratio of hole mobilities along poly(phenylenevinylene) and polythiophene chains was found to be in agreement with experimental findings. For both polymers, estimated mobilities become consistent with the experimental values if polymerization defects and chain end effects are included in the calculations. This suggests that even higher mobilities than those reported here can be realized by improving the effective conjugation along the polymer chain.

## 1. Introduction

Conjugated polymers are of considerable current interest, because of their semiconducting and light emitting properties.<sup>1</sup> These properties, combined with their relatively low cost and good processability as compared to inorganic semiconductors, make them attractive candidates for application in low-cost field-effect transistors (FETs) for disposable electronics and as the emissive material in light emitting diodes (LEDs) and large area displays.<sup>2–5</sup> The mobility of charge carriers in conjugated polymers is one of the key parameters determining the performance characteristics (e.g., switching times and maximum current) of organic LED and FET devices. A thorough understanding of the mechanism of charge transport in conjugated polymers is therefore of obvious importance for the development of devices based on these materials. For these reasons, it is hardly surprising that a vast amount of experimental work has been carried out in attempts to probe transport properties of conjugated polymers.<sup>6–10</sup>

The majority of investigations made so far, are focused on bulk materials, mainly using direct current (DC) detection techniques such as time-of-flight measurements (TOF)<sup>9</sup> and experiments involving FET devices.<sup>10</sup> In these DC measurements, charge carriers drift under the influence of an applied constant electric field over macroscopic distances of typically a few tens of microns. As a consequence, the charge transport that is probed involves not only motion along the polymer chains

but also much slower processes such as the transfer of charge between neighboring chains and migration across grain boundaries. Because the overall mobility is limited by the slowest process, the apparent transport properties of conjugated polymers as measured using DC techniques depends to a large extent on the macroscopic morphology of the material studied.

The difficulties associated with DC measurements are largely circumvented with the time-resolved microwave-conductivity (TRMC) technique, where the mobility of charge carriers is determined using high frequency (~30 GHz) microwaves.<sup>11–13</sup> With this technique, there is no need to apply electrodes, and the high frequency ensures that the movement of charges within relatively ordered domains is probed. Therefore, the charge carrier mobilities obtained from TRMC measurements are mainly determined by the intrinsic properties of the materials studied rather than by the preparation method of the device used to determine the mobility. TRMC measurements have been performed on a variety of conjugated polymers including a number of poly(phenylenevinylene)s (PPVs) and polythiophenes.<sup>14–17</sup>

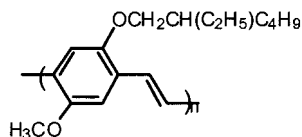
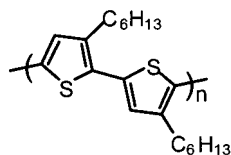
Recently, it was shown that the TRMC method can also be used to obtain direct information about the mobility of charge carriers on isolated polymer chains in solution.<sup>18,19</sup> The type of measurements described above offer unique data on charge transport along molecular wires which is very useful for gaining insight into the relation between the molecular structure of conjugated polymers and their conductive properties. The results are especially interesting, because isolated polymer chains are also tractable for theoretical treatments that take the inherently disordered nature of polymers into account. Moreover, direct measurements of the intramolecular mobility for different polymers can present a useful guideline for design of molecular

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**MEH-PPV****P3HT****Figure 1.** Molecular structure of MEH-PPV and P3HT.

wires with transport properties that meet requirements of nanoscale electronics.

Measurement of mobilities of positive charges along isolated polymer chains have been performed for a variety of  $\pi$ -conjugated polymers as reported recently. The results obtained show that there are significant differences in the ability of MEH-PPV and P3HT (see Figure 1 for the structure) to transport positive charges. The hole-mobility on MEH-PPV was found to be  $0.43 \text{ cm}^2/\text{Vs}$ , whereas for poly-3-hexylthiophene, a value of  $\sim 0.02 \text{ cm}^2/\text{Vs}$  was obtained. A qualitative explanation for this large difference is the difference in the amount of torsional disorder in the polymer chain. Torsion in the polymer chain causes a breaking of the conjugated pathway and hence impedes the transport of charge.

