# **Opto-Electronic Properties**

of

## **Conjugated Molecular Wires**

F.C. Grozema

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The research described in this thesis was performed at the Radiation Chemistry department (SC) of the Interfaculty Reactor Institute (IRI), Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands.

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## **General Introduction**

#### 1.1 History

Conjugated polymers form a class of polymers that have been studied extensively over the last two decades for possible applications in electronics. Most organic polymers are electrically insulating. Therefore, their primary use in electronics is as an insulating layer around copper wires. In recent years, however, an alternative use of organic polymers has emerged. In 1977 Shirakawa, MacDiarmid and Heeger discovered that films of polyacetylene, the simplest example of a conjugated polymer, become highly conducting after oxidative doping.<sup>1</sup> It was found that exposure to iodine vapor made the polyacetylene films 10<sup>9</sup> times more conductive than they are in their undoped (pristine) state. For this discovery they were awarded the Nobel-prize in chemistry in 2000.<sup>2-4</sup>

A second breakthrough in the field of conjugated polymers was the observation of electro-luminescence for poly(p-phenylene vinylene) by Burroughes et al.<sup>5</sup> This discovery has opened the way to application of conjugated polymers in electronics not only as (semi-) conducting materials but also as light-emitting materials for use in e.g. light-emitting diodes. Moreover, the optical properties of conjugated polymers make them suitable for application in photovoltaic devices as the light absorbing layer.<sup>6</sup>

One of the main advantages of conjugated polymers over traditional inorganic materials is their relatively low processing cost. In crystalline inorganic devices the active layer is usually deposited by (expensive) vapor phase deposition. Conjugated polymers can be cast from solution, which makes them suitable for application in large area displays and solar cells. The first commercial applications of devices based conjugated polymers have recently emerged. Light emitting diodes (LEDs) with a conjugated polymer as the emissive layer are currently being used as the back-light for LCD displays. The first examples of video displays with pixels consisting of polymer LEDs<sup>7</sup> have also been presented recently and several companies are working on the commercialization of such devices.

#### 1.2 Conjugated polymers

Conjugated polymers consist of an alternating sequence of single and double bonds between the carbon atoms. The structure of some important  $\pi$ -conjugated polymers are shown in Figure 1.1. The simplest polymer in this class is polyacetylene, which consists of a chain of carbon atoms connected alternatingly by single and double bonds. This was the first conjugated polymer in which a high conductivity was measured, as mentioned above.<sup>1</sup> A second, much used example is polythiophene, a chain of five-membered heterocycles containing a sulfur atom. This polymer is more stable than polyacetylene and is presently one of the most used conjugated polymers for field effect transistors (FETs). Poly(p-phenylene vinylene) was the first material in which electro-luminescence was observed.<sup>5</sup> This polymer is therefore an excellent candidate for the emissive layer in LEDs.



Figure 1.1: Backbone structure of some conjugated polymers.

Poly(p-phenylenes) form a class of polymers that have received a considerable amount of attention, especially because of their fluorescence in the blue part of the spectrum. Polyfluorene is a derivative of PPP that becomes liquid crystalline at temperatures between 150 and 200 °C, the actual phase transition temperature depending on the substituents. If a suitable alignment layer is used, it is possible to make highly aligned polymer layer in which the chains lie preferentially in one direction.<sup>8,9</sup> This makes it possible to make LED devices that emit polarized light,<sup>10,11</sup> which has interesting technological applications. It has been shown that increased ordering in thin polyfluorene films also has interesting consequences for the charge transport properties. A large in-plane anisotropy has been measured, showing that charge transport along the polymer chain direction is much more efficient than transport perpendicular to the polymer direction.<sup>12</sup> Moreover, it has been shown in time-of-flight

measurements, that the charge carrier mobility even perpendicular to the chain direction is increased by an order of magnitude due to the alignment of the polymer.<sup>13</sup>

Another PPP derivative is ladder type PPP. In this polymer the intra-molecular (torsional) disorder is reduced to a minimum by interconnecting the consecutive ring with a methylene bridge. This reduced structural disorder causes the charge carrier mobility obtained from time-of-flight measurements to be relatively temperature independent.<sup>14,15</sup>



**Figure 1.2**: Structures of two substituted conjugated polymers that are commonly used in light-emitting diodes (MEH-PPV) and field effect transistors (P3HT).

The first conjugated polymers that were synthesized contained no side chains and were insoluble. This makes it rather hard to purify the polymers. Moreover, soluble polymers are much easier to process into thin films; *e.g.* by spin coating. Conjugated polymers with alkylor alkoxy- side chains have been synthesized in order to obtain soluble polymers. Two well-known examples of substituted conjugated polymers are shown in Figure 1.2, poly-3-hexyl-thiophene (P3HT) and poly(2-methoxy-5-[2'-ethyl-hexyloxy]-phenylene vinylene) (MEH-PPV). Introduction of side-chains has led to great improvements in the purity of conjugated polymers and some of these materials are now commercially available. The introduction of side chains has additional advantages in the supra-molecular ordering of the chains in a solid material. If side chains are introduced in polythiophene in a regular way the polymer organizes itself in a lamellar structure which is advantageous for charge transport.<sup>16,17</sup>

#### 1.3 Applications of conjugated polymers

Conjugated polymers are being considered as the active materials in several types of electronic devices. This section briefly discusses the three most important applications. In all of these devices the polymer is used in a thin film of solid material. Such a thin polymer layer can be deposited from solution; *e.g.* by spin coating or drop casting. For commercial applications ink-jet printing has become the method of choice

#### Field effect transistors

Field effect transistors based on conjugated polymers are being studied for possible applications in plastic electronics.<sup>18</sup> In principle, this could lead to low-cost, flexible electronic devices for use as smart electronic tags<sup>19,20</sup> that can be read out from a distance.

Polymer transistors have also been demonstrated to be useful as the switching element in (flexible) flat panel displays.<sup>21</sup> The basic design of a field effect transistor is shown in Figure 1.3. The current passing between two electrodes, the source and the drain, is controlled by applying a voltage to the third electrode, the gate. The performance (e.g. the switching time and maximum current) of the device depend critically on the mobility of the charges in the active conjugated polymer layer adjacent to the insulator. Another important parameter is the on/off ratio which should be as high as possible.



**Figure 1.3**: Schematic drawing of a conjugated polymer based field effect transistor device.

Excellent results have been obtained for FET devices based on oligomers (oligothiophenes, pentacene) that are deposited from the vapor phase.<sup>22,23</sup> Great progress has also been made in polymer based devices in which the active material is deposited from solution. For devices based on regio-regular P3HT a mobility of ~0.1 cm<sup>2</sup>/Vs has been reported.<sup>16</sup> This is still several orders of magnitude lower than the mobility in crystalline silicon ( $10^3 \text{ cm}^2/\text{Vs}$ ), however, it is sufficient for the applications mentioned above. In these applications the emphasis is on the low cost rather than on high performance. Fully flexible integrated circuits based on conjugated polymers have been demonstrated already.<sup>19,20</sup>

#### Light emitting devices

The second application of conjugated polymers is as the emissive layer in light-emitting diodes. In 1990 Burroughes et al.<sup>5</sup> demonstrated that luminescence can be produced by charge injection into poly(phenylene vinylene). It was found that the electro-luminescence spectrum showed a close resemblance to the photoluminescence spectrum, suggesting that the emission is from the same excited state. A schematic picture of a light emitting diode is shown in Figure 1.4. Electrons and holes are injected from opposite electrodes and migrate towards each other through the conjugated polymer thin film under the influence of an applied field. Combination of an electron and a hole leads to the formation of an exciton which can decay radiatively if it is in a singlet spin state.

The device characteristics of polymer based LEDs (electro-luminescence yield, color of the light) can be tailored by chemical modification of the luminescent polymers used. The color of the light emitted by LED devices can be tuned by using polymers with different backbone structures. LEDs based on PPP<sup>24</sup>, PPV<sup>5,25</sup> and polythiophene<sup>26</sup> show emission in the blue, green-orange and red wavelength region, respectively. The emissive color can also be

influenced by substitution of the polymer with electron donating or withdrawing groups.<sup>27,28</sup> Moreover the optical properties can be changed by deliberately introducing conjugation breaks in the polymer.<sup>29</sup> The chemical modifications mentioned above also have an influence on the electro-luminescence yield.



Figure 1.4: Schematic drawing of simple light-emitting diode device.

One of the advantages of conjugated polymers for use as the active layer in light emitting devices is that they can be processed from solution. Thin films of the emissive material can be created e.g. by spin coating. Recently, it has been shown that it is even possible to make large area displays and electronic circuits by ink-jet printing.<sup>7,30,31</sup> Prototypes of full color displays based on conjugated polymers have already been made and commercial applications are expected shortly.

#### Photovoltaic cells

Conjugated polymers can also be applied as the absorbing layer in photovoltaic devices, in which the processes occurring in LEDs are reversed.<sup>6,32-34</sup> Figure 1.5 schematically shows the design of a photovoltaic bi-layer device. The device consists of a conjugated polymer layer on top of a large band-gap, inorganic semiconductor material,  $TiO_2$  in this case.<sup>35</sup> The cell is illuminated through the optically transparent anode and  $TiO_2$  layer, creating singlet excited states (excitons) in the conjugated polymer. These excitons can migrate through the material until they reach the interface with the  $TiO_2$ , where electron transfer takes place. The electron is transported through the  $TiO_2$  layer to the anode. The positive charge is left behind in the conjugated polymer and has to travel through the polymer layer to reach the cathode.

The requirements of the conjugated polymers used in photovoltaic devices are somewhat different than those used for LEDs. Whereas in LEDs it is often required that the emitted light has one well-defined color, in photovoltaic devices the polymer preferably absorbs light with a spectral range as broad as possible. Both types of device have in common that the polymer must be able to transport charge. An additional requirement for photovoltaics is that the exciton must, during its lifetime, diffuse to the interface. Therefore, the exciton should have an appreciable life-time and/or a relatively high diffusion constant. A huge increase in the lifetime of excitons can be achieved by using the triplet excited state rather than the singlet. A

drawback of such triplet sensitization is that the diffusion constant of the triplet exciton is usually a few orders of magnitude lower than for singlet excitons. Recently it was demonstrated however, that triplet excitons can migrate over large distances through thin films of palladium porphyrin to a  $TiO_2$  layer, where charge separation takes place.<sup>36</sup> This illustrates the potential of photovoltaic cells using a triplet sensitizer.



Figure 1.5: Schematic drawing of a bilayer photovoltaic device.

Another approach to improve the performance of polymer based solar cells is to reduce the distance over which an exciton has to migrate. This is realized by maximizing the contact area between the absorbing materials (the conjugated polymer) and the electron acceptor (TiO<sub>2</sub> or an organic material e.g.  $C_{60}$ ) by using nanoporous layers or blends of the two components.<sup>6,37</sup> These so-called bulk hetero-junction solar cells lead to devices with a considerably higher efficiency than bi-layer devices. A prerequisite is that a percolation path for charge migration to the electrodes exists.

#### **1.4 Molecular electronics**

In the devices described in the previous section, conjugated polymers are used in the form of thin films. These applications make use of the simplified ways of processing the polymers, as compared to inorganic semi-conductors. A second possible application is their use as molecular wires in single molecule electronics or nanoscale devices.<sup>38,39</sup> According to the predictions of Gordon Moore in 1965 the number of transistors per square centimeter of silicon doubles every 18 months.<sup>40</sup> This requires that the size of transistors and their interconnects decreases at the same rate. Up until now this miniaturization has been realized by improvements in photolithographic techniques. These techniques will reach their fundamental limit in the near future, as the dimensions of the components approach a few tens of nanometers. Therefore much research is focussed on going directly to the smallest components that are likely to be functional, that is components consisting of single molecules or groups of molecules.

Already in 1959 the eminent physicist Richard Feynman<sup>41</sup> discussed the possibilities of devices of extremely small dimensions:

"I don't know how to do this on a small scale in a practical way, but I do know that computing machines are very large; they fill rooms. Why can't we make them very small, make them of little wires, little elements — and by little I mean little. For instance, the wires should be 10 or 100 atoms in diameter, and the circuits should be a few thousand angstroms across...there is plenty of room to make them smaller. There is nothing that I can see in the laws of physics that says the computer elements cannot be made enormously smaller than they are now." <sup>41</sup>

#### Molecular rectifiers

The first concrete idea for an electronic component consisting of a single molecule was the molecular rectifier described by Aviram and Ratner in 1974.<sup>42,43</sup> The molecular rectifier that they considered consisted of an electron donating moiety, tetrathiafulvalene, that was connected to an electron accepting group, tetracyanoquinodimethane, by an "insulating"  $\sigma$ -bonded spacer, see Figure 1.6a. This molecule can be considered as an analogue of *p*-*n* junctions common to the design of traditional solid-state rectifiers. Quantum chemical calculations suggested that this molecule should indeed exhibit rectifying behavior.



**Figure 1.6**: A: Structure of the molecular recifier proposed by Aviram and Ratner.<sup>42</sup> B: Intramolecular junction between a metallic and semiconducting nanotube section which exhibits rectifying behavoir.<sup>44</sup>

A second example of a rectifier consisting of a single molecule is the carbon nanotube intramolecular junction reported by the group of Dekker.<sup>44</sup> Single-walled nanotubes can be either metallic or semi-conducting depending on their diameter and helicity.<sup>7</sup> An intramolecular junction between a metallic and a semi-conducting nanotube section can be realized by introducing a pentagon and a heptagon into the hexagonal carbon lattice, see Figure 1.6b. Electrical transport measurements on a single carbon nanotube intramolecular metal-semi-conductor junction have been performed by Yao et al.<sup>44</sup> It was shown that the

transport characteristics were strongly asymmetric with respect to the bias polarity, thus exhibiting the behavior of a rectifying diode.

#### Molecular switches

The basic control element in electronic architecture is the switch, which allows the control of current-flow. Switches can be used on their own but can also be connected in arrays of multiple switches to implement logic operations.



**Figure 1.7**: Structure of the dithienyl photochromic switch. Reversible switching between the open and closed forms is achieved by irradiation with visible and UV light.

One example of a switch on a molecular scale is the photochromic switch consisting of a dithienylethene molecule, see Figure 1.7.<sup>45-48</sup> The connection between the thienyl rings can be made or broken by illuminating with different wavelengths of light. In the open form the thienyl rings are not connected and therefore the conjugation across the molecule is broken. If the molecule is illuminated with ultra-violet light (UV) the closed form is obtained. The molecule can be switched back to its open form by irradiation with visible light. Such a light switchable molecule can be used as a memory element, using the open and closed form as "on" and "off" bits. The photochromic switch can also, in principle, be used for switching currents "on" or "off" on a molecular level when it is incorporated into a molecular wire. The conjugated conductive pathway through the molecule can be opened or closed by illumination. Note that the closed form of the switch is planar whereas the open form is not.

A second example is the transistor demonstrated by the group of Dekker,<sup>49</sup> which consists of a semi-conducting single-walled nanotube positioned across two Pt electrodes on a silicon oxide substrate with doped silicon as the back gate. The current through the nanotube can be manipulated by changing the voltage applied at the gate electrode. It has also been demonstrated that these devices can be assembled into one-, two-, and three-transistor circuits that perform a range of digital logic operations such as an inverter or a memory cell.<sup>50</sup>

#### Molecular wires: connecting devices

The molecular devices described above have to be connected to form electronic circuits in order to be able to use them in a functional way. These conducting interconnects have to be of molecular dimensions. The connections can be made using metallic carbon nanotubes.<sup>51</sup> This would make it possible together with the nanotube rectifier and transistor described above to create electronic circuits completely consisting of nanotubes. One of the problems in building actual nanotube circuits is the control over synthesis and organization. At this time it is not possible to specifically synthesize the nanotube rectifiers described above. Control over the

"supramolecular" organization is needed if the nanotubes are to be positioned into actual circuits. An interesting idea for positioning nanotubes was put forward by Dekker and coworkers recently.<sup>52</sup> These authors connected a section of DNA to carbon nanotubes. The highly specific supramolecular organization properties of DNA can in principle be used in this way to position the nanotube-wires.

The interconnects can also be realized by using conjugated polymers or oligomers such as those shown in Figures 1.1 and 1.2. One of the advantages of these molecules over carbon nanotubes is that their properties can be controlled to a high degree by chemical methods.<sup>28,53</sup> Supramolecular ordering can possibly be induced by attaching e.g. hydrogen bonding units, as explored by Meijer et al.<sup>54-56</sup>, in order to create self-organizing circuits. A possible problem for these materials as molecular wires can be their instability especially in their oxidized or reduced state in which they readily undergo reactions with water or oxygen.

#### 1.5 Models of charge transport in conjugated polymers

In solid materials there are two extreme types of charge carrier motion. In band-transport the charge are highly delocalized and have a mean free path towards scattering very much larger than the intermolecular or interatomic distances. This type of transport is often encountered in highly ordered (crystalline) materials. The other extreme is hopping transport in which the charge is highly localized and scattering occurs at virtually every hopping step. Such transport is usually found in disordered materials. The two charge transport models are characterized by the magnitude and temperature dependence of the charge carrier mobility. In band transport the mobilities are usually high (>> 1 cm<sup>2</sup>/Vs) and increase with decreasing temperature. In hopping, much lower mobilities are found in general (<< 1 cm<sup>2</sup>/Vs) and the mobility usually increases with increasing temperature.

#### Band structure theory

In inorganic semiconductor research the electronic properties of the materials are commonly described in terms of band theory.<sup>57</sup> The formation of bands in a periodic array of 'repeat units' is illustrated in Figure 1.8. At infinite separation the electrons in the repeat units do not interact and in both units there are a number of discrete molecular orbitals. If two units are brought together the interaction between the electrons in both units (the electronic coupling) causes the energy levels to adapt. In the simple case where the interaction is only between a single orbital on unit A and a single orbital on unit B the electronic coupling induces the formation of two new levels, one of higher and one of lower energy than that of the original orbitals in the separate units. On neglect of the spatial overlap between the orbitals the energetic splitting between the two new levels is equal to twice the electronic coupling.<sup>58</sup> In the limit of an infinite number of repeat units the new levels will form a continuous band, with an energy spread or band-width which is equal to four times the electronic coupling between neighboring units. This formation of bands arises for the occupied molecular orbitals leading to the valence band, but also for the unoccupied orbitals leading to formation of the conduction band. The electrons in the solid can be considered to be completely delocalized over the entire material.



#### Infinite number of interacting units



**Figure 1.8**: Development of bands by interaction of HOMO and LUMO orbitals in repeat units. The interaction between two units leads to two new levels with an energy splitting of twice the electronic coupling, b, between the orbitals. For an infinite number of repeat units a continuous band of levels develops with a bandwidth of 4*b*.

Excess charge carriers can be introduced in the valence or conduction band for example by chemical doping, photo-excitation or injection from electrodes. The steady-state velocity, V, with which an ensemble of these charges move through the material under the influence of an external electrical field, E, is determined by the charge carrier mobility,  $\mu$ :

$$V = \mu E \tag{1.1}$$

In the simplest description of charge transport, the Drude model,<sup>57</sup> the mobility is given by

$$\mu = \frac{e\tau}{m} \tag{1.2}$$

with *e* the elementary charge,  $\tau$  the momentum transfer scattering time and *m* the mass of the charge carrier. In band theory this mass is actually an effective mass, which can differ significantly from the actual mass of an electron. The scattering events in such a model involve interactions with lattice vibrations (or phonons) and/or structural defects. The scattering time will therefore become smaller as the vibrational energy increases, causing the charge carrier mobility to decrease with increasing temperature.



**Figure 1.9**: Example of a potential energy landscape in hopping transport. The charge carrier 'hops' over barriers of height  $E_b$  between the localization sites.

#### Thermally activated hopping transport

Band theory is known to give a good description in many cases of crystalline materials where the approximation of a periodic structure is quite accurate. This is not the case for disordered solid materials such as polymer films.<sup>59</sup> In these materials the charge carriers are generally believed to be localized to a greater or lesser extent. Charge transport in disordered materials is often described in terms of a thermally activated hopping mechanism.<sup>60,61</sup> According to this mechanism the charge performs thermally activated 'hops' between different localization sites. An example of a potential energy landscape in a disordered material is shown in Figure 1.9. The localization sites are separated by energy barriers of different height. For the case considered in Figure 1.9, the over-the-barrier (OVB) hopping mechanism the rate for a jump over a barrier of energy  $E_b$  is

$$W = w_0 \exp\left(-\frac{E_b}{k_B T}\right) \tag{1.3}$$

where  $w_0$  is a prefactor, the so-called attempt frequency. In the OVB hopping mechanism the site energies are equal, the energetic disorder is in the barriers between them. This model has been shown to give a good description of charge transport in columnar stacks of discotic molecules where all localization sites (the individual molecules) are the same. <sup>62</sup>

A second often-used hopping model is the Miller-Abrahams model for tunneling assisted hopping.<sup>63</sup> In this case the site energies are different and the charge moves from site to site by tunneling. The tunneling probability depends on the energy difference between the sites and on the electronic coupling between the sites.

Charge transport has been studied numerically by Monte Carlo simulations of charges moving in an energy landscape with a gaussian or exponential distribution of site energies or barrier heights.<sup>62,64</sup> There are also analytical approximations for some types of hopping that can be used to describe experimental results.<sup>62,65</sup> Hopping models have been used to describe experimental results on solid materials with reasonable success, however the parameters that are obtained from such fits (e.g. the energetic disorder) give little insight into the relation between charge transport properties and the structure at a molecular level. Moreover, the approximation that the charges are always localized and move only by fully incoherent hopping events is likely to be an oversimplified view.

In the work described in this thesis, where the focus is on charge transport along isolated molecular wires in solution, a model is required that includes elements of both transport models. A band-description would be appropriate for an infinitely long periodic polymer chain, however, in solution the conformation of the polymer chain is far from periodic. There will, however, be relatively ordered stretches of polymer, the length depending on the backbone structure and substituents, where the charge transport is very efficient and the coherent effects have to be considered. A model describing charge transport along isolated chains is presented in Chapter 7.

#### 1.6 Measuring the mobility of charges

#### DC techniques

In most experimental studies of charge transport in conjugated polymers the mobility of charges is obtained from DC-techniques such as time-of flight (TOF) measurements or measurements on field-effect transistor devices (see Figure 1.5). In TOF methods a constant electric field is applied to the sample. Charge carriers are generated by illuminating the sample through the (grid) electrode. The photocurrent is monitored in a time-resolved way and from the transit time, the time at which the current starts decaying, the charge carrier mobility is obtained. In measurements on FET devices the mobility is obtained from the current voltage characteristics. In both of these DC-techniques the charge carrier has to travel through the entire sample in order to contribute to the current from one electrode to the other. The mobility of the charge is a combination of several different processes as illustrated in Figure 1.10. Firstly, the charge can move along a single chain of a conjugated polymer. In order to move over macroscopic distances the charge also has to move from one polymer chain to the other. These interchain processes are generally believed to be slower than intrachain transport. Depending on the morphology of the material the sample between the electrodes may consist of different domains ('grains') with a relative well ordered internal structure. The transport between the grains can be expected to be even less efficient than interchain transport because of the limited contact between the polymer chains in different

domains. The mobility obtained by DC measurements is determined by the least efficient charge transfer step, which generally leads to relatively low mobilities in disordered materials.



**Figure 1.10**: Schematic representation of a disordered polymer material. Arrow 1, 2 and 3 represent intrachain, interchain and interdomain charge transport, respectively.

#### High frequency techniques: microwave conductivity

In this thesis the mobility of charge carriers is probed at a high frequency (~30 GHz) using microwaves.<sup>66,67</sup> With this technique there is no need to apply electrodes and it is relatively free of domain boundary and dielectric polarization effects due to the fast reversal time of the microwave field (a few tens of picoseconds). The charge carriers do not undergo a net displacement from one electrode to the other as in DC experiments. Therefore a charge can move back and forth inside a single monodomain of the sample and still contribute to the (AC) conductivity. This means that the most efficient charge transfer step; i.e. charge transport in a single polymer chain or in an ordered domain; determines the mobility measured. In DC experiments the slowest processes, such as charge transfer between different ordered domains or from electrodes to the polymer, determine the overall charge carrier mobility. The lack of electrodes also means that the mobility of charges along polymer chains in solution can be probed.

Recently, the first papers describing charge migration probed at Tera-Hertz frequencies have appeared.<sup>68</sup> In this case, the charge carrier mobility is monitored on an even smaller distance scale. The advantage is that charge transport can be probed using a very high time-resolution, on the order of 100 femtoseconds. Probing the motion of charge carriers using a wide range of different frequencies (from DC to THz) can give useful information on the nature of charge transport on distance scales from molecular dimensions to the macroscopic dimensions needed in electronic devices.

#### Frequency dependence of the charge carrier mobility

In general the mobility of charges in disordered materials is frequency dependent,<sup>69</sup> which means that a mobility measured at 30 GHz is not necessarily the same as the DC mobility measured in a device. This is even more so for terahertz frequencies. The frequency at which the mobility starts deviating from the DC value is dependent on factors such as the morphology of the material (crystallinity, disorder) and the temperature. Figure 1.11 shows as an example the charge carrier mobility in solid samples of dihexyl-quater-thiophene (DH4T) as a function of temperature obtained from microwave measurements and from DC measurements in a FET device.<sup>70</sup> At room temperature the DC mobility and the 30 GHz mobility are of the same order of magnitude. On decreasing the temperature from 300 K to 100 K, the DC mobility decreases by two orders of magnitude, while the 30 GHz mobility stays almost constant over this temperature range.



**Figure 1.11**: Comparison of the temperature dependence of the charge carrier mobility obtained from microwave conductivity (filled circles) and field effect transistor measurements from ref. 70.

This large difference in temperature dependence between the DC and AC mobility can be understood by considering the charge transport to take place via a thermally activated hopping mechanism. In a DC experiment a charge carrier moving in a potential energy 'landscape' such as the one shown in Figure 1.9 has to overcome all energy barriers along its path from one electrode to the other. At room temperature the charge carrier can acquire enough energy from the vibrating 'lattice' to overcome all the energy barriers, including the 'high barriers' indicated in Figure 1.9. At lower temperatures the charge can not gain enough energy to overcome the high barriers and it does not contribute to the current anymore. This causes a dramatic decrease in the average DC charge carrier mobility.

If the mobility of a charge is probed with an oscillating electric field the charge can move back and forth between the two high barriers and still contribute to the AC conductivity, even at low temperatures. It should be noted that the AC-conductivity is also influenced by the distance between the high barriers. If this distance is so small (or the mobility so high) that the charge runs into a very high barrier, e.g. a grain boundary, before the electric field reverses, the measured mobility will be lowered. In a material consisting of a collection of very small nano-particles the microwave mobility will be dependent on the size of these particles up to a certain limit. The same applies to the mobility of charges along isolated conjugated chains. For long polymer chains the charge hardly ever runs into a chain end. In the case of short oligomers or conjugation breaks in polymers the mobility is dependent on the chain length or percentage of conjugation breaks. In chapter 5 the effect of conjugation breaks on the (microwave) mobility along isolated chains is studied experimentally. In chapter 7 the frequency dependence of the charge carrier mobility along isolated polymer chains is discussed in more detail.

#### 1.7 Outline of this thesis

This thesis describes experimental and theoretical studies of the opto-electronic properties of isolated conjugated polymer and oligomer chains in solution. The experimental methods used are described in chapter 2. In chapter 3 the quantum chemical methods used in the theoretical work in chapters 7-10 are briefly described.

#### Mobility of charges along isolated polymer chains

In chapters 4-6 experimental studies of charge transport along isolated conjugated polymer chains in dilute benzene solution are described. These measurements offer unique insight into the relation between the molecular structure of the polymers and their conductive properties. The results are especially interesting since isolated polymer chains are also tractable for theoretical treatments that take the disordered conformation of the polymer into account. Such theoretical studies are presented in Chapter 7. The measurements can also present useful guidelines for the design of molecular wires with charge transport properties that meet the requirements for applications in molecular electronics.

The kinetics of formation and decay of positively charged polymer chains in solution on pulse radiolysis and the way in which charge carriers mobilities are derived from these measurements are described in Chapter 4, taking MEH-PPV as an example. Chapter 5 discusses the effect of conjugation breaks on the charge transport along MEH-PPV chains. Measurements of charge carrier mobilities along polymer chains with backbone structures different from PPV, both  $\pi$ -conjugated and  $\sigma$ -conjugated, are reported in Chapter 6.

#### Optical absorption spectra of charged species

The optical absorption spectra of charged conjugated polymers or oligomers contain additional information on the properties of such charged species. The absorption maxima depend on the length of the conjugated chains but also on the substituents. In chapter 5 the optical absorption spectra of positively charged MEH-PPV chains with broken conjugation are discussed. Chapter 8 describes a combined theoretical and experimental study of the optical absorption spectra of positively charged phenylenevinylene oligomers. The effects of the chain length and alkoxy substitution are also considered in this chapter.

#### Excited state properties

The last two chapters of this thesis (chapters 9 and 10) deal with the polarizability of conjugated chains in their electronically excited state. The excited states in conjugated molecules are of interest since they are the intermediary state in light-emitting and photovoltaic devices. The increase in polarizability upon excitation (excess polarizability) gives an indication of the degree of delocalization or 'size' of the exciton, which may be one of the factors determining the probability of formation of an exciton when an electron and a hole approach each other. The exciton polarizability can also be considered as a measure of the exciton binding energy, the attraction between the electron and the hole. A large excess polarizability implies a small exciton binding energy, which may be favorable for exciton dissociation in photovoltaic devices.

Chapter 9 discusses a method for calculating excited state polarizabilities using timedependent density functional theory. The method is applied to three different types of conjugated chains, thiophenes, diphenyl polyenes and phenylenevinylenes. In chapter 10 the possibility of tuning the excited state polarizability of phenylenevinylene oligomers by changing the substituents or by modifications in the conjugated backbone is explored theoretically.

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## **Experimental Techniques**

#### 2.1 Introduction

The experimental work in this thesis deals mainly with the study of singly charged isolated chains of conjugated oligomers and polymers. Charged molecules were generated by pulse-radiolysis.<sup>1</sup> With this technique the sample of interest is irradiated with a short pulse (~ nanoseconds) of high-energy electrons which induce ionizations and electronic excitations in the medium. The nature and reaction kinetics of the ionic species formed are studied in a time-resolved way using two different techniques. Mobile charge carriers can be probed using the time-resolved microwave conductivity technique (TRMC) in which conductivity changes upon irradiation are monitored using high-frequency (~30 GHz) microwaves. Alternatively, the time-resolved optical absorption method can be applied to give information on the electronic absorption spectra of the charged species. These optical spectra offer additional insight into the properties of the charged species, such as electronic energy levels and oscillator strengths. With both techniques it is possible to follow the formation and decay kinetics of the charged species of interest. This provides a unique insight into the kinetics of the reactions that the charge carriers undergo.

In the following sections the experimental techniques used in this thesis are briefly described. Firstly, the pulse radiolysis method that was used to generate charge carriers is discussed, followed by the two detection techniques, TRMC and time-resolved optical absorption. This chapter is not a complete review of the experimental techniques used, but serves only to provide the aspects that are required for the understanding of the results described in later chapters. For an in-depth description of the techniques the reader is referred to original and review papers that are cited in the following sections.

