

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231667560>

Charge Mobilities in Conjugated Polymers Measured by Pulse Radiolysis Time-Resolved Microwave Conductivity: From Single Chains to Solids

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · NOVEMBER 2011

Impact Factor: 7.46 · DOI: 10.1021/jz201229a

CITATIONS

30

READS

25

2 AUTHORS:



F.C. Grozema

Delft University of Technology

129 PUBLICATIONS **3,721** CITATIONS

SEE PROFILE



Laurens D A Siebbeles

Delft University of Technology

249 PUBLICATIONS **7,267** CITATIONS

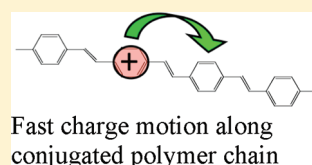
SEE PROFILE

Charge Mobilities in Conjugated Polymers Measured by Pulse Radiolysis Time-Resolved Microwave Conductivity: From Single Chains to Solids

Ferdinand C. Grozema and Laurens D. A. Siebbeles*

Optoelectronic Materials Section, Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands

ABSTRACT: We discuss how the mobility of a charge moving along a conjugated polymer chain is affected by different types of disorder. The intrachain mobility has been determined by using pulse radiolysis in combination with microwave conductivity measurements. The intrachain mobility of charges on isolated planar ladder-type poly(*p*-phenylene) chains in solution is as high as 600 cm²/(V s). In solid samples, the intrachain mobility is only 30 cm²/(V s) due to disorder caused by interactions between different polymer chains. Interestingly, this mobility is 4 orders of magnitude higher than the DC device mobility, which is limited by charge hopping between different chains. Torsional disorder along poly(*p*-phenylene vinylene) chains limits the intrachain mobility to 60 cm²/(V s), while in polyfluorenes, coiling of the chains strongly reduces the mobility. The results imply that higher charge mobilities can be realized in devices if the polymer chains directly interconnect the electrodes and adopt a straight, planar structure in a homogeneous environment.



Conjugated Polymers for Opto-Electronics. The optical and electronic properties of conjugated polymers are of considerable importance because of the applications of these materials in plastic electronic devices.^{1,2} Some of the reasons for the attractiveness of conjugated polymers for device applications are their low weight and flexibility and the fact that they can be processed more cheaply than inorganic semiconductors, for example, by inkjet printing.³ Conjugated polymers can be used as the charge-transport layer in field effect transistors^{4,5} (FETs) or as the light-absorbing/emitting layer in solar cells^{4,6–8} and light-emitting diodes.⁴ In these applications, the performance (maximum current, switching time, etc.) critically depends on the mobility of charges through the polymer layer. The charge mobility, μ , determines the velocity, v , in an electric field, E , via the relation $v = \mu E$.

Although conjugated polymers have some interesting advantages over conventionally used inorganic semiconductors, the mobility of charges in these materials is generally several orders of magnitude lower. In crystalline inorganic semiconductors, charge carrier mobilities are typically on the order of thousands of cm²/(V s), while for conjugated polymers, mobilities obtained from device studies are lower by 4–9 orders of magnitude. For polymers with strong interchain coupling and favorable π – π stacking in FETs, values in the range between 0.1 and 1 cm²/(V s) are among the highest mobilities.^{9,10} The mobility of a charge in a semiconductor is inversely proportional to the effective mass. The effective mass decreases with the bandwidth, and therefore, a larger bandwidth implies a higher charge mobility.¹¹ Interestingly, when the widths of the electronic bands in conjugated polymers are compared to those in inorganic semiconductors, very similar values of a few electron volts are found. If the scattering times in both materials are assumed to be of the same order of magnitude, this would imply similar mobility values.^{11,12}

The obvious reason for the lower mobility in polymers is the presence of structural disorder. Whereas inorganic semiconductors

are mostly highly ordered crystalline materials, conjugated polymer materials are typically disordered and often consist of chains with a wide range of lengths, conformations, and chemical defects. The problem of disorder is closely related to the length scale on which charge transport is probed.^{12–17} On a very small length scale, for instance, a single-crystalline domain or a planar stretch of conjugated polymer, much higher charge carrier mobilities should be measured than those on a macroscopic scale where the charge has to pass boundaries between the ordered domains. In this Perspective, we outline how charge carrier mobilities can be measured on a distance scale of tens of nanometers by using a fast oscillating microwave field in combination with the generation of charges by irradiation with high-energy electrons. We demonstrate that the inherent mobility of charges in conjugated polymers can be as high as that for inorganic semiconductors, and we discuss how different types of disorder limit the mobility. Finally, we relate the high mobility found on the nanometer scale to values found on longer distance scales and point out possibilities of improving the charge carrier mobilities in devices based on conjugated polymers.

The inherent mobility of charges in conjugated polymers can be as high as that for inorganic semiconductors.

Received: September 9, 2011

Accepted: November 4, 2011

Published: November 04, 2011

Electrodeless Conductivity Measurements on Charges Produced by Pulse Radiolysis. The typical distance scale on which charge transport is probed in direct-current (DC) experiments, for instance in, a FET device or by time-of-flight measurements, is dictated by the minimum spacing between the electrodes or the minimum layer thickness needed to prevent short circuits. In most cases, this means that the distance over which charge transport is probed exceeds 100 nm. Much smaller distance scales can be reached by using electrodeless techniques in which transport is probed by a fast oscillating electric field. Such alternating-current (AC) techniques include time-resolved microwave conductivity^{18,19} and terahertz conductivity^{16,17,20} measurements with probing frequencies of a few tens and thousands of GHz, respectively. At these high frequencies, the charges can move back and forth inside of a single small domain of a material without having to migrate over long distances to electrodes. The distance scale on which charge transport is probed depends on the electric field frequency used; the higher the frequency, the smaller the distance scale.^{13–15} The microwave or terahertz mobility of a charge is a complex quantity that determines the velocity in the oscillating electric field, $E(t) = E_0 \cos(\omega t)$, according to $v(t) = \mu_R(\omega)E_0 \cos(\omega t) + \mu_I(\omega)E_0 \sin(\omega t)$, with $\mu_R(\omega)$ and $\mu_I(\omega)$ the real and imaginary components of the mobility, respectively, ω the oscillation frequency, and t the time. The real component of the mobility describes the velocity in phase with the electric field, while the imaginary component describes the out-of-phase velocity. The latter becomes important in the presence of barriers to charge transport. The DC mobility corresponds with the real component of the mobility at zero frequency $\mu_{DC} = \mu_R(\omega = 0)$. The DC mobility is related to the diffusion constant, D , by the Einstein relation $\mu_{DC} = (e/k_B T)D$, with e as the elementary charge, k_B the Boltzmann constant, and T the temperature. The AC mobility at electric field frequency $\omega = 2\pi/\tau_{os}$ is determined by charge motion over a distance that is approximately equal to $(D\tau_{os})^{1/2}$. If this is less than the distance between barriers to transport in the material, the AC mobility corresponds to the ultimate inherent mobility of charges.