In this paper, the effects of torsional disorder and chemical defects in conjugated polymers are studied theoretically. The mobilities of charges are calculated using a quantum mechanical model described in section 2. The model includes a detailed description of the effects of torsional disorder on the mobility of charges along conjugated polymer chains. One of the important features of the model used here is that it does not assume a periodic structure for the polymer as is the case in band structure calculations. Polymers in solution are known to have rather disordered conformations, which is substantiated by the fact that the optical properties are very similar to those expected for a distribution of oligomers of limited length. Therefore, a theoretical treatment of the charge carrier mobility should include effects of (torsional) disorder. Such a description is more appropriate than a description in terms of an effective mass of the charge carriers obtained from band structure calculations on polymers with an ordered periodic structure.

The results in section 3 show that such torsional disorder is indeed an important factor governing the mobility of charges. A comparison of theoretical and experimental results indicates that the influence of polymerization defects and finite polymer chain length cannot be neglected.

## 2. Theoretical Framework

The method used for the calculation of intramolecular transport of charge carriers is based on the tight-binding approximation combined with static disorder along the chain.<sup>20,21</sup> Following this approximation, a polymer is modeled by a chain

of  $N$  sites that correspond to the monomer repeat-units, and charge migration on this chain is described by the Hamiltonian

$$H_q = \sum_n [\epsilon_n a_n^+ a_n - b(\Delta\theta_{n,n+1})(a_{n+1}^+ a_n + a_n^+ a_{n+1})] \quad (1)$$

In this equation,  $\epsilon_n$  is the energy of the charge at the  $n$ th site, while  $a_n^+$  and  $a_n$  are the creation and annihilation operators for a charge at this site. The charge-transfer integral  $b(\Delta\theta_{n,n+1})$ , which is a measure of the electronic coupling between neighboring sites, depends on the interunit angle,  $\Delta\theta_{n,n+1}$ , between the  $n$ th and  $(n+1)$ th monomer units in the polymer and can be calculated using quantum chemical methods, see below. The energy of a positive charge localized on a singly polymer unit,  $\epsilon_n$ , is essentially the ionization potential of such a unit. For polythiophene, all monomer units are identical. However, a PPV chain consists of an alternating sequence of phenylene and vinylene units. The ionization potential of a vinylene unit was calculated to be 1.1 eV higher than that of a phenylene unit. This energy difference was taken into account in the simulations for PPV.

The wave function,  $|\Psi(t)\rangle$ , of a hole is expressed as a superposition of states  $|n\rangle$  located on the different sites with coefficients  $c_n$ :

$$|\Psi(t)\rangle = \sum_n c_n(t) |n\rangle \quad (2)$$

At  $t = 0$ , a positive charge is localized on a single unit; that is,  $c_i(t = 0) = 1$  and all other coefficients are zero. The time-dependent coefficients,  $c_n(t)$ , are obtained by numerical integration of the first-order differential equations that follow from the substitution of the wave function in eq 6 into the time-dependent Schrödinger equation  $i\hbar \partial|\Psi(t)\rangle/\partial t = H|\Psi(t)\rangle$ . The coefficients are propagated until a preset time is reached.

Once the coefficients  $c_n(t)$  are known as a function of time, the mean-square displacement,  $\Delta^2(t)$ , of the charge carrier can be calculated according to

$$\Delta^2(t) = \langle \Psi(t) | n^2 | \Psi(t) \rangle \lambda^2 = \sum_n |c_n(t)|^2 n^2 \lambda^2 \quad (3)$$

where  $\lambda$  is the distance between the centers of two adjacent monomer units. The frequency dependent mobility of the charge carriers can now be obtained from the Kubo formula:<sup>22–24</sup>

$$\mu(\omega) = \frac{-e\omega^2}{2k_B T} \text{Re} \left[ \int_0^\infty \Delta^2(t) \exp(-i\omega t) dt \right] \quad (4a)$$

in which  $e$  is the elementary charge,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $\omega$  is the radian frequency of the probing electric field, and 'Re' denotes that the real part of the integral is taken. Note that, for normal diffusive motion,  $\Delta^2(t) = 2Dt$  and the diffusion constant  $D$  is related to the mobility,  $\mu$ , by the Einstein relation