#### 2.2 Generation of charge carriers: pulse radiolysis

In pulse radiolysis experiments the sample of interest is irradiated with a short pulse of highenergy, ionizing radiation, usually in the form of electrons with kinetic energies in the MeV range produced by an electron accelerator.<sup>1</sup> The use of ionizing radiation has certain advantages over other techniques for pulsed generation of charge carriers such as laser flashphotolysis. Ionizing radiation is non-specific in the sense that energy deposition in the sample is dependent only on the electron density of the medium, regardless of the color or morphology. Another advantage is the relatively large penetration depth of high-energy radiation. If a laser is used, excitations are created with a concentration depth profile that depends on the extinction coefficient of the material at the wavelength used. In the case of ionizing radiation a close to uniform distribution of ionizations/excitations can be produced in bulk solid or liquid materials for depths of several millimeters.<sup>2</sup>



**Figure 2.1**: A schematic representation of the Van de Graaff accelerator.

#### The Van de Graaff accelerator

In the present work a Van de Graaff accelerator, shown schematically in Figure 2.1, is used to produce short pulses of high energy electrons. A hollow, metal hemispherical capacitor is charged to 3 MV by transporting electrons to it using an insulating rubber belt. A heated cathode emits electrons that are accelerated over 3 MV through a constant gradient electric

field in the accelerator section of the flight tube. The electrons gain a kinetic energy of 3 MeV and exit the flight tube through a thin aluminum window at close to the speed of light. Electron pulses are produced by temporarily removing the negative bias on a grid close to the surface of the cathode. Pulses of durations ranging from 2 to 250 ns are generated using a line pulser whose pulse forming coaxial cable length determines the pulse duration. Short sub-nanosecond pulses (down to 200 ps) are created using reflecting stubs. The pulse durations routinely used in this thesis are between 2 ns and 50 ns.

The flight tube widens at the end into the scanner. Electromagnetic coils make it possible to focus and align the electron beam or deflect it onto a coaxial target that is positioned inside the scanner. The amount of charge per pulse can be routinely measured by an electrometer connected to this target. The maximum current in the pulse is *circa* 4 A, which means that a 5 ns second pulse delivers *circa* 20 nC of charge. Pulse-to-pulse fluctuations in the amount of charge are generally less than a 2 percent. Detailed descriptions of the IRI Van de Graaff accelerator have been published previously<sup>3-6</sup> and the reader is referred to these accounts for more extensive information.

#### Energy deposition

3 MeV (primary) electrons that impinge on a sample transfer energy in discrete excitation and ionization events along their path through the medium.<sup>7,8</sup> The incident high-energy electrons interact with the molecules in the medium via the Coulomb force. When an electron passes through a medium it induces a rapidly changing electric field, analogous to the oscillating electric field of a photon, but with a very broad frequency spectrum. This interaction leads to inelastic scattering events and a distribution of ionizations and excitations along the path of the primary electron. The average energy that is transferred per ionization or excitation event is approximately 40 eV for hydrocarbon liquids and solids. The average distance between separate energy transfer events is approximately 200 nm.<sup>7,9</sup> A large fraction of the energy transfer events leads to ionization of molecules in the medium with the formation of secondary electrons. Secondary electrons with sufficient kinetic energy can induce further ionizations and electronic excitations. Eventually the secondary electrons become thermalized by excitation of vibrational, librational and translational modes of the molecules of the medium. The average distance,  $R_{\pm}$ , between the electron and its parent positive ion after thermalization is ca. 5-10 nm for organic materials.<sup>10</sup> This average distance is considerably less than the Onsager escape distance,  $R_c$ , which is defined as the distance at which the Coulomb attraction is equal to the characteristic thermal energy  $k_BT$ ; *i.e.* 

$$R_c = \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T} \tag{2.1}$$

with  $\varepsilon_0$  the permittivity of vacuum,  $\varepsilon$  the relative permittivity of the medium, *e* the elementary charge,  $k_B$  the Boltzmann constant and *T* the temperature. For liquid benzene, the solvent used in the experiments in this thesis,  $\varepsilon = 2.28$  and  $R_c = 25$  nm.

The probability,  $\phi(R_{\pm})$ , that the electron and its parent positive ion, formed at distance  $R_{\pm}$ , escape from their mutual attraction is

$$\phi(R_{\pm}) = e^{-R_c/R_{\pm}}$$
(2.2)

Because  $R_{\pm}$  is much smaller than  $R_c$  at room temperature, a large fraction of the initial ionization events are followed by rapid, "geminate" charge recombination on a subnanosecond timescale.<sup>11,12</sup> Only a small fraction, on the order of one percent, escapes from geminate recombination resulting in the formation of relatively long-lived, homogeneously distributed "free ions". The yield of free ions,  $G_{fi}$ , is usually expressed as the number produced per 100 eV energy absorbed in the material. This "free-ion yield" is obtained by averaging the escape probability,  $\phi(R_{\pm})$ , over the initial separation distribution of the ion pairs,  $f(R_{\pm})$ ,

$$G_{fi} = G_{tot} \int f(R_{\pm}) \,\phi(R_{\pm}) \,dR_{\pm}, \tag{2.3}$$

where  $G_{tot}$  is the initial yield of ion pairs.

The free-ion yield in benzene has been determined to be  $0.053 (100 \text{ eV})^{-1}$ .<sup>13,14</sup> These free ions can decay by homogeneous recombination or react with a solute, e.g. a deliberately added conjugated oligomer or polymer as in the present work. It is this small fraction of free ions that is of interest for the work in this thesis.

#### Dosimetry

The energy of a high-energy electron that is transferred to the medium per unit track length dE/dx is proportional to the electron density of the material. For organic materials composed of light elements dE/dx is close to being proportional to simply the mass density,  $\rho$  (kg/m<sup>3</sup>). The total amount of energy transferred to the medium is usually expressed as the absorbed dose *D*, in Gray (Gy) which is defined as the amount of energy deposited per unit mass (1Gy = 1 J/kg). For analysis of the conductivity and optical absorption data it is more convenient to deal with the energy per unit volume. Therefore, in the remainder of this thesis the absorbed dose per unit volume,  $D_V$ , in Jm<sup>-3</sup>, is used.

For many organic solvents the yield of "free" charge carriers per unit dose absorbed is accurately known.<sup>15</sup> Therefore, if the dose delivered to the sample is known, an accurate estimate of the number of free ion pairs produced can be made. In order to estimate the dose delivered it is convenient to relate the dose to the incident beam charge, which can be measured routinely with high accuracy in the pulse radiolysis set-up, as mentioned above.

The energy deposited in the sample per nanoCoulomb beam charge in the microwave conductivity experiments (see section 2.3) was determined using thin film radiochromic dosimeters (Far West Technology Nr. 92). The dosimeters consist of 50  $\mu$ m thin film nylon foils impregnated with a radiation sensitive dye. On exposure to ionizing radiation the dye changes from colorless to blue. After irradiation, the change in optical density was measured

at 510 nm and converted to the amount of energy deposited per unit mass using a calibration curve supplied by Far West Technologies. The dose was determined at different depths in the sample cell by placing six radiochromic foils between 0.53 mm thick polyethylene plates of 0.947 g/cm<sup>3</sup>. This medium was irradiated with 3 MeV electrons from the Van de Graaff accelerator and the beam charge per pulse was also measured. The radiation dose along the 27.4 mm long microwave conductivity cell was not fully homogeneous because of the intensity variation over the cross section of the electron beam. The dose absorbed at the ends of the cell was up to 50 percent lower than that in the center. The dose-depth distribution was found to be similar to earlier reports in which the dosimetry in shorter microwave sample cells was described.<sup>2</sup> The average dose absorbed per unit volume in the cell was 540 Jm<sup>-3</sup> per nanocoulomb of beam charge for benzene.

The radiation dose delivered to a sample in the optical absorption cell is related to the beam charge per pulse in the same way as in the TRMC experiments. Dosimetry is performed using the aqueous electron dosimeter.<sup>16</sup> The radiation dose deposited in the medium per nC of beam charge was determined to be 1230 Jm<sup>-3</sup>.

The charged species generated by pulsed irradiation are transient and must be detected using fast, time resolved detection techniques. The techniques used in this thesis, timeresolved microwave conductivity and time resolved optical absorption, are discussed in the following sections.

#### 2.3 Time-resolved microwave conductivity detection

Using the time-resolved microwave conductivity technique the change in conductivity of a sample upon irradiation is measured using microwaves. The use of microwaves for the time-resolved study of ionic processes in the gas phase was introduced by Biondi and Brown,<sup>17,18</sup> applying the knowledge from the development of radar technology during the second world war. In this initial method the change in the wavelength of microwaves due to ionization of the gas-phase medium was measured. This corresponds to measuring a change in the imaginary component of the conductivity.

In the early 70's Warman and De Haas developed the time-resolved microwave conductivity or TRMC technique for measuring the *absorption* of microwaves in a conductive medium.<sup>19,20</sup> In this case, it is the change in the real component of the conductivity or the dielectric loss that is probed. Microwave absorption measurements are more appropriate than the phase shift method for the study of ionic processes in condensed phases of (low mobility) organic materials because the imaginary conductivity component is in general much smaller than the real conductivity in this case. Figure 2.2 schematically shows the attenuation of microwave power when microwaves propagate through a conducting medium. In a weakly conducting medium, only a small fraction ( $\Delta P/P$ ) of the incident microwave power is absorbed.

Over the last thirty years the TRMC technique, combined with charge carrier generation by pulse radiolysis, has been applied to the study of a wide variety of systems, including pure hydrocarbon liquids,<sup>11,21</sup> ice,<sup>22-25</sup> (rare) gasses,<sup>26-28</sup> discotic liquid crystalline materials<sup>29-34</sup> and

solid polymer samples.<sup>35-41</sup> Using the TRMC technique, it is not only possible to determine the mobility of charged species in these materials but also the kinetics of the reactions that these species undergo can be studied. Examples of such reactions include the formation and decay of highly mobile charges on polymer chains in solution as will be described in chapters 4-6.



**Figure 2.2:** Schematic representation of the attenuation of microwaves when propagating through a weakly conducting dielectric medium.

The use of an ultra high frequency oscillating electro-magnetic field has certain advantages over conventional DC techniques. With the TRMC technique there is no need to apply electrodes. The conductivity obtained from TRMC measurements is therefore not affected by charge injection processes at electrodes, which may limit the current in DC experiments. The absence of electrodes also makes it possible to measure the conductivity due to charges moving along isolated polymer chains in dilute solution as has been shown by Hoofman et al.<sup>42</sup> Detailed studies of conductivity experiments on dilute polymer solutions are described in chapters 4-6.

#### The microwave conductivity apparatus

A schematic diagram of the TRMC equipment used in the experiments is shown in Figure 2.3.  $TE_{10}$  mode microwaves (see Figure 2.4) are generated by a Gunn-diode mounted in a tunable cavity. For this mode, the electric field vector of the microwaves is aligned along the short axis (*b*, see Figure 2.4) of the waveguide. The frequency of the microwaves can be tuned from 26.5 to 40 GHz (K<sub>a</sub>-band) with a power output of ca. 100 mW. The microwave circuitry is built from rectangular K<sub>a</sub>-band wave guide sections with inner dimensions of 7.1 x 3.55 mm<sup>2</sup> (width *a* times height *b*, see Figure 2.4) that are connected by flanges. The microwaves pass through a ferrite isolator that protects the source and reduces effects due to reflections in the system. The microwaves, after passing a variable attenuator, are then guided into the sample cell via a circulator. The cell consists of a piece of K<sub>a</sub>-band waveguide that is short-circuited at the end with a metal plate, see Figure 2.4. The waves that are reflected at the end-plate

return to the circulator which directs them to microwave detectors; either a slow response, linear power meter or a fast, non-linear Schottky barrier diode. The time-resolved signal from the detector diode is amplified 33.5 times by a cascade of amplifiers and is monitored on either a linear time base with a Tektronix TDS 680B digitizer or on a logarithmic time-base using a Sony/Tektronix RTD 710 digitizer. All of the active components are enclosed in a Faraday cage, as indicated in Figure 2.3, in order to reduce electromagnetically induced noise emanating from the accelerator pulse.



Figure 2.3: Scheme of the microwave circuitry

The steady-state power reflected by the sample cell is monitored by the power meter. For time resolved measurements of the changes in the reflected microwave power a detector diode with a rise time of *circa* 0.6 ns is used. The voltage output of this detector, V, is not a linear function of the incident power. For small fractional changes in the power level at the detector,  $\Delta P/P$ , the relation to the change in detector output,  $\Delta V/V$ , is

$$\frac{\Delta P}{P} = N_{fact} \frac{\Delta V}{V} \tag{2.4}$$

The power proportionality factor  $N_{fact}$  depends on both the microwave frequency and the power level and was obtained by calibration of the Schottky barrier diode using the slow response linear power meter.

#### А

Ka-band wave guide



В






#### The sample cell

The microwave cell used for measurements on dilute polymer solutions is shown in Figure 2.4. The cell consists of a 27.4 mm long piece of  $K_a$ -band waveguide which is terminated at one end with a copper end-plate and at the other end with a 50 micron thick, vacuum-tight kapton or aramide window. The top wall of the cell was reduced to approximately 0.4 mm thickness to minimize the attenuation of the electron beam. The cells were gold-plated via a redox exchange of copper with gold using a 10% diluted "Atomex Gold solution" (Engelhardt) to make them chemically inert. The cells are connected, via a metal to glass transition, to a glass bulb (*ca* 2 ml) that is closed by a vacuum-tight valve. The glass bulb can be connected to a vacuum line for sample preparation.

#### The sensitivity factor

As discussed above, the primary information that is obtained from time-resolved microwave conductivity measurements is the change in microwave power reflected by the sample cell. This change in reflected power is directly proportional to the change in conductivity of the sample upon irradiation,

$$\frac{\Delta P}{P} = -A\Delta\sigma \tag{2.5}$$

where  $\Delta\sigma$  is the change in conductivity and A is the sensitivity factor. The magnitude of the sensitivity factor, A, is dependent on the geometry of the cell and on the frequency of the microwaves due to multiple reflections that occur at dielectric interfaces.<sup>19,43</sup>



**Figure 2.5**: Microwave absorption as a function of frequency for a change of  $10^{-3}$  Sm<sup>-1</sup> in the conductivity of a benzene or cyclohexane solution in a cell similar to that shown in Figure 2.4.

Figure 2.5 shows the (calculated) fractional change in reflected microwave power by a sample medium of length 27.4 mm due to a conductivity change of  $10^{-3}$  Sm<sup>-1</sup> as a function of the frequency for relative dielectric constants of 2.28 (benzene) and 2.02 (cyclohexane). It can be seen that the maximum value of  $\Delta P/P$  (i.e. the highest sensitivity factor) is almost insensitive to the dielectric constant. For the microwave reflection cell containing a uniform dielectric material of length *d* (the polymer solution), adjacent to the short circuit a relatively simple analytical expression can be derived that relates  $\Delta P/P$  to  $\Delta \sigma$  for the frequency of maximum sensitivity:<sup>19,43</sup>

$$\left(\frac{\Delta P}{P}\right)^{\max} = -\frac{2\lambda_a f_{\max} d}{\varepsilon_0 c^2} \,\Delta\sigma \tag{2.6}$$

where  $\lambda_a$  is the wavelength of the microwaves in air (inside the waveguide), *d* is the total length of the dielectric medium,  $\varepsilon_0$  is the permittivity of free space and *c* is the velocity of light in vacuum. The frequency where the sensitivity is maximum is determined by the dielectric constant of the medium as evident from Figure 2.5. It can be shown that these maxima occur when the medium is exactly an odd number of quarter wavelengths long;<sup>19</sup> i.e.

$$d = (2n+1)\frac{\lambda_l}{4} \tag{2.7}$$

In this equation  $\lambda_l$  is the wavelength inside the sample. The frequencies at which maxima in absorption occur for a given sample-length *d* are

$$f_{\max} = \frac{c}{2\sqrt{\varepsilon_r}} \left[ \left(\frac{2n+1}{2d}\right)^2 + \left(\frac{1}{a}\right)^2 \right]^{\frac{1}{2}}$$
(2.8)

with  $\varepsilon_r$  the relative dielectric constant of the medium and *a* the broad dimension of the waveguide. The value of  $\lambda_a$  that corresponds to  $f_{max}$  is given by

$$\lambda_a = \frac{2\pi}{\left[\left(\frac{2\pi f_{\text{max}}}{c}\right)^2 - \left(\frac{\pi}{a}\right)^2\right]^{\frac{1}{2}}}$$
(2.9)

The values for  $f_{max}$  and  $\lambda_a$  can be substituted into Eq. 2.6 to obtain the sensitivity factor. In the case of the cell used in the present work the solution inside the cell is not irradiated over the entire length *d* because of the presence of a flange by which the cell is connected to the microwave circuitry. As shown in Figure 2.4 only 23.4 mm of the solution is irradiated. This must be taken into account in Eq. 2.6 by inclusion of a correction factor  $F(d_i/d)$ 

$$\left(\frac{\Delta P}{P}\right)^{\max} = -\frac{2\lambda_a f_{\max} d}{\varepsilon_0 c^2} F(d_i/d) \Delta \sigma$$
(2.10)

For the maxima in absorption  $F(d_i/d)$  can be shown to be<sup>19</sup>

$$F(d_i/d) = \frac{d_i}{d} - \frac{\sin[(2n+1)\pi d_i/d]}{(2n+1)\pi}$$
(2.11)

#### Charge carrier mobility

In the preceding section it was discussed how the microwave power absorbed by a sample is related to the conductivity. The conductivity,  $\sigma$ , of a medium due to the presence of mobile charge carriers is related to the mobility,  $\mu_i$ , and number densities,  $N_i$  of all charge carriers in that medium by

$$\sigma = e \sum_{i} N_{i} \mu_{i} \tag{2.12}$$

where *e* is the elementary charge. The charge carrier mobility,  $\mu$ , is defined as the ratio of the drift velocity,  $v_E$ , to the externally applied electric field. It is a measure of the ease with which charges can move through a medium under the influence of the field, *E*.

$$\mu = \frac{v_E}{E} \tag{2.13}$$

As noted in chapter 1, the mobility (or conductivity) in disordered materials is, in general, frequency dependent,<sup>44</sup> which means that a value measured at 30 GHz is not necessarily the same as the DC mobility in an electronic device, even for bulk solids. The difference is due to the length-scale on which the motion of charges is probed. In DC measurements charges have to move over macroscopic distances through materials from one electrode to the other. If high barriers to charge transport, such as grain boundaries, are encountered on this path the measured mobility will be considerably lowered. In TRMC measurements a charge can move back and forth between boundaries and still contribute to the mobility without ever crossing the boundaries. The frequency at which the AC mobility starts deviating from the DC value depends on the characteristics of the material (crystallinity, disorder etc.), the temperature at which measurements are performed<sup>32,45</sup> and the mobility of the charges.<sup>46-48</sup> In chapter 7, where a theoretical study of charge transport along conjugated polymer chains solution is presented, the frequency dependence of the mobility of charges in such systems is discussed in more detail.

#### Time-resolved measurements

Pulsed irradiation of a sample leads to the formation of transient charged species. If these charges are mobile their formation and decay can be monitored as a function of time using TRMC. An example of a time-resolved microwave conductivity transient recorded using a linear time-base is shown in Figure 2.6a. During the pulse from the accelerator the conductivity of the sample increases as mobile charges are created, reaching a maximum at the end of the pulse. After the pulse the conductivity signal decays due to trapping and recombination of the charged species.



**Figure 2.6**: Conductivity transient obtained on pulsed irradiation of (A) pure benzene on a linear time-base and (B) a solution of MEH-PPV in benzene on a logarithmic time-base.

In Figure 2.6b an example of a TRMC transient is shown using a logarithmic time-base digitizer (RTD 710). In this case the sample is a solution containing conjugated polymer chains. In the same graph the conductivity recorded on a linear time-base (TDS 680B) during the first hundred nanoseconds after the pulse is shown as a dashed line. The combination of the transients from both digitizers gives the complete conductivity transient shown in the figure. After a rapid initial decay of the conductivity the signal starts rising again. This increase after the pulse is due the formation of positively charged polymer chains; positive charges have a higher mobility on the polymer chain than in solution. The formation and decay of the positively charged polymer chains can be followed in time after a pulse from a time-scale of a few nanoseconds up to milliseconds.

#### 2.4 Time-resolved optical absorption detection

When mobile charge carriers are formed in a medium, the change in conductivity of that medium can be determined by measuring the absorption of microwaves, as outlined in the previous section. The optical properties of a medium can also change due to the presence of the charge carriers. These transient changes in the optical absorption spectrum of a sample upon irradiation with an electron pulse can be measured using the time resolved optical absorption technique. The time-resolved optical absorption set-up is shown schematically in Figure 2.7.



**Figure 2.7**: Scheme of the time-resolved optical absorption apparatus.

The light source is an Osram XBO high-pressure Xe-lamp (450 W) which is pulsed to circa 20 times its constant intensity for approximately 1 ms during the recording of each transient. The solution under investigation is flowed continuously through a quartz cell (optical path length 12.5 mm) using a slight overpressure of benzene-saturated oxygen in order to minimize decomposition due to photolysis of the sample. Cut-off filters and a fast shutter are used to further reduce such damage.

The transmitted light is analyzed using a Jobin Yvon HL 300 monochromator. For detection at near infrared wavelengths a short-wavelength enhanced InGaAs photodiode (Hamamatsu, Japan) is used. In the visible and UV spectral regions a photomultiplier is used as a detector. Transient changes in the optical absorption are recorded using the same Tektronix TDS680B digitizer as used in the TRMC experiments.

#### Optical absorption spectra

Optical absorption spectra of ionic species and/or excited states are obtained by measuring the changes in absorbance at different wavelengths. An example of such an optical absorption spectrum of a charged conjugated molecule is shown in Figure 2.8. Transient absorption spectra are recorded using relatively high solute concentrations and a 50 ns electron pulse in order to obtain a good signal-to-noise ratio, also in the regions of the spectrum where the absorbance is low. The lower energy limit of the spectra that can be obtained using the present apparatus is 0.9 eV.



**Figure 2.8**: Optical absorption spectrum in benzene solution of the radical cation shown, determined using the pulse radiolysis time-resolved optial absorption equipment. The absorption of the neutral compound starts at energies higher than 2.8 eV.

From the absorbance it is possible to obtain the extinction coefficient,  $\varepsilon$ , for electronic transitions using the Beer-Lambert law:

$$A = -\log_{10} \left( \frac{I_{transmitted}}{I_{incident}} \right) = \varepsilon cl$$
(2.14)

where *l* is the optical path length and *c* is the concentration of the absorbing species. The total intensity of a transition is obtained after integration of  $\varepsilon$  over the whole absorption band. This integrated total intensity is related to the oscillator strength of a transition.

Time-resolved optical absorption measurements can also be used to follow the kinetics of formation and decay of a particular transient radical species. The same kinetic information is obtained from TRMC experiments described in the previous section, however, the TRMC technique is only sensitive to mobile charged species. In optical absorption it is also possible to study immobile charges or uncharged transient species such as triplet excited states. An example of the kinetics of formation and decay of positively charged conjugated polymer chains in benzene solution is shown in Figure 2.9. The dashed line is the same time-resolved microwave conductivity transient as show in Figure 2.6b in the previous section. The solid line represents the transient optical absorption at 1.3 eV due to absorption by positively charged polymer chains, which is shown to have exactly the same temporal dependence as the TRMC transient.



**Figure 2.9**: Kinetics of the formation of MEH-PPV radical cations monitored by TRMC (dashed, left axis) and by optical absorption measured at 1.3 eV (solid line, right axis).

#### 2.4 Determination of physical information

Quantitative data (absolute charge carrier mobilities and extinction coefficients or oscillator strengths) can be obtained from both TRMC and time-resolved optical absorption experiments, provided that the concentration of the charged species of interest is known. From pulse radiolysis experiments much is known about the yield of radiolytic products and the mobilities of the charged species formed in pure hydrocarbon solutions.<sup>9,11,15</sup> These data are very important when pulse radiolysis experiments are being performed on more complicated systems such as solutions of conjugated molecules in organic liquids. In such solutions the species formed initially on irradiation are created in the solvent with virtually the

same yield as in the pure solvent. The charged species can diffuse through the solvent and can undergo charge transfer to the dissolved molecules leading to formation of charged conjugated molecules. These reactions are involved in the studies described in chapters 4-6 (polymers) and chapter 8 (oligomers) to study the optical absorption spectrum and charge carrier mobility of positive charges on conjugated polymers and oligomers in benzene solution. Chapter 4 also gives an extensive account of the radiolytic processes occurring in benzene on pulse radiolysis and the kinetics of the formation reactions by which the positively charged polymers and oligomers are formed.

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## Chapter 3

### **Quantum Chemical Methods**

#### **3.1 Introduction**

Over the last ten years the use of computational methods in chemistry has rapidly increased. This is partly due to the developments in theoretical chemistry but even more due to the enormously fast development in computer technology. The speed of normal desktop computers is now sufficient to perform quantum chemical calculations on moderately sized molecules at a high level of theory.

Computational methods in chemistry are useful for several reasons. Calculations often give information that aids the interpretation of experimental results. An example of this is found in spectroscopy where experimental spectra can be compared to calculated spectra in order to make a correct assignment of the origin of different electronic transitions. Another reason for the use of computational methods is to predict electronic or structural properties of molecules that have not (yet) been synthesized. In addition, calculations can give information that is impossible or very hard to obtain from experiments, such as the electron distribution within a molecule or the properties of excited states.

Computational chemistry is basically a collection of a wide variety of methods. These methods range from completely classical methods such as molecular dynamics calculations with empirical force fields to high-level quantum mechanical electronic structure calculations.<sup>1</sup>

Completely classical methods are useful for studying the interactions between molecules. In this case there is no need to have a detailed description of the electron distribution inside the molecule. The interaction between molecules can be expressed as the sum of four types of 'classical' interactions: the electrostatic interaction, dispersion, dipole/induced-dipole interactions (induction) and short-range repulsion. Such descriptions are especially useful for studying properties of solutions since the low level of theory enables the application of these methods to very large systems, containing hundreds of molecules.<sup>2</sup>

If more detailed information on the electronic properties of (isolated) molecules or small clusters of molecules is required one has to use a quantum mechanical description. The quantum mechanical methods for electronic structure calculations form a sub-set of computational chemistry methods which is usually referred to as quantum chemistry.

The first approximation that is usually made in quantum chemistry is the Born-Oppenheimer approximation, which states that the motion of the electron in a molecule can be separated from the motion of the nuclei since the latter are much heavier (this is the case even for the smallest nucleus, the proton, which has a mass that is 1836 times larger than that of an electron). Because of this large difference in mass, the electrons can respond instantaneously to changes in the positions of the nuclei. Therefore it is usually possible to perform a relatively accurate calculation of the electronic wavefunction and energy while fixing the positions of the nuclei. Quantum chemistry therefore deals primarily with finding solutions to the time-independent <u>electronic</u> Schrödinger equation<sup>3</sup> which in short-hand operator form is given as

$$\hat{H}\Psi = E\Psi \tag{3.1}$$

in which  $\Psi$  is the many-electron wavefunction,  $\hat{H}$  is the Hamilton operator or Hamiltonian and E is the energy.

When the Born-Oppenheimer approximation is used the electronic part of the Hamiltonian for a molecule containing N electrons, in atomic units, is given by:

$$\hat{H} = -\sum_{i}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{i}^{N} \sum_{a} \frac{Z_{a}}{|\mathbf{R}_{a} - \mathbf{r}_{i}|} + \sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} + \sum_{a,b} \frac{Z_{a}Z_{b}}{|\mathbf{R}_{a} - \mathbf{R}_{b}|}$$
(3.2)

The first term describes the kinetic energy of the electrons, while the second term accounts for the attraction between the electrons and the nuclei. The third term describes the electronelectron repulsion. The last term represents the nuclear repulsion energy, which is not dependent on the electron coordinates and is a constant.

An exact solution to this equation is possible only for systems containing one electron such as the hydrogen atom. Therefore, for chemically interesting molecules that can contain up to thousands of electrons, one has to resort to an approximate solution of the Schrödinger equation. Finding such approximate solutions for  $\Psi$  that describe the electronic properties of interest as accurately as possible is the central issue of quantum chemistry.

There are many ways to approximate the exact  $\Psi$  and a number of excellent textbooks are available that describe these methods. It is the purpose of this chapter to give a brief overview of the quantum chemical methods that are used in chapters 7-10. For a more complete description the reader is referred to textbooks on this subject.<sup>1,3,4</sup>

#### 3.2 The Hartree-Fock self-consistent field approximation

The Hartree-Fock self-consistent field approximation<sup>4</sup> is very often the starting point for a quantum chemical study. Moreover, a large part of chemical understanding is rooted in the concepts present in Hartree-Fock theory.

The many electron wavefunction that is generally used in HF calulation is the so-called Slater determinant:

$$\Phi_{0}(\mathbf{x}_{1},\mathbf{x}_{2},...,\mathbf{x}_{N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_{i}(\mathbf{x}_{1}) & \chi_{j}(\mathbf{x}_{1}) & \cdots & \chi_{k}(\mathbf{x}_{1}) \\ \chi_{i}(\mathbf{x}_{2}) & \chi_{j}(\mathbf{x}_{2}) & \cdots & \chi_{k}(\mathbf{x}_{2}) \\ \vdots & \vdots & \vdots \\ \chi_{i}(\mathbf{x}_{N}) & \chi_{j}(\mathbf{x}_{N}) & \cdots & \chi_{k}(\mathbf{x}_{N}) \end{vmatrix}$$
(3.3)

Such a determinant yields an anti-symmetrized sum of all products of one-electron functions. Interchanging two electrons results in the interchanging of two columns of the matrix in Eq. 3.3, which causes the determinant to change sign. The expectation value of the energy of such a determinant

$$E_0 = \left\langle \Phi_0 \middle| \dot{H} \middle| \Phi_0 \right\rangle \tag{3.4}$$

can be evaluated by inserting the Hamiltonian (Eq. 3.2) and the wavefunction consisting of a single Slater determinant (Eq. 3.3) into Eq. 3.4. Although the expansion of the determinant in Eq. 3.3 leads to a complicated expression for the wavefunction, the expression for the energy of such a determinant turns out to be relatively simple. For the one electron part of the Hamilton operator, h, containing the first two terms of the Hamiltonian in Eq. 3.2, only terms involving one electron remain.

$$\left\langle \Phi_{0} \left| h \right| \Phi_{0} \right\rangle = \sum_{i}^{N} \left\langle i \left| h \right| i \right\rangle$$
(3.5)

where the bracket notation is used for the one-electron integrals

$$\langle i|h|i\rangle = \langle \chi_i|h|\chi_i\rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_i(\mathbf{x}_1)$$
(3.6)

The two-electron part of the Hamiltonian gives rise to term with  $1/|\mathbf{r}_1 - \mathbf{r}_2| = r_{12}^{-1}$ , given by:

$$\left\langle \Phi_{0} \left| r_{12}^{-1} \right| \Phi_{0} \right\rangle = \sum_{i}^{N} \sum_{j>i}^{N} \left( \left\langle ij \left| ij \right\rangle - \left\langle ij \right| ji \right\rangle \right)$$
(3.7)

The first term in the summation on the right denotes the Coulomb type two-electron integrals,

$$\langle ij|ij\rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \boldsymbol{\chi}_i^*(\mathbf{x}_1) \boldsymbol{\chi}_j^*(\mathbf{x}_2) r_{12}^{-1} \boldsymbol{\chi}_i(\mathbf{x}_1) \boldsymbol{\chi}_j(\mathbf{x}_2)$$
(3.8)

which brings into account the 'classical' Coulomb repulsion between the charge distribution of electrons with coordinates  $x_1$  and  $x_2$ . The second term on the right side of equation 3.7 represents the two-electron integrals of the type,

$$\langle ij|ji\rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \boldsymbol{\chi}_i^*(\mathbf{x}_1) \boldsymbol{\chi}_j^*(\mathbf{x}_2) r_{12}^{-1} \boldsymbol{\chi}_j(\mathbf{x}_1) \boldsymbol{\chi}_i(\mathbf{x}_2)$$
(3.9)

which is only non-zero for electrons having the same spin coordinate. This exchange term results from the anti-symmetrization of the wavefunction by introduction of the Slater determinant. The exchange interaction between electrons has no classical analogue.