In electrodeless conductivity measurements, charges cannot be generated by injection from electrodes, which is the usual practice in DC measurements. Microwave and terahertz conductivity studies on thin-film samples are carried out by producing charges by photoexcitation.^{19,21–26} A drawback of photoexcitation is that the quantum yield of charges is usually unknown, which hampers quantitative determination of the mobility from the measured conductivity. In addition, the penetration depth of the incident (visible or UV) laser light is on the order of 100 nm; therefore, the thicker samples cannot be excited homogeneously. In bulk solid polymer samples and polymer solutions, charges can be efficiently generated by pulse radiolysis.^{18,27–32}

In the pulse radiolysis experiments described below, charges are generated by irradiation of the sample with 3 MeV electron pulses with a duration of typically 10 ns. The sample is contained in a rectangular microwave (34 GHz) conductivity cell. The incident high-energy electrons undergo scattering in the sample and transfer energy by inducing ionizations along their tracks. In this way, a close to uniform distribution of positive charges (holes) and (secondary, ternary, etc.) electrons is produced in the sample. The penetration depth of 3 MeV electrons is ~ 1.5 cm, which largely exceeds the thickness of the microwave cavity (0.5 cm). Hence, the incident 3 MeV electrons pass through the sample, and charging does not occur.

Production of mobile charges in the sample leads to a fractional absorption of microwave power that is proportional to the real component of the radiation-induced conductivity. A possible charge velocity out of phase with the microwave field gives rise to an imaginary radiation-induced conductivity component. The change in real (imaginary) conductivity of the sample is determined by the product of the charge concentration and the real (imaginary) mobility. The mobility can thus be determined quantitatively if the concentration is known. The initial concentration of charges is obtained from the experimental radiation dose in the sample due to the 3 MeV electron pulse and the average energy that is needed to generate an electron–hole pair. For the case of bulk solid samples, the electron–hole pair formation energy for ionization of a polymer backbone can be estimated on the basis of the semiempirical result for inorganic semiconductors provided by Alig et al.^{27,33} The electron–hole pair formation energy for hydrocarbon side group substituents or a hydrocarbon solvent is obtained from pulse radiolysis studies of charge yields in hydrocarbon liquids.^{34,35} For experiments on polymer chains in dilute solutions, the incident 3 MeV electrons ionize the solvent rather than the small amount of polymer chains. In this case, accurate values of the electron–hole pair formation energy from the literature can be used to determine the initial concentration of charges.^{34,35} Interestingly, charge yields in hydrocarbon liquids determined by pulse radiolysis of hydrocarbon liquids two decades or longer ago are now used to determine charge mobilities in organic materials for optoelectronic applications. This application of results of fundamental radiation chemical studies is highly fascinating and was not foreseen.

The combination of pulse radiolysis with time-resolved microwave conductivity detection described above can be used to study charge transport in small well-organized domains in bulk solids, as well as to measure the mobility of charges along isolated chains of a conjugated polymer in solution. In the latter case, the charges move up and down a polymer chain in the oscillating microwave field.

Pulse radiolysis with time-resolved microwave conductivity detection can be used to study the mobility of charges along isolated polymer chains.

Charge Transport along Isolated Planar Polymer Chains. As discussed above, the electronic bandwidth in conjugated polymers is similar to typical values found in inorganic semiconductors, implying mobility values of $\sim 10^3$ cm²/(V s). Such a high mobility of charges can be expected for a highly ordered polymer chain in which the conjugation length is not limited by the chain conformation. Examples of such polymers are the ladder-type poly(*p*-phenylene)s (LPPPs), shown in Figure 1. The individual phenylene units are restricted to a planar ribbon-like conformation that is optimal for charge transport along the chain.

In Figure 1, we present the conductivity after the generation of charge carriers by pulse radiolysis of solutions of the ladder-type

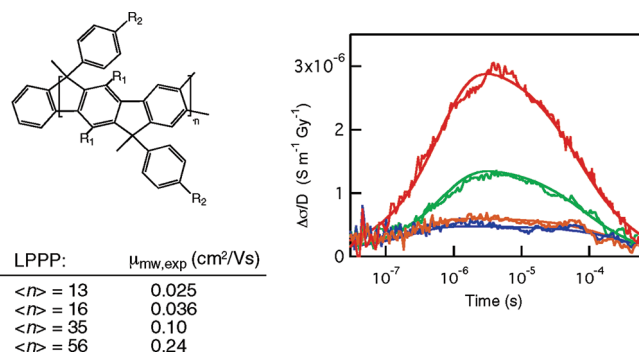
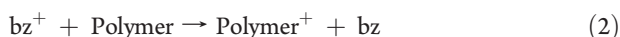


Figure 1. (Left) Molecular structure and experimental charge mobilities for the ladder-type polymer (LPPP) of varying average chain length. (Right) Pulse radiolysis time-resolved microwave conductivity transients for different average polymer chain lengths (red: $\langle n \rangle = 56$; green: $\langle n \rangle = 35$; orange: $\langle n \rangle = 16$; blue: $\langle n \rangle = 13$).