$$\mu = \frac{e}{k_B T} D \quad (4b)$$

The data presented below were obtained by averaging the results for the mean-square displacement of the charge over several thousands of polymer chains with different realizations of the interunit angles. This was found to be sufficient for numerical convergence. The torsional disorder is included in the tight-binding calculations by using the value of the electronic coupling,  $b(\Delta\theta_{n,n+1})$ , corresponding to the angle between

neighboring units. The interunit angles were sampled from a Boltzmann distribution using the rotational potential energy profiles for the polymer under consideration. No correlation between neighboring angles was assumed; that is, all angles were determined independently of each other. This assumption is quite reasonable for polymer chains in dilute solution where the (solvent) environment is reasonably homogeneous. A strong correlation between the angles can of course be expected in solid state films of conjugated polymers where interchain interactions can induce highly ordered regions with little torsional disorder separated by more disordered regions. These interchain effect do not play a role for isolated polymer chains in dilute solution.

The potential energy profiles for the polymers studied here, polythiophene and poly(phenylenevinylene) as unsubstituted model systems for P3HT and MEH-PPV, were obtained from ab initio quantum chemical calculations on small model systems of the polymers. For PPV, this model system consists of a single phenylenevinylene unit (i.e., a styrene molecule), whereas for polythiophene, an unsubstituted bithiophene molecule was taken. The geometries of the model systems were fully optimized at the Hartree-Fock level using Dunning's cc-pVDZ basis set.<sup>25</sup> The potential energy profile was then calculated using Hartree-Fock plus second-order Møller-Plesset perturbation theory in the same basis set by taking the minimum energy conformation and rotating around the interunit angle in steps of 15°. The geometry was not optimized for each angle. Consequently, the calculated rotational barrier is an upper limit to the actual rotation barrier.

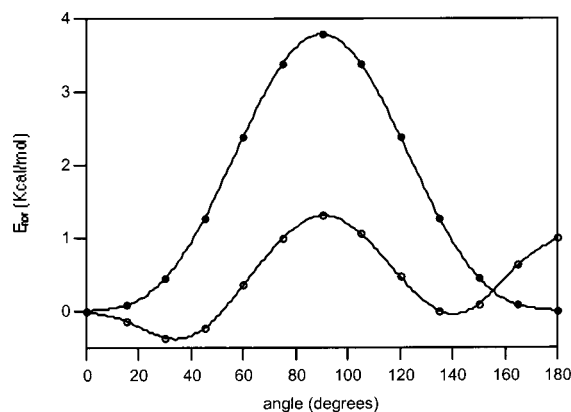
The values of the charge-transfer integral  $b(\Delta\theta_{n,n+1})$  were estimated from the energy splitting between the two highest occupied molecular orbitals (HOMOs) in the same model systems as used above for the potential energy profiles. For these estimations, the energy splitting between the HOMOs in the dimer ( $E_+ - E_-$ ) and the energy difference of the HOMOs in the separate units at infinite distance ( $E_1 - E_2$ ) were calculated. Once these energies are known,  $b(\Delta\theta_{n,n+1})$  can be evaluated from the familiar expression<sup>26</sup>

$$|b(\Delta\theta_{n,n+1})| = \frac{1}{2} \sqrt{(E_+ - E_-)^2 - (E_1 - E_2)^2} \quad (5)$$