The total energy expectation value for a single determinant wavefunction in terms of spin-orbitals now becomes:

$$E_{0} = \langle \Phi_{0} | \hat{H} | \Phi_{0} \rangle = \sum_{i}^{N} \langle i | h | i \rangle + \sum_{i}^{N} \sum_{j>i}^{N} \left( \langle ij | ij \rangle - \langle ij | ji \rangle \right)$$
(3.10)

The aim of a Hartree-Fock calculation is to find the best possible approximation to the ground state wavefunction of an N-electron system, which means finding the optimal set of one-electron spin-orbitals,  $\chi_i(r_j)$ , in the Slater determinant. According to the variation principle<sup>3</sup> the best spin-orbitals are those that minimize the total electronic energy in Eq. 3.10.

Up to this point the discussion has been in terms of a general set of one electron spinorbitals,  $\{\chi_i\}$ . In order to perform an actual calculation it is convenient to write the spin orbitals as a linear combination of a set of known spatial basis functions, as was proposed independently by Roothaan<sup>5</sup> and Hall.<sup>6</sup>

$$\chi_i = \sum_{\mu}^{\kappa} C_{\mu i} \phi_{\mu} \tag{3.11}$$

where K is the total number of basis functions. If this expansion of the orbitals is introduced the coefficients of the basis functions,  $C_{\mu i}$ , are obtained by minimization of the total energy (Eq. 3.11) by variation of these coefficients. These  $C_{\mu i}$  are obtained by solving a matrix eigenvalue problem:

$$\mathbf{FC} = \mathbf{SC}\varepsilon \tag{3.12}$$

In Eq 3.12, **F** is the Fock-operator matrix, **C** is the matrix of eigenvectors, **S** is the overlap matrix and  $\boldsymbol{\varepsilon}$  is a diagonal matrix containing the eigenvalues. The elements of the Fock matrix depend on the eigenvectors, **C**:

$$F_{\mu\nu} = \langle \mu | h(1) | \nu \rangle + \sum_{a}^{N/2} \sum_{\lambda,\sigma}^{K} C_{\lambda a}^{*} C_{\sigma a} \left[ 2 \langle \mu \lambda | \nu \sigma \rangle - \langle \mu \lambda | \sigma \nu \rangle \right]$$
(3.13)

where a transition has been made to doubly occupied spatial orbitals rather than the singly occupied spin orbitals used above. Because of the dependence of the Fock operator,  $\mathbf{F}$ , on the coefficients, Eq. 1.12 is solved iteratively, until self-consistency is reached. The first term in eq. 3.14 is the one-electron part which does not depend on  $\mathbf{C}$ . The two electron part depends on the density which is represented by the orbitals coefficients  $\mathbf{C}$ . The two electron integrals have become integrals over the basis functions:

$$\langle \mu \lambda | \nu \sigma \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_{\mu}^*(\mathbf{r}_1) \phi_{\lambda}^*(\mathbf{r}_2) r_{12}^{-1} \phi_{\nu}(\mathbf{r}_1) \phi_{\sigma}(\mathbf{r}_2)$$
(3.14)

The evaluation and manipulation of the two-electron integrals over the basis functions is the most computationally demanding part of a Hartree-Fock calculation, since the number of these integrals scales with the fourth power of the number of basis functions. Attempts to reduce the amount of two-electron integrals to be evaluated have resulted in semi-empirical methods, as will be discussed below.

#### Restricted versus unrestricted Hartree-Fock

In general, molecules in their neutral ground state can be well-described as closed shell systems; *i.e.* all electrons are paired up, one with alpha-spin and one with beta-spin, both having the same spatial distribution. However, in this thesis, an important part deals with the radical cations of conjugated molecules, which obviously are open shell systems. One way to describe an open-shell system in Hartree-Fock theory involves the use of an unrestricted Hartree-Fock (UHF) wavefunction. In this case the spatial part of the spin-orbitals of the alpha and beta electrons are not restricted to be the same. A rather severe disadvantage of UHF is that the resulting wavefunction is, in general, not an eigenfunction of the spin operator  $S^2$ , corresponding to the square of the total spin angular momentum.<sup>1</sup> This means that in the case of a singlet ground state the wavefunction may contain (spurious) contributions from other spin states. In the case of radical cations in their electronic ground state, which are of doublet multiplicity, contributions from higher lying quartet, sextet states, etc contribute to the wavefunction. This mixing of higher multiplicity is also called spin-contamination.

One way to overcome the spin-contamination problem is to use a restricted open-shell Hartree-Fock (ROHF) wavefunction. In ROHF all electrons, except those occupying open-shell orbitals, are forced to occupy doubly occupied spatial orbitals. In this case the wavefunction obtained for e.g. the doublet ground state of a radical cation is an eigenfunction of  $S^2$  and is a pure doublet. There are also some disadvantages of the ROHF method. One of the fundamental problems is that in ROHF theory the orbital energies are not uniquely defined. Therefore they cannot be equated to the ionization potential of a molecule using the Koopmans' theorem. Furthermore, the orbital energy problem also introduces difficulties when electron correlation is to be included using perturbation theory.

#### 3.3 Basis sets

In principle, the basis set used to expand the orbitals should be complete (*i.e.* an infinite number of basis function should be used) in order to obtain the exact solution of the Hartree-Fock equations. This exact limit is called the Hartree-Fock limit. Note that this does not correspond to the exact many-electron wavefunction  $\Psi$ , it is merely the best possible wavefunction that can be obtained within the approximations made in HF theory. In practice, a finite set of basis functions is used. A variety of basis sets have been developed in order to find an optimal balance between reaching accurate results and keeping the computational cost as small as possible.<sup>1</sup> For the expansion of the wavefunction in basis functions as in eq 3.12 a choice of the type of basis function has to be made. A natural choice is to take so-called Slater-type orbitals (STOs) since these exponentially decaying functions represent the exact solutions for atomic one-electron systems.<sup>3</sup>

In practice it turns out that the evaluation of one- and two-electron integrals over STOs centered on multiple atomic centers is rather time-consuming, which has lead to the introduction of gaussian type functions (GTO). The advantage of the use of GTOs is that the evaluation of the multi-center two-electron integrals can be performed analytically, however the number of individual functions that have to be used to get a reliable description is much larger. In general, basis sets are used in which each (radial) basis function consists of a linear combination of 'primitive' gaussians. For example in the well-known 6-31G basis set, the core basis functions (e.g. a 1s orbital on carbon) consist of 6 primitive gaussians and one uncontracted gaussian.

*Ab initio* calculations are usually performed using basis sets consisting of gaussian functions. In semi-empirical methods such as the intermediate neglect of differential overlap method (INDO), used in chapters 8, it is common to use a minimal STO basis set. Another exception to the general use of GTOs is found in the Amsterdam Density Functional (ADF) program,<sup>7,8</sup> which has been used extensively for the work described in chapters 8-10. ADF uses STO basis functions with a very efficient numerical algorithm to evaluate the integrals in Eq. 3.15.

The results of quantum chemical calculations depend critically on the size and type of basis set used. Calculations using minimal basis sets often give a reasonable first impression. In a minimal basis set, the number of functions per atom is just sufficient to accommodate all the electrons of that atom. For hydrogen only a single s-type function is used, while for carbon two s-functions and a p-shell (three p-functions,  $p_x$ ,  $p_y$ , and  $p_z$ ) are used giving a total of 5 basis functions. If high accuracy is desired it is necessary to use large basis sets. For calculations of reasonable accuracy it is recommendable to use at least a so-called double-zeta basis set including polarization functions (DZP). This means that, compared to the situation for the minimal basis, the number of basis function is a basis function of higher angular momentum than the occupied orbitals in the atom. In a DZP basis set for hydrogen there are 4 s-functions (double zeta) and one set of three p-functions, whereas for carbon there are 4 s-functions two sets of three p-functions and a single set of five d-type functions. For calculations of high accuracy the basis set can be extended with more functions, for example

by using a triple-zeta or quadruple zeta basis set or by including functions of higher orbital angular momentum such as g-functions. Furthermore, if the basis sets are to be used in calculations including electron correlation (MP2 or CI) there are other requirements than for HF calculations. Special basis sets have been developed for use with correlated methods such as the series of correlation consistent basis sets (cc-pVDZ, cc-pVTZ,...) by Dunning et al.<sup>9</sup>

#### 3.4 Semi-empirical methods: INDO/s

In a Hartree-Fock calculation the calculation of the two-electron integrals over basis functions in Eq. 3.15 is the most computationally demanding part, as mentioned above. The computational cost of HF calculations scales with the fourth power of the number of basis functions (in absence of using methods to reduce the number of integrals to be calculated). In order to be able to perform quantum chemical calculations on large systems there has been a search for approximations in addition to those made in the HF method. This has led to the formulation of semi-empirical methods in which the goal is a considerable reduction in the number of two-electron integrals that have to be evaluated.<sup>1</sup> The first step in reducing the computational cost in semi-empirical methods is to consider only the valence electrons explicitly. The core electrons are accounted for by reducing the nuclear charge or by introducing functions to model the repulsion due to core electrons. For the valence electron only a minimal basis set is used. From ab initio calculations it is known that minimal basis sets generally give a rather poor description of the molecular orbitals. The quality of the wavefunction is further decreased by neglecting certain integrals. Examples of integrals that are neglected are the three- and four-center two-electron integrals, by far the most numerous. The deficiencies introduced by these approximations are repaired by replacing some, or all of the remaining integrals by parameters. These parameters can be obtained either from higher level quantum chemical calculations or from fitting to (atomic or molecular) experimental data such as, e.g. ionization potentials or heats of formation.

With the developments in computer speed the use of semi-empirical methods has decreased since *ab initio* methods (including density functional methods) can now be applied to large systems. One of the exceptions is the intermediate neglect of differential overlap method (INDO) which was originally proposed by Pople et al.<sup>10</sup> and independently by Dixon.<sup>11</sup> The INDO method has been especially parametrized, by Zerner and co-workers,<sup>12-14</sup> for calculating electronic spectra of large molecules or systems containing heavy atoms. This INDO/s parameterization has been used to calculate electronic spectra for a wide variety of molecules and is generally known to give excellent results at a very low computational cost.

#### 3.5 Configuration interaction

In a Hartree-Fock calculation the assumption is made that each electron interacts with the average charge distribution of all the other electrons. In reality, however, the electrons interact instantaneously. Therefore, in the exact wavefunction, the electrons avoid each other more than they do in the HF wavefunction. This means, that in the exact many-electron wavefunction, the Coulomb repulsion between the electron is always less than in the HF

wavefunction, and hence the exact wavefunction will always have a lower energy. This type of correlation is also called dynamic correlation.

Several ways have been developed to include electron correlation in electronic structure calculations. Most of the conventional methods use the HF wavefunction as a starting point, but there are also alternative methods such as density functional theory, which will be described separately in the next section. The configuration interaction (CI) method is conceptually (but not practically) the most simple way to include electron correlation<sup>4</sup> where the HF single-determinant wavefunction is taken as the starting point. In CI the wavefunction is a linear combination of singly excited, doubly excited, etc. Slater determinants.

$$\Phi_{CI} = c_0 |\Phi_0\rangle + \sum_{ar} c_a^r |\Phi_a^r\rangle + \sum_{\substack{a < b \\ r < s}} c_{ab}^{rs} \sum |\Phi_{ab}^{rs}\rangle + \sum_{\substack{a < b < c \\ r < s < t}} c_{abc}^{rst} |\Phi_{abc}^{rst}\rangle + \dots$$
(3.15)

The reference determinant,  $\Phi_0$ , is the HF ground state wave function.  $\Phi_a^r$  is a singly excited determinant in which an electron is taken from (HF) orbital *a* and is transferred to orbital *r* which was unoccupied in the HF reference wavefunction.  $c_a^r$  is the corresponding expansion coefficient for this determinant.  $\Phi_{ab}^{rs}$  are doubly excited determinants, etc. If all possible excited determinants based on a certain Slater determinant are included within a given basis set the full-CI expansion is obtained. Although the full-CI wavefunction is exact within a certain basis set, it is generally not possible to obtain the full-CI solution except for the smallest systems (such as H<sub>2</sub>). Therefore the CI expansion is usually truncated, e.g. by including only singly and doubly excited determinants (CI-SD). CI-SD is often used to include *dynamic* electron correlation<sup>1</sup> in calculations on molecules in the ground state.

Diagonalization of the CI matrix not only yields the ground state CI wavefunction but also solutions for excited states. Therefore a CI calculation can be used to calculate the electronic absorption spectra of molecules. Sometimes the excited state consists mainly of only one Slater determinant. Generally, there are more determinants that give a significant contribution, for instance a linear combination of two excited determinants. The determinants that are absolutely necessary to give a first order description of an excited state give a description of the so-called *static* correlation.<sup>1</sup>

In many cases a reasonable description of an excited state can be obtained by using a CI expansion containing only singly excited determinants (CIS). Such an expansion contains mainly static correlation and very little dynamic correlation. The HF reference wavefunction for construction of the excited determinants can be an *ab initio* HF wavefunction but it is also possible to use a semi-empirical calculation to obtain the reference wavefunction. In chapter 8 an INDO/s calculation is used to obtain the reference determinant. This reference determinant is used in a CIS calculation to obtain the wavefunctions for the excited states. The combination INDO/s-CIS is known to give a very good description of electronic spectra at only a relatively small computational cost.

#### **3.6 Density functional theory**

An alternative way to include electron correlation in electronic structure theory is Density Functional Theory (DFT), which is not based on a HF wavefunction as a starting point. In DFT the central quantity is the electron density rather than the many-electron wavefunction as in 'conventional' quantum chemistry. The proof given by Hohenberg and Kohn<sup>15</sup> shows that there is a one-to-one connection between the electron density,  $\rho$ , and the total electronic energy,  $E(\rho)$ . The ground state energy, and all other ground-state properties, are uniquely defined by the electron density. The goal is to find the electron density that minimizes the energy for a given set of nuclear coordinates.

The central issue of DFT is that the functional that connects the ground state electronic energy to the electron density is not known. Much of the development work in DFT is therefore directed at designing density functionals that approach the exact density functional as much as possible.<sup>16,17</sup>

The DFT total electronic energy can be written as a sum of the kinetic energy, T, the nuclear attraction energy,  $E_{ne}$ , the Coulomb repulsion between the electrons, J, and the exchange-correlation energy  $E_{XC}$ :<sup>1,17</sup>

$$E_{DFT}[\rho] = T[\rho] + E_{ne}[\rho] + J[\rho] + E_{XC}[\rho]$$
(3.16)

in which all terms are a functional of the electron density. Comparison with the expression for the Hartree-Fock total energy shows that it is analogous, apart from the inclusion of the correlation energy in  $E_{XC}$ . Early attempts to construct functionals for the kinetic and exchange energies were derived by considering a non-interacting uniform electron gas. It was found however that this leads to a poor description of the kinetic energy.

An alternative approach was proposed by Kohn and Sham<sup>18</sup> in which the (approximate) density is written in terms of a set of auxiliary one-electron functions as

$$\rho(r) = \sum_{i=1}^{N} |\phi_i|^2$$
(3.17)

The kinetic energy can be calculated from

$$T = \sum_{i=1}^{N} \left\langle \phi_i \Big|_{-\frac{1}{2}} \nabla^2 \Big| \phi_i \right\rangle$$
(3.18)

The electron-electron Coulomb repulsion  $(J[\rho])$  is calculated in the same way as in HF (see Eq. 3.8 and 3.9) using the auxiliary basis functions. The exchange and correlation energy are calculated from a functional of the density. In principle, the exchange energy could also be calculated 'exactly' using the basis functions and leave only the electron correlation to be calculated from a density functional. However, this approach is known to give rather poor results.<sup>1</sup> The reason for this is related to the actual definition of the correlation energy, which is not the same as in HF theory.<sup>16,19,20</sup> In DFT the exchange and correlation are intimately

related, one part correcting for errors in the other, and combining a correlation functional with exact calculation of the exchange (using the basis functions) generally gives inaccurate results.

The introduction of basis functions in DFT results in a set of pseudo-eigenvalue equations, known as the Kohn-Sham equations:

$$\mathbf{h}_{KS}\phi_i = \varepsilon_i\phi_i \tag{3.19}$$

The Kohn-Sham equations have to be solved in an iterative way since the Kohn-Sham operator,  $\mathbf{h}_{KS}$ , depends on the density and thus on the orbitals,  $\phi_i$ . The computational cost of solving these equations is therefore similar to that of solving the HF equations. An advantage of DFT is, however, that it is in principle able to provide more accurate results. It should be noted that the 'orbitals' obtained from DFT calculations (the Kohn-Sham orbitals) and the eigenvalues,  $\varepsilon_i$ , cannot be compared directly to the orbitals and eigenvalues from HF calculations. It has been shown recently that the eigenvalues in DFT are related to ionization potentials although not in the same way as in HF.<sup>21</sup> Furthermore, it has been argued that the Kohn-Sham orbitals are a good basis for a qualitative interpretation of the molecular orbitals.<sup>16,22</sup>

#### Density functionals<sup>17</sup>

In most exchange-correlation functionals the starting point is the local density approximation (LDA) in which it is assumed that the density can be treated locally as a uniform electron gas.<sup>23</sup> This may seem like a rather crude approximation for molecular systems but the results are often of similar accuracy as obtained from HF methods.

More sophisticated methods have to consider systems in which the density is not uniform. A step in this direction is to make the exchange and correlation energies also dependent on the derivative of the electron density, leading to the generalized gradient approximation (GGA). Many gradient corrected density functionals have been proposed, either as corrections to the LDA or as separate gradient corrected functionals. The construction of exchange correlation functionals can be based on physical considerations, such as for example in the construction of an asymptotically correct functional by Van Leeuwen and Baerends.<sup>24</sup> In other methods a functional is constructed by optimizing its parameters (sometimes up to 15) by fitting them to optimally reproduce experimental data (ion energetics, dissociation energies etc.) for a certain 'learning set' of molecules.<sup>25</sup> In the latter approach DFT is actually considered as a sort of semi-empirical method.

#### Advantages of DFT

Over the last decade DFT methods have become widely used in chemistry. The main advantage of DFT over 'conventional' correlated methods is the computational cost. DFT using gradient corrected functionals generally gives results that are comparable in accuracy

(or better) than *e.g.* Møller-Plesset second-order perturbation theory (MP2) results at a cost comparable to that of HF calculations. This makes it possible to perform correlated calculations on very large molecules, which are not possible using conventional correlated methods.

DFT is used to optimize the geometry of large conjugated molecules in chapter 8 of this thesis. It is also possible to use density functional theory for calculating excitation spectra by using response theory, or time-dependent density functional theory.<sup>26-28</sup> This method is employed in chapter 9 to study the properties of conjugated molecules in electronically excited states.

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## **Chapter 4**

# The Formation and Recombination Kinetics of Positively Charged MEH-PPV Chains in Solution<sup>\*</sup>

This chapter describes how the mobility of positive charges ("holes") along isolated conjugated polymer chains is derived from the results of pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) experiments on dilute polymer solutions. The method is illustrated with results for oxygen-saturated, benzene solutions of the well-known poly(phenylene vinylene) derivative, MEH-PPV. Nanosecond pulsed irradiation results initially in ionization of the solvent with the formation of excess electrons and benzene radical cations,  $Bz^{\dagger}$ . The former rapidly (< 1 ns) undergo attachment to  $O_2$  to form  $O_2^{-}$  with a rate constant of 1.5x10<sup>11</sup> M<sup>-1</sup>s<sup>-1</sup>. The Bz<sup>+</sup> ions diffuse through the solvent and react with the (lower ionization potential) polymer chains via electron abstraction forming holes on the polymer backbone. This is accompanied by a large increase in the conductivity of the solution after the pulse, demonstrating that the mobility of holes on the polymer chains is very much larger than the mobility, via molecular diffusion, of Bz<sup>+</sup> ions in the solvent. To describe the after-pulse growth in conductivity a large effective reaction radius, Reff. of ca 400 Å is required for the diffusion-controlled reaction of  $Bz^{+}$  with MEH-PPV chains. This requires taking into account the time-dependent term in the rate coefficient. The conductivity eventually decays due to the recombination of the positively charged polymer chains with negative counterions ( $O_2$ ) with a rate coefficient of 1.2x10<sup>11</sup> M<sup>-1</sup>s<sup>-1</sup>. No evidence could be found for first-order trapping of the mobile positive charge on the polymer chains prior to recombination. The pseudo-one-dimensional mobility of holes along the polymer backbone derived from the absolute magnitude of the conductivity transients is 0.46  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ .

#### **4.1 Introduction**

The mechanism of charge transport in conjugated polymers is a topic of considerable interest since these materials are being considered for application in electronic devices.<sup>1-6</sup> Examples of such devices include field effect transistors (FETs), light emitting diodes (LEDs) and

<sup>&</sup>lt;sup>\*</sup> This chapter is based on: F.C. Grozema, R.J.O.M. Hoofman, L.P. Candeias, M.P. de Haas, J.M. Warman and L.D.A. Siebbeles, *J. Phys. Chem. A*, in press.

photovoltaic cells. The performance characteristics (e.g. switching times and maximum current) of these devices are critically dependent on the mobility of the charge carriers. We have recently shown that it is possible to measure the mobility of charges along isolated chains of conjugated polymers in solution using the pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC).<sup>7,8</sup> The mobility of charge along an isolated polymer chain in solution cannot be compared directly with charge carrier mobilities in the corresponding bulk solid; the state in which these materials are used in devices. In the solid, charge transport can occur via interchain as well as intrachain mechanisms. In addition, the static and dynamic disorder within the backbone of the polymer is expected to be quite different in the two phases.

Measurements of charge transport on isolated chains do, however, provide unique data on charge transport along molecular wires; information that is 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.<sup>9</sup> Moreover, direct measurements of the *intra*-molecular mobility for different polymers can present a useful guideline for the design of molecular wires with transport properties that meet the requirements of nano-scale electronics.

Recently, we have reported mobilities of positive charges along isolated polymer chains in benzene solution for a variety of  $\sigma$ - and  $\pi$ -conjugated polymers.<sup>7</sup> For both types of polymer the mobility was found to depend strongly on the molecular structure of the polymer backbone and on the nature of the side-chains.

It is the purpose of this chapter to give a detailed account of the kinetic fitting procedure that was used to obtain the charge carrier mobility from the time-resolved microwave conductivity measurements, using a poly(phenylene vinylene) derivative, MEH-PPV (see Figure 4.1) as an example. This requires a detailed description of the kinetics of formation and decay of the positively charged polymer chains. Both the formation and decay involve diffusion-limited reactions between a small mobile entity and a large, relatively immobile, polymer chain. The complex kinetics of such reactions are not only relevant for the particular problem that is addressed in this work but are of general importance.<sup>10</sup> Examples of diffusion limited reactions of the type discussed here include fluorescence quenching,<sup>11,12</sup>, reaction of small reactive species with polymers<sup>13</sup> and the binding of a small substrate to the catalytic site of an enzyme.<sup>14</sup> There have been many theoretical studies of such processes, using both analytical<sup>15-22</sup> and numerical methods.<sup>20-22</sup>



Figure 4.1: Molecular structure of MEH-PPV

We first discuss the experimental procedures used to measure the radiation-induced conductivity and the radiolytic processes that occur. We then describe the analysis of the kinetics of the diffusion controlled formation and decay reactions of positively charged polymer chains and the procedure used to fit the conductivity transients observed.

#### 4.2 Experimental details

The chemical structure of the poly(phenylene vinylene) derivative studied in this work, poly(2-methoxy-5-[2'-ethyl-hexyloxy]-phenylene vinylene), MEH-PPV, is shown in Figure 4.1. According to gel permeation chromatography (GPC) measurements the polymer has an estimated number averaged molecular weight,  $M_n$ , of  $200\pm100$  kDa, which corresponds to  $800\pm400$  monomer units. The alkoxy side-chains make it possible to dissolve the polymer in a variety of organic solvents. Dilute solutions in benzene (Merck UV spectroscopic grade) were freshly prepared before each experiment. The concentrations ranged from 0.2 mM to 1.0 mM in monomer units. This corresponds to polymer chain concentrations from 0.25 to 1.25  $\mu$ M for a molecular weight of 200 kDa. No indication of polymer aggregation was observed. The solutions were bubbled with oxygen for at least 10 minutes before transferring them to a vacuum tight microwave cell. The O<sub>2</sub> concentration in a saturated solution is ca. 12 mM.



Figure 4.2: Schematic drawing of the PR-TRMC setup.

A schematic drawing of the experimental setup used for the experiments described in this chapter is shown in Figure 4.2. Excess charge carriers were produced in the solution by

pulsed irradiation with 3 MeV electrons from a Van de Graaff accelerator using pulse durations from 2 ns to 50 ns. Electrons with an energy of 3 MeV have a penetration depth of 15 mm in benzene, which is much larger than the 3.55 mm thickness of the microwave cell that contains the polymer solution. Energy deposition by the electron beam as it traverses the sample is therefore close to uniform. In a multi-component medium, energy is initially distributed between the individual components according to their fractional contribution to the overall electron density. In the case of the solutions used in the present work the contribution of the polymer to the electron density was less than 0.1% even for the highest polymer concentration used. Therefore energy is initially deposited almost exclusively in the benzene solvent. A more detailed description of the experimental set-up can be found in chapter 2.

The initial concentration of charge carriers is proportional to the amount of energy deposited per unit volume; the radiation dose,  $D_v$  (Jm<sup>-3</sup>). The dose was calibrated using thin film radiochromic dosimeters (Far West Technology) and was 530 Jm<sup>-3</sup> per nanocoulomb beam charge. The integrated beam charge per pulse, Q (nC), was routinely measured for each pulse. The concentration in moles per liter of a radiolytic product X formed within a pulse is given by

$$[X] = \frac{530Q}{6.02 \times 10^{26} e_{X}} \tag{4.1}$$

with  $E_X$  the average energy in eV absorbed per product X formed. As an example, for a 10 ns pulse Q is *ca* 40 nC. Taking this together with the value of 1900 eV for the average energy to form one free ion pair in benzene,<sup>23,24</sup> results in an estimated concentration of ion pairs formed of 0.12  $\mu$ M.

Irradiation of benzene leads to the formation of radiochemical products, such as biphenyl, which can react with the initially formed excess electrons and benzene radical cations.<sup>25</sup> The accumulated irradiation dose used in the experiments described in the following sections was therefore kept sufficiently low that such radiolytic products did not affect the conductivity transients measured. No change in the magnitude or shape of a conductivity transient for a given solution was observed for the total accumulated dose used in a series of measurements on a single solution. From separate, steady-state radiolysis experiments it has been found that a total dose of more than an order of magnitude larger than the doses used in the present pulsed experiments is required to induce a detectable change in the optical absorption of oxygen saturated MEH-PPV solutions.

The radiation-induced conductivity in the solutions was measured using the time-resolved microwave conductivity (TRMC) technique.<sup>26-28</sup> The microwave system is constructed of rectangular waveguide with internal cross section  $7.1x3.55 \text{ mm}^2$ . Microwave frequencies in the K<sub>a</sub>-band (26.5 - 40 GHz) were used, corresponding to a reciprocal radian frequency of ca. 5 ps. The average microwave power level was 100 mW, which corresponds to an electric field amplitude within the cell of ca. 10 Vcm<sup>-1</sup>. The microwave cell containing the polymer solution is closed at one end with a metal plate and at the other end with a vacuum-tight polyimide window, see Figure 4.2. The probing microwaves are reflected at the metal end-plate and form a standing wave pattern in the cell.

Changes in the conductivity inside the cell upon pulsed irradiation were monitored as changes in the microwave power reflected by the cell. The output of the microwave detector diode was monitored using either a linear time-base with a Tektronix TDS 680B two-channel digital real-time oscilloscope or a logarithmic time-base using a Sony/Tektronix RTD 710 digitizer. Using the latter combination, conductivity transients could be monitored from 10 ns to 1 ms using a single accelerator pulse.

The change in the microwave power reflected by the cell,  $\Delta P_R$ , is directly proportional to the change in the conductivity of the sample,  $\Delta \sigma$ , for small changes in the conductivity,

$$\frac{\Delta P_R}{P_R} = A\Delta\sigma \tag{4.2}$$

The sensitivity factor, A, can be calculated from the geometric and dielectric properties of the sample and the microwave frequency used, as described previously.<sup>26-28</sup> The radiation-induced conductivity is related to the mobility of the charge carriers formed,  $\mu_i$ , according to

$$\Delta \sigma(t) = e \sum_{i} N_{i}(t) \mu_{i}$$
(4.3)

In Eq. 4.3,  $N_i(t)$  is the number density of charge carriers of type *i* existing at time *t* and *e* is the elementary charge. The radiation-induced conductivity is usually given as the dose normalized quantity  $\Delta \sigma / D_v$  (Sm<sup>2</sup>J<sup>-1</sup>).

#### 4.3 Results and discussion

As mentioned in the introduction, it is the purpose of this chapter to present a detailed description of the method of data analysis used to derive the mobilities of charge carriers on conjugated polymer chains from TRMC measurements on pulse-irradiated dilute polymer solutions.<sup>7,8</sup> The emphasis is therefore more on the reaction mechanisms and kinetics which underlie the growth and decay of the conductivity after the pulse, rather than the absolute value of the mobility derived, which has been published previously.<sup>7,8</sup> The method of data treatment and the type of information obtained are illustrated by measurements on dilute, oxygen saturated solutions of the conjugated polymer MEH-PPV. As pointed out in the experimental section, energy from the incident 3 MeV electrons will be transferred initially almost exclusively to molecules of the solvent. Because of this, we first discuss the radiolytic processes occurring in the solutions subsequent to pulsed irradiation.