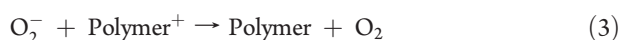
polymer in benzene. Results are presented for average chain lengths ranging from 13 to 56 repeat units.²⁹ In order to selectively study the mobility of holes along the polymer chains, the solution was saturated with oxygen. Because of the relatively high concentration (12 mM) and electron affinity of oxygen, the excess electrons generated in the benzene solvent during the electron pulse (e_{bz}^-) rapidly react with the oxygen molecules (O_2), forming the oxygen anion (O_2^-) via the reaction



In this way, the transfer of negative charges to the polymer chains is prevented. Because the mobility of the oxygen anion in benzene is low, the contribution of the oxygen anion to the observed change in conductivity is negligible. The benzene cations generated during the 10 ns electron pulse (bz^+) can react with the ladder-type polymer by a diffusion-controlled reaction, yielding positively charged polymer chains, according to



As this reaction proceeds, an increase in the transient conductivity is observed on a time scale of hundreds of nanoseconds. This increase directly indicates that the positive charge on the polymer chain is more mobile than the benzene cation in benzene solution. On a time scale of ten to hundreds of microseconds, a decrease in the conductivity signal is observed. The time scale of this decay decreases with increasing initial concentration of charge carriers and is therefore attributed to charge recombination between the oxygen anion and the positive charge on the polymer chain via the reaction



A more extensive description of the reactions upon irradiation with high-energy electrons and the resulting transient conductivity of dilute polymer solutions can be found elsewhere.³⁶ To obtain the microwave mobility of charges from the measured conductivity shown in Figure 1, the concentration of positively charged polymer chains must be known at each point in time. These concentrations were obtained from a kinetic analysis of the conductivity transients, involving reactions (1–3). From this kinetic analysis, the mobility of charges along the polymer chains is obtained.³⁶

The resulting microwave mobility for average chain lengths of 13, 16, 35, and 54 repeat units was found to be 0.025, 0.036, and 0.10 to 0.24 cm²/(V s), respectively.²⁹ The strong dependence of

the microwave mobility on the chain length of the ladder-type polymers shows that for the chain lengths considered, the motion of charge along the polymer chains is severely hindered by the chain ends. This means that the charges can diffuse fast enough along the polymer chains to encounter a chain end during the 30 ps cycle of the microwave electric field. The 30 GHz frequency of the microwave field is not high enough to probe the motion of the charge on a length scale shorter than the chain lengths. The measured mobility does not correspond with the inherent mobility that would be obtained for very long chains or, equivalently, for very high probing frequencies. However, variation of the mobility with chain length does contain information about the inherent charge carrier mobility.

In the limit of a small electric field, it is the diffusive motion of a charge that determines its mobility. Applying the theory of Kubo,^{15,37} we can calculate the microwave mobility (at a probing frequency of 34 GHz) of charges along polymer chains of finite length if the diffusion coefficient or the (DC) intrachain mobility is known. In this model, the charge is assumed to diffuse along a one-dimensional flat energy surface between two infinitely high reflecting barriers.^{29,38} By comparing the experimentally obtained chain length dependence of the charge carrier mobility to the results from this analysis, we have arrived at the conclusion that the inherent intrachain mobility for the ladder-type polymers is close to 600 cm²/(V s).²⁹ This is of the same order of magnitude as expected when the bandwidths for hole transport in this type of polymer are compared to those in inorganic semiconductors. Interestingly, the intrachain mobility of the ladder-type polymers is more than 5 orders of magnitude higher than the DC mobility determined from time-of-flight measurements.³⁹ This is due to the fact that the DC mobility is limited by relatively slow charge-transfer steps between different polymer chains.

The inherent intrachain mobility for the ladder-type polymers is close to 600 cm²/(V s).

Effect of Intrachain Disorder. In the ladder-type polymers that were discussed above, the molecular structure is kept planar by bridging atoms between the repeat units. Most conjugated polymers that are being applied in plastic electronic devices do not have structures that are forced to be planar. In the most studied conjugated polymers, poly(*p*-phenylene vinylene) (PPV) and polythiophene, the repeat units are connected by (formally) single bonds. The result is that the individual units in these polymers have much more “torsional” freedom, leading to a more disordered chain conformation for isolated chains of these polymers.^{40–42} Larger torsional angles between repeat units reduce the bandwidth, which should have a negative effect on the mobility of charges along the chains.

In order to establish the effect of such torsional disorder on the charge carrier mobility, we have performed time-resolved microwave conductivity measurement such as those described above for a series of phenylene vinylene oligomers (oligo-PV) and polymers.⁴³ Experiments have been performed for two well-defined oligomers consisting of 13 and 17 repeat units and for a series of PPVs with a well-defined fraction of chemical

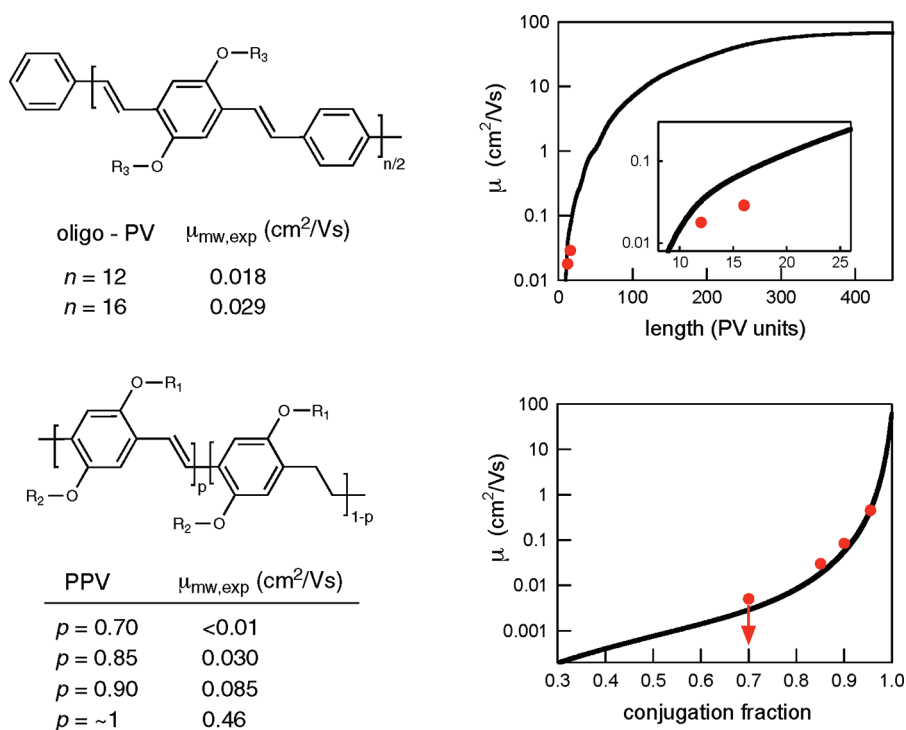


Figure 2. (Left) Molecular structures and microwave mobility values for holes moving along chains of phenylene vinylene oligomers (oligo-PV) with well-defined chain length n or along PPV with a fraction of the conjugated bonds given by p . (Right) Calculated microwave mobility as a function of the chain length and the conjugation fraction. The experimental data are included for comparison as filled circles.