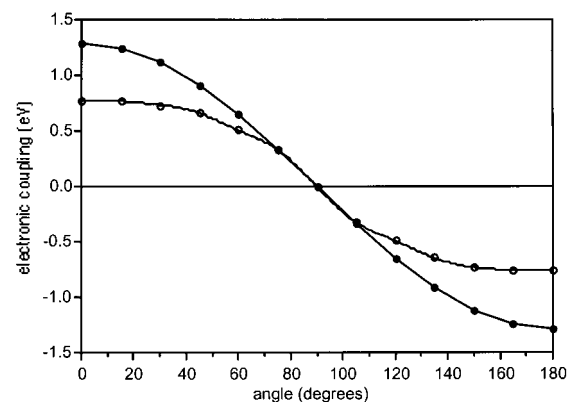
### 3. Results and Discussion

The potential energy profiles for styrene and bithiophene molecules, taken as model systems for PPV and polythiophene chains, are plotted in Figure 2. As evident from this figure, the potential energy profile calculated for PPV has a minimum that corresponds to a fully planar conformation with the torsion angle  $\theta_{\text{tor}} = 0^\circ$ . Upon rotation around the inter unit bond, the energy steeply increases, attains a maximum value  $E_{\text{tor}}^{\text{max}} = 3.8 \text{ Kcal mol}^{-1}$  at  $\theta_{\text{tor}} = 90^\circ$  and then decreases for angles up to  $180^\circ$ . Because at room temperature  $E_{\text{tor}}^{\text{max}} \gg kT$ , an isolated PPV polymer chain will be relatively planar, thus providing a good geometry for intramolecular charge transport. Note, that the conjugation length in solution can be considerably larger than in solid films where intermolecular interactions can lead to the occurrence of large angles. For example, in thin films of unsubstituted PPV, an effective coherence length of about 8 PV units has been reported.<sup>27</sup> In the solid state, the preparation method of a sample has a large effect on the amount of disorder, and techniques such as annealing at higher temperatures can significantly improve the charge transport properties.<sup>15,14</sup>

For polythiophene, the potential energy profile for polythiophene is very different from that for PPV (see Figure 2). In



**Figure 2.** Potential energy profiles for torsion motion of structural units in PPV (filled circles) and polythiophene (open circles) chains. Calculations were performed at the MP2/cc-pVDZ level for styrene and bithiophene model systems. Points correspond to the energy difference,  $E_{\text{tor}}$ , between configurations with torsion and with planar geometry.

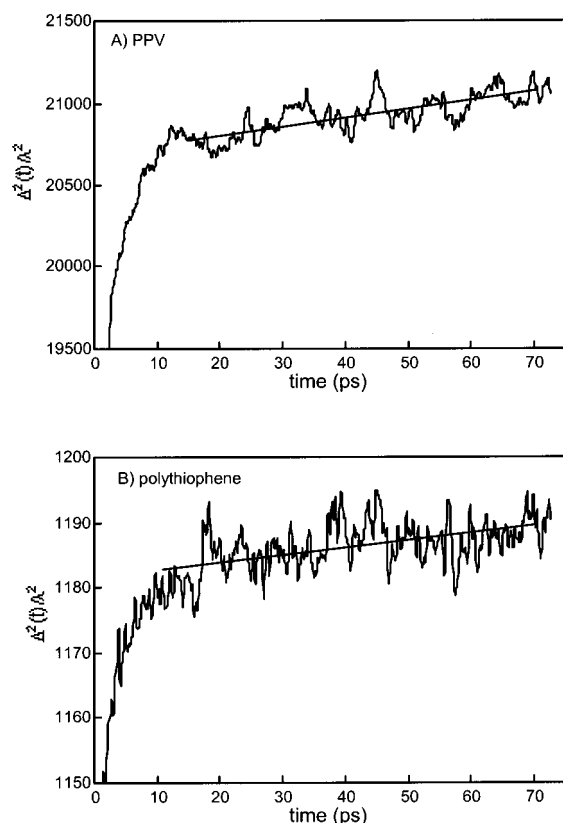


**Figure 3.** Charge-transfer integral between monomer repeat units of PPV (filled circles) and polythiophene (open circles) as a function of the torsion angle. Numerical results shown in the figure were obtained for styrene and bithiophene model systems.

this case, the potential energy has a minimum at a torsion angle near  $30^\circ$ . In addition, the height of the barrier for torsional motion in polythiophene measured from the minimum to the maximum of the potential energy profile is only  $1.7 \text{ kcal mol}^{-1}$  which is lower than the analogous barrier found for PPV. Consequently, the probability of deviations from a coplanar alignment of monomer repeat units within a polymer chain in solution is higher in polythiophene than in PPV. Note again that the situation in dilute solution is different from that in polythiophene films where intermolecular interaction are known to induce the formation of highly ordered regions.<sup>10</sup>

The electronic coupling,  $b(\Delta\theta_{n,n+1})$ , obtained by the calculations described in the previous section, is plotted against the interunit angle for both polymers in Figure 3. For both compounds, the coupling is maximal at a planar geometry, as expected. The electronic coupling for this coplanar alignment is higher for PPV than it is for thiophene. The coupling decreases when the angle is increased and becomes (almost) zero at a perpendicular geometry. For such a geometry, the motion of a charge between the repeat units involved is impossible.