#### Radiolytic processes

Radiolysis of benzene results initially in ionization and excitation of individual molecules of the medium leading to the formation of benzene radical cations,  $Bz^+$ , excess electrons,  $e^-$ , and excited states, represented by  $Bz^*$ . In the present conductivity study we are principally

interested in the charged species since these are specifically monitored using the TRMC technique. These are initially formed as coulomb-correlated pairs,  $\{Bz^+ + e^-\}$  with an average separation distance,  $R_{\pm}$  of approximately 50 Å,<sup>29</sup> which is considerably less than the Onsager escape distance,  $R_c$ .

$$Bz \sim \sim \sim \geq \{Bz^{+} + e^{-}\}$$
(A)

 $R_c$  is the distance at which the coulomb energy is equal to the characteristic thermal energy  $k_BT$  (*ca* 0.025 eV at room temperature) and is given in terms of the relative dielectric constant,  $\varepsilon$ , by

$$R_c = \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T} \tag{4.4}$$

with  $\varepsilon_0$  the permittivity of vacuum, *e* the elementary charge,  $k_B$  the Boltzmann constant and *T* the temperature. For liquid benzene  $\varepsilon = 2.28$  and  $R_c = 250$  Å. Because  $R_{\pm}$  is much smaller than  $R_c$  at room temperature, a large fraction of the initial ionization events are followed by rapid, "geminate" charge recombination on a sub-nanosecond timescale.<sup>27</sup>

$$\{Bz^+ + e^-\} \longrightarrow Bz^*$$
 (B)

Only a small fraction,  $F_{fp}$ , of the initially formed pairs is capable of undergoing diffusional escape resulting in the formation of relatively long-lived, homogeneously-distributed "free" ions.

$$\{Bz^+ + e^-\} \xrightarrow{F_{fp}} Bz^+ + e^-$$
 (C)

The yield of free ions in benzene at room temperature has been determined, in DC conductivity experiments, to be 0.053 per 100 eV absorbed.<sup>23,24</sup> This corresponds to an average energy for the formation of a free ion pair,  $E_{fp}$ , of 1900 eV and to a value of  $F_{fp}$  of approximately 1%. It is this small escaped fraction that is relevant in the present work since these free ions can diffuse throughout the solvent and react with dissolved solutes. The geminately recombining ions, on the other hand, will have decayed well within the shortest time scale of a few nanoseconds prevailing in the present experiments.

The conductivity resulting on nanosecond pulse-radiolysis of pure benzene is given by,

$$\Delta \sigma = eN_{fp} \left[ \mu(e^{-}) + \mu(Bz^{+}) \right] \tag{4.5}$$

with  $\mu(e)$  and  $\mu(Bz^+)$  the mobility of the excess electron and solvent radical cation respectively, and  $N_{fp}$  the concentration of free ions. If no decay of free ions occurs during the pulse then the end-of-pulse value of  $N_{fp}$  for a dose in the pulse of  $D_v$  in Jm<sup>-3</sup>, will be,

$$N_{fp}(0) = \frac{D_{v}}{E_{fp}}$$
(4.6)

Substitution for  $N_{fp}(0)$  from Eq.4.6 in Eq. 4.5 and rearrangement gives for the experimentally measurable quantity  $[\Delta\sigma/D_{\nu}]_0$ ,

$$\left[\Delta\sigma / D_{\nu}\right]_{0} = \frac{e\left[\mu(e^{-}) + \mu(Bz^{+})\right]}{E_{fp}}$$

$$\tag{4.7}$$

DC conductivity experiments have shown the excess electron to be the major charge carrier in benzene with a mobility of  $0.13 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  at room temperature.<sup>23,30</sup> A mobility of  $1.2 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for Bz<sup>+</sup> has been estimated previously from PR-TRMC measurements using an X-band resonant cavity. This value is close to that which would be expected for diffusive molecular motion within a liquid of viscosity 0.65 cP; *i.e.* it corresponds to a diffusion coefficient, *D*, of  $3 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$  according to the Einstein relationship,

$$D = \frac{\mu k_B T}{e} \tag{4.8}$$

Substituting the above mobilities and the value of  $E_{fp}$  in Eq. 4.7 yields a predicted value of  $[\Delta\sigma/D_{\nu}]_0$  for pure benzene of  $6.9 \times 10^{-9} \text{ Sm}^2 \text{J}^{-1}$ .

A dose-normalized TRMC transient obtained on pulse-radiolysis of pure benzene using a 2 ns pulse is shown in Figure 4.3. The initial rapid decay of the conductivity during the first 2-5 ns is attributed to a tail of the geminately recombining ion pairs. The conductivity at longer times is due to free ion pairs that have escaped from geminate recombination. The first half-life of the decay of this conductivity component, as indicated by the dashed line in Figure 4.3, is *ca* 70 ns. Since this is considerably longer than the 2 ns pulse-length used, we conclude that only a small fraction of the free ions will have recombined within the pulse. The end-ofpulse value of  $\Delta\sigma/D_{\nu}$  should therefore be close to the value of  $[\Delta\sigma/D_{\nu}]_0$  given above. The value found by extrapolation of the relatively slowly decaying conductivity component to the end of the pulse is  $8.0 \times 10^{-9}$  Sm<sup>2</sup>J<sup>-1</sup>. This is approximately 15% higher than the value of  $6.9 \times 10^{-9}$  Sm<sup>2</sup>J<sup>-1</sup> predicted on the basis of previous DC measurements. In view of the very different experimental techniques used to derive  $[\Delta\sigma/D_v]_0$ , we consider the agreement to be reasonable. The larger value of  $[\Delta\sigma/D_v]_0$  found in the present work could be due to a higher mobility and/or a larger free-ion yield (lower value of  $E_{fp}$ ) than measured in the DC experiments. Since the value of  $E_{fp}=1900$  eV has been independently determined by two different groups, we have consistently used this value to calculate the concentration of free ions formed. If the value of  $E_{fp}$  is in fact 15% lower, then the values of the polymer hole mobility calculated on the basis of  $E_{fp} = 1900$  eV would be approximately 15% too high.



**Figure 4.3**: Radiation induced conductivity in neat benzene (solid line), and oxygen saturated benzene (dotted line) using a 2 ns electron pulse. The dashed line is an exponential fit to the transient for neat benzene.

Since the electron is by far the most mobile charge carrier in pure benzene, the after-pulse decay of the conductivity reflects mainly the decay of this species. In the absence of electron attaching impurities or additives, decay will occur by homogeneous charge recombination according to

$$Bz^{+} + e^{-} \longrightarrow Bz$$
 (D)

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In molecular liquids the reaction coefficient for charge recombination,  $k_r$ , is given in general by the Debye relation<sup>31</sup>

$$k_{r} = \frac{e[\mu_{+} + \mu_{-}]}{\varepsilon \varepsilon_{0}} = 4\pi R_{c}[D_{+} + D_{-}]$$
(4.9)

with  $\mu_+$  and  $\mu_-$  the mobilities of the recombining ions and  $D_+$  and  $D_-$  the corresponding diffusion constants (see Eq. 4.8). The resulting time dependence of the free-ion concentration after the pulse should then be given by

$$\frac{N_{fp}(t)}{N_{fp}(0)} = \frac{1}{1 + N_{fp}(0)k_r t}$$
(4.10)

The first half-life due to recombination alone,  $\tau_r$ , is therefore

$$\tau_r = \frac{1}{N_{fp}(0)k_r}$$
(4.11)

Substituting in Eq. 4.11 for  $N_{fp}(0)$  from Eq. 4.6 and for  $k_r$  from Eq. 4.9 leads to the following expression,

$$\tau_r = \frac{E_{fp} \varepsilon \varepsilon_0}{e D_v [\mu_+ + \mu_-]} \tag{4.12}$$

Taking the known values of  $E_{fp}$ ,  $\varepsilon$ , and  $[\mu_+ + \mu_-]$  corresponding to reaction D together with the dose of  $4.2 \cdot 10^3$  Jm<sup>-3</sup> used for the transient in Figure 4.3 results in a predicted value for  $\tau_r$  of *ca* 700 ns.

This half-life estimated for recombination alone is substantially longer than the actual half-life of 70 ns derived from the transient in Figure 4.3. An additional decay channel to D for electrons must therefore be operative. This is attributed to the occurrence of electron attachment to spurious impurities,  $I_e$ , in the nominally pure solvent.

$$e^{-} + I_e \xrightarrow{k_E} I_e^{-}$$
 (E)

For an electron mobility of 0.13 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> the rate constant for reaction (E) could be as high as  $3x10^{12}$  M<sup>-1</sup>s<sup>-1</sup>.<sup>27</sup> An impurity concentration of as little as 5 micromolar (corresponding to only *ca.* 1 ppm) would therefore be sufficient to result in the half-life of 70 ns found.

Neat benzene may also contain small concentrations of spurious impurities, which can scavenge the initially formed  $Bz^+$  radical cations.

$$Bz^{+} + I_{h} \xrightarrow{k_{F}} Bz + I_{h}^{+}$$
(F)

Because of the much lower diffusion coefficient of  $Bz^+$  the rate coefficient for this reaction will, however, be much smaller than that for reaction E and close to the value of  $1x10^{10}$  M<sup>-1</sup>s<sup>-1</sup> expected for a diffusion controlled reaction between molecular species.

As pointed out above, only small amounts of electron attaching compounds are sufficient to considerably shorten the electron lifetime. By deliberately adding such an electron "scavenger" the conductivity signal due to excess electrons can be almost completely suppressed. This is shown in Figure 4.3 by the TRMC transient for an oxygen saturated (12 mM) solution in which electron attachment occurs via G.

$$e^{-} + O_2 \qquad \xrightarrow{k_G} O_2^{-} \qquad (G)$$

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From the decay of the conductivity in solutions containing a lower concentration of oxygen, we have determined the rate constant for electron scavenging by  $O_2$  to be  $k_G=1.5 \times 10^{11} \text{ M}^{-1} \text{s}^{-1}$ . For an  $O_2$  saturated solution the concentration is therefore high enough to reduce the electron lifetime to less than a nanosecond as shown in Figure 4.3.

In the present work we have used oxygen as an electron scavenger rather than  $CCl_4$  which was used in a previously reported study.<sup>8</sup> This was motivated by the fact that electron attachment to  $O_2$  is non-dissociative and does not produce a strongly oxidizing free-radical species such as  $CCl_3$  on pulse-radiolysis which could possibly lead to subsequent oxidation of the polymer.

When using  $O_2$ -saturated solutions care has to be taken that the sample is not exposed for extensive periods of time to light. This was achieved in the present work by transferring the solutions to the microwave cell within a few minutes after saturation with oxygen. We have previously carried out a quantitative study of the UV photo-oxidative degradation of MEH-PPV in benzene solution<sup>32</sup> and found a 10% reduction in the microwave photoconductivity for a total absorbed dose of UV radiation of *ca* 20 J/cm<sup>3</sup>. An exposure of many hours would be required to reach this level of photo-degradation under normal laboratory lighting conditions. As far as radiolytic degradation goes, we have observed no significant change in the temporal form or absolute magnitude of the conductivity transients during the course of a series of experiments. Deliberate exposure of  $O_2$ -saturated MEH-PPV solutions to large doses of ionizing radiation in a Cobalt-60 source have shown only small, < 10%, changes in the optical absorption for doses 10 times the total accumulated dose used in the present pulse-radiolysis experiments.

Benzene radical cations do not react with oxygen but diffuse through the solvent and eventually undergo charge transfer to the conjugated polymer chains (reaction H), which have a lower ionization potential.

$$Bz^+ + PPV \longrightarrow Bz + PPV^+$$
 (H)

Figure 4.4 shows the time-dependence of the microwave conductivity after pulsed irradiation for polymer concentrations ranging from 0.25  $\mu$ M to 1.25  $\mu$ M. The conductivity is seen to increase initially after the pulse on a time scale of hundreds to thousands of nanoseconds. As is evident from Figure 4.4, this after-pulse growth becomes faster with increasing polymer concentration, in accordance with expectations based on reaction H as the underlying source. These results provide immediate qualitative evidence that the mobility of positive charges on MEH-PPV chains is considerably higher than that of Bz<sup>+</sup> ions in benzene. Note that the large increase in mobility is due to motion of charge along the polymer chain rather than diffusional motion of the polymer chains as a whole.



**Figure 4.4**: Dose normalized radiation-induced conductivity in benzene solutions of MEH-PPV for different concentrations obtained using a 10 ns pulse. From top to bottom: 1.25  $\mu$ M, 1.0  $\mu$ M, 0.75  $\mu$ M 0.5  $\mu$ M and 0.25  $\mu$ M (polymer concentrations). The dotted lines represent kinetic fits for which all parameters were held constant apart from the polymer concentration.

The conductivity eventually decays on a time scale of tens to hundreds of microseconds as shown in Figures 4.4 and 4.5. In Figure 4.5 the time scale of the decay of the conductivity is seen to become shorter as the pulse duration increases, i.e. as the concentration of ion pairs formed in the pulse is increased. Accordingly, we attribute this decay to second order charge recombination of PPV<sup>+</sup> with  $O_2^-$ .

$$PPV^{+} + O_{2}^{-} \qquad \xrightarrow{\kappa_{I}} \qquad PPV + O_{2} \qquad (I)$$

In order to obtain the absolute value for the mobility, the concentration of charged polymer chains in the solution must be known as a function of time. This can be obtained from a kinetic scheme that includes all the relevant reactions that occur upon pulsed irradiation of the polymer solutions. The rate coefficients and mobilities that are unknown are adjusted such that an optimal correspondence between the calculated conductivity transients and the experimental data in Figures 4.4 and 4.5 is obtained. This fitting procedure and the resulting rate coefficients and mobility are discussed in the following sections.

#### Reaction kinetics

The kinetics of the reactions A-I can be described by a set of differential equations for the formation and decay of the five relevant species ( $e^{-}$ ,  $Bz^{+}$ ,  $PPV^{+}$ ,  $O_{2}^{-}$ ,  $I_{h}^{+}$ ). Freely diffusing  $Bz^{+}$ 

and e<sup>-</sup> are formed during the electron pulse by processes A and C. As discussed above the geminate recombination process, reaction B takes place on a time-scale of less than a nanosecond, whereas the reactions that we are mainly interested in occur on time scales of tens of nanoseconds or longer. Therefore, only the 'free' ions that escape from geminate recombination by reaction C are considered in the kinetic analysis.



**Figure 4.5**: Dose normalized radiation induced conductivity in benzene solutions of MEH-PPV (1 mM in monomer units) for different pulse durations, from top to bottom: 5 ns, 10 ns, 20 ns and 50 ns. The dotted lines represent kinetic fits for which all parameters were held constant apart from the concentration of ion pairs formed in the pulse.

Since the time-profile of the Van de Graaff electron pulses is close to rectangular with rise and fall times of ca 100 ps, the formation of free ions during the pulse can be well described by

$$\frac{dN_{fp}}{dt} = \frac{D_v}{E_{fp}\Delta\tau} \qquad (0 < t < \Delta\tau)$$
(4.13)

where  $\Delta \tau$  is the pulse duration. This results in a linear increase of  $[Bz^+]$  and  $[e^-]$  with time during the pulse. The decay of excess electrons occurs mainly by reaction with the dissolved oxygen:

$$\frac{d[e^{-}]}{dt} = -k_G[e^{-}][O_2]$$
(4.14)

Reaction of excess electrons via D or E is insignificant compared to the rate of attachment to  $O_2$ .

For the benzene radical cations there are four possible decay pathways: homogeneous recombination with  $e^{-}$  (reaction D), reaction with MEH-PPV (reaction H), reaction with hole scavenging impurities (reaction F) and, finally charge recombination with  $O_2^{-}$  (reaction J).

$$Bz^{+} + O_{2}^{-} \qquad \xrightarrow{k_{J}} \qquad Bz + O_{2} \qquad (J)$$

These decay pathways lead to the following differential equation for the decay of  $Bz^+$ :

$$\frac{d[Bz^+]}{dt} = -k_D[e^-][Bz^+] - k_F[Bz^+][I_h] - k_H[Bz^+][PPV] - k_J[Bz^+][O_2^-]$$
(4.15)

Positive charges can become trapped at hole-scavenging impurities, denoted by  $I_h$ , by reaction F and can subsequently recombine by reaction with  $O_2^-$  via reaction K,

$$I_h^+ + O_2^- \longrightarrow I_h + O_2$$
 (K)

which gives for the evolution of  $[I_h^+]$  with time.

$$\frac{d[I_h^+]}{dt} = +k_F[I_h][Bz^+] - k_K[I_h^+][O_2^-]$$
(4.16)

 $PPV^+$  is formed by charge transfer from  $Bz^+$  and decays by charge recombination with  $O_2^-$ :

$$\frac{d[PPV^+]}{dt} = +k_H [Bz^+] [PPV] - k_I [O_2^-] [PPV^+]$$
(4.17)

The charge recombination reaction of  $PPV^+$  with e<sup>-</sup> can be neglected since the fraction of e<sup>-</sup> that has not yet reacted with O<sub>2</sub> on the time-scale on which  $PPV^+$  is formed is negligible.

The formation of  $O_2^-$  occurs via reaction G while its decay is due to charge recombination with  $Bz^+$ ,  $PPV^+$  and  $I_h^+$ .

$$\frac{d[O_2^-]}{dt} = +k_G[e^-][O_2] - k_J[Bz^+][O_2^-] - k_I[O_2^-][PPV^+] - k_K[I_h^+][O_2^-]$$
(4.18)

The concentrations of charged species as a function of time and the mobility of the species together determine the conductivity of the solution according to Eq. 4.3. Fits to the experimental data in Figures 4.4 and 4.5 were obtained by numerically integrating the

differential equations 4.13-4.18 using the Runge-Kutta method. In the fitting procedure the rate coefficients of reactions H and I are the variables which mainly determine the shape of the radiation-induced conductivity transients, while the charge mobility on MEH-PPV mainly determines the absolute magnitude of the transients. In the following section we discuss the values of the rate coefficients and mobilities used in this fitting procedure with particular attention given to the (possible) time dependence of the former.

#### Mobilities and rate coefficients (small molecular species)

Numerical integration of the differential rate equations given in the previous section and calculation of the time dependence of the conductivity requires, as input, values of the mobilities of the charged species listed in Table 4.1 and the rate coefficients of the reactions listed in Table 4.2. For the small (as opposed to polymeric) molecular species these parameters are known from previous work or have been determined in separate experiments as mentioned earlier in this article. Summarizing the mobility values:  $\mu(e^{-}) = 0.13 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  has been determined by time-of-flight measurements<sup>23,30</sup>;  $\mu(Bz^+) \approx 1.2 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  was obtained from previously unreported PR-TRMC measurements on electron-scavenged benzene solutions using a more sensitive X-band resonant cavity method<sup>33</sup>;  $\mu(I_h^+) \approx \mu(Bz^+)$  is a reasonable assumption since  $\mu(Bz^+)$  is close to the value expected for molecular diffusion in a liquid with the viscosity of benzene (0.65 cP);  $\mu(O_2^-) \approx 1.0 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  was estimated by interpolation between the values of  $\mu(O_2^-)$  determined by time-of-flight measurements in the hydrocarbon solvents cyclohexane ( $\eta = 1.0 \text{ cP}$ ) and iso-octane ( $\eta = 0.35 \text{ cP}$ )<sup>34</sup>.

lon	Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Comments
e	0.13	from refs. 28 and 30
Bz⁺	0.0012	from ref. 33
0 <sub>2</sub> <sup>-</sup>	0.001	from ref. 34 <sup>a</sup>
l <sub>h</sub> +	0.0012	assumed $\approx \mu(Bz^{+})$
P⁺	0.000004	from ref. 39 <sup>C</sup>
h⁺/P	0.46 (1-D) <sup>b</sup>	this work

Table 4.1: Mobility values used in the fitting procedure

(a) From  $\mu(O_2)$  determined in liquid cyclohexane and iso-octane in ref. 33 adjusted to the viscosity of liquid benzene.

(b) Three times the isotropic value of  $0.153 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  used to fit the experimental conductivity transients.

(c) from D(P) determined by dynamic light scattering.

The following rate coefficients were taken as fixed parameters:  $k_E = 1.0 \times 10^7 \text{ s}^{-1}$  derived from the excess electron decay in nominally pure, de-aerated benzene;  $k_G = 1.5 \times 10^{11} \text{ M}^{-1} \text{s}^{-1}$ from the excess electron decay in air-saturated benzene;  $k_D$ ,  $k_J$  and  $k_K$  were calculated using the Debye relation for diffusion-controlled recombination (Eq. 4.9) with the relevant mobility values taken from Table 4.1 and  $R_C = 250 \text{ Å}$ . Inclusion of reaction F, with a rate of  $1.0 \times 10^5 \text{ s}^{-1}$ , was found to be necessary in order to provide a satisfactory description of the concentration dependence. This reaction has however little influence on the temporal form of the calculated transients.
Reaction	Reactants	Rate coefficient	Comments
D	Bz⁺ + e⁻	6.2x10 <sup>13</sup> M <sup>-1</sup> s <sup>-1</sup>	$k_D = [\mu(Bz^+) + \mu(e)]e/\epsilon\epsilon_0^{(a)}$
Е	e <sup>-</sup> + I <sub>e</sub>	1.4x10 <sup>7</sup> s <sup>-1</sup>	this work, electron decay in "pure" benzene
F	Bz⁺ + I <sub>h</sub>	1.0x10 <sup>5</sup> s⁻¹	this work, from fits for PPV solutions
G	e <sup>-</sup> + O <sub>2</sub>	1.5x10 <sup>11</sup> M⁻¹s⁻¹	this work, electron decay in benzene + O <sub>2</sub>
			soltn.
Н	$Bz^{+} + PPV$	eq. 23-24	D(Bz⁺)=3x10⁻⁵, R <sub>eff</sub> =360 Å
I	$PPV^+ + O_2^-$	1.2x10 <sup>11</sup> M <sup>-1</sup> s <sup>-1</sup>	this work, from fits for PPV solutions
J	$Bz^+ + O_2^-$	1.2x10 <sup>12</sup> M <sup>-1</sup> s <sup>-1</sup>	$k_J = [\mu(Bz^+) + \mu(O_2)]e/\epsilon \varepsilon_0^{(a)}$
К	$I_{h}^{+} + O_{2}^{-}$	1.2x10 <sup>12</sup> M <sup>-1</sup> s <sup>-1</sup>	$k_{K} = k_{J}$

Table 4.2: Rate coefficients used in the fitting procedure

(a) The Debye relation for diffusion-controlled charge recombination; Eq. 4.9 in text.

A factor that must be considered in the calculations is the possibility that the rate coefficients are time dependent on the time scale of the measurements. Smoluchowski<sup>16</sup> has shown that the rate coefficient for a diffusion-controlled reaction between two small (spherical) reactants *i* and *j* should be time-dependent according to,

$$k_{ij}(t) = 4\pi R_{ij} D_{ij} \left[ 1 + \frac{R_{ij}}{\sqrt{(\pi D_{ij}t)}} \right]$$
(4.19)

In Eq. 4.19,  $R_{ij}$  is the distance apart at which reaction is considered to occur irreversibly (the "reaction radius") and  $D_{ij} (= D_i + D_j)$  is the sum of the diffusion coefficients of the reactants. From Eq. 4.19 it can be seen that for times much longer than  $R_{ij}^2/\pi D_{ij}$  the time-dependent term becomes negligible and reaction proceeds with the limiting, time-independent rate *constant*,  $k_{ij}$ .

$$k_{ij} = 4\pi R_{ij} D_{ij} \tag{4.20}$$

For the contribution of the time-dependent term to be less than 10%, the following inequality for the time scale on which reaction occurs must be fulfilled.

$$t > \frac{10R_{ij}^2}{\pi D_{ij}} \tag{4.21}$$

For reactions between an ion and a neutral molecule, values of  $R_{ij}$  on the order of 5 Å are found for species with dimensions of a few Ångstroms.<sup>35</sup> The rate coefficients for such reactions can therefore be taken to be constant for times longer than  $8 \times 10^{-15}/D_{ij}$  seconds, for  $D_{ij}$  in units of cm<sup>2</sup>s<sup>-1</sup>. For excess electron reactions in benzene  $D_{ij}$  is dominated by the high electron diffusion coefficient of  $3.3 \times 10^{-3}$  cm<sup>2</sup>s<sup>-1</sup>. The values of  $k_E$  and  $k_G$  may therefore be considered to be time-independent for times in excess of approximately 2 ps, a condition which is amply fulfilled in the present experiments. For reaction F the value of  $D_{ij}$  will be approximately  $5 \times 10^{-5}$  cm<sup>2</sup>s<sup>-1</sup> and the assumption of a constant value of  $k_F$  will therefore be valid for times longer than *ca* 200 ps. Since this reaction is operative on the same time scale as the after-pulse growth of the conductivity, *i.e.* several hundred nanoseconds, the condition in Eq. 4.21 will also be fulfilled for reaction F.

The recombination reactions D, J and K between small charged species have an effective value of  $R_{ij}$  equal to the Onsager radius  $R_C$  (see Eq. 4.4) which is 250 Å for benzene. This results in a time of  $2 \times 10^{-11}/D_{ij}$  seconds above which the time-independent value of the rate coefficient given by the Debye expression (Eq. 4.19) can be assumed to apply. Taking the diffusion coefficients corresponding to the mobilities given in Table 4.1 results in limiting times of 6 ns for reaction D and *ca* 400 ns for reactions J and K. The former limit is considerably shorter than the decay time of electrons in pure benzene and the latter is much shorter than the time scale of many microseconds on which recombination of molecular ions occurs, as indicated by the decay of the conductivity transients in the polymer solutions. The assumption of a constant rate coefficient for the recombination reactions D, J and K, as given by Eq. 4.19, is therefore justified.

### Mobilities and rate coefficients (polymeric species)

As mentioned previously, three parameters have a dominant influence on the temporal form and absolute magnitude of the conductivity transients in the present experiments. These are 1) the rate coefficient for charge transfer from  $Bz^+$  to the polymer,  $k_H$ , which governs the afterpulse growth of the conductivity, 2) the rate coefficient for neutralization of the charged polymer chains by  $O_2^-$ ,  $k_I$ , which governs the eventual decay of the conductivity, and 3) the mobility of positive charge ("holes" or "radical cation sites") along the polymer backbone,  $\mu(h^+/P)$ , which governs the absolute magnitude of the conductivity. All three parameters will depend to a greater or lesser extent on the length and the conformation of the polymer chains in solution. We begin therefore with a discussion of existing information relevant to these properties.

The weight-averaged molecular weight,  $M_w$ , of the MEH-PPV sample used, as determined by GPC using polystyrene standards, was *ca* 600 kDa with a poly-dispersity index of *ca* 3 corresponding therefore to a number-averaged molecular weight,  $M_n$ , of *ca* 200 kDa. The average number of monomer units per chain,  $n = M_n/M_m$  with  $M_m$  the monomer molecular weight (260 g mol<sup>-1</sup>), is therefore approximately 800 with a broad distribution around this number. If anything the value of  $M_w$ , hence  $M_n$  and n may be overestimates because of the more "rigid-rod" character of the PPV backbone compared with that of the polystyrene standards used. The value of  $M_n = 200$  kDa was however consistently used to estimate the concentration of polymer chains in solution based on the known weight per unit volume of MEH-PPV dissolved.

Aggregation of PPV derivatives in solution via  $\pi$ - $\pi$  interactions between different segments of the same chain or between separate polymer chains is a well-known phenomenon, which can lead ultimately to the formation of gels and solid precipitates. Even prior to phase separation, aggregation is usually apparent as a red-shifted shoulder in the

absorption band and a red shift in the fluorescence.<sup>36-38</sup> We have found no evidence for aggregation, in the form of red shifts in the absorption or emission bands, for benzene solutions of MEH-PPV up to the maximum concentration used in the present experiments; *ca* 1 milli-molar in monomer units. Further support for the lack of aggregation has been provided by dynamic light-scattering measurements on *p*-xylene solutions of MEH-PPV which show the hydrodynamic radius of the polymer to be concentration independent up to monomer unit concentrations of 0.4 mM; the maximum investigated.<sup>39</sup> We conclude that the solutions studied in the present work consist of homogeneous suspensions of individual polymer chains free from inter- or intra-chain  $\pi$ - $\pi$  interactions. Evidence that such interactions do ultimately occur at higher concentrations of MEH-PPV in chlorobenzene and tetrahydrofuran solvents has been presented in the form of a red shift in the photoluminescence excitation spectrum and a decrease in the effective hydrodynamic radius.<sup>40</sup> These effects are, however, only significant for concentrations that are an order of magnitude or more higher than the maximum used in the present work.

Because of the relatively large barrier of *ca* 0.2 eV towards rotation out of an all-planar configuration of the phenylene vinylene backbone,<sup>9</sup> PPV derivatives are expected to have properties characteristic of "rigid-rod" type polymers. This is confirmed by the long persistence lengths, from 10 up to more than 60 monomer units, determined by static light-scattering measurements on dilute solutions of dialkoxy-PPV's in *p*-xylene.<sup>39</sup> As a result, individual polymer chains of MEH-PPV, with a (weight-averaged) molecular weight of *ca* 600 kDa, are found to have open structures with relatively large hydrodynamic radii, *R*<sub>H</sub>, of 359 Å, 215 Å and 125 Å in *p*-xylene, chlorobenzene, and tetrahydrofuran respectively.<sup>39,40</sup> These values are to be compared with a radius of only *ca* 40 Å expected for a compact spheroid of  $M_n \approx 200$  kDa and density *ca* 1 g cm<sup>-3</sup>.

Since the molecular weight of the polymer used in the present work is similar to that in the dynamic light scattering studies, we make the reasonable assumption that  $R_H$  will also be similar and close to the value of 359 Å determined in *p*-xylene, an aromatic solvent very similar to benzene.<sup>39</sup> This value of  $R_H$  corresponds to a diffusion coefficient of the polymer chains (via Brownian motion), D(P), of  $1.0 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>, as given by the Stokes-Einstein equation,

$$D(P) = \frac{k_B T}{6\pi\eta R_H} \tag{4.22}$$

with  $k_B$  the Boltzmann constant and  $\eta$  the viscosity of the solvent (0.65 cP for benzene). Assuming the chain conformation and hence the diffusion coefficient to remain unchanged on abstraction of an electron, the mobility of the charged polymer chain as a whole,  $\mu(P^+)$ , can be estimated using Eq. 4.8 to be  $ca 4 \times 10^{-6}$  cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>. This is more than two orders of magnitude lower than  $\mu(Bz^+)$ . Therefore, as mentioned previously, the *increase* in conductivity observed on transfer of charge from Bz<sup>+</sup> to a polymer chain can only be explained by the occurrence of rapid hole migration within the polymer agglomerate.

Because of the very open structure of the polymer chains, as evidenced by the large hydrodynamic radius, and the lack of intrachain aggregation, the migration of holes will occur pseudo-one-dimensionally along the phenylene-vinylene backbone with a diffusion coefficient  $D(h^+/P)$ . The corresponding pseudo-one-dimensional, intrachain hole mobility is related to  $D(h^+/P)$  via the Einstein relation,

$$\mu(h^+ / P) = \frac{eD(h^+ / P)}{k_B T}$$
(4.23)

Since the polymer backbone within an agglomerate as well as the agglomerates themselves will have a random orientation with respect to the electric field vector of the microwaves, the motion of the charge will be vectorially randomized. Therefore, the measured mobility will be an effective, isotropic value. The value of the mobility used in the fitting procedure was therefore taken to be  $\mu(h^+/P)/3$ .