conjugation breaks (see Figure 2). The microwave mobility values obtained from these measurements are listed in Figure 2. The results show that the microwave mobility of charges along the chains depends strongly on the chain length and the degree of conjugation. Therefore, similar to the situation for the ladder-type polymer, the inherent intrachain mobility is considerably higher than the microwave mobility that is directly obtained from analysis of the experimental results. Unfortunately, we cannot apply the same analysis of the chain length dependence in this case due to the torsional disorder that is present along the PPV chains. A charge moving along a conjugated piece of polymer will encounter a variety of interunit angles and will therefore not move with a constant mobility along the chains.

In order to learn more about the inherent mobility of positive charges along PPV chains, we have performed quantum mechanical simulations of charge motion in which the dynamical disorder in the torsion angles between different units is taken into account by a rotational diffusion time of the phenyl units of 200 ps.^{43,44} Variation of the rotational diffusion time by a factor of 2 does not significantly affect the simulated mobility. Interestingly, for static torsion angles, the simulated mobility is more than an order of magnitude smaller because the mobility is limited by the largest torsion angles between PV units. Random fluctuations in the site energies and charge-transfer integrals due to other vibrational modes than torsional motion were found to change the simulated mobility by only about a factor of 2 and are therefore not taken into account in the results described below. Further details about the calculations can be found elsewhere.^{43,44}

Mobilities obtained from the simulations are shown in Figure 2 as a function of the PPV chain length. The microwave mobility is seen to be strongly dependent on the chain length, as expected. For chains longer than 400 repeat units, the simulated microwave

mobility attains a constant value of approximately $60 \text{ cm}^2/(\text{V s})$. For such long chains, the microwave frequency is high enough to directly probe the inherent mobility of charges along PPV chains. For shorter chains, the frequency is not sufficiently high, and the chain ends have a strong negative influence on the microwave mobility. Indeed the measured microwave mobility for the two oligomers consisting of 13 and 17 repeat units is much lower than $60 \text{ cm}^2/(\text{V s})$ and close to the calculated microwave mobility values for these chain lengths (see Figure 2).

The calculated values of the microwave mobility for different chain lengths can be used to obtain the dependence of the microwave mobility on the fraction of chemical conjugation breaks along the chain. This is shown in Figure 2, assuming a Flory distribution of conjugation lengths.^{43,44} The calculated microwave mobilities for the PPVs with conjugation breaks are close to the measured values.

From the good correspondence between the calculated and experimental results, we conclude that our calculations give a good description of the charge transport along PPV chains with torsional disorder. This means that the inherent mobility of charges along PPV chains is approximately $60 \text{ cm}^2/(\text{V s})$, an order of magnitude lower than that found above for the ladder-type polymers. Clearly, the inherent mobility of charges along polymer chains strongly depends on the degree of torsional disorder along the chains. A similar conclusion was reached previously for a comparison of PPV and polythiophene, for which the torsional disorder is much more pronounced.⁴⁰

The results discussed above involve mobilities of positive charges (holes). We have found that electrons on PPV or poly(thienylene vinylene) chains have a mobility similar to that for holes.^{45,46} This can be understood theoretically because the valence and conduction band widths are comparable.⁴⁴

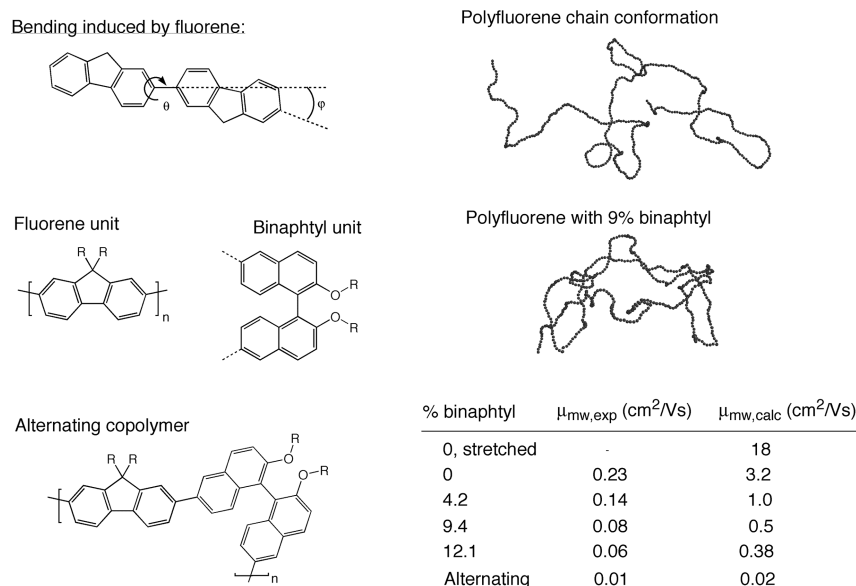


Figure 3. (Left) Molecular structures of the units in the fluorene–binaphthyl copolymers. The binaphthyl units are statically distributed in the random copolymers. (Right) Coiled chain conformation of polyfluorene with and without binaphthyl and the experimental and calculated mobility of holes along chains of the different polyfluorene derivatives.