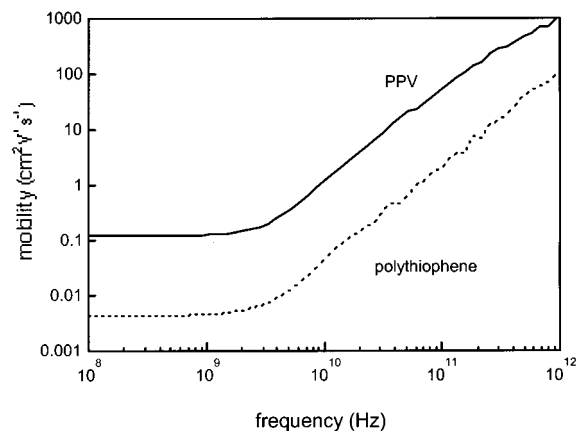
The potential energy profiles and the angular dependence of the transfer integral were used in the tight-binding model described above to study the influence of torsional disorder on intramolecular motion of holes numerically. The time evolution of  $\Delta^2(t)$  for holes moving along isolated chains of polythiophene and PPV with static torsional disorder is shown in Figure 4.



**Figure 4.** Dimensionless mean-square displacement of charge carriers as a function of time for PPV (panel A) and polythiophene (panel B). The straight lines indicate the linear increase of  $\Delta^2(t)$  with time in the second stage of the simulations.

The results plotted in this figure correspond to the case where the number of sites  $N$  is sufficiently large to avoid the effects of chain ends on the motion of charge carriers. The numerical data reveal two characteristic stages of the transport process common for both polymers investigated. At the early stage, the mean-square displacement rapidly increases with time and exhibits nonlinear temporal behavior, whereas after about 10 ps, the value of  $\Delta^2(t)$  rises much slower with an essentially linear time dependence. The nonlinear rise of the mean-square displacement at small  $t$  suggests that initially holes undergo fast delocalization over an almost planar stretch of the polymer chain. However, after some time, a moving hole will inevitably reach a site with a large interunit torsion angle, where the electronic coupling is very small. As a consequence, charge motion will slow and will become diffusive at long times. Note that the value of  $\Delta^2(t)$ , at which the transition from the fast initial spreading of the wave function to the slower diffusive motion occurs, is much larger for PPV than for polythiophene. This is consistent with a more planar configuration of the PPV chains as compared to polythiophene.

The two stages of the charge transport process mentioned above manifest themselves in the dependence of the intramolecular hole mobility,  $\mu$ , on the frequency,  $\omega$ , of the probing electric field (Figure 5). Indeed, according to eq 4a the low frequency mobility should mainly be determined by the temporal behavior of holes in the long-time limit  $t > 10$  ps, where  $\Delta^2(t) \sim t$  and the migration of the charge resembles normal diffusion. Therefore, at frequencies below a few GHz, the value of  $\mu$  calculated for isolated PPV and polythiophene chains should be independent of  $\omega$ , in agreement with the numerical results in Figure 5. This ceases to be true at higher frequencies, where the charge carriers can follow the external electric field



**Figure 5.** Frequency dependence of the intramolecular mobility of holes along PPV and polythiophene chains, obtained from the data of Figure 5 using eq 8a.

by moving back and forth between sites with large interunit angles. In this case the main contribution to the integral in eq 4 and hence to  $\mu$  originates from the fast nonlinear initial increase of  $\Delta^2(t)$  with time at the early stage of the transport process. As a consequence, at high frequencies, the mobility rises almost as  $\omega^2$  for both PPV and polythiophene, see Figure 5.