**Figure 4.6**: A short section of a phenylenevinylene polymer modelled as a chain of reactive spherical sinks of reaction radius  $R_M$  and distance between the units a.

The rate coefficient for the reaction of  $Bz^+$  with the polymer,  $k_H$ , should be proportional to the sum of the diffusion coefficients of the reactants, *i.e.*  $[D(Bz^+) + D(P)]$ . However since D(P) is two orders of magnitude smaller than  $D(Bz^+)$ ,  $k_H$  will be given to a good approximation by

$$k_{H} = 4\pi D(Bz^{+})R_{eff} \left[ 1 + \frac{R_{eff}}{\sqrt{\pi D(Bz^{+})t}} \right]$$
(4.24)

The form of Eq. 4.24, including the time-dependent term, has been taken to be the same as that derived for small reactants, Eq. 4.19, with however the "reaction radius",  $R_{ij}$ , replaced by an "effective reaction radius",  $R_{eff}$ . The validity of taking an equation of the form of 4.24 to be generally applicable even for large, non-spherical molecular entities is supported by the

analytical expression derived by Traytak for the case of a linear chain of *n* reactive moieties separated by a distance *a* each with a reaction radius  $R_M$  as separate entities, see Figure 4.6.<sup>17–19</sup> In the Traytak solution  $R_{eff}$  is given by

$$R_{eff} = \frac{nR_M}{1 + \frac{2R_M}{a}\ln n}$$
(4.25)

 $R_{eff}$  is clearly no longer a radius in the true sense of the word but is simply a length parameter.



**Figure 4.7**: Full line: experimental conductivity transient on 10 ns pulsed irradiation of a 1.25  $\mu$ M solution of MEH-PPV in benzene. Dashed lines: calculated kinetic fits in which the main variable is the effective reaction radius,  $R_{eff}$ , in equation (24) for the rate coefficient for charge transfer from Bz<sup>+</sup> to the polymer with  $D(Bz^+) = 3x10^{-5} \text{ cm}^2 \text{s}^{-1}$ .

In Figure 4.7 we show attempted fits to the conductivity transient for a 1.25  $\mu$ M PPV (1x10<sup>-3</sup> mM PV monomer) solution using  $R_{eff}$  values in Eq. 4.24 of 40 Å (close to the radius of a compact sphere of molecular weight 200 kDa), 400 Å (close to the hydrodynamic radius, R<sub>H</sub>), and 1000 Å (considerably larger than R<sub>H</sub>). In all three cases  $D(Bz^+)$  was held constant at  $3x10^{-5}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and  $k_I$  and  $\mu(h^+/P)$  were varied to obtain the best fit to the long time decay and the maximum value of the conductivity. For the three values of  $R_{eff}$  used the best fit values of  $k_I$  and  $\mu(h^+/P)$  were 1.63 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and 3.6x10<sup>11</sup> M<sup>-1</sup>s<sup>-1</sup>, 0.42 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and 1.2x10<sup>11</sup> M<sup>-1</sup>s<sup>-1</sup> respectively.

The fit to the experimental transient in Figure 4.7, in the region of the after-pulse growth, is seen to be considerable better for  $R_{eff} = 400$  Å than for either the smaller or larger values of  $R_{eff}$ . For  $R_{eff} = 400$  Å and  $D = 3 \times 10^{-5}$  cm<sup>2</sup>s<sup>-1</sup>, inequality 4.21 indicates that the time-dependent term in k<sub>H</sub> can only be neglected for times longer than *ca* 2 µs. Since the growth of the conductivity occurs on a timescale much shorter than this, the time-dependence of  $k_H$  plays an important role in the early-time kinetics. The influence of the time-dependent term is illustrated in Figure 4.8 by the transient calculated using  $R_{eff} = 400$  Å but neglecting the time-dependent term.



**Figure 4.8**: Full line: experimental conductivity transient on 10 ns pulsed irradiation of a 1.25  $\mu$ M solution of MEH-PPV in benzene. Dotted and dashed lines: calculated kinetic fits for  $R_{eff}$  = 40 nm and  $D(Bz^{+}) = 3x10^{-5} \text{ cm}^2 \text{s}^{-1}$  with and without the time-dependent term in the rate coefficient for charge transfer from Bz<sup>+</sup> to the polymer, equation (4.24), respectively.

From fits to all of the transients shown in Figures 4.5 and 4.6, we have determined overall "best-fit" values for  $\mu(h^+/P)$  and  $k_I$  of 0.46 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, 1.2x10<sup>11</sup> M<sup>-1</sup>s<sup>-1</sup>, and  $k_H$  given by Eq. 4.24 with  $D(Bz^+) = 3x10^{-5}$  cm<sup>2</sup>s<sup>-1</sup> and R<sub>eff</sub> = 360 Å. The calculated curves shown in Figures 4.5 and 4.6 were obtained using these fixed values. The agreement with the experimental transients is seen to be reasonably good except for the highest dose pulse.

The value of  $R_{eff} = 360$  Å for charge transfer from Bz<sup>+</sup> to MEH-PPV chains is very much larger than the 5 to 10 Å usually found for electron transfer reactions involving relatively small molecular species. This is not particularly surprising since each of the *ca*. 800 phenylene vinylene units comprising a polymer chain may be considered to be a potential reactive site. As mentioned above, an analytical solution for the rate coefficient for the reaction of a small reactant with a linear chain of *n* reactive moieties of individual reaction radius  $R_M$  and center-to-center separation distance *a* has been derived by Traytak.<sup>17-19</sup> The corresponding effective reaction radius for such a linear array is given by Eq. 4.25. Since  $R_M$  is expected to be similar in magnitude to half of the length of a PV unit (*a*/2), Eq. 4.25 can be approximated for large *n* by

$$R_{eff} \approx \frac{na}{2\ln n} \tag{4.26}$$

Substituting in Eq. 4.26 a = 6.7 Å (the actual length of a phenylene vinylene unit) and n = 800, (determined by GPC and used in the fitting procedure,  $R_{eff}$  is estimated to be 401 Å, *i.e.* close to the value of 360 Å found. As Eq. 4.26 shows, for large n the value of  $R_{eff}$  is (relatively) insensitive to the value taken for  $R_M$ . Using the full expression for  $R_{eff}$ , Eq. 4.25, with  $R_M$  values of a (6.7 Å) and a/2 (3.35 Å) results in  $R_{eff}$  values of 373 Å and 349 Å respectively, which are even closer to the experimentally determined value. While a straight, linear array of reactive centers is without doubt an unrealistic representation of the much more complex three-dimensional structure of an MEH-PPV chain in solution, it does appear to provide a good description of the reaction kinetics using known quantities.

For comparison, we consider the effective reaction radius for a three-dimensional, cubic array of the reactive sinks with, as before, an individual reaction radius  $R_M$  and a center-to-center distance *a* between sinks. The solution derived by Traytak is, <sup>17</sup>

$$R_{eff} = \frac{nR_{M}}{1 + \frac{2CR_{M}n^{(1-1/d)}}{a}}$$
(4.27)

with C a constant and d (= 3) the dimensionality. The large n approximation of Eq. 4.27 is

$$R_{eff} \approx \frac{na}{2Cn^{(1-1/d)}} \tag{4.28}$$

Tseng *et al.*<sup>41</sup> have considered the "touching spheres" case, *i.e.*  $2R_m = a$ , and have derived a value of C = 0.80 for diffusion-limited reaction with a cubic lattice. Taking n = 800 and a = 6.7 Å, which corresponds to a highly compact, globular structure, yields a value of  $R_{eff} = 39$  Å. Using the full expression (Eq. 4.27) with  $R_M$  values of 3.35 Å and 6.7 Å results in no significant change in the value of  $R_{eff}$  calculated. Clearly, a highly compact structure is not capable of describing the reaction kinetics observed, as shown by the attempted fit using  $R_{eff} = 40$  Å in Figure 4.7. This is not unexpected in view of the large value found for the hydrodynamic radius which indicates the polymer agglomerates to have very open structures encompassing a volume several hundred times that expected for a compact sphere.

An open, three-dimensional structure can be simulated by allowing the cubic lattice parameter *a* in Eq. 4.27 and Eq. 4.28 to increase to values significantly larger than the individual reaction radius, *i.e.*  $a \gg 2R_M$ . The value of *a* required to explain a given value of the effective reaction radius can then be determined from

$$a \approx \frac{2Cn^{(1-1/d)}R_{eff}}{n} \tag{4.29}$$

For n = 800, a value of a = 62 Å is required to explain the value of 360 Å found for  $R_{eff}$ . Therefore the average distance between reactive sinks needs be approximately 10 times the distance between PV units along a polymer backbone in order to explain the kinetics observed.

For a>>2 $R_M$  and large *n*, the length of a side of the cubic array, *L*, will be

$$L \approx a \Big[ n^{1/3} - 1 \Big] \tag{4.30}$$

For the above value of a = 62 Å, L is therefore 512 Å. The radius of a sphere with the same volume would be 318 Å which is quite close to the value of 359 Å found for the hydrodynamic radius determined by light scattering. That there should be a close, quantitative relationship between the kinetic and hydrodynamic parameters of molecular clusters has previously been suggested by Tseng *et al.*<sup>21,41</sup>

Clearly, neither the simple linear chain nor the expanded cubic lattice are realistic representations of the actual MEH-PPV polymer chain conformation in dilute solution. The present kinetic results do however serve to confirm the conclusions from the light scattering results of a very open structure with extensive, close-to-linear backbone segments. In this regard it is worth pointing out that even the "best" PPV polymers invariably contain a few percent of chemical defects in the form of saturated (sp<sub>3</sub>) and dehydrogenated (sp<sub>1</sub>) vinylene moieties. Even a small percentage of such defects could have a controlling influence on the overall structure of a polymer agglomerate since they allow much more ready bending and twisting than the phenylene vinylene backbone itself.<sup>42,43</sup>

Finally we consider the value of the rate constant for charge recombination,  $k_I$ , which was taken to be time-independent on the basis of an expected reaction radius of 250 Å (R<sub>c</sub> in benzene) and  $[D(O_2^-) + D(P^+)] = 2.5 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ . The time-dependent term in the recombination coefficient, according to Eq. 4.21, should therefore be negligible for times longer than *ca* 1 µs. From the time scales of the transient decays, this condition is seen to be fulfilled for all but the highest dose pulse. The value of  $k_I = 1.2 \times 10^{11} \text{ M}^{-1} \text{s}^{-1}$  found is considerably smaller than the value of  $4.7 \times 10^{11} \text{ M}^{-1} \text{s}^{-1}$  expected on the basis of  $k_I = 4\pi R_c [D(O_2^-) + D(P^+)]$ . The fact that the Debije relation does not provide a good estimate of  $k_I$  for this particular reaction is perhaps not surprising in view of the fact that the hydrodynamic radius of the polymer is in fact significantly larger than the Onsager escape distance; 360 Å versus 250 Å. The lower value of  $k_I$  could therefore be due to a substantially lower diffusion coefficient of  $O_2^-$  within the polymer agglomerate than in bulk benzene or to a lower effective reaction radius resulting from the one-dimensionally confined and possibly highly delocalized nature of the positive charge.

### 4.4 Summary and conclusions

In this paper we measure and discuss the kinetics of formation and decay of positively charged MEH-PPV polymer chains in pulse-irradiated benzene solutions. The progress of the reactions was monitored continuously as the change in the microwave conductivity of the solution over a time scale from nanoseconds to milliseconds using a single pulse. The kinetics of formation of MEH-PPV<sup>+</sup> by charge transfer from benzene radical cations occurs with an extremely large effective reaction radius,  $R_{eff}$ , of close to 400 Å. Because of this the time-dependent term in the rate coefficient must be taken into account in the fitting procedure. The value of  $R_{eff}$  is in agreement with theoretical expectations for a linear chain of reactive sites of length equal to one phenylene vinylene unit. Comparison with predictions for a hypothetical three-dimensional cubic lattice arrangement of the PV units, indicates the polymer agglomerates to have a very open, gel-like structure in agreement with the large hydrodynamic radius found in previous light scattering measurements.

From the dependence of the decay kinetics of the conductivity on the initially generated ion concentration we conclude that MEH-PPV<sup>+</sup> decays with a rate constant of  $1.2 \times 10^{11}$  M<sup>-1</sup>s<sup>-1</sup> by second order recombination with O<sub>2</sub><sup>-</sup> ions formed by electron attachment to oxygen. This rate constant is a factor of approximately 4 lower than expected for recombination according to the Debye equation which is most probably related to the fact that the hydrodynamic radius of the agglomerates (360 Å) is in fact considerably larger than the Onsager distance in benzene (250 Å). No indication was found for a first order component in the decay of the conductivity. Trapping of positive charge on the polymer chains (at chemical defect sites for example) does not appear to occur within a time scale of several hundred microseconds at least.

The good agreement between the calculated and experimental conductivity transients for a range of polymer and initial charge carrier concentrations enables us to obtain an accurate value of 0.46 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the pseudo-one-dimensional mobility of positive charge along isolated MEH-PPV chains in dilute solution.

### 4.5 References

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## Positive Charge Carriers on Isolated Chains of

## MEH-PPV with Broken Conjugation<sup>\*</sup>

### **Optical Absorption and Mobility**

Pulse radiolysis of oxygen-saturated dilute solutions of poly[2-methoxy-5-(2'ethylhexyloxy)-1,4-phenylene vinylene]s in benzene showed charge-transfer from the solvent radical-cation to the polymer, yielding positive charge carriers (radical-cations or "holes") on the isolated chains. The radical-cation of the fully conjugated polymer exhibited an absorption maximum at 1.32 eV. The absorption maximum shifted to higher energies with decreasing conjugated fraction, in a way consistent with thermal equilibration of the positive charge over the conjugated segments of different length. The mobility of the positive charge along the fully conjugated MEH-PPV chains was determined to be 0.46 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The introduction of conjugation breaks decreased the charge mobility strongly, which is attributed to the disruption of the  $\pi$ -conjugation and/or the conformational disorder caused by the flexibility of the chains at the sites of conjugation breaks.

### **5.1 Introduction**

Poly(phenylene vinylene)s are a class of luminescent, conjugated polymers with potential applications in organic electro-optical devices.<sup>1-3</sup> The investigation of the properties of the charge carriers on the polymer chains is not only of practical relevance, but has also raised interesting, fundamental questions, such as how the optical absorption and charge-transport properties of a chain depend on the conjugation length and backbone flexibility.

Recently, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene]s have been synthesized in which a controlled fraction of the vinylene groups have been saturated, generating soluble polymer chains with a conjugated fraction x MEH-PPV-(x) (Figure 5.1).<sup>4</sup>

<sup>&</sup>lt;sup>\*</sup> This chapter is based on: L.P. Candeias, F.C. Grozema, G. Padmanaban, S. Ramakrishnan, L.D.A. Siebbeles, J.M. Warman, *J. Phys. Chem. B*, **107** (2003), 1554-1558.

The saturated C–C bonds decrease the conjugation length, block triplet energy transfer along the polymer chains<sup>5</sup> and increase the chain flexibility.



**Figure 5.1**: Molecular structures of the broken conjugation MEH-PPV polymers with conjugated fraction *x*.

In this chapter we discuss the effect of these conjugation breaks on the optical properties and mobility of the positive charge carriers on isolated chains of MEH-PPV-(x) in dilute solution. The method used was pulse radiolysis with two detection techniques: time-resolved UV/VIS/NIR spectroscopy and time-resolved microwave conductivity (TRMC).<sup>5-8</sup> Pulses of high-energy electrons were used to generate charge carriers and the optical properties, kinetics of formation and decay, and mobility of the charge carriers were investigated.

### 5.2 Experimental details

The polymers MEH-PPV-(x) used for the present experiments had conjugated fractions x between 0.2 and 1. It should be noted that due to chemical damage during synthesis and handling the "fully conjugated" polymer may contain up to 2 % of conjugation breaks (x  $\geq$  0.98). The molecular weight of the polymers was 220 – 260 kDa, corresponding to ca. 1000 monomer units per chain.<sup>4</sup> Dilute solutions (typically 0.2 to 1 mM) of MEH-PPV-(x) in UV-spectroscopic grade benzene were freshly prepared before each experiment and were bubbled with benzene-saturated oxygen for at least 10 minutes. All experiments were performed at room temperature.

The pulse radiolysis methods using time-resolved microwave conductivity (TRMC) or transient optical absorption detection were essentially as described in chapter 4. In these techniques, the samples are irradiated with pulses of high-energy electrons, which generate charged- and excited-states. The amount of these species is proportional to the radiation dose deposited in the sample, usually expressed in gray (1 Gy = 1 J kg<sup>-1</sup>). The ratio between the concentration of the primary species and the absorbed dose is the radiation-chemical yield, expressed in mol  $J^{-1}$  (or in number of ions or excited-states per 100 eV). Radiation-chemical yields for a variety of systems have been measured.

A Van de Graaff accelerator is used to generate 0.2 - 50 ns pulses of 3 MeV electrons. The solutions were flowed through the quartz cell (optical path 1.2 cm) by a slight overpressure of benzene-saturated oxygen. The source of detection light was a pulsed highpressure Xe-lamp (450 W). Cut-off filters and a fast shutter were used to minimize photolysis of the solution by the detection light. NIR detection was achieved with a short-wavelength enhanced InGaAs photodiode (Hamamatsu, Japan). The transients were recorded by a Tektronix TDS680 digitizer.

For the TRMC measurements, the solutions were contained in a gold-coated Q-band microwave cell. They were first degassed by freeze-pump-thaw cycles on a vacuum line and then saturated with oxygen and sealed. The dose per pulse was varied between 4 Gy and 40 Gy. The transients were recorded on a logarithmic time-scale using a Tektronix RTD 710 digitizer. A detailed description of the experimental equipment is given in chapter 4.



**Figure 5.2**: Formation of MEH-PPV-(x)<sup>•</sup><sup>+</sup>, monitored by the dosenormalized optical absorption at the maximum, for polymer concentration 10<sup>-6</sup> M and dose per pulse 20 Gy. The smooth lines are fits using a time-dependent rate coefficient as described in chapter 4.

#### 5.3 Results and Discussion

### Absorption spectra of MEH-PPV-(x) radical-cations

Irradiation of benzene (Bz) generates radical-cations (Bz<sup>+</sup>), excited states (Bz<sup>\*</sup>), and excess electrons  $(e_{Bz}^{-})$  (Eq 5.1).<sup>9,10</sup>

$$Bz \quad \sim \sim \sim \gg \quad Bz^+, Bz^*, e_{Bz}^- \tag{5.1}$$

In pure benzene, these primary radiolysis products react with each other, or with parent benzene. However, in the presence of other molecules and at low radiation doses, reaction of the primary products with those molecules prevails. For example, in oxygen-saturated benzene ( $[O_2] = 11.9$  mM at 1 atm and 25 °C), the excited states and the excess electrons are rapidly scavenged within a few nanoseconds (Eqs. 5.2 and 5.3, see also chapter 4),<sup>11</sup> while the benzene radical-cations are not affected.

$$Bz^* + O_2 \longrightarrow Bz^{+1}O_2$$
(5.2)

$$e_{B_z}^- + O_2 \longrightarrow O_2^-$$
 (5.3)

Pulse radiolysis of MEH-PPV-(x) solutions in oxygen-saturated benzene resulted in absorptions in the range 0.9 - 2.2 eV which grew in after the pulse on a time-scale of microseconds (Figure 5.2). The growth rate increased with increasing polymer concentration. In an experiment with the fully conjugated polymer MEH-PPV-(1), a concomitant decrease of absorbance in the same time-domain was observed at 2.5 eV (500 nm), where the polymer absorbs.



**Figure 5.3**: Transient absorption at 1.3 eV measured by pulse radiolysis of solutions of fully conjugated MEH-PPV in O<sub>2</sub> saturated benzene after 20 Gy pulses. The polymer concentration, from the lowest to the highest curve, were:  $2 \times 10^{-7}$  M,  $4 \times 10^{-7}$  M,  $6 \times 10^{-7}$  M and  $1 \times 10^{-6}$  M. The smooth lines are numerical fits based on the reaction mechanism described in the text.

These results show that the absorbance changes are due to the reaction of a primary species produced in benzene (Eq 5.1) with MEH-PPV-(x). On the basis of these results, and considering the scavenging effect of oxygen on the excited states and excess electrons (Eq. 5.2 and 5.3), the absorbance changes are attributed to the transfer of positive charge from the benzene radical-cations to MEH-PPV-(x), yielding polymer radical-cations, MEH-PPV-(x)<sup>+</sup> (Eq 5.4).

$$Bz^+$$
 + MEH-PPV-(x)  $\longrightarrow Bz$  + MEH-PPV-(x)<sup>+</sup> (5.4)

To verify this assignment, similar experiments were performed with solutions containing triethylamine (0.07 M), a well-known radical-cation scavenger. Under these conditions, the absorbance changes were suppressed, showing that they were due to the formation of MEH-PPV- $(x)^+$ . Additional evidence was provided by the TRMC experiments (see below), which show the production of mobile, charged species with the same growth kinetics as the optical absorption (Figures 5.3 and 5.4).



**Figure 5.4**: Dose-normalized transient conductivity observed on pulse radiolysis of solutions of MEH-PPV-(*x*)  $(10^{-6} \text{ M})$  in O<sub>2</sub>-saturated benzene, after pulses of 20 Gy. The transients for *x* = 0.85 and *x* = 0.7 have been multiplied by a factor of five.

The absorption spectra of MEH-PPV-(x)<sup>+</sup> were obtained by measuring the transient changes of absorbance at different photon energies (Figure 5.5). The energies of the absorption maxima (Table 5.1) showed a systematic blue shift with decreasing conjugated fraction. For the fully conjugated polymer the spectrum of the radical-cation was the same as that previously obtained in chloroform solution.<sup>12</sup> The radical-cation absorptions at energies lower than that of the neutral molecule have been attributed to transitions involving two polaronic states, POL1 and POL2, lying in the gap between the valence band and the conduction band (see Fig 5.6, a more detailed theoretical discussion of the optical properties of phenylenevinylene cations can be found in chapter 8).<sup>13</sup> According to this interpretation, the absorption band observed here with DE = 1.3 eV corresponds (mainly) to the POL1 $\rightarrow$ POL2 transition. Two other absorption bands are predicted, one overlapping the parent absorption at ca. 2.5 eV, and another at ca. 0.6 eV [= (2.5 - 1.3) / 2], which is outside the detection range of our equipment. The fact that a decrease of absorption was observed at 2.5 eV indicates that the extinction coefficient of the



**Figure 5.5**: Absorption spectra of the MEH-PPV-(x) radical-cations (conjugated fraction x given in the figure).



**Figure 5.6**: Energy levels of MEH-PPV<sup>+</sup> in the approximate band formalism. POL1, POL2: polaron levels. Allowed transitions and their energies are shown. (The short arrow indicates the unpaired electron on POL1.)

radical-cation for this transition is less than for the band-gap transition in the neutral molecule (ca.  $1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ).

x	$\Delta E_{\max}$ (eV) <sup>a</sup>	ε (10 <sup>5</sup> M <sup>-1</sup> cm <sup>-1</sup> ) <sup>b</sup>	μ⁺ <sub>1D</sub> (cm²/Vs) °
0.2	1.60	0.18	_
0.45	1.47	0.55	< 0.005
0.7	1.44	0.63	≈ 0.01
0.85	1.40	0.66	0.04
1	1.32	0.92	0.46

**Table 5.1**: Absorption maximum ( $\Delta E_{max}$ ), extinction coefficient ( $\epsilon$ ), and charge mobility ( $\mu^{+}_{1D}$ ) of the MEH-PPV-(*x*) radical-cations.

a ± 0.01 eV

 $b \pm 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ 

c from the fitting procedure described in the text; uncertainty  $ca.\ 20\ \%.$ 

The absorption maxima of the radical-cations of oligomers of phenylene vinylene have been found to shift to higher energies with decreasing chain length.<sup>14</sup> This chain length effect can partially explain the observed shift of the absorption maximum of MEH-PPV- $(x)^+$  to higher energies with decreasing x. These polymers consist of a distribution of conjugated segments of n consecutive phenylene vinylene (PV) units, separated by broken conjugation sites (phenylene ethylidine units). As discussed in the following paragraphs, the distribution of the excess positive charge over the conjugated segments can be derived from statistical, kinetic and thermodynamic arguments. On the basis of this distribution, and the reported absorption spectra of PV oligomers,<sup>14</sup> the absorption maxima of MEH-PPV- $(x)^+$  can be predicted and compared with the experimentally measured values.



**Figure 5.7:** Distribution of positive charges over conjugated segments of length *n* calculated by a: the mass-weighted distribution W(n,x), and b: Boltzmann distribution U(n,x). Panel c shows the energy of the maxima of the optical absorption obtained from W(n,x) (open squares), from U(n,x) (open triangles), and measured experimentally (solid circles).

The probability P(n,x) of finding a segment of *n* consecutive PV units in a polymer of conjugated fraction x is given by Eq. 5.5.

$$P(n,x) = (1-x)x^{n}$$
(5.5)

Assuming that the diffusion-controlled charge-transfer from  $bz^+$  to the polymer chain results in charges located with equal probability on conjugated and non-conjugated sites, the distribution of charge over conjugated segments of length *n* is proportional to the mass fraction of these segments W(n,x) (Eq 5.6).

$$W(n,x) = (n+1)(1-x)^2 x^n$$
(5.6)

The most probable conjugation lengths n, i.e. the maxima of W(n,x), for x = 0.85, x = 0.7, and  $x \le 0.45$  are 5, 2, and 0, respectively (Fig 5.7a). (Conjugation length 0 corresponds to the saturation of consecutive vinylene groups.) The radical-cations of the PV oligomers of this length have absorption maxima at energies higher than experimentally measured (Fig. 5.7c). Alternatively, it may be assumed that the excess-charge rapidly reaches thermodynamic equilibrium. In this case the energy-weighted charge distribution U(n,x) is given by a Boltzmann distribution (Eq. 5.7 and Figure 5.7b).

$$U(n,x) = \frac{P(n,x)\exp\left(\frac{-E_n}{RT}\right)}{\sum_{n} P(n,x)\exp\left(\frac{-E_n}{RT}\right)}$$
(5.7)

In Eq. 5.7,  $E_n$  is the energy of the charge on a segment of conjugated length *n*; the experimentally determined reduction potentials of the radical-cations of PV oligomers are a measure of  $E_n$ .<sup>14</sup> (For n = 0, we used the reduction potential of the 1,4-dimethoxybenzene radical-cation  $E_0 = 1.34$  V vs. SCE.) This method predicts absorption maxima of MEH-PPV-(x)<sup>+</sup> with a shallow dependence on the conjugated fraction, in agreement with the experimental observation (Fig 5.7c). This suggests that the excess-charge is indeed thermodynamically equilibrated over the conjugated segments of different length and that the time-scale for this equilibration is shorter than the time for the formation of charge-transfer from Bz<sup>+</sup> under the conditions of our experiments ( $\leq 3$  ms).

#### Kinetics of formation and decay of MEH-PPV-x radical-cations

The kinetics of formation of MEH-PPV- $(1)^+$  were monitored by transient absorbance at 1.3 eV, and by TRMC experiments as discussed in chapter 4. The two techniques give the same kinetics of formation and decay of MEH-PPV radical cations, as evident from Figure 2.9. Numerical fits were made to the time-dependent absorbance at 1.3 eV measured experimentally with the fully conjugated polymer (Fig 5.3). The details of this procedure are described in chapter 4.

The same numerical procedure was applied to fit the formation of the broken conjugation radical-cations. The extinction coefficients of the radical cations at the maxima obtained from the fitting procedure are listed in Table 5.1. They show a systematic decrease with the decreasing degree of conjugation. This observation can in part be explained by the distribution of charges over conjugated segments of different lengths discussed in the previous section. The fraction of charges localized on short conjugated segments increases with decreasing x; these charges have their absorption at high energies (VIS and UV) and do not contribute to the NIR absorption.

### Mobility of the positive charge on MEH-PPV-(x) chains

In order to investigate the mobility of the positive charge along the broken conjugation chains, experiments with the MEH-PPV-(x) solutions were carried out using time-resolved microwave conductivity (TRMC). For the polymers with the highest conjugated fractions (x  $\geq$  0.7) an increase of conductivity following the pulse was observed, followed by a decay (Figure 5.4), with the same kinetics as the formation and decay of MEH-PPV-(x)<sup>+</sup> under the same conditions of concentration and dose, as monitored by transient optical absorption. The conductivity increase shows that the transfer of the positive charge to the polymer chains on reaction of Bz<sup>+</sup> with MEH-PPV-(x) results in an increase of the mobility, i.e. the positive charge mobility along the polymer chains is higher than that of Bz<sup>+</sup> itself. The one-dimensional mobility of the positive charges along the polymer chains  $\mu_{1D}^+$  (in cm<sup>2</sup>/Vs) is related to the transient conductivity  $\Delta \sigma$  (in Scm<sup>-1</sup>) by Eq. 5.8, where *e* is the elementary charge (1.6 x 10<sup>-19</sup> C), and  $N_{\text{MEH-PPV+}}$  is the concentration of charge carriers on MEH-PPV chains (in charges/cm<sup>3</sup>). The factor 1/3 converts the measured conductivity in randomly oriented polymer chains to the one-dimensional mobility.

$$\Delta \sigma = \frac{1}{3} e \mu_{\rm 1D}^* N_{\rm MEH-PPV^+} \tag{5.8}$$

Using this equation,  $\mu_{1D}^+$  can be calculated from the time-dependent MEH-PPV-(x)<sup>+</sup> concentration obtained from the kinetic fits to the transient absorption results described above. The values obtained (Table 5.1) show that conjugation breaks strongly decrease the mobility of the positive charge. A similar effect was previously observed in solid samples of related poly(phenylene vinylene)s.<sup>21,22</sup> Both electronic and steric reasons may lie behind the decrease of mobility with decreasing *x*: the saturated C–C bonds not only interrupt the  $\pi$ -conjugation but their torsional freedom also introduces conformational disorder that decreases the charge mobility.

The high "hole" mobility measured for the fully conjugated polymer ( $\mu_{1D}^{+} = 0.46$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) demonstrates the remarkable conducting properties of the polymer chains. Previously, the sum of the mobilities of the positive and negative charges in a solid sample of MEH-PPV was measured by pulse radiolysis-TRMC, and a much lower value (ca.  $10^{-3}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) was obtained.<sup>21</sup> The comparison of these results suggests that in the bulk solid the polymer chains are forced into conformations that are detrimental to charge migration. The positive charge mobility value obtained by current-voltage measurements on PPV-based devices is even lower (ca.  $10^{-7}$  to  $10^{-5}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>).<sup>19,22,23</sup> In this case, inter-chain charge transfer and the necessity for charge-transfer across domain boundaries appear to have a further detrimental effect on charge transport through the bulk solid.