Effect of Coiling on Mobility. Both the ladder-type polymer and PPV consist of relatively rigid, straight chains with high persistence lengths. This means that the spatial extent of the polymers in solution, or the hydrodynamic radius, is rather large. There are also conjugated polymers, such as polyfluorene, that are extensively coiled, as illustrated in Figure 3. In this case, the motion of charges along the polymer chains cannot be considered one-dimensional. The effect of coiling on the charge mobility has been studied by pulse radiolysis experiments as described above on dilute solutions of a series of polyfluorene derivatives with different degrees of coiling.²⁸ The different degrees of coiling are obtained by incorporating different predetermined fractions of binaphthyl units in the polyfluorene chain. The calculated dihedral angle between the naphthyl units in a binaphthyl moiety is in the range of 60–120°.²⁸ The structures and experimentally obtained microwave mobilities of positive charges are given in Figure 3. The experimental data show that the incorporation of more binaphthyl units leads to lower microwave mobility values. However, the dependence on the fraction of binaphthyl units is less pronounced, as found above for “chemical” conjugation breaks in PPV. This indicates that the binaphthyl units do not break the conjugation along the fluorene chains completely. This is confirmed by the results on the fluorene–binaphthyl alternating copolymer, where the mobility should have vanished in the case of complete conjugation breaking. The data in Figure 3 show that both the calculated and the experimental microwave mobility decrease considerably when the polymer becomes more coiled. This is understandable because the spatial extent of the polymer coil decreases and charges have to travel a longer distance along the contour of the polymer chain to move from one end of the coil to the other. The calculated mobility for the hypothetical case of a one-dimensional “stretched” polyfluorene is 18 cm²/(V s), which is significantly higher than the value of 3.2 cm²/(V s) for the coiled polyfluorene. Hence, coiling substantially hinders the charge from moving along the direction of an applied electric field and leads to a lower mobility. In the simulations of the charge mobility, the length of the polymer chains was taken to be

2500 molecular units, which was sufficiently long for chain end effects to be unimportant.

As discussed above, the experimental microwave mobility of charges is a lower limit to the mobility (or diffusion coefficient) of charges moving along the contour of a coiled polyfluorene chain. Interestingly, even the experimental microwave mobility is about 2 orders of magnitude higher than the mobilities for charges moving along the contour of polyfluorene chains obtained from pulse radiolysis with optical detection by Asaoka et al.³⁰ As discussed in ref 30, the mobility in the experiments with optical detection can be limited by polaronic effects resulting from charge-induced reorientation of the polar tetrahydrofuran solvent molecules. Such polaronic effects are less important in the microwave experiments where nonpolar benzene is used as the solvent. In addition in the experiments with optical detection,³⁰ charges must move toward traps at the end of the polyfluorene chains. Consequently, the mobility is determined by a longer distance scale than that in the microwave experiments. A longer distance scale of charge transport reduces the mobility because encounter of a barrier in the form of a large torsional angle between fluorene units is more likely.

Effect of Interchain Interactions. In addition to intrachain torsional disorder and coiling of the polymer chains, the mobility can also be reduced by disorder that originates from interchain interactions. In general, solid conjugated polymers are structurally disordered, which means that there are considerable differences in the environment that a charge experiences on different segments along the chains. Places where the backbones of neighboring polymer chains closely interact might act as localization sites that are energetically favorable for charge carriers. Therefore, the potential energy landscape encountered by a charge moving along the backbone of a polymer chain can be significantly altered by the presence of neighboring polymer chains.

We have studied the effect of such interchain interactions on the mobility of charges along the chains by performing pulse radiolysis microwave conductivity experiments on solid samples

of the LPPPs of varying average chain lengths, as shown in Figure 1.²⁷ In these experiments, both the real and the imaginary components of the conductivity were determined. The real part of the conductivity is observed as absorption of microwave power, whereas the imaginary part causes a phase shift of the microwaves that are traveling through the sample. An imaginary component indicates that the velocity of charges is at least partially out of phase with respect to the applied microwave field, that is, the charge velocity is not always in the same direction as the direction of the electric field. As discussed above, the electron–hole pair formation energy for solid polymer samples must be estimated, which leads to an uncertainty in the absolute value of the charge mobility. Fortunately, by measuring both the real and imaginary components of the conductivity, we were able to obtain an accurate value of the mobility. This could be realized by comparing the ratio of both components with the results obtained using the analytic model of one-dimensional diffusion along a polymer chain.²⁷ The charge carrier mobility that was obtained from this analysis is $30 \text{ cm}^2/(\text{V s})$, a factor of 20 lower than the value of $600 \text{ cm}^2/(\text{V s})$ that we obtained for isolated chains of the same polymers in solution.

In principle, the mobility measured for these solid samples should contain contributions from both intrachain transport and interchain charge-transfer events. The latter process is expected to be much less efficient because the electronic coupling between different chains is generally much smaller than the intrachain coupling. In microwave conductivity measurements, the most efficient charge-transfer steps give the largest contribution to the conductivity signal. This means that the microwave mobility derived from the experiments on solid samples are mostly due to charge transport along the ladder-type polymer chains. Indeed, the intrachain mobility of the ladder-type polymers in a solid sample is more than 4 orders of magnitude higher than the DC mobility of $10^{-3} \text{ cm}^2/(\text{V s})$ determined from time-of-flight measurements.³⁹

Note that the chain conformation of the individual polymer chains is the same as that in solution because of the rigid nature of the polymer backbone. The result that the intrachain mobility decreases by a factor of 20 when going from solution to solid indicates that the interactions between different chains in the solid give rise to a significant amount of energetic disorder along the polymer chain. This immediately points to an interesting direction to improve the charge carrier mobility in these materials—creation of a more homogeneous environment for the polymer chains in the solid. This can be achieved by inducing a more ordered supramolecular structure.

Strategies to Enhance the Charge Mobility in Devices. Most of the experimental and simulated data discussed in the preceding sections refer to isolated chains of conjugated polymers in solution rather than the solids, the state in which these materials are used in devices. However, in particular, the experiments in solution give interesting insights in the separate effects of the different types of disorder that can occur in conjugated polymers. In this section, we use these insights to point out some directions that can be taken to improve the charge carrier mobility in devices.