Although the dependencies of the intramolecular charge mobility on  $\omega$  exhibit general features that are common for PPV and polythiophene, the absolute  $\mu$  values obtained for these polymers are quite different. The results plotted in Figure 5 suggest that the calculated mobility of holes on infinitely long PPV chains is approximately 30 times higher than for polythiophene chains within the entire frequency range investigated. This large difference is due to a considerably lower average electron coupling between the repeat units in polythiophene caused by the higher degree of torsional disorder in polythiophene in comparison with PPV.

The calculated mobilities discussed so far were obtained for infinitely long polymer chains without chemical defects. However, the experimental data were obtained for polymers with a finite chain length and polymerization defects. In particular, because of side reactions, polymer macromolecules can contain single or triple bonds instead of the normal double bonds.<sup>28</sup> These polymerization mismatches disrupt the conjugated  $\pi$  system and can act as reflecting boundaries for charge transport, thus limiting the length of the pathway for intramolecular charge transport.

To investigate the effects of such polymerization mismatches, the mean-square displacement and intramolecular mobility of charge carriers on polymer chains with limited length were calculated. In these simulations, it was assumed that the initial generation of a hole on each site of the chain is equally probable.

The mobility of  $0.43 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  measured for PPV at a microwave frequency of 34 GHz could be reproduced taking PPV chains consisting of 180 PV units. This effective (chemical) conjugation length is reasonable. Although the PPV chains used in the experiments consist of  $800 \pm 400$  phenylenevinylene units, they could contain up to  $\sim 2\%$  polymerization defects, leading to a limited effective chain length for charge transport. Note that this value for the effective length of 180 repeat units refers only to the presence of chemical defects. The motion of a charge is further reduced torsional disorder.

The experimental hole mobility of  $0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  on polythiophene chains measured at 34 GHz can be reproduced by calculations on chains consisting of 135 thiophene units. This



chain length is not very different from those in the polythiophene sample, which have an average length of 55 thiophene units and a polydispersity index equal to 1.4. A more detailed quantitative comparison of the experimental and calculated mobilities is hampered by the lack of knowledge of the precise shape of the distribution of the effective conjugation lengths in the polymer samples used.

It should be noted that dynamic fluctuations in the polymer chains may increase the mobility, because monomer units that are initially perpendicular may rotate to a more planar conformation, which enables a charge to pass such a point after some time. Further, the effect of a possible self-localization of the charge by formation of a polaron also needs to be considered. Although experimental observations are usually explained in terms of self-localized polarons, there are some studies where it is argued that self-localization of polarons is unlikely. From band structure calculations by Gomes da Costa et al. on PPV, it was concluded that the presence of localized charge carriers should be attributed to the presence of defects or impurities rather than to a self-localized polaron.<sup>29</sup> Furthermore, Brocks has performed density functional theory calculations on thiophenes that show that self-localized polarons are not very likely in polythiophene.<sup>30</sup> The effects of dynamic fluctuations and polaron formation are under active investigation at present. Finally, another factor that has been neglected in the calculations presented here is the effect of substituents, which are present in both polymers studied experimentally. Substituents will alter the potential energy profile, which will result in a somewhat different amount of torsional disorder. Furthermore, the ionization potential of the monomer units which enter the simulation as the site energy  $\epsilon_n$ , see eq 5, will also be affected by the presence of substituents. These steric and electronic effects of the substituents will have some influence on the magnitude of the mobility obtained for both MEH-PPV and P3HT. However, the large difference in mobility between both polymers will remain because it arises mainly from the torsional disorder, which is already described in detail in the present model.

#### 4. Conclusions

Recently it was shown experimentally that the mobility of positive charges along isolated PPV chains is an order of magnitude higher than that obtained for polythiophene. This large difference can be explained by considering the torsional disorder along the polymer chain. Theoretical studies show that PPV chains are expected to have a much more planar structure in dilute solution than polythiophene chains. This results in a mobility for PPV that is more than an order of magnitude higher than that for polythiophene. A comparison of the absolute values of the calculated and experimental mobilities shows that chain ends or breaks of the conjugation reduce the mobility measured on isolated polymer chains considerably. Quantitative agreement between experimental and calculated results is obtained if the limited conjugation length is included in the calculations.

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