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## Hole Conduction Along Molecular Wires<sup>\*</sup>

 $\sigma$ -bonded Silicon Versus  $\pi$ -Bond-Conjugated Carbon

### **6.1 Introduction**

According to Moore's Law<sup>1</sup>, by the year 2020 the dimensions of integrated circuit components will have been reduced to approximately 10 nanometers. The interconnecting wires within such circuits will by then have approached the ultimate limit; that of a linear array of single atoms. Potential candidates for such semiconductive "molecular wires" are  $\sigma$ -bonded chains of silicon and  $\pi$ -bond-conjugated chains of carbon. In recent years, readily soluble, high molecular weight polymeric chains of both types have been synthesised. This has made it possible to study their optoelectronic properties in isolation, free from the interchain interactions and morphological complexities which dominate their electronic properties in the bulk solid phase. Here we show that mobilities well in excess of 0.1 cm<sup>2</sup>/Vs are possible for hole transport along isolated chains of both  $\sigma$ -bonded silicon and  $\pi$ -bond-conjugated carbon. In both cases disorder within the backbone plays a decisive role in determining the magnitude of the mobility and we conclude that values in excess of 1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> should be realisable, even at room temperature, if the disorder can be reduced by either chemical or physical means.

### **6.2 Experimental details**

Oxygen saturated, dilute benzene solutions (corresponding to *ca* 1 mM monomer units) of the polymers shown in Figure 6.1 were contained in a microwave cell of internal dimensions  $3.5x7.1x24 \text{ mm}^3$ . The solutions were irradiated with 5 or 10 ns pulses of 3 MeV electrons from a Van de Graaff accelerator with a total absorbed dose per pulse, D, of approximately  $1x10^4 \text{ J/m}^3$  which was accurately measured for each experiment. This resulted initially in the formation of a uniform concentration of *ca* 0.1  $\mu$ M of excess electrons and benzene radical cations. The resulting change in the conductivity of the solution was measured as the change

<sup>&</sup>lt;sup>\*</sup> This chapter is based on: F.C. Grozema, L.D.A. Siebbeles, J.M. Warman, S. Seki, S. Tagawa, U. Scherf, *Adv. Mater*, **14** (2002), 228-231.

in the power of microwaves (26-38 GHz) reflected by the cell. Using only a single pulse the radiation-induced conductivity could be monitored from 10 ns to 1 ms using a pseudo-logarithmic time-base. The experimental methodology and data reduction procedures have been described in detail in chapters 2 and  $4^{2,3}$ .



**Figure 6.1**: The molecular structures of the polymers investigated in the present work together with their pseudonyms (left) and onedimensional, intra-chain hole mobilities (right) determined from the experimental data shown in Figure 6.2.

### 6.3 Results and discussion

The molecular structures of the polymers studied are shown in Figure 6.1. All had molecular weights in excess of 10 kDa and consisted of chains of approximately 100 or more monomer units. They could be readily dissolved in benzene with no evidence of aggregation for the conditions used (monomer-unit concentration ca 1 mM at room temperature). The solutions were saturated with oxygen prior to irradiation with single nanosecond pulses of 3 MeV electrons from a Van de Graaff accelerator.

Irradiation produces initially a close to uniform concentration of benzene radical cations,  $Bz^+$ , and excess electrons, e<sup>-</sup>. The latter are highly mobile ( $\mu(e^-) = 0.13 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ )<sup>4</sup> and react within a nanosecond with the dissolved oxygen to form  $O_2^-$ . The  $Bz^+$  ions are unaffected by  $O_2$  and can diffuse to polymer chains where they undergo charge transfer to the lower ionization potential polymer resulting in the formation of a "radical cation site" or "hole" on the polymer backbone.

$$Bz^{+} + P \qquad \xrightarrow{k_{CT}} \qquad Bz + P^{+} \qquad (6.1)$$

If the mobility of the positive charge on the polymer chain is larger than the mobility of  $Bz^+$  in the solution ( $\mu(Bz^+) = 0.4x10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1})^5$  then the conductivity of the solution should initially increase after the pulse as reaction (6.1) proceeds.

The change in the conductivity of a solution on pulsed irradiation was monitored using the time-resolved microwave conductivity technique (TRMC) at a frequency of *ca* 30 GHz. This ultra-high frequency method of measuring conductivity changes has been described fully elsewhere<sup>2,3</sup> and its application to the determination of the electron and hole mobilities on isolated chains of MEH-PPV has been previously reported.<sup>6</sup> By using a transient digitizer with a pseudo-logarithmic time-base the radiation-induced conductivity could be monitored from *ca* 10 ns to *ca* 1 ms after a single pulse. Examples of the conductivity transients observed are shown in Figure 2. For a given solution no change in the magnitude or form of the conductivity transient was observed for the total accumulated dose used in a series of measurements (*ca* 1MJ m<sup>-3</sup>).

For most of the polymer solutions an increase in conductivity over the first several hundred nanoseconds after the pulse was observed as shown in Figure 6.2. As mentioned above, this provides immediate, qualitative evidence that the mobility of holes on the polymer chains is indeed considerably larger than the value of  $0.4 \times 10^{-3}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the initially formed Bz<sup>+</sup> ions.

The initial increase in conductivity is seen to be followed by an eventual decrease for times in the region of tens to hundreds of microseconds. The timescale of this decay has been found to decrease with increasing dose in the pulse, *i.e.* increasing concentration of ion pairs. It is accordingly attributed to the second order charge recombination of  $P^+$  with  $O_2^-$ .

$$P^+ + O_2^- \longrightarrow P + O_2$$
 (6.2)

No evidence has been found for a first order component in the decay kinetics, from which we conclude that trapping of holes on the polymer chains does not occur; at least not on a sub-millisecond timescale.

The conductivity at a given time after the pulse is given by

$$\Delta \sigma(t) = e \sum_{i} N_i(t) \mu_i \tag{6.3}$$

with,  $N_i(t)$  and  $\mu_i$  the concentration and mobility of the *i*-th charged species present and e the elementary charge. Quantitative fits to the experimental data have been made by numerically solving the differential rate equations for the concentrations of Bz<sup>+</sup>, O<sub>2</sub><sup>-</sup> and P<sup>+</sup>. The initial concentration of free ion pairs formed in the pulse,  $N_{fp}$ , is calculated from the energy deposited per unit volume in the solution, D (J m<sup>-3</sup>), and the average energy required to form



**Figure 6.2**: Dose-normalised changes in the microwave conductivity on pulse-radiolysis of dilute, oxygen-saturated benzene solutions of the polymers shown in Figure 6.1; upper,  $\pi$ -bond conjugated-carbon polymers; lower,  $\sigma$ -bonded silicon polymers. In all cases the monomer-unit concentration was close to 1 mM. The transients were obtained using single 5 or 10 ns pulses and were monitored, from 10 ns to 1 ms using a transient-digitizer with a pseudo-logarithmic time-base. The smooth full lines drawn through the data for MEH-PPV and PAPS6 are examples of calculated fits from which the hole mobility was determined.

one Bz<sup>+</sup>/e<sup>-</sup> pair,  $E_{fp}$ . The former parameter is known to within 5% from dosimetry and by routine monitoring of the beam charge per pulse. The value of  $E_{fp}$  for benzene is also well-known with two different groups<sup>7,8</sup> reporting the same value of 1900 eV. Since the mobilities of Bz<sup>+</sup> and O<sub>2</sub><sup>-</sup> (0.8x10<sup>-3</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>)<sup>9</sup> are known, only three adjustable parameters remain in the fitting procedure: the rate coefficients for reactions (1) and (2),  $k_{CT}$  and  $k_{CR}$  respectively,

and the hole mobility,  $\mu(h_p^+)$ . The last parameter is defined as the one-dimensional mobility along the polymer backbone. To take into account the random orientation of the polymer chains in solution a value of  $\mu(h_p^+)/3$  is used in the calculations. The three parameters were varied to give best fits to the shape and the magnitude of the conductivity transients. Examples of such fits are shown for MEH-PPV and PAPS6 in Fig. 6.2. The values of  $\mu(h_p^+)$ ,  $k_{CT}$  and  $k_{CR}$  derived from the fits are listed in Table 6.1. In the case of  $k_{CT}$  account was taken of the time-dependence of the rate coefficient at short times using the expression of Smoluchowski,<sup>10,11</sup> i.e.

$$k(t) = 4\pi R D \left[ 1 + \frac{R}{\sqrt{(\pi D t)}} \right]$$
(6.4)

with the value of D taken to be given by the Einstein expression,

$$D = \frac{\mu(Bz^{+})e}{k_{B}T} = 1.0 \times 10^{-5} \,\mathrm{cm}^{2}/\mathrm{Vs}$$
(6.5)

The value of  $k_{CT}$  given in the table is the long-time limit,  $4\pi RD$ , and is based on the concentration of monomer units of the polymer.

Polymer <sup>a</sup>	$\mu(h_p^+)$ , cm <sup>2</sup> /Vs	$k_{CT}^{b}$ , $M^{-1}s^{-1}$	<i>k<sub>CR</sub></i> , M <sup>-1</sup> s <sup>-1</sup>
DEH-PF	0.74	1.3·10 <sup>9</sup>	3.9·10 <sup>11</sup>
MEH-PPV	0.46	5.8·10 <sup>8</sup>	1.2·10 <sup>11</sup>
MeLPPP	0.16	2.7·10 <sup>9</sup>	1.5·10 <sup>11</sup>
P3HT	0.02	1.7·10 <sup>9</sup>	1.5·10 <sup>11</sup>
PAPS2	<0.01	-	-
PAPS4	0.03	7.5·10 <sup>8</sup>	1.5·10 <sup>11</sup>
PAPS6	0.23	7.5·10 <sup>8</sup>	1.5·10 <sup>11</sup>
PAPS8	0.17	9.8·10 <sup>8</sup>	1.0·10 <sup>11</sup>

**Table 6.1**: The rate coefficients for reactions (6.1) and (6.2) required to fit the temporal shape of the conductivity transients in Figure 6.2 and the hole mobility  $\mu(h_p^{+})$ , required to fit the absolute magnitude of the conductivity.

<sup>a</sup> see Fig. 1 for molecular structure

<sup>b</sup> the long time limit based on the monomer unit concentration

We emphasise that the temporal dependence of a conductivity transient (the shape) is determined mainly by the two rate coefficients and the absolute magnitude mainly by the value of  $\mu(h_p^+)$ . Furthermore, since the timescales of the growth and decay differ considerably, all three parameters can be separately determined. It is also worth pointing out that the concentration of charge carriers formed per pulse is only approximately  $1 \times 10^{-7}$  M which is more than an order of magnitude lower than the polymer chain concentration in all cases. The occurrence of multiple ionization of an individual chain should therefore be negligible. A more detailed account of the fitting procedure, including the values of  $k_{CT}$  and  $k_{CR}$  derived, will be given in a subsequent publication. Suffice to say that the rate coefficients derived were close to values which would be expected for diffusion controlled reactions.

The values of  $\mu(h_p^+)$  determined are given in Figure 6.1. The error is estimated to be  $\pm$  10% or  $\pm$  0.01 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> whichever is the larger. As can be seen the values cover a wide range for both types of polymer. While there is a tendency for the values for the carbon-based backbones to be somewhat higher than for silicon, both classes contain some compounds with mobilities well in excess of 0.1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and others close to the lower limit of the measurements.

In the case of polysilane chains, a perfect *all-trans* arrangement of the sigma-bonds has been shown to be the optimal configuration for intrachain electronic coupling.<sup>12-15</sup> On the basis of this, the lower mobility values for the shorter alkyl-chain compounds, PAPS2 and PAPS4, are attributed to lower barriers to conformations other than *all-trans* which results in greater conformational disorder and a decrease in the overall electronic coupling. A higher degree of backbone disorder in PAPS2 and PAPS4 is indicated by the considerably greater half-width of their UV absorption bands, 0.53 and 0.24 eV respectively, compared with 0.17 eV for PAPS6 and PAPS8.

In the case of the carbon-based polymers, a perfectly coplanar arrangement of the aromatic/ethylinic moieties should be optimal for electronic coupling between neighbouring p-orbitals and should favour rapid charge transport along the chain. This could explain the much lower mobility found for the polythiophene compound since the barrier to relative torsional rotation between neighbouring units is much lower than for poly(phenylene vinylene)s, see chapter 7.<sup>16</sup> Greater conformational disorder results in a smaller average electronic coupling, which can be interpreted as a larger effective mass of the charge carrier. On the basis of this, a lower mobility is predicted for the more disordered conjugated backbone of P3HT.<sup>16</sup> In addition the "regioregular" P3HT used in the present work is known to contain *ca* 15% of head-to-head alkyl-chain defects which have been shown to have a dramatic negative effect on the charge carrier mobility in FET devices.<sup>17</sup> This almost certainly explains why the maximum mobility of 0.1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> found for a 4% defect sample in the FET work is considerably larger than the value of  $0.02 \text{ cm}^2 V^{-1} \text{s}^{-1}$  found in the present study. We can however not completely rule out the explanation that interchain charge transport is the dominant mechanism in the solid material.

The large mobility found for DEH-PF would appear to be anomalous since rotation of the neighbouring fluorene units about the connecting  $\sigma$ -bond might also be expected to occur. This compound and a similar 9,9'-dioctyl derivative have however been found to have an exceptional propensity for self-alignment indicating a high degree of order along the chains.<sup>17-19</sup> This characteristic would appear to be operative even in the dilute solutions and may explain the particularly high mobility observed.

An initially unexpected result was that the mobility for the ladder polymer, MeLPPP, which should have the most rigid, coplanar backbone of all, was lower than for MEH-PPV and DEH-PF. The explanation for this apparent anomaly probably lies in the fact that MeLPPP has a branched structure with non-conjugated branching points every 20 to 30

monomer units. We believe that these structural defects, which decrease the effective conjugation length, are responsible for the relatively low mobility observed and that if longer, un-branched chains of this ladder polymer could be synthesised much higher mobilities would be found.

### 6.4 Conclusions

In conclusion, we have shown that radical cation centres or holes can have mobilities well in excess of 0.1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> on isolated chains of both  $\sigma$ -bonded silicon and  $\pi$ -bond conjugated carbon. While the latter tend to have somewhat higher mobilities than the former, even the highest mobilities (up to 0.74 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) are probably still limited by conformational disorder and structural defects in the backbone. If these can be reduced by chemical or physical means we believe that mobilities well in excess of 1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> should be realisable, even at room temperature.

Apart from P3HT the present, isolated chain mobilities are considerably larger than those recently determined by DC time-of-flight or field-effect transistor measurements on solid materials.<sup>17,19-25</sup> This could in part be due to the ultra-high frequency and low amplitude ( $E_{max} \approx 10 \text{ V/cm}$ ) electric field used to probe the samples. As a result only a very small perturbation of the normal random diffusional motion of the charge carriers occurs. In DC measurements on the other hand, charge carriers are drifted over distances much larger than the molecular dimensions and mobility determinations are therefore sensitive to morphological disorder and domain boundaries. Considerable improvements in the conductive properties of thin layers for device applications should therefore be possible by better (self-) alignment of the polymers, particularly if the inter-electrode distance can be reduced to the length of a single chain, *i.e.* approximately one micron or less. Relevant to this is our finding that trapping of holes on the polymer chains themselves does not appear to occur.

### 6.5 References

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## Intramolecular Charge Transport Along Isolated Chains

## of Conjugated Polymers<sup>\*</sup>

### Effect of Torsional Disorder and Polymerization Defects

Recently it has become possible to measure the mobility of charges along isolated chains of conjugated polymers. The mobility of holes along poly(phenylene vinylene) and polythiophene backbones were reported to be 0.46 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> 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-(phenylene vinylene) 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 intra-molecular 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(phenylene vinylene) 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.

### 7.1 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

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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. Since 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 ( $\approx$ 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-(phenylene vinylene)s (PPVs) and polythiophenes.<sup>14-17</sup>

In chapters 4-6 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, since isolated polymer chains are also tractable for theoretical treatments that take the inherently disordered nature of polymers into account. Moreover, direct measurements of the intra-molecular wires with transport properties that meet requirements of nanoscale electronics.

The results described in chapter 6 show that there are significant differences in the ability of MEH-PPV and P3HT (see Figure 6.1 for the structure) to transport positive charges. The hole-mobility on MEH-PPV was found to be  $0.46 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  whereas for poly-3-hexylthiophene a value of ~ $0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  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 chapter, 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 7.2. 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.



Figure 7.1: Molecular structure of MEH-PPV and P3HT

The results in section 7.3 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.

### 7.2 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

$$H_{q} = \sum_{n} \left[ \varepsilon_{n} a_{n}^{\dagger} a_{n} - b(\Delta \theta_{n,n+1}) \left( a_{n+1}^{\dagger} a_{n} + a_{n}^{\dagger} a_{n+1} \right) \right]$$
(7.1)

In this equation  $\varepsilon_n$  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 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,  $\varepsilon_n$ , 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  $c_n$ :

$$\left|\Psi(t)\right\rangle = \sum_{n} c_{n}(t) \left|n\right\rangle \tag{7.2}$$

At t=0 a positive charge is localized on a single unit; *i.e.*  $c_i(t=0)=1$  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 wavefunction in Eq. 7.2 into the time-dependent Schrödinger equation

$$i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = H |\Psi(t)\rangle$$
(7.3)

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

$$\Delta^{2}(t) = \left\langle \Psi(t) \middle| n^{2} \middle| \Psi(t) \right\rangle \lambda^{2} = \sum_{n} \left| c_{n}(t) \right|^{2} n^{2} \lambda^{2},$$
(7.4)

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>

$$\mu(\omega) = \frac{-e\omega^2}{2k_B T} \operatorname{Re}\left[\int_{0}^{\infty} \Delta^2(t) \exp(-i\omega t) dt\right],$$
(7.5a)

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

$$\mu = \frac{e}{k_{\scriptscriptstyle B}T}D\tag{7.5b}$$

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 inter-unit 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 inter-unit 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; i.e. 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 effects do not play a role for isolated polymer chains in dilute solution.

The potential energy profiles for the polymers studied here, polythiophene and poly-(phenylene vinylene) 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), while 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 inter-unit angle in steps of 15 degrees. 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>

$$\left| b(\Delta \theta_{n,n+1}) \right| = \frac{1}{2} \sqrt{\left(E_{+} - E_{-}\right)^{2} - \left(E_{1} - E_{2}\right)^{2}}$$
(7.5)

## 7.3 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 7.2. 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  $\theta_{tor}=0^{\circ}$ . Upon rotation around the inter-unit bond, the energy steeply increases, attains a maximum value  $E_{tor}^{max}=3.8$  Kcal mol<sup>-1</sup> at  $\theta_{tor}=90^{\circ}$ , and then decreases for angles up to 180°. Since at room temperature  $E_{tor}^{max}>>kT$ , 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>14,15</sup>



**Figure 7.2**: Potential energy profiles for torsional motion of structural units in PPV (filled circles) and polythiophene (open circles) chains. Calculations were performed at MP2/cc-pVDZ level for styrene and bithiophene model systems. Points correspond to the energy difference,  $E_{tor}$ , between configurations with torsion and with planar geometry.

For polythiophene the potential energy profile for polythiophene is very different from that for PPV (see Figure 7.2). In this case the potential energy has a minimum at a torsion angle near 30°. 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 kcal mol<sup>-1</sup> 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 inter-unit angle for both polymers in Figure 7.3. For both compounds the coupling is maximal at a planar geometry, as expected. The electronic coupling for this co-planar 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 7.4. The results plotted in this figure correspond to the case where the number of sites



**Figure 7.3**: Charge transfer integral between monomer repeatunits 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.

*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 non-linear temporal behavior, while after about 10 ps the value of  $\Delta^2(t)$  rises much slower with an essentially linear time dependence. The non-linear 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 inter-unit torsion angle, where the electronic coupling is very small. As a consequence, charge motion will slow down 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 7.5). Indeed, according to Eq. 7.5a the low frequency mobility should mainly be determined by the temporal behavior of holes in the long-time limit t>10ps, 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 7.5. This ceases to be true at higher frequencies, where the charge carriers can follow the external electric field by moving back and forth between sites with large inter-unit angles. In this case the main contribution to the integral in Eq. 7.5 and hence to  $\mu$  originates from the fast non-linear initial increase of  $\Delta^2(t)$  with time at the early stage of the transport process. As a consequence,



**Figure 7.4**: 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.

at high frequencies the mobility rises almost as  $\omega^2$  for both PPV and polythiophene, see Figure 7.5.

Although the dependencies of the intramolecular charge mobility on  $\omega$  exhibits 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 7.5 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.



**Figure 7.5**: Frequency dependence of the intramolecular mobility of holes along PPV and polythiophene chains, obtained from the data of Figure 7.4 using Eq. 7.5a.

The calculated mobilities discussed so far were obtained for infinitely long the polymer chains without chemical defects. However the experimental data were obtained for polymers with a finite chain length and polymerization defects. In particular, due to 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.

In order 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 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> 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±400 phenylenevinylene units, they could contain up to ~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 poly-dispersity 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, since 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 selflocalized 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  $\varepsilon_n$ , see Eq. 7.5, 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 since it arises mainly from the torsional disorder, which is already described in detail in the present model.

# 7.4 Conclusions

Recently is 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 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.

## 7.5 References

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# **Chapter 8**

# **Opto-Electronic Properties of Positively Charged**

# Oligo(phenylene vinylene)s<sup>\*</sup>

# Effects of Chain Length and Alkoxy Substitution

In this chapter a combined experimental and quantum chemical study of the geometry and opto-electronic properties of unsubstituted and dialkoxy-sustituted phenylenevinylene oligomers (PV's) is presented. The optical absorption spectra for PV cations with different chain lengths and substitution patterns were measured using pulse radiolysis with time-resolved spectrophotometric detection from 1380 to 500 nm (0.9 to 2.5 eV) . The geometries of the PV's studied were optimized using density functional theory (DFT) for both the neutral and singly charged molecule. The spectra for the PV radical cations were then calculated using singly excited configuration interaction with an intermediate neglect of differential overlap reference wavefunction (INDO/s-CIS) method together with the DFT geometry. The agreement between experimental and theoretical absorption energies is excellent; most of the calculated radical cation absorption energies are within 0.15 eV of the experimental values. The pattern of dialkoxy-substitution is found to have a large effect on the optical absorption spectrum of the cation. Using the calculated charge distribution it is shown that the degree of delocalization of the charge correlates with the energy of the lowest absorption band. If alkoxy side chains are present on some of the rings the positive charge tends to localize at those sites.

## 8.1 Introduction

Conjugated polymers have an alternating sequence of single and double bonds, giving rise to  $\pi$ -orbitals that are delocalized over several monomer units. In general these materials are wide band-gap semiconductors in their pristine state, but can become conducting on oxidative or reductive doping. Some members of this class of polymers emit light when electrons and positive charges are injected through electrodes. These physical properties, combined with the low cost and ready processability, make these materials interesting candidates for

<sup>&</sup>lt;sup>\*</sup> This chapter is based on: F.C. Grozema, L.P. Candeias, M. Swart, P.T. van Duijnen, J. Wildeman, G. Hadziioannou, L.D.A. Siebbeles and J.M. Warman, *J. Chem. Phys.*, **117** (2002), 11366-11378.

(opto)electronic applications such as field-effect transistors, light emitting diodes and photovoltaic cells.<sup>1-3</sup>

Poly(phenylene vinylene) (PPV) and its derivatives are conjugated polymers that have been studied extensively for application as the emitting layer in light emitting diodes and solid-state lasers.<sup>4,5</sup> They are also being considered as the absorbing antenna layer in photovoltaic devices.<sup>2,6</sup> The first demonstration of a conjugated polymer light-emitting diode (LED) was based on an unsubstituted PPV<sup>7</sup> which is insoluble and thus excludes processability from common organic solvents. Attachment of substituents such as alkyl- and alkoxy side-chains provides soluble polymers that can be processed for instance by spin coating. Introduction of alkoxy groups also offers the possibility to tune the absorption and emission wavelength and improve the electro-luminescence yield of LED's.<sup>8-10</sup>

The application of PPV's in LED's and photovoltaic cells relies critically on the ability of the polymer to transport charges. A detailed knowledge of the nature of charge carriers in PPV's is therefore essential. The properties of charged defects on phenylene vinylene chains have been studied experimentally by optical absorption measurements, ESR and vibrational spectroscopy.<sup>11</sup> Studies of well-defined phenylene-vinylene (PV) oligomers in solution have shown that the optical absorption spectrum of singly charged PV's is characterized by two electronic transitions below the lowest energy absorption band of the neutral compound. The assignment of these absorptions to the radical ions is supported by an ESR signal that indicates the presence of an unpaired spin.<sup>12</sup> For doubly charged PV's the optical absorption spectrum has been predicted to exhibit a single strong transition.<sup>13</sup> Such an absorption feature has been observed for an oligomer containing three phenylene rings (PV2) in a doped solid film.<sup>14</sup>



**Figure 8.1:** Band structure model (a) and molecular orbital model (b) for sub-gap absorption feature in singly charged phenylene vinylenes

The radical cation optical absorption spectra of conjugated polymers (and also of oligomers) are usually discussed in terms of a one-electron band structure model.<sup>15</sup> In this model the introduction of a localized, singly charged defect leads to the formation of two electronic levels inside the gap between the valence band and the conduction band (Figure 1a)

which are responsible for the sub-gap absorption features in the spectrum of the cation. The three possible sub-gap excitations are indicated by arrows in Figure 8.1a. A band structure model infers an infinitely long conjugated polymer chain with a periodic structure. However, the present work involves oligomers where discrete energy levels are present instead of bands, as indicated in Figure 8.1b. Moreover, even for polymers a band structure model is not directly applicable since polymers are usually rather disordered and consist of a distribution of conjugation lengths. Consequently, they usually have electronic properties that are more similar to that of a distribution of oligomers of different length, rather than those expected for an infinitely long periodic chain.<sup>16</sup> Although the band structure model is not directly applicable for oligomers the terminology is generally used and is therefore also adopted in this chapter. In this terminology the lower 'polaron' level, which is singly occupied, is called P1 and the lowest unoccupied level is called P2. Note that in this system the electronic level called LUMO or L is actually the second empty level while the HOMO level or H is the highest doubly occupied orbital, see Figure 1b.

Quantum chemical calculations can yield valuable information on the molecular level which cannot be obtained by experimental methods. Semi-empirical calculations on the formation of polarons on phenylene vinylene oligomers have been performed by Cornil et al.<sup>13</sup> From geometry optimizations using the AM1 method it was concluded that a positive charge on a PV chain is self-localized and its spatial extent was estimated to be circa three repeat units. The geometries obtained from these calculations were used to calculate the electronic spectra using the intermediate neglect of differential overlap Hamiltonian (INDO) combined with the singly excited configuration interaction (CIS) method. The calculations indeed showed two allowed electronic transitions below the onset of the optical absorption of the neutral compound, however, the absolute agreement with the experimental absorption energies was rather poor. The work by Cornil et al. was also limited to unsubstituted PV's which makes comparison to experimental work difficult since PV's and PPV's used in experimental work usually contain substituents, either to make them soluble or to tune their optical properties as mentioned above. The presence of side-chains can be expected to have a considerable effect on the spatial extent and optical absorption spectra of charges on PV chains.

The aim of this chapter is to provide insight into the effect of chain length and alkoxy substituents on the opto-electronic properties of singly positively charged PV oligomers. A combined experimental and theoretical study of the electronic structure and spatial extent of polarons on phenylene-vinylene oligomers is presented. Optical absorption spectra of positively charged oligomers have been measured by performing pulse radiolysis experiments for a variety of PV's differing in chain length and substitution pattern. The charge distribution and excitation energies of singly charged PV's are determined theoretically using a combination of density functional theory (DFT) and semiempirical INDO/s calculations. The geometry of neutral and charged PV's were optimized using DFT. These geometries were used in INDO/s-CIS calculations in order to calculate the optical absorption spectra of the cations. Excitation energies calculated for different chain lengths and a variety of substitution patterns are compared to optical spectra of radical cations obtained from pulse radiolysis experiments described here and to spectra previously reported in the literature. The results provide a unique insight into the subtle effects of substituents on the geometry and electronic

structure of singly oxidized PV's. The structures of the phenylene vinylene derivatives investigated in the present work and their pseudonyms are shown in Figure 8.2.



**Figure 8.2:** Structures of PV oligomers for which calculations have been performed. In this chapter the notation PVn(x da) is used, in which n is the number of phenylene vinylene units and x is the number of dialkoxy substituted phenyl rings

# 8.2 Experimental details

The compounds  $PVn(n/2 \ da)$  and  $PV4(1 \ da)$  shown in Figure 8.2 were synthesized and purified as reported earlier.<sup>17,18</sup> Solutions (ca.  $10^{-4}$  M) in UV-spectroscopic grade benzene were freshly prepared before each experiment and bubbled with benzene-saturated oxygen for at least ten minutes. All experiments were performed at room temperature.

The pulse radiolysis method using transient optical absorption detection was essentially the same as used previously for the measurement of triplet spectra of the PVn(n/2 da) oligomers.<sup>19,20</sup> Solutions were irradiated using 50 ns pulses of 3 MeV electrons from a Van de Graaff accelerator in order to create PV radical cations as described in section 8.4. The solutions were flowed continuously through a quartz cell (optical path length 12.5 mm) using a slight overpressure of benzene-saturated oxygen. The source of detection light was a pulsed high-pressure Xe-lamp (450 W). Cut-off filters and a fast shutter were used to minimize photolysis of the solution by the detection light. NIR detection was achieved using a short-wavelength enhanced InGaAs photodiode (Hamamatsu, Japan). Transient changes in the optical absorption were recorded using a Tektronix TDS680 digitizer. The lower limit of the photon energy was ca. 0.9 eV.

## 8.3 Computational methodology

The geometries of all the phenylene-vinylene oligomers studied in this work were optimized using the Amsterdam Density Functional program (ADF).<sup>21,22</sup> The geometry optimizations were performed using the Local Density Approximation (LDA) with the exchange and correlation functionals based on the parameterization of the electron gas data given by Vosko, Wilk and Nusair (VWN).<sup>23</sup> Generalized Gradient Approximation corrections by Becke (exchange) and Perdew (correlation) were included.<sup>24,25</sup> All calculations were performed using a basis set of double-zeta quality including polarization functions (DZP, basis set III in ADF) consisting of Slater-type functions. Test calculations for short oligomers showed that there are no significant changes in geometry if a larger basis set is used. For the charged oligomers the restricted open shell method was used in order to avoid artifacts due to spin contamination. The geometries were restricted to C<sub>2h</sub> symmetry.