The most optimal situation for charge transport in conjugated polymers is transport along planar chains such as the ladder-type polymer discussed above. Unfortunately, the high mobility value of $\sim 600 \text{ cm}^2/(\text{V s})$ can only be achieved in devices if the distance between the electrodes, typically on the order of 100 nm, can be bridged by a single ladder-type polymer chain, as indicated in

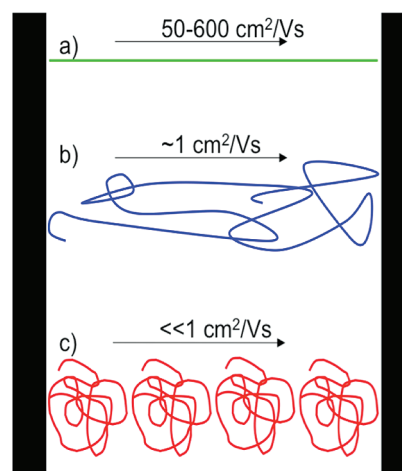


Figure 4. Schematic representation of conjugated polymer chains in devices, where the distance between the contacts is bridged by (a) a single stretched polymer chain, (b) a single coiled polymer chain, and (c) multiple strongly coiled polymer chains.

Figure 4a. For polymers that exhibit torsional disorder, such as PPV, the charge carrier mobility along the chain can already be reduced by an order of magnitude, to $\sim 60 \text{ cm}^2/(\text{V s})$. This problem can be overcome by ensuring that the polymer in the bulk material self-assembles in an organized structure in which the individual chains are planarized by intermolecular interactions. This has been shown to be important in poly-3-hexylthiophene, where an ordered arrangement of the side chains leads to highly organized structures, resulting in much higher mobilities than those in disordered polythiophene materials.⁴⁷

If the distance between the electrodes is not bridged by stretched polymer chains but by coils of a single chain (see Figure 4b), the mobility is already considerably lower. In this case, the transport of charge takes place with a mobility that corresponds to the inherent DC mobility calculated here for a charge moving along a coiled polymer chain in three dimensions, that is, on the order of $1 \text{ cm}^2/(\text{V s})$. This value for the charge carrier mobility assumes that the charge only moves along the contour of the polymer chain and that no interchain charge-transfer steps from one part of the polymer to another take place. This is a reasonable assumption because the interchain transport is much less efficient than intrachain charge transport.

At a certain degree of coiling, the spatial extent of the polymer chains becomes so small that a single polymer coil is not sufficient to bridge the gap between the two electrodes (see Figure 4c). This means that charge transport has to take place via multiple polymer chains, which involves interchain charge-transfer steps. These interchain charge-transfer events are the slowest steps in the charge motion and therefore limit the mobility that is obtained from measurements in devices, with the highest values in FETs being close to $1 \text{ cm}^2/(\text{V s})$.¹⁰

An additional effect that limits the mobility in a solid material results from interactions between different polymer chains. The presence of interchain interactions also influences the inherent mobility of charges along straight planar conjugated chains, as discussed above for the ladder-type polymer. An inhomogeneous environment that surrounds the chains results in energetic disorder along the chain. This was shown to decrease the mobility along the ladder-type polymer chain by a factor of 20. Such reduction of the mobility can be overcome by ensuring that

the environment of the polymer chains in the solid is more homogeneous by improving the order in the material.

Higher charge mobilities can be realized in devices if polymer chains directly interconnect electrodes and adopt a straight, planar structure in a homogeneous environment.

The results discussed above show that the mobility of charges in conjugated polymers is not inherently lower than in inorganic semiconductors. For conjugated polymers with high intrachain order, the mobility of charges along the backbone can be as high as $600 \text{ cm}^2/(\text{V s})$. This is consistent with the electronic bandwidth in these polymers, a few electronvolts, which is very similar to typical bandwidths in inorganic semiconductors. There are several factors that lead to reduction of charge mobilities in the solid state. The polymer backbone can exhibit torsional disorder, resulting in conjugation breaks that limit the mobility. Additionally, many conjugated polymers will exhibit rather coiled structures with a small spatial extent in the solid. This not only reduces the mobility within the polymer coil but also leads to the requirement of interchain charge transport in devices with an electrode spacing exceeding the coil diameter. Finally, interchain interactions lead to energetic disorder along polymer chains, which can reduce the mobility of charges along the individual chains by more than an order of magnitude.

The most important question arising from the results presented in this Perspective pertains to the identifications of strategies that lead to higher charge carrier mobilities in devices. How should conjugated polymers be organized in solid-state devices so that the intrinsically high charge carrier mobility along the chains can be exploited? We believe the answer lies in the improvements of supramolecular order in the material. Much higher charge mobilities can be obtained if the polymer chains directly interconnect the electrodes and adopt a straight, planar structure with a homogeneous environment.

AUTHOR INFORMATION

Corresponding Author

*E-mail: L.D.A.Siebbeles@tudelft.nl.

BIOGRAPHIES

Ferdinand C. Grozema (1973) studied chemistry at the University of Groningen and obtained his Ph.D. degree at the Delft University of Technology. In 2007, he spent 7 months working as a visiting scholar at Northwestern University in Evanston, IN, U.S.A. Currently, he is an associate professor in the opto-electronic materials section at the Chemical Engineering Department of the Delft University of Technology in Delft. His research interests consist of theoretical and experimental studies of the properties and dynamics of excited states in

bio/organic materials. The main focus of this research has been on charge transport in conjugated molecular wires and in DNA.

Laurens D. A. Siebbeles (1963) studied chemistry at The Free University in Amsterdam and obtained his Ph.D. degree at the FOM-institute for Atomic and Molecular Physics in Amsterdam. He was a Postdoc at the University of Paris Sud in France. Currently, he is professor in opto-electronic materials at the Delft University of Technology in The Netherlands. He studies the dynamics of charges and excitons in molecular materials and semiconductor nanocrystals. Charges and excitons are produced with high-energy electron or laser pulses and probed by time-resolved optical and microwave or terahertz measurements. The experiments are supported by theory of charge and exciton dynamics.