The excitation spectra for the singly charged oligomers were calculated as follows. A restricted open shell Hartree-Fock (ROHF) calculation, using the intermediate neglect of differential overlap (INDO/s)<sup>26-29</sup> Hamiltonian, was performed for the ground state. The Coulomb repulsion terms were described using the Mataga-Nishimoto parameters which have been especially developed for spectroscopic calculations. The electronic spectra were obtained from singly excited configuration interaction (CIS) calculations using the groundstate ROHF wave function as the reference determinant. The smallest CI expansion used in the calculations contained all configurations involving single excitations from the 20 highest occupied molecular orbitals into the 20 lowest unoccupied molecular orbitals of the ROHF reference wave function. This was found to be sufficient for convergence of the excitation energies for oligomers with a chain length up to 4 PV units. For longer oligomers it was found that larger CI expansions were necessary. The largest CI space used in this work contained all configurations involving single excitations from the 40 highest occupied molecular orbitals into the 40 lowest unoccupied orbitals, giving a total of 3200 configurations for the doublet multiplicity. The energy of the lowest allowed transition of the radical cation (RC1) was found to be less sensitive to the size of the CI expansion than those of transitions to higher states (RC2 and RC3). In the oligomers for which two or more close lying allowed transitions were calculated the convergence of the high energy transitions with the size of CI space was rather slow, especially with regard to the oscillator strength. The method for calculation of spectra outlined here is known to give an excellent description of electronic spectra of neutral molecules if an accurate geometry is used.<sup>28</sup>

## 8.4 Results and discussion

The phenylene-vinylene oligomers studied in this work are shown in Figure 8.2. The oligomers include three series of increasing length. The first series consists of phenylene vinylene oligomers, PVn, which are para-substituted with methyl groups on the outermost phenylene rings. Experimental data on the optical absorption spectra of the cations of these oligomers up to n=3 is available from experiments by Furukawa et al.<sup>14</sup> (see Table 8.1). The second series of oligomers, PVn(n+1 da) contains two alkoxy substituents on all phenyl rings.

Cation spectra for these oligomers are available from the work of Van Hal et al.<sup>30</sup> (see Table 8.2) who studied photo-induced charge transfer between PV's and a fullerene derivative.

In the third series, PVn(n/2 da), every other phenylene ring is substituted with two alkoxy side chains. The optical absorption spectra of the PVn(n/2 da) cations were obtained from pulse radiolysis experiments performed in the present work (see Table 8.3). In order to study the effect of substituents in more detail, experiments and calculations were performed on one more oligomer, PV4(1 da), which is dialkoxy substituted only on the central phenylene moiety.

## 8.4.1 Measurements of PV radical cation spectra

Irradiation of benzene (Bz) leads to the formation of radical cations (Bz<sup>+</sup>), excited states (Bz<sup>\*</sup>), and excess electrons ( $e^{-}$ )<sup>31-33</sup>

Bz 
$$\rightarrow$$
 Bz<sup>+</sup>, Bz<sup>\*</sup>, e<sup>-</sup> (8.1)

In oxygen-saturated solution (  $[O_2] = 11.9$  mM at 1 atm. and 25 °C), the excited states and the excess electrons are scavenged within a few nanoseconds, Eqs. 8.2 and 8.3.

$$Bz^* + O_2 \rightarrow O_2(^1\Delta) + Bz$$
 (8.2)

$$e^{-} + O_2 \longrightarrow O_2^{-}$$
 (8.3)

The  $Bz^+$  ions are unreactive towards  $O_2$  and can diffuse to the dissolved PV oligomers where they undergo charge transfer (Eq. 8.4), since these conjugated oligomers have a lower ionization potential than benzene. This results in the abstraction of an electron from the oligomer, forming the radical cation or "hole".

$$Bz^+ + PV \longrightarrow Bz + PV^+$$
 (8.4)

The absorption spectra of the radical cations were obtained by measuring the transient changes in the absorbance of the solution at different wavelengths. The absorption spectra obtained for the  $PVn(n/2 \ da)$  series are shown in Figure 8.3. The energies at which the absorption maxima occur are listed in Table 8.3.

For the radical cation of PV2(1 da) two well-separated bands are observed, one at 1.24 eV and the other at 2.03 eV. These bands are denoted RC1 and RC2, respectively. The appearance of two absorption maxima in the radical cation spectra of PV's is in agreement with earlier experiments<sup>14</sup> and quantum chemical calculations by Cornil *et al.*<sup>13</sup> For the longer oligomers in the PVn(n/2 da) series the low energy band, RC1, shifts below 0.9 eV and cannot be observed with the optical absorption set-up used in the present work. The high-energy absorption band, RC2, also shifts to lower energy when the chain length is increased but remains within the detection range. Interestingly, this high energy band clearly exhibits two maxima for PV4(2 da) and PV6(3 da). These maxima are denoted RC2 and RC3 in Table

8.3. The assignment of these bands to two separate electronic transitions is supported by the results from the calculations described in section 8.4.2. The energy difference between RC2 and RC3 decreases from 0.19 eV for PV4(3 da) to 0.12 eV for PV6(2 da). In the spectra for PV8(4 da) through PV16(8 da) only a single broad maximum can be discerned. In view of the results for the shorter oligomers this absorption band is considered to be due to the fusion of two individual electronic transitions at close lying energies. This combined absorption band RC2/RC3 exhibits only a very small spectral shift in going from PV4(2 da) to longer chains.



**Figure 8.3:** Optical absorption spectra of the radical cations of the PVn (n/2 da) series.

Figure 8.4 shows a comparison of the absorption spectra for the radical cations of PV4(2 da) and PV4(1 da). It is evident from this comparison that the cation optical absorption spectrum of a phenylene vinylene tetramer depends strongly on the number of alkoxy substituents and their positions. The low energy absorption band, RC1, which is below 0.9 eV for PV4(2 da) and could therefore not be observed in the present experiments, has moved to considerably higher energy in PV4(1 da). The RC1 energy is in fact close to that observed for PV2(1 da) which indicates that the charge carrier is more localized in these two compounds than in PV4(2 da). The RC1 band appears to be more sensitive to the delocalization length of the charge carrier than the RC2 or RC3 bands. The spectrum of PV4(1 da) exhibits a shoulder on the high energy side of RC2 which is attributed to the second high energy transition, RC3, as observed for the PV4(2 da) and PV6(3 da).



**Figure 8.4:** Comparison of the optical absorption spectra of radical cations of PV4 (2 *da*) and PV4 (1 *da*).

# 8.4.2 Calculated absorption spectra of PV cations

The electronic transitions of the radical cations of all PV oligomers shown in Figure 8.2 have been calculated using the methodology outlined in section 8.3. For the calculations on these compounds, the alkoxy substituents were taken to be methoxy groups. This simplification is not expected to significantly influence the results with regard to electronic effects of the substituents. Of course bulky alkyl groups could possibly have a steric effect especially in the case of the PVn(n+1 *da*) series in the experiments of Van Hal et al.<sup>30</sup> since these contain branched alkoxy side chains on all phenyl rings. The PV1, PV2 and PV3 oligomers used in the experimental work of Furukawa et al.<sup>14</sup> contained two methyl groups, para-substituted on the outermost phenyl rings. These methyl groups were omitted in the calculations.

The calculated radical cation transition energies are collected in Table 8.1 together with the experimental data from the present pulse radiolysis experiments and values from the literature. The agreement between the calculated excitation energies and the experimental data is in general very good, with most of the calculated energies differing by less than 0.15 eV

from the experimental absorption maxima. In what follows we give a fuller discussion of the theoretical results and the comparison with experiment.

Compound	Band	$\Delta E_{+}$	$\Delta E_{+}$	f (Calc.)	Main CI-expansion coefficients
		(Exp.) <sup>a</sup>	(Calc.)		
		in eV	in eV		
PV1	RC1	1.54	1.71	0.04 <sup>b</sup>	-0.51(H-2 →P1) - 0.50(H→P1) + 0.52(H→P2)
	RC2	2.45	2.20	0.80	-0.46(H-2 →P1) - 0.37(H→P1) - 0.70(P1→P2)
PV2	RC1	1.03	1.13	0.36	-0.87(H→P1) - 0.33(H→P2)
	RC2	1.95	1.89	1.01	-0.35(H→P1) + 0.78(P1→P2)
PV3	RC1	0.80	0.87	0.62	-0.87(H→P1)
	RC2	1.74	1.69	1.14	0.77(P1→P2)
PV4	RC1	-	0.71	0.89	-0.87(H→P1)
	RC2	-	1.65	1.03	0.39(H→L) + 0.65 (P1→P2)
	RC3	-	1.91	0.22	0.52(H-2 →P1) - 0.49(P1→P2)
PV6	RC1	-	0.55	1.13	0.49(H-2 →P1) - 0.78(H→P1)
	RC2	-	1.44	0.14	0.35(H-6 →P1) - 0.48(H-2→P1)
	RC3	-	1.58	1.00	0.41(H→P1) + 0.63(P1→P2)
PV8	RC1	-	0.49	1.29	0.33(H-4→P1) + 0.60(H-2→P1) + 0.64(H→P1)
	RC2	-	1.57	0.80	0.45(P1→P2)
	RC3	-	1.81	0.38	0.55(P1→P2)
PV10	RC1	-	0.46	1.33	
	RC2	-	1.47	0.23	
	RC3	-	1.60	0.27	
PV12	RC1	-	0.45	1.39	
	RC2	-	1.60	0.43	
	RC3	-	1.72	0.34	

**Table 8.1:** Calculated and experimental transition energies ( $\Delta E_+$ ), calculated oscillator strengths (f) and main CI expansion coefficients for radical cations of PVn oligomers. Only transitions with an oscillator strength higher than 0.1 are given.

<sup>a</sup> Experimental data were taken from ref. 13

<sup>b</sup> For unsubstituted PV2 the calculated oscillator strength was found to be smaller than 0.1

# Unsubstituted oligomers, PVn

First, the unsubstituted PVn series is considered. The transition energies ( $\Delta E_+$ ), oscillator strengths and main CI expansion coefficients for this series are given in Table 8.1. For the shorter oligomers up to PV3 two transitions with energies lower than the absorption onset of the neutral molecule are found. This is in agreement with the general appearance of spectra of singly oxidized PV's.<sup>13,14</sup> The agreement with the experimental  $\Delta E_+$  data improves in going from PV1 through PV3 which can be attributed to the use of a larger effective basis set upon increasing the size of the system studied. For unsubstituted oligomers longer than PV3 there is no experimental data. The calculations show however that the radical cations of oligomers PV4 through PV12 should exhibit a third allowed transition in the spectrum, denoted RC3 in Table 8.1.

As evident from Table 8.1 the RC1 transition is dominated in all cases by the configuration corresponding to an excitation from the doubly occupied HOMO (H) level to the singly occupied P1 level. In the following, such a configuration is denoted as  $(H\rightarrow P1)$ . The oscillator strength for RC1 increases markedly with the length of the oligomer, as observed also in earlier theoretical studies.<sup>13</sup>

For all PVn, the RC2 transition contains a large contribution from a configuration that corresponds to a singly excited determinant resulting from a transition from the singly occupied P1 orbital to the lowest unoccupied P2 orbital. This configuration is indicated as P1 $\rightarrow$ P2. For longer oligomers the contribution from this transition to RC2 becomes somewhat less and configurations involving lower lying orbitals (such as H-2 $\rightarrow$ P1 and H-4 $\rightarrow$ P1) start mixing in more. These contributions due to lower lying orbitals are caused by a decrease of the energy difference between the orbital energy of P1 and the energies of the lower lying orbitals (H-2, H-4) as the chain length increases. This also leads to the formation of the third allowed transition which contains a considerable amount of P1 $\rightarrow$ P2 character but also contributions such as H-2 $\rightarrow$ P1 and H-4 $\rightarrow$ P1.

Note that for the PVn series there are no contributions such as H-1 $\rightarrow$ P1 and H-3 $\rightarrow$ P1 to the allowed electronic transitions, see Table 8.1. This can be understood by symmetry arguments. It was found that for PVn the frontier orbitals alternately have  $a_u$  and  $b_g$  symmetry, as illustrated in Figure 8.1b. The H-1 $\rightarrow$ P1 configuration is due to a transition between orbitals that are both of  $b_g$  symmetry and therefore the transition dipole moment between these configurations is zero by symmetry. Thus these configurations do not contribute to the allowed electronic transitions. For RC2 the oscillator strength increases initially with chain length. However, when the third sub-gap absorption appears this trend is lost. In general, if the energies of the transitions RC1, RC2 and RC3 are compared it can be seen that RC1 is more sensitive to changes in the length of the chain than RC2 or RC3.



**Figure 8.5:** Chain length dependence of the radical cation absorption energies RC1 (open symbols) and RC2 (closed symbols) determined experimentally (circles) or calculated (squares). The results of previous calculations by Cornil *et al.* (ref. 13) are also shown (triangles).

RC1 decreases from 1.71 eV for PV1 to 0.49 for PV8, a decrease by a factor of 3.5 while RC2 decreases by less than 20%.

In Figure 8.5 the transition energies for RC1 and RC2 are compared to experimental data from the work of Furukawa<sup>14</sup> (see also Table 8.1) and to previous theoretical work by Cornil et al.<sup>13</sup> The correspondence between the present calculations and experimental data is very good for PV1 to PV3 and is considerably better than in the work of Cornil *et al.*. The present method used to calculate the spectra is basically the same as that used by Cornil *et al.* The only difference is in the geometry used in the INDO/s-CIS calculation of the spectrum. Cornil et al. used geometries optimized using the semiempirical AM1 Hamiltonian, whereas in the present work the geometry optimizations were performed using density functional theory, see section 8.3. As will be shown below there are considerable differences between the geometries obtained with the AM1 and DFT methods.

The INDO/s-CIS method used here to calculate the excitation energies is especially parameterized for the calculation of absorption spectra of neutral molecules. The results obtained are usually very good if accurate molecular geometries are used in the calculations. The good correspondence between the excitation energies calculated in the present work and the experimental data therefore suggests that the geometries obtained from DFT calculations are more accurate than those obtained using the AM1 method, at least up to PV3. Due to the lack of experimental data for longer unsubstituted PV's it is not possible to draw definite conclusions about the quality of the geometry for these longer oligomers.

Compound	Band	$\Delta E_{+}$	$\Delta E_{+}$	f (Calc.)	Main CI-expansion coefficients
		(Exp.) <sup>a</sup>	(Calc.)		
		in eV	in eV		
PV2(3 <i>da</i> )	RC1	0.76	0.90	0.30	-0.85(H→P1)
	RC2	1.71	1.66	0.64	0.74(P1→P2) + 0.34(H→P1)
	RC3	~2.0	1.99	0.23	0.78(H-2→P1)
PV3(4 <i>da</i> )	RC1	0.66	0.71	0.43	0.77(H→P1) + 0.42(H-2→P1)
	RC2	1.52	1.34	0.34	0.37(H-4→P1) - 0.41(H-2→P1) - 0.51(P1→P2)
	RC3	~1.7	1.56	0.61	0.39(H→P1) - 0.57(P1→P2) + 0.34(H-4→P1) -
					0.44(H-2→P1)
PV4(5 <i>da</i>	RC1	0.59	0.68	0.58	-0.77(H→P1) - 0.40(H-3→P1)
	RC2	1.43	1.35	0.96	0.68(P1→P2)
	RC3	~1.6	1.61	0.11	-0.42(H-3→P1) - 0.40(P1→P2)
PV5(6 <i>da</i> )	RC1	0.54	0.57	0.74	-0.73(H→P1) +0.32(H-4→P1) + 0.42(H-2→P1)
	RC2	1.40	1.24	0.31	0.47(H-4→P1) - 0.37(P1→P2)
	RC3	~1.6	1.40	0.85	0.39(H-4→P1) 0.37(H→P1) 0.65(P1→P2)

**Table 8.2**: Calculated and experimental transition energies ( $\Delta E_+$ ), calculated oscillator strengths (f) and main CI expansion coefficients for radical cations of PVn (n+1 da) oligomers. Only transitions with an oscillator strength higher than 0.1 are given.

<sup>a</sup> Experimental data taken from ref. 30

# Fully dialkoxy substituted oligomers, PVn(n+1 da)

The cation absorption energies in the series of PV's containing two alkoxy substituents on all phenylene rings (PVn(n+1 da) are all lower than those in the corresponding unsubstituted PV's, see Tables 8.1 and 8.2. The calculated results are in reasonable agreement with the experimental data obtained by Van Hal *et al.*<sup>30</sup> for these compounds, see Table 8.2. Interestingly, the calculations show that there is a third sub-gap absorption band, even for the shortest oligomer of this series, PV2(3 da). A third absorption band is clearly present in the experimental spectra of Van Hal *et al.* However, this additional band is not assigned to a separate electronic transition by the authors. The calculated energy of RC3 agrees well with that obtained from the experimental spectra, see Table 8.2. Also for the longer PV's studied by Van Hal *et al.* a second high energy band, or at least a shoulder towards the higher energy side of RC2, can be distinguished in the spectrum, in agreement with the calculated spectra.

In Table 8.2 the oscillator strengths and main CI-coefficients for the PVn(n+1 da) oligomers are also given. The lowest energy transition is dominated by the  $H\rightarrow P1$  contribution in all cases, as was observed for the PVn series. For PV2(3 da) the second band, RC2, is mainly due to the P1 $\rightarrow$ P2 configuration, while RC3 has predominantly H-2 $\rightarrow$ P1 character. For the longer oligomers the RC2 and RC3 bands cannot clearly be attributed to a single CI configuration. Both excited states are mixtures that consist mainly of P1 $\rightarrow$ P2 and of configurations such as H-2 $\rightarrow$ P2 and H-4 $\rightarrow$ P2. The introduction of the alkoxy side-chains effectively lowers the energy difference between these lower lying orbitals and P1. This causes the third absorption feature to appear already in PV2(3 da), while for the unsubstituted PV's the first appearance of RC3 was in PV4.

#### Partially dialkoxy substituted oligomers, PVn(n/2 da)

The PVn(n/2 da) oligomers are dialkoxy substituted on every second phenylene unit. The experimental radical cation spectra are shown in Figure 8.3. The allowed transitions that were calculated for this series of oligomers are compared to the experimental data in Table 8.3. The agreement is seen to be excellent. For PV2(1 da) both the calculated RC1 (1.26 eV) and RC2 (2.02) band are very close to the experimental values of 1.27 eV and 2.07 eV respectively. For PV4(2 da) the low energy band RC1 is predicted to shift to a considerably lower energy (0.51 eV) which is lower than the experimental limit of ca. 0.9 eV. Accordingly it could not be experimentally observed.

The energies of RC2 and RC3 are calculated to be 1.49 eV and 1.74 eV respectively. This is in excellent agreement with the experimental spectrum in Figure 8.3 which displays two maxima at 1.51 eV and 1.70 eV. The similar magnitude of the two bands is in agreement with the calculated oscillator strengths for RC2 and RC3 of 0.56 and 0.53 respectively. When the chain length is increased to PV6(3 *da*) the energy difference between the RC2 and RC3 bands becomes smaller; 0.25 eV for PV4(2 *da*) versus 0.09 eV for PV6(3 *da*), in agreement with the experimental spectra in Figure 8.3. The calculated spectra for the longer oligomers show that increasing the chain length beyond PV6 has little further effect on RC2 and RC3 energies actually increase slightly after n=8, see Table 8.3. This is probably due to the fact that the largest CI

expansions used here are still not sufficient. As mentioned in section 8.3 the RC2 and RC3 energies are more sensitive to the size of the CI expansion than RC1.

**Table 8.3:** Calculated and experimental transition energies ( $\Delta E_+$ ), calculated oscillator strengths (f) and main CI expansion coefficients for radical cations of PVn (n/2 da) oligomers. Only transitions with an oscillator strength higher than 0.1 are given.

Compound	Band	$\Delta E_{+}$	$\Delta E_{+}$	f (Calc.)	Main CI-expansion coefficients
		(Exp.) <sup>a</sup>	(Calc.)		
		in eV	in eV		
PV2(1 da)	RC1	1.26	1.26	0.04 <sup>c</sup>	0.63(H→P1) + 0.52(P1→P2)
	RC	2.07	2.02	1.08	0.63(H→P1) - 0.61(P1→P2)
PV4(2 <i>da</i> )	RC1	-	0.51	0.75	-0.91(HP1)
	RC2	1.51	1.49	0.56	-0.33(H-2→P1) + 0.62(P1→P2) - 0.32 (H→L)
	RC3	1.70	1.74	0.53	0.62(H-2→P1) + 0.47(P1→P2)
PV6(3 <i>da</i> )	RC1	-	0.75	0.86	-0.77(H→P1) + 0.33(H-4→P1)
	RC2	1.49	1.47	0.44	0.32(H-4→P1)
	RC3	1.61	1.56	0.72	0.44(H→P1) + 0.63(P1→P2)
	RC4	-	1.91	0.30	0.42(H-4→P1) - 0.34(P1→P2)
PV8(4 <i>da</i> )	RC1	-	0.38	1.03	-0.72(H-2→P1) + 0.54(H→P1)
	RC2	1 E1b	1.41	0.77	-0.52(P1→P2)
	RC3	1.51	1.56	0.10	0.40(P1→P2)
	RC4		1.72	0.29	-0.41(P1→P2) +0.33(H-2→P1) -0.39(H-6→P1)
					+ 0.43(H-10→P1)
PV10(5 <i>da)</i>	RC1	-	0.66	1.08	
	RC2		1.47	0.30	
	RC3	-	1.65	0.81	
	RC4	-	1.92	0.49	
PV12(6 <i>da</i> )	RC1		0.34	1.15	
	RC2	1 40 <sup>b</sup>	1.51	0.56	
	RC3	1.49~	1.59	1.19	
	RC4		1.72	0.38	
PV16(8 <i>da)</i>	RC2	1 10 <sup>b</sup>	-	-	
	RC3	1.48	-	-	
PV4(1 da)	RC1	~0.9	1.03	0.44	
	RC2	1.6	1.77	1.47	
	Rc3	1.97	1.94	0.14	

<sup>a</sup> Experimental data obtained from spectra in Figures 3 and 4

<sup>b</sup> Could not be separated

<sup>c</sup> For PV2(1 *da*) the calculated oscillator strength was found to be smaller than 0.1

When the calculated RC1 energies are considered, an intriguing odd/even trend emerges. Figure 8.6 shows a comparison of the chain length dependence of the RC1 energy for the PVn(n/2 da) series and the unsubstituted PVn series. The PVn(n/2 da) oligomers with an even number of dialkoxy substituted phenylene rings all have an RC1 energy lower than that obtained for the corresponding PVn derivative, whereas for those PVn(n/2 da) oligomers with

an odd number of dialkoxy substituted phenylene rings the energy is always higher than that of the unsubstituted analogue. It is worth noting that for the "odd" compounds the central phenylene ring is dialkoxy substituted but unsubstituted for the "even" compounds. This oddeven effect is discussed in more detail below when the effect of the substitution pattern on the charge distribution is considered.

#### Effect of the dialkoxy substitution pattern

In order to investigate the effect of the substitution pattern on the electronic properties of the PV cations in more detail the compound PV4(1 da) with dialkoxy substitution only at the central phenylene moiety was investigated. The low energy RC1 band of this compound is predicted to shift to considerably higher energy compared to the spectra of PV4 and PV4(2 da). This large blue shift of the RC1 band of PV4(1 da) is observed experimentally as shown in Figure 8.4.



**Figure 8.6**: Comparison of the calculated transition energy corresponding to the lowest energy absorption band, RC1, of the unsubstituted PV series, PVn (open circles, solid line) and the partially dialkoxy-substituted series, PVn(n/2 da) (filled circles, dashed line) as a function of chain length.

These results show that the precise position of an alkoxy group can have a considerable effect on the delocalization length of a charge on the phenylene vinylene chain. This means that there must be a significant mixing of the p-type orbitals on the oxygen atom of the alkoxy groups with the p-orbitals of the conjugated  $\pi$ -system. The highest occupied molecular orbital in PV4(1 *da*) obtained from INDO/s calculations was indeed found to have significant density on the oxygen atom in the side chain. Therefore the angle between the alkoxy group and the plane of the conjugated chain can be expected to have a pronounced influence on the energy of RC1. The calculated data given in Table 8.2 and 8.3 for alkoxy substituted PV's refer to the geometry in which the dihedral angle between the side chain and the conjugated chain is zero; i.e. the carbon atoms of the methoxy groups are in the plane of the molecule. This planar configuration was found to be the minimum energy geometry. When the substituents are twisted to a dihedral angle of 90 degrees the energy of RC1 becomes 0.86 eV, which is 0.17

eV lower than found for the planar geometry. This shows that the orientation of the substituents indeed influences the degree of delocalization of the charge.

#### 8.4.3 Effect of substituents on the charge distribution

More direct insight into the effect of the substituents on the delocalization of a charge carrier on a phenylene vinylene oligomer can be obtained by examining the actual charge distribution along the PV chain. In Figure 8.7 the distributions of an excess positive charge on phenylene vinylene tetramers with different substitution patterns are shown. The charge distributions were obtained from a Mulliken population analysis performed on the same wave functions used to calculate the electronic absorption spectra; i.e. the INDO charge distribution. The figure shows the increase in positive charge,  $\Delta_+$ , on the (dialkoxy-)phenylene and vinylene moieties in the chain when an electron is removed. This increase was calculated by adding the Mulliken charges on all atoms in a unit and subtracting the charge that was present on that unit in the neutral molecule.

For the unsubstituted oligomer a maximum in the charge distribution is found at the central phenylene unit of the chain. In general the vinylene units have a lower charge density than their neighboring phenylene units . The presence of more charge on the phenylene units is related to a considerably lower ionization potential of these units compared with the vinylene units. Introduction of methoxy substituents on the phenyl rings leads to a further lowering of their ionization potential which is accompanied by a further shift of charge from the vinylene groups to the phenyl rings as evident from Figure 8.7. If only the central phenylene ring contains methoxy groups, as in PV4(1 *da*), almost 40% of the charge becomes localized there. If methoxy substituents are present on the second and fourth phenyl ring, PV4(2 *da*), the charge is more evenly distributed than in PV4. The lowering of the ionization potential of these two phenylene units leads to an increase of positive charge on these rings, accompanied by a decrease of charge on the middle phenylene ring and its neighboring vinylene units. Finally, if all phenylene rings are dialkoxy substituted, as in the PV4(5 da) oligomer, the charge distribution is almost the same as found for the unsubstituted PV4 oligomer.

In order to gain more insight into the relationship between the charge distribution and the radical cation optical absorption spectra presented above, it is useful to express the degree of delocalization of charge in terms of the so-called 'participation ratio', *P*, which is defined as:

$$P = \left[\sum_{i=1}^{N} Q_i^2\right]^{-1} \tag{5}$$

where  $Q_i$  is the fraction of the total charge present on the *i*-*th* unit and *N* is the number of monomer units. *P* is equal to 1 if the all of the excess charge is localized on a single unit while P=N if a charge is evenly spread over all *N* units of a chain.

The participation ratio was calculated for PV oligomers with different substitution patterns by taking for  $Q_i$  the increase in charge on the phenylene and vinylene units upon introduction of a charge. The calculated values of P for selected oligomers are listed in Table 8.4.



**Figure 8.7:** Effect of dialkoxy substitution on the distribution of an excess positive charge,  $\Delta_+$ , in PV tetramers with different dialkoxy substitution patterns obtained from Mulliken population analysis on wavefunctions obtained from INDO/s calculation. Phenylene and vinylene moieties are indicated by p and v respectively.

First consider the values for the unsubstituted PV oligomers. The value of P gradually increases with increasing chain length, indicating an increased degree of delocalization. This increase in the degree of delocalization is accompanied by a gradual decrease of the lowest cation absorption energy RC1 (See Table 8.1).

If two methoxy groups are substituted at the central phenylene unit of PV4 to give  $PV4(1 \ da)$ , *P* decreases to 5.1 which is significantly smaller that the value of 7.1 for PV4 but close to the value of 4.6 found for PV2. Therefore it is concluded that in PV4(1 da) the charge is delocalized over a distance similar to the degree of delocalization in PV2. This result

directly explains the very similar RC1 absorption energies of these two molecules; i.e. 1.13 eV and 1.03 eV for PV2 and PV4(1 *da*) respectively.

Compound	Р	Compound	Р
PV2	4.6 <i>(4.6)</i>	PV2(1 <i>da</i> )	3.3 (4.2)
PV4	7.1 (8.3)	PV4(2 <i>da</i> )	7.2 (7.5)
PV6	8.2 (12.0)	PV6(3 <i>da</i> )	6.1 <i>(10.9)</i>
PV8	8.6 (15.6)	PV8(4 <i>da</i> )	8.8 (14.1)
PV4(1 <i>da</i> )	5.1 (7.7)		
PV4(5 <i>da</i> )	6.4 (7.4)		

**Table 8.4:** Participation ratio, P, (see Eq. 8.5) from INDO/s Mulliken population analysis. Values of P from the DFT charge distribution are given in parentheses.

At this point it is interesting to recall the odd-even trend in the RC1 energies for the  $PVn(n/2 \ da)$  oligomer series, shown in Figure 8.6. For  $PV2(1 \ da)$  a higher RC1 energy is found than for PV2. This is consistent with the values for P which are 4.6 and 3.3 for PV2 and PV2(1 da) respectively. The presence of the methoxy substituents on the middle ring causes a more localized charge distribution and therefore a lower P. For PV4(2 da) the RC1 energy is lower than that for PV4 due to the more delocalized charge, the values of P for PV4(2 da) is slightly larger that for PV4. The presence of methoxy groups on the second and fourth phenylene units "draws" the charge away from the middle ring leading to a more evenly distributed charge as illustrated in Figure 8.7. For PV6(3 da) the calculated RC1 energy is considerably higher than for both PV4(2 da) and PV6, which is consistent with the lower value of P for PV6(3 da). For PV8(4 da) the RC1 energy is lower than that for PV8 in agreement with the higher value of P. According to these INDO/s calculation, the presence of methoxy substituents on the central phenylene ring (in PV3(1 da), PV6(3 da) and PV10(5 da)) leads to a more localized charge distribution. If methoxy substituents are not present on the central ring but only on phenylene rings closer to the chain ends, the charge is drawn away from the middle, which gives a more delocalized charge distribution leading to lower RC1 energies.

It should be noted that calculation of the participation ratio using the Mulliken charges obtained from the DFT calculation yields a different result. The differences between the INDO and DFT charge distribution are discussed in more detail below.



**Figure 8.8**: Changes in C-C bond length upon removal of an electron for the unsubstituted PVn series from DFT calculations. The numbering of the bonds is indicated in the scheme.

# 8.4.4 Geometry changes upon introduction of a charge

The removal of an electron from a phenylene vinylene chain is known to result in deformations of the geometry, most prominently seen as changes of the C-C bond lengths. Previously, Cornil *et al.*<sup>13</sup> have shown, using semi-empirical AM1 calculations, that these

geometry deformations are not uniformly distributed over the whole phenylene vinylene chain. The geometry deformations were calculated to extend over a chain length encompassing approximately only three phenylene vinylene units. The changes in the C-C bond lengths outside this three-unit central region were found to be negligible.

When the geometry deformations that are obtained from the present DFT calculations are considered, a different picture emerges. Figure 8.8 shows the changes in C–C bond lengths in PV2, PV4, PV6 and PV8. The numbering of the C-C bonds is indicated in Figure 8.8. As evident from this figure, the maximum change in C-C bond length is ~0.02 Å for PV2. The largest changes are found in the vinylene units and the bonds between the vinylene units and the phenyl rings, the bond length changes in the phenylene units are considerably smaller. Upon increasing the length of the PV oligomers the C-C bond changes become smaller, for PV8 the maximum change are is less than 0.01 Å. The introduction of alkoxy substituents has no significant effect on the geometry deformations.

The results described here are very different from the earlier work by Cornil *et al.*<sup>13</sup> who found C-C bond length changes up to ~0.04 Å in the central part of the molecule. Furthermore, the geometry deformations in the DFT calculations are evenly spread over the whole PV chain and exhibit no features characteristic of the formation of a self-localized polaron, in contrast to the earlier AM1 results. Similar differences between DFT and Hartree-Fock calculations have been found for thiophene oligomers. Moro *et al.*<sup>34</sup> have performed DFT geometry optimizations for thiophenes and also found that the geometry deformation was evenly spread over the entire oligomer while earlier AM1 calculations<sup>35</sup> yielded a polaron localized on five thiophene rings.

Compound	E <sub>ion</sub> in eV	E <sub>relax</sub> in eV
PV1	7.882	0.105
PV2	7.131	0.081
PV3	6.723	0.066
PV4	6.462	0.056
PV6	6.146	0.040
PV8	5.956	0.033
PV10	5.824	0.025
PV12	5.724	0.022

 Table 8.5:
 Ionization energies and relaxation energies

 calculated using DFT for selected PV's.

The smaller geometry changes in longer PV's are consistent with the smaller relaxation energies, see Table 8.5. The relaxation energies were obtained from the DFT calculations as the difference between the vertical ionization energy, also given in Table 8.5, and the adiabatic ionization energy. As expected, the ionization energy was found to decrease gradually with increasing chain length. The relaxation energy is 0.08 eV for PV3 and decreases to close to 0.02 eV for PV12 which is comparable to the thermal energy at room temperature ( $k_BT\approx0.025$  eV at 293 K). This means that, according to the present DFT calculations, the formation of a self-trapped polaron, as predicted by AM1 calculations is unlikely. The DFT results therefore suggest that the existence of localized charges in solids should be attributed to impurities or defects in the films or crystals.<sup>36</sup> These defects can be of

a chemical nature, such as polymerization mistakes causing cross-links or broken conjugation.<sup>37</sup> Moreover, localization of charges can be induced by conformational defects caused by inter-chain interactions.

#### 8.4.5 Comparison of DFT results with Hartree-Fock calculations

As mentioned in the previous sections, there are considerable differences between results obtained using DFT and those using HF methods. DFT calculations are known to give a more delocalized charge distribution for charged conjugated oligomers.<sup>34,38,39</sup> In Figure 8.9 the charge distribution for PV4 obtained from a Mulliken population analysis of the charge density obtained from the DFT calculations is shown. The charge distribution is evenly spread over the entire PV chain, with more charge on the phenylene rings than on the vinylene moieties. This result is in agreement with the delocalized geometry deformations obtained from DFT calculations as shown above. Ab initio Hartree-Fock (HF) calculations performed on PV4 using Dunning's cc-pVDZ basis set<sup>40</sup> (which is of similar quality as the DZP-type basis set consisting of Slater functions used in ADF) give results very similar to the charge distribution from the INDO/s Hartree-Fock calculations as evident from comparison of Figures 8.7 and 8.9b. The same difference between DFT and HF calculations is observed in the geometry deformations shown in Figure 8.10. The deformations obtained from the HF/ccpVDZ calculations occur mostly in the vinylene units in the middle of the chain, and are very small in the outermost units. Note that the C-C bond length change is about 0.04 Å in the ab *initio* HF calculations, similar to the earlier semi-empirical AM1 calculations.<sup>13</sup>



**Figure 8.9:** Distribution of excess positive charge,  $\Delta_+$ , in PV4 from DFT and HF/cc-pVDZ calculations. Phenylene and vinylene moieties are indicated by p and v respectively.

There can be several explanations for these large differences between Hartree-Fock and DFT. In the DFT calculations electron correlation is included, which can lead to a more evenly spread charge distribution. However, there are also indications that in DFT the delocalization of a charge on a conjugated chain is overestimated.<sup>41</sup> The good agreement

between the spectra calculated using INDO/s-CIS with DFT geometries and experimental spectra suggests that the geometry deformations in PV cations are evenly distributed over the whole chain. However, it should be realized that the good agreement may be fortuitous since a combination of a uniform geometrical deformation (DFT) and a more localized charge distribution (INDO/s) is used. The INDO/s calculation is a Hartree-Fock type calculation and



**Figure 8.10:** Changes in C-C bond length on abstraction of an electron from PV4. Comparison of DFT/DZP (dotted line) and HF/cc-pVDZ (solid line) results.

does not contain (dynamic) correlation. The charge distribution that is obtained from the INDO/s calculation has a rather localized character, even if no substituents are present (see PV4 in Figure 8.7). The use of a delocalized geometry deformation opposes this tendency to localize leading to a sort of half-way charge distribution.

These differences between DFT and HF are also reflected in the odd-even effect for the PVn(n/2 da) series. The oscillating behavior of the RC1 energy is consistent with the degree of delocalization (e.g. reflected in the participation ratio, Table 8.4) calculated from the INDO/s charge distribution. However, if the values of *P* obtained from the DFT charge distributions are considered (see Table 8.4 in parentheses) a gradually decreasing trend is observed.

It seems clear that the delocalization length of a polaron on a conjugated chain obtained from Hartree-Fock calculations is too small. The polaron 'size' of 3 or 4 PV units obtained from AM1 calculations implies that no changes in the optical absorption spectra should be observed for oligomers longer than this. In the experimental results by Van Hal *et al.*<sup>30</sup> the energy of RC1 decreases gradually up to the longest PV studied in that work, which contains seven phenylene units. Moreover, for thiophene oligomers, AM1<sup>35</sup> calculations have predicted a polaron confined to approximately five thiophene rings, while changes in the radical cation spectra up to a thiophene oligomer containing twelve rings have been observed experimentally.<sup>42</sup> This indicates that HF calculations underestimate the spatial extent of charge carriers on conjugated chains considerably, probably due to the absence of (dynamic) electron correlation. DFT calculations have been performed for singly charged thiophene oligomers by Moro et al.<sup>34</sup> and by Brocks<sup>38</sup> and both found results similar to those obtained here for phenylene vinylenes; i.e. the charge distribution and geometry deformations are fully delocalized over the entire chain.

It would be of interest to establish whether the larger delocalization of the charge in DFT calculations is caused by inclusion of electron correlation or is an artifact in the DFT calculations. This issue could be resolved by comparison with correlated calculations at the

MP2 level of theory. This requires the use of large basis sets suitable for calculations including electron correlation such as, for example, the correlation-consistent series of basis sets constructed by Dunning<sup>40</sup>. Such calculations should be performed on PV oligomers of at least *circa* 8 repeat units and would require large computational power. Therefore these calculations are beyond the scope of the present work.

It is of particular importance to extend the experimental data on cations of PV's. Cation spectra for  $PVn(n/2 \ da)$  should be extended to lower photon energies in order to establish whether there is actually an odd/even effect in the RC1 energies. This would make it possible to decide which charge distribution is more reliable, that of the INDO/s wavefunction that predicts an odd-even trend or that from the DFT charge distribution where the degree of delocalization increases gradually with the chain length.

#### 8.5 Summary and conclusions

This chapter describes a combined experimental and theoretical study of electronic and structural properties of radical cations of phenylene vinylene (PV) oligomers. PV cations in solution were produced using pulse radiolysis. The cation optical absorption spectra were measured for a variety of PV's differing in chain length and substitution pattern. The introduction of alkoxy substituents was found to have a large effect on the optical absorption spectra of the cations. The cation optical absorption spectrum was found to depend strongly on the pattern of substitution. This indicates that substituents influence the degree of delocalization considerably.

INDO/s-CIS calculations of the cation optical absorption spectra have been performed using geometries optimized by density functional theory (DFT) calculations. The resulting absorption energies for the cations were found to be in excellent agreement with experiments. This shows that the combination of DFT geometries with INDO/s-CIS calculation of the electronic spectra gives a reliable way of predicting cation spectra of conjugated oligomers. It was found that for several oligomers a third and sometimes a fourth sub-gap absorption feature can arise especially for longer oligomers. These findings are in full agreement with experimental results.

Analysis of the charge distribution along the PV chains shows that the presence of alkoxy substituents can lead to a more localized charge if the substituents are not present on all phenylene rings. The degree of delocalization correlates with the radical cation absorption spectrum. The lowest energy absorption band, RC1, was shown to be most sensitive to charge delocalization. For a series of PV oligomers containing alkoxy substituents on every second phenylene ring an interesting odd/even effect in the energy of the low energy absorption band, RC1, is predicted. This odd/even effect correlates with the degree of delocalization of the charge obtained from the INDO/s wavefunction. The RC1 energy is higher if substituents are present on the middle phenylene ring and lower if no substituents are present there. These predictions could not be verified experimentally since the optical absorption occurs at energies outside the range accessible in the experimental set-up used in this work. Different results for the degree of delocalization were obtained from the DFT charge distribution. It is therefore of considerable interest to extend the experimental spectra to lower energies.

Large differences were observed between the charge distributions obtained from DFT calculation and those obtained using Hartree-Fock theory. Hartree-Fock calculations show the

formation of a stable self-trapped polaron, in agreement with earlier HF calculations. In contrast, according to the DFT results a positive charge is almost evenly distributed over the entire PV chain up to an oligomer containing twelve repeat units which argues against the formation of a self-trapped polaron. Therefore, on basis of the DFT results it should be concluded that the presence of localized charges in bulk solids or in solution should be attributed to defects, such as polymerization mistakes or disordered chain conformations. Additional quantum chemical calculations (such as MP2 calculation) are called for in order to establish whether the DFT method gives a correct description of charges on conjugated chains.

# 8.6 References

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#### Chapter 8

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# **Chapter 9**

# Excited State Polarizabilities of Conjugated Molecules<sup>\*</sup> A Time-Dependent Density Functional Theory Study

In this chapter time dependent density functional theory (TDDFT) calculations of excited state polarizabilities of conjugated molecules are presented. The increase in polarizability upon excitation was obtained by evaluating the dependence of the excitation energy on an applied static electric field. The excitation energy was found to vary quadratically with the field strength. The excess polarizabilities obtained for singlet excited states are in reasonable agreement with the experimental results for the shorter oligomers, particularly if the experimental uncertainties are considered. For longer oligomers the excess polarizability is considerably overestimated, similar to DFT calculations of ground state polarizabilities. Excess polarizabilities of triplet states were found to be smaller than those for the corresponding singlet state, which agrees with experimental results that are available for triplet polarizabilities. Negative polarizabilities are obtained for the lowest singlet A<sub>g</sub> states of longer oligomers. The polarizability of the lowest B<sub>u</sub> and A<sub>g</sub> excited states of the conjugated molecules studied here are determined mainly by the interaction between these two states. Upon application of a static electric field a quadratic Stark effect is observed in which the lower B<sub>u</sub> state has a positive excess polarizability and the upper A<sub>g</sub> state exhibits a decrease in polarizability upon excitation. All results are explained in terms of a sum-over-states description for the polarizability.

## 9.1 Introduction

The electrostatic properties of molecules in their electronically excited states are of considerable interest since they determine many of their observable properties and they contain information on the nature of excited states. Upon excitation both dipole moment and polarizability of a molecule can change. These changes can for instance result in a large effect of an environment, e.g. a solvent shell, on the absorption spectrum.<sup>1</sup> Changes in dipole moment alter the electrostatic interaction with the solvent in the ground and excited state, which causes a shift in the absorption maximum. These effects are used in solvent polarity scales such as the well-known  $ET_{30}$  scale.<sup>2</sup> A less recognized environment effect is caused by changes in polarizability, which causes a change in the dispersion (Van der Waals attraction) interaction between a molecule and its surroundings.<sup>1,3</sup> A striking example of environment effects on electronic spectra is found in the biologically important retinal where the absorption

<sup>&</sup>lt;sup>\*</sup> This chapter is based on: F.C. Grozema, R. Telesca, H.T. Jonkman, L.D.A. Siebbeles and J.G. Snijders, J. Chem. Phys., **115** (2001), 10014-10021.

maximum shifts from 450 nm in solution to 568 nm when it is embedded in bacteriorhodopsin.<sup>4</sup>

Changes in polarizability upon excitation also contain valuable information on the nature of molecules in their electronically excited state, the so-called exciton state.<sup>5-7</sup> This is of particular interest in the research of  $\pi$ -conjugated polymers and oligomers. These materials are intensively studied at present because of their semiconducting and light-emitting properties which makes them attractive candidates for application in polymer or molecular electronic devices such as light emitting diodes (LEDs) and field effect transistors (FETs). The increase in polarizability upon excitation (excess polarizability,  $\Delta \alpha$ ) can be considered as a measure for the spatial extent of the exciton. The lowest singlet exciton is the intermediary state in organic LEDs<sup>8</sup> and photovoltaic devices.<sup>9,10</sup>

Finally, the electrostatic properties of excited states are important for studying materials, which exhibit nonlinear optical (NLO) behavior.<sup>11</sup> In the two-state model the first hyperpolarizability is proportional to the change in dipole moment upon excitation,  $\Delta\mu$ . In solution  $\Delta\mu$  is affected also by the change in polarizability since the electric field of the surrounding solvent induces a dipole moment of a different size.

For the experimental determination of excited state electrostatic properties there are mainly two techniques available. The first is the Stark spectroscopy or electroabsorption/emission method.<sup>12</sup> In this method the effect of a strong external electric field on the absorption or emission spectrum is evaluated. The effect of the electric field is observed as a broadening of the absorption band if there is a change in the dipole moment upon excitation, which is a result of the random orientation of molecules with respect to the applied field. A change in polarizability causes a shift of the absorption/emission band, which is quadratically dependent on the applied field. The method can be used either in absorption or emission spectroscopy. In the case of electro-absorption, information is obtained on the properties of the relaxed excited state. This method has often been applied in studies of chromophores in biologically important systems<sup>13-16</sup> but also in the study of donor-acceptor molecules for NLO applications.<sup>11,17</sup>

The second method by which information on the excited state electrostatic properties can be obtained is the flash photolysis time-resolved microwave-conductivity (FP-TRMC) technique.<sup>5,7,18-20</sup> In this technique the changes in molecular properties upon excitation with a short nanosecond laser pulse are probed using microwaves. A change in dipole moment results in absorption of microwaves while a change in the polarizability (which changes the dielectric constant of the sample) causes a phase shift of the microwaves. The information obtained in this way usually corresponds to the relaxed excited state, generally the lowest singlet state. In materials with an appreciable singlet-triplet transition probability such as oligothiophenes also the properties of the lowest triplet state can be obtained.<sup>21</sup>

While there is a large amount of experimental data available on excited state properties there have been very few theoretical studies, especially for the calculation of excess polarizabilities. This is not very surprising since experimental studies very often involve large molecules not accessible to accurate *ab initio* methods taking electron correlation in

consideration, such as configuration interaction including single and double excitations (CISD) or complete active space multi-configuration self-consistent field (CASSCF) methods combined with large basis sets. This restricts the applicability of these methods to rather small molecules such as benzene and polyenes.<sup>22,23</sup> Semi-empirical methods have also been used for calculating excited state polarizabilities. Such methods have been applied with reasonable success for the calculation of excess polarizabilities in biphenyl polyenes, however, considerable deviations from experimental results were observed in the case of donor-acceptor substituted polyenes.<sup>13,24</sup>

Recently, Van der Horst *et al.*<sup>25</sup> have calculated polarizabilities of exciton states of conjugated polymers by applying the Bethe-Salpeter equation (BSE) for the description of an electron-hole pair. The results obtained from these calculations were in reasonable agreement with experimental data, however they were performed for infinitely long and periodic polymer chains. This is a rather crude approximation since conjugated polymers in solution in general have a disordered structure.

Density functional theory (DFT) offers a very attractive alternative to the traditional correlated *ab initio* methods since it can treat very large systems at the correlated level at a computational cost comparable to that for Hartree-Fock calculations. DFT is in principle a ground state theory, however the recent implementations of time-dependent density functional theory (TDDFT)<sup>26</sup> have made the evaluation of excitation spectra possible and it has been shown that reliable results can be obtained from this method.

In this chapter we demonstrate the use of time dependent density functional theory combined with a static electric field for the calculation of the change in polarizability upon excitation,  $\Delta \alpha$ , for conjugated oligomers of three different types: oligothiophenes, oligophenylenevinylenes and diphenylpolyenes. The molecular structures of these oligomers are shown in Figure 9.1, together with the nomenclature used in this paper. Calculations are performed for molecules in vacuum and the results are compared to experimental data from both Stark spectroscopy and FP-TRMC for isolated molecules in solution.

# 9.2 Theory and Computational Details

All the calculations described below were performed using the Time Dependent Density Functional Theory code as implemented in the Amsterdam Density Functional Program Package (ADF). <sup>27-30</sup>

For the ground state calculations the Local Density Approximation (LDA) for the exchange and correlation functional based on the parameterization of the electron gas data given by Vosko, Wilk and Nusair (VWN)<sup>31</sup> was used, together with the Generalized Gradient Approximation corrections by Becke<sup>32</sup> (exchange) and Perdew<sup>33</sup> (correlation).

The basis set used for the calculations below was of Triple Zeta quality including polarization functions (TZP, basis set IV in ADF) consisting of Slater-type functions. Polarizabilities of these systems were calculated using response theory based on time dependent density functional Theory (TDDFT) as implemented in the RESPONSE code of ADF,<sup>26,30,34</sup> in combination with a static electric field (see below).



**Figure 9.1**: Molecular structure and nomenclature for molecules studied in this work, note that OPV2 is the same as DPE.

TDDFT provides a method for calculating frequency-dependent (and static) polarizabilities, excitation energies and several other response properties. The calculation of excitation energies and oscillator strengths goes practically through the solution of the following eigenvalue equation<sup>26</sup>

$$\Omega F_i = w_i^2 F_i \tag{9.1}$$

where the four-index matrix  $\Omega$  has components given by

$$\Omega_{ias,jbt} = d_{st} d_{ij} d_{ab} (e_{as} - e_{is})^2 + 2\sqrt{(e_{as} - e_{is})} K_{ias,jbt} \sqrt{(e_{bt} - e_{jt})}$$
(9.2)

In this equation the squared differences between occupied and virtual KS orbital energies (*a*, *b* refer to unoccupied and *i*, *j* refer to occupied ones, while  $\sigma$  and  $\tau$  are spin indices) are included as well as a coupling matrix, *K* containing Coulomb and Exchange Correlation (XC) parts. The square of the desired excitation energies are the eigenvalues  $\omega_i^2$ , while the oscillator strengths are simply related to the eigenvectors  $F_i$ . The elements of the eigenvectors  $F_i$  are roughly comparable to the CI coefficients in a Singly Excited Configuration Interaction (SECI) calculation and are a measure to what extent the corresponding excitation can be interpreted as a pure single particle excitation or if several such excitations play a crucial role in the transition. The Coulomb part of the coupling matrix is given by
$$K_{ijs,klt}^{Coul} = \int dr \int dr' f_{is}(r) f_{js}(r) \times \frac{1}{|r-r'|} f_{kt}(r') f_{lt}(r')$$
(9.3)

While the exchange correlation part

$$K_{ijs,kl\tau}^{xc}(w) = \int dr \int dr' f_{is}(r) f_{js}(r) \times f_{xc}^{st}(r,r',w) f_{kt}(r') f_{lt}(r')$$
(9.4)

is related to the so called exchange correlation kernel

$$f_{xc}^{st}(r,r',t-t') = \frac{dv_{xc}^{s}(r,t)}{dr_{t}(r',t')}$$
(9.5)

In the so called Adiabatic Local Density Approximation (ALDA) used here the exchange correlation kernel is simply given by

$$f_{xc}^{ALDA,st}(r,r',w) = d(r-r') \frac{dv_{xc}^{LDA,s}(r,t)}{dr_t} \bigg|_{r_t = r_{0,t}(r)}$$
(9.6)

The matrix  $\Omega$  can become rather large, however, since one is usually interested in the lowest few excitations, efficient algorithms such as the Davidson algorithm can be used.<sup>35-37</sup> The TDDFT method as implemented in ADF can be used to calculate accurate excitation energies and has been successfully applied to the excited states of oligothiophenes.<sup>38</sup>

The combination of TDDFT with a static uniform electric field makes possible to analyze the electrostatic properties of molecules in their excited state. The dependence of the excitation energy on a static external electric field depends on the changes in dipole moment and polarizability upon excitation. A change in dipole moment gives a linear dependence on the applied electric field whereas a change in polarizability causes a quadratic field dependence of the excitation energy:

$$E_{exc}(F) = E_{exc}(0) - \Delta\mu F - \frac{1}{2}\Delta\alpha F^2$$
(9.7)

where F is the static electric field. This method for the calculation of the changes in electrostatic properties is in fact analogous to the way in which excited state properties are obtained in electroabsorption measurements. The advantage of calculations is however that there is full control of the orientation of the system that is studied and therefore a change in dipole moment will also cause a shift of the excitation energy as opposed to a broadening of the spectrum which is obtained experimentally because of the random orientation of molecules in the solution or matrix. The molecules that are considered in this work exhibit only an increase in polarizability upon excitation. Hence, the excitation energy varies quadratically with increasing field strength as a results of the quadratic Stark effect. Such a quadratic dependence is demonstrated by the



**Figure 9.2**: Excitation energy plotted versus electric field strength for lowest singlet excitation in OPV3. The squares represent calculated values, the line is a parabolic fit.

TDDFT calculations as shown in Figure 9.2 for PV2 (see Figure 9.1 for nomenclature). Excess polarizabilities reported below were obtained by calculating the excitation energy at zero field and at three different field strengths ranging from  $5 \cdot 10^7$  V m<sup>-1</sup> ( $1 \cdot 10^{-4}$  au) to  $1.5 \cdot 10^8$  V m<sup>-1</sup> ( $3 \cdot 10^{-4}$  au) and fitting of a parabolic function to the results. The only significant contribution to the excess polarizability was found to be in the direction along the long axis of the molecules studied. The values given below are average values for the increase in polarizability, i.e. averaged over all three directions. The change in dipole moment ( $\Delta \mu$ ) was found to be zero for all studied molecules, as expected. The dependence of the results on the size of the basis set used is shown in Table 9.1 for PV1 (or DPE). Sizes of the basis set range from a minimal basis set (SZ, basis I in ADF)) to triple zeta plus polarization functions (TZP, IV in ADF). All basis sets consist of Slater type functions. The calculated excitation energy decreases with increasing size of the basis set, however the calculated excess polarizability does not seem to depend much on the size of the

**Table 9.1**: Basis set dependence of the excitation energy and excess polarizability for the lowest  $B_u$  state of PV1. ADF basis set names are given in parentheses in the first column.

Basis set	E <sub>exc</sub> (eV)	$\Delta \alpha (\text{\AA}^3)$
SZ (I)	4.46	64
DZ (II)	3.81	46
DZP (III)	3.68	44
TZP (IV)	3.61	47
Experimental	3.71	-

basis set, except for the smallest basis where the polarizability is considerably larger. The differences in  $\Delta \alpha$  obtained using the other basis sets are very small and are probably due to

numerical imprecision in the Davidson algorithm and in the fitting of the results to parabolic functions. The basis set used for the calculations reported below (TZP, IV) can be considered sufficient for accurate results.

#### 9.3 Results and discussion

#### Singlet B<sub>u</sub> excitons

The method described in the previous section was used to calculate excess polarizabilities for three series of  $\pi$ -conjugated oligomers that are of interest for application in plastic electronic devices (see Figure 9.1).

The excess polarizabilities calculated for the lowest singlet excitons (of  $B_u$  symmetry) of the molecules in Figure 9.1 are listed in Table 9.2 together with the experimental data collected from both Stark spectroscopy<sup>39,40</sup> and FP-TRMC measurements.<sup>5,19,21</sup> The calculated results for shorter oligomers are shown to be in reasonable agreement with experimental data, especially when the experimental error margins are considered. For longer oligomers (T6, PV3 and DPD) the polarizability is considerably overestimated in these calculations. This is shown graphically in Figure 9.3 for the series of biphenyl polyenes. The calculated results correspond reasonably to the Stark spectroscopy values up to DPO. The calculated  $\Delta\alpha$  for DPD deviates considerably from the experimental value. This overestimate for long conjugated system has also been found for ground state polarizabilities of polyenes as reported by Champagne et al.<sup>41</sup> This incorrect behavior for long (conjugated) molecules is related to the short-sightedness of present XC potentials which mainly feel the local density and are relatively insensitive to polarization charges induced by an external electric field at the chain ends.<sup>41</sup>



**Figure 9.3**: Trend in excess polarizability of the diphenylpolyenes for the lowest singlet excited state. Triangles are calculated values, circles are experimental values from electroabsorption measurements.

For short oligomers this problem does not arise. For PV2 the calculated excess polarizability  $(351 \text{ Å}^3)$  is in reasonable agreement with the Stark value  $(420 \text{ Å}^3)^{40}$  as well as with the FP-TRMC result  $(300 \pm 50 \text{ Å}^3)$ ,<sup>5</sup> this shows that for shorter oligomers the results are reliable. PV2 is the only oligomer on which both experimental techniques have been applied and the difference can be interpreted as a rough estimate of the experimental errors, although the difference may also arise because of fundamental differences between both techniques. In FP-TRMC the excess polarizability is measured as the difference between the ground state polarizability in the ground state geometry and the exciton state in its relaxed excited state geometry, whereas in Stark spectroscopy the un-relaxed, initially excited state is probed.

Compound	$\Delta \alpha (^{1}B_{u})$	Δα ( <sup>1</sup> B <sub>u</sub> )	$\Delta \alpha$ ( <sup>3</sup> B <sub>u</sub> )	$\Delta \alpha$ ( <sup>3</sup> B <sub>u</sub> )	$\Delta \alpha$ ( <sup>1</sup> A <sub>g</sub> )	$\Delta \alpha (^{3}A_{g})$
Compound	(Calc.)	(Exp.)	(Calc.)	(Exp.)	(Calc.)	(Calc.)
T2	11	125 ± 100	3	4.5 <sup>e</sup>	24	34
		а				
Т3	84	370 ± 100	16	11 <sup>e</sup>	-20	12
		а				
T4	189	400 ± 100	47	19 <sup>e</sup>	-356	24
		а				
Т5	567	355±50 °	103	23 <sup>e</sup>	-425	51
Т6	1429	370±50 <sup>a</sup>	198	23 <sup>e</sup>	-1183	84
PV1	47	-	<10	-	66	59
PV2	351	$300 \pm 50$ <sup>b</sup> ,	63	-	-273	20
		420 °				
PV3	1283	$530 \pm 50$ <sup>b</sup>	205	-	-1023	89
DPE	47	-	<10	-	66	59
DPB	65	53 <sup>d</sup>	14	-	78	43
DPH	100	91 <sup>d</sup>	17	-	-61	20
DPO	145	116 <sup>d</sup>	21	-	-104	24
DPD	265	140 <sup>d</sup>	26	-	-199	25

**Table 9.2**: Excess polarizabilities for different singlet and triplet excited states (in  $Å^3$ ) compared to experimental data, where available.

Experimental data from:

<sup>a</sup> FPTRMC, ref. 19

<sup>b</sup> FPTRMC, ref. 5

<sup>c</sup> Electroabsorption, ref.40

<sup>d</sup> Electroabsorption, ref.39

<sup>e</sup> ref. 21

Oligothiophenes and oligophenylenevinylenes can be expected to have different excited state properties than diphenylpolyenes. The diphenylpolyenes are phenyl-endcapped polyacetylenes in which there exist bound exciton states just below the conduction band edge. According to the work of Shibahara et al. these excitons have binding energies around 0.2  $eV^{42}$  and theoretical studies have shown that they are delocalized over a long distance.<sup>43</sup> A low exciton binding energy for polyacetylene would explain the trend in the experimental values of

the excited state polarizabilities very well. In this case, for polyacetylenes the relevant excitonic states are delocalized, and a linear increase in the excited state polarizabilities with the size of the system can be expected, which is indeed observed for the shorter polyenes presented here. The upper limit of the polarizability is probably determined by the degree of structural disorder in these systems. The TDDFT calculations give good numerical agreement with experimental results. One indeed observes a linear increase of the polarizability up to DPO, for longer chains TDDFT overestimates the excited state polarizabilities. This discrepancy is inherent to the theoretical method used and can be attributed to the local character of the XC potentials currently used, as it was explained before.

For the oligothiophenes the situation is somewhat different. Much higher exciton binding energies (0.5 - 1.0 eV) have been reported in this case. This would lead to the formation a Frenkel type exciton which is localized over a much smaller length than the exciton in polyacetylene. The experimental excess polarizability seems to saturate already for T3 which would agree with these arguments. It should be noted however, that the experimental data for the thiophenes are not reliable enough (because of a large uncertainty in the excited state life-time<sup>19</sup>) to draw definite conclusions in this respect. The TDDFT values are in reasonable agreement for the small oligomers up to T3, there is a large discrepancy with experiment for the larger ones. Oligothiophenes can in general be described as long one dimensional chains of weakly interacting monomer units. It should be clear that the diphenylpolyenes have a different character because of their low exciton binding energy and may in fact be considered as simple conjugated entities. For the OPVs the same behaviour as for the oligothiophenes may be expected, although the excitonic states have a smaller binding energy and the localization length of the exciton is somewhat larger. Here again up to OPV3 there is good agreement between experiment and theory.

Differences in experimental and calculated values for the OPVs and oligothiophenes may be caused by the effect of substituents on the excess polarizability. The calculations all refer to unsubstituted oligomers whereas most of the experimentally studied compounds have substituents. In the case of the OPVs this effect is probably not very large since the substituents in this case are *t*-butyl groups at the two outermost rings of the molecule.<sup>5</sup> These alkyl side-chains are not expected to have a large electronic effect on the excess polarizability. The same argument applies to the oligothiophenes up to T5, the experimental results in this case are end-capped by a butyl chains connecting the  $\alpha$  and  $\beta$  carbon atoms of the thiophene ring.<sup>19</sup>

Another potential source for differences between experimental and calculated results is the environment effect. Experiments are performed in solution or in a solid matrix (or frozen solutions) whereas the calculations correspond to the gas phase. The environment may alter the actual polarizability by intermolecular interactions as it has been shown theoretically<sup>44</sup> but it also complicates the analysis of experimental results from electro-absorption measurements. The change in the excitation energy is related to the local electric field that is 'felt' by the molecule, this field may differ from the externally applied field because of screening by the surrounding solvent. This shielding factor is unknown and is not corrected for in the evaluation of the results.

#### Triplet $B_u$ excitons

In Table 9.2 the excess polarizabilities for states other than the lowest singlet state are also listed for the compounds in Figure 9.1. The excess polarizabilities found for the triplet  $B_{\mu}$ excitons are considerably lower than those found for the singlet excitons. Experimentally, there is very little information on excess polarizabilities of triplet states since these states are not accessible by direct excitation from the ground state. Therefore no triplet data is available from electroabsorption measurements. Long living triplet states can be studied using the FP-TRMC technique if the quantum yield for intersystem crossing is large enough. Triplet polarizabilities have been published only for thiophene oligomers<sup>21</sup> which have an appreciable intersystem crossing yield and the excess polarizabilities were found to be almost an order of magnitude lower than those for singlet excitons which corresponds nicely with the TDDFT calculations presented here. For these triplet polarizabilities there is also a reasonable agreement between the experimental