REFERENCES

- (1) Blythe, T.; Bloor, D. *Electrical Properties of Polymers*; Cambridge University Press: Cambridge, U.K., 2005.
- (2) Moliton, A. *Optoelectronics of Molecules and Polymers*; Springer: New York, 2006.
- (3) Krebs, F. C.; Tromholt, T.; Jorgensen, M. Upscaling of Polymer Solar Cell Fabrication using Full Roll-to-Roll Processing. *Nanoscale* **2010**, 2, 873–886.
- (4) Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. Materials and Applications for Large Area Electronics: Solution-Based Approaches. *Chem. Rev.* **2010**, 110, 3–24.
- (5) Jung, B. J.; Tremblay, N. J.; Yeh, M. L.; Katz, H. E. Molecular Design and Synthetic Approaches to Electron-Transporting Organic Transistor Semiconductors. *Chem. Mater.* **2011**, 23, S68–S82.
- (6) Gunes, S.; Neugebauer, H.; Saricifti, N. S. Conjugated Polymer-Based Organic Solar Cells. *Chem. Rev.* **2007**, 107, 1324–1338.
- (7) Xue, J. G. Perspectives on Organic Photovoltaics. *Polym. Rev.* **2010**, 50, 411–419.
- (8) Anthony, J. E. Small-Molecule, Nonfullerene Acceptors for Polymer Bulk Heterojunction Organic Photovoltaics. *Chem. Mater.* **2011**, 23, 583–590.
- (9) Zhang, M.; Tsao, H. N.; Pisula, W.; Yang, C. D.; Mishra, A. K.; Mullen, K. Field-Effect Transistors Based on a Benzothiadiazole–Cyclopentadithiophene Copolymer. *J. Am. Chem. Soc.* **2007**, 129, 3472–+.
- (10) Sonar, P.; Singh, S. P.; Li, Y. N.; Ooi, Z. E.; Ha, T. J.; Wong, I.; Soh, M. S.; Dodabalapur, A. High Mobility Organic Thin Film Transistor And Efficient Photovoltaic Devices Using Versatile Donor–Acceptor Polymer Semiconductor by Molecular Design. *Encycl. Environ. Sci.* **2011**, 4, 2288–2296.
- (11) Grozema, F. C.; Siebbeles, L. D. A. Mechanism of Charge Transport in Self-Organizing Organic Materials. *Int. Rev. Phys. Chem.* **2008**, 27, 87–138.
- (12) Laquai, F.; Wegner, G.; Bassler, H. What Determines the Mobility of Charge Carriers in Conjugated Polymers? *Philos. Trans. R. Soc. London, Ser. A* **2007**, 365, 1473–1487.
- (13) Hilt, O.; Siebbeles, L. D. A. Time And Frequency Dependent Charge Carrier Mobility of One-Dimensional Chains with Energetic Disorder. *Chem. Phys. Lett.* **1997**, 269, 257–262.
- (14) Hilt, O.; Siebbeles, L. D. A. Time and Frequency Dependent Charge Carrier Mobility on One-Dimensional Chains with Energetic Disorder for Polaron and Miller–Abrahams Type Hopping. *Chem. Phys.* **1998**, 229, 257–263.
- (15) Dyre, J. C.; Schröder, T. B. Universality of AC Conduction in Disordered Solids. *Rev. Mod. Phys.* **2000**, 72, 873–892.
- (16) Nemes, H.; Kuzel, P.; Sundstrom, V. Charge Transport in Nanostructured Materials for Solar Energy Conversion Studied by Time-Resolved Terahertz Spectroscopy. *J. Photochem. Photobiol., A* **2010**, 215, 123–139.
- (17) Ulbricht, R.; Hendry, E.; Shan, J.; Heinz, T. F.; Bonn, M. Carrier Dynamics in Semiconductors Studied with Time-Resolved Terahertz Spectroscopy. *Rev. Mod. Phys.* **2011**, 83, S43–S86.

- (18) Warman, J. M.; de Haas, M. P.; Dicker, G.; Grozema, F. C.; Piris, J.; Debije, M. G. Charge Mobilities in Organic Semiconducting Materials Determined by Pulse Radiolysis Time-Resolved Microwave Conductivity: π -Bond-Conjugated Polymers Versus π - π -Stacked Discotics. *Chem. Mater.* **2004**, *16*, 4600–4609.
- (19) Kroeze, J. E.; Savenije, T. J.; Warman, J. M. Electrodeless Determination of the Trap Density, Decay Kinetics, and Charge Separation Efficiency of Dye-Sensitized Nanocrystalline TiO_2 . *J. Am. Chem. Soc.* **2004**, *126*, 7608–7618.
- (20) Hendry, E.; Schins, J. M.; Candeias, L. P.; Siebbeles, L. D. A.; Bonn, M. Efficiency of Exciton and Charge Carrier Photogeneration in a Semiconducting Polymer. *Phys. Rev. Lett.* **2004**, *92*, 196601.
- (21) Grzegorzczak, W. J.; Savenije, T. J.; Dykstra, T. E.; Piris, J.; Schins, J. M.; Siebbeles, L. D. A. Temperature-Independent Charge Carrier Photogeneration in P3HT–PCBM Blends with Different Morphology. *J. Phys. Chem. C* **2010**, *114*, 5182–5186.
- (22) Ferguson, A. J.; Kopidakis, N.; Shaheen, S. E.; Rumbles, G. Quenching of Excitons by Holes in Poly(3-hexylthiophene) Films. *J. Phys. Chem. C* **2008**, *112*, 9865–9871.
- (23) Holt, J. M.; Ferguson, A. J.; Kopidakis, N.; Larsen, B. A.; Bult, J.; Rumbles, G.; Blackburn, J. L. Prolonging Charge Separation in P3HT–SWNT Composites Using Highly Enriched Semiconducting Nanotubes. *Nano Lett.* **2010**, *10*, 4627–4633.
- (24) Rance, W. L.; Ferguson, A. J.; McCarthy-Ward, T.; Heeney, M.; Ginley, D. S.; Olson, D. C.; Rumbles, G.; Kopidakis, N. Photoinduced Carrier Generation and Decay Dynamics in Intercalated and Non-intercalated Polymer:Fullerene Bulk Heterojunctions. *ACS Nano* **2011**, *5*, 5635–5646.
- (25) Katoh, R.; Furube, A.; Yamanaka, K.; Morikawa, T. Charge Separation and Trapping in N-Doped TiO_2 Photocatalysts: A Time-Resolved Microwave Conductivity Study. *J. Phys. Chem. Lett.* **2010**, *1*, 3261–3265.
- (26) Saeki, A.; Tsuji, M.; Seki, S. Direct Evaluation of Intrinsic Optoelectronic Performance of Organic Photovoltaic Cells with Minimizing Impurity and Degradation Effects. *Adv. Energy Mater.* **2011**, *1*, 661–669.
- (27) Prins, P.; Grozema, F. C.; Schins, J. M.; Savenije, T. J.; Patil, S.; Scherf, U.; Siebbeles, L. D. A. Effect of Intermolecular Disorder on the Intrachain Charge Transport in Ladder-Type Poly(p-phenylenes). *Phys. Rev. B* **2006**, *73*, 045204.
- (28) Prins, P.; Grozema, F. C.; Galbrecht, F.; Scherf, U.; Siebbeles, L. D. A. Charge Transport Along Coiled Conjugated Polymer Chains. *J. Phys. Chem. C* **2007**, *111*, 11104–11112.
- (29) Prins, P.; Grozema, F. C.; Schins, J. M.; Patil, S.; Scherf, U.; Siebbeles, L. D. A. High Intrachain Hole Mobility on Molecular Wires of Ladder-Type Poly(p-phenylenes). *Phys. Rev. Lett.* **2006**, *96*, 146601.
- (30) Asaoka, S.; Takeda, N.; Lyoda, T.; Cook, A. R.; Miller, J. R. Electron and Hole Transport to Trap Groups at the Ends of Conjugated Polyfluorenes. *J. Am. Chem. Soc.* **2008**, *130*, 11912–11920.
- (31) Sreearunothai, P.; Asaoka, S.; Cook, A. R.; Miller, J. R. Length and Time-Dependent Rates in Diffusion-Controlled Reactions with Conjugated Polymers. *J. Phys. Chem. A* **2009**, *113*, 2786–2795.
- (32) Keller, J. M.; Glusac, K. D.; Danilov, E. O.; McIlroy, S.; Sreearunothai, P.; Cook, A. R.; Jiang, H.; Miller, J. R.; Schanze, K. S. Negative Polaron and Triplet Exciton Diffusion in Organometallic “Molecular Wires”. *J. Am. Chem. Soc.* **2011**, *133*, 11289–11298.
- (33) Alig, R. C.; Bloom, S.; Struck, C. W. Scattering by Ionization and Phonon Emission in Semiconductors. *Phys. Rev. B* **1980**, *22*, 5565–5582.
- (34) Gee, N.; Freeman, G. R. Electron Thermalization Distances and Free-Ion Yields in Dense Gaseous and Liquid Benzene. *Can. J. Chem.* **1992**, *70*, 1618–1622.
- (35) Hummel, A. In *The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1992; pp 743–780.
- (36) Grozema, F. C.; Hoofman, R. J. O. M.; Candeias, L. P.; de Haas, M. P.; Warman, J. M.; Siebbeles, L. D. A. The Formation and Recombination Kinetics of Positively Charged Poly(phenylene vinylene) Chains in Pulse-Irradiated Dilute Solutions. *J. Phys. Chem. A* **2003**, *107*, 5976–5986.
- (37) Kubo, R. Statistical-Mechanical Theory of Irreversible Processes I. General Theory and Simple Applications to Magnetic and Conduction Problems. *J. Phys. Soc. Jpn.* **1957**, *12*, 570–586.
- (38) Prins, P.; Grozema, F. C.; Schins, J. M.; Siebbeles, L. D. A. Frequency Dependent Mobility of Charge Carriers Along Polymer Chains with Finite Length. *Phys. Status Solidi B* **2006**, *243*, 382–386.
- (39) Hertel, D.; Scherf, U.; Bässler, H. Charge Carrier Mobility in a Ladder-Type Conjugated Polymer. *Adv. Mater.* **1998**, *10*, 1119–1122.
- (40) Grozema, F. C.; van Duijnen, P. T.; Berlin, Y. A.; Ratner, M. A.; Siebbeles, L. D. A. Intramolecular Charge Transport Along Isolated Chains of Conjugated Polymers: Effect of Torsional Disorder and Polymerization Defects. *J. Phys. Chem. B* **2002**, *106*, 7791–7795.
- (41) Darling, S. B. Isolating the Effect of Torsional Defects on Mobility and Band Gap in Conjugated Polymers. *J. Phys. Chem. B* **2008**, *112*, 8891–8895.
- (42) Adachi, T.; Brazard, J.; Ono, R. J.; Hanson, B.; Traub, M. C.; Wu, Z. Q.; Li, Z. C.; Bolinger, J. C.; Ganesan, V.; Bielawski, C. W.; et al. Regioregularity and Single Polythiophene Chain Conformation. *J. Phys. Chem. Lett.* **2011**, *2*, 1400–1404.
- (43) Prins, P.; Grozema, F. C.; Siebbeles, L. D. A. Efficient Charge Transport Along Phenylene-Vinylene Molecular Wires. *J. Phys. Chem. B* **2006**, *110*, 14659–14666.
- (44) Prins, P.; Grozema, F. C.; Siebbeles, L. D. A. Charge Transport Along Phenylenevinylene Molecular Wires. *Mol. Simul.* **2006**, *32*, 695–705.
- (45) Hoofman, R. J. O. M.; de Haas, M. P.; Siebbeles, L. D. A.; Warman, J. M. Highly Mobile Electrons and Holes on Isolated Chains of the Semiconducting Polymer Poly(phenylenevinylene). *Nature* **1998**, *392*, 54–56.
- (46) Prins, P.; Candeias, L. P.; Van Breemen, A. J. J. M.; Sweelssen, J.; Herwig, P. T.; Schoo, H. F. M.; Siebbeles, L. D. A. Electron and Hole Dynamics on Isolated Chains of a Solution Processible Poly(thienylene vinylene) Derivative in Dilute Solution. *Adv. Mater.* **2005**, *17*, 718–723.
- (47) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. Two-Dimensional Charge Transport in Self-Organized, High-Mobility Conjugated Polymers. *Nature* **1999**, *401*, 685–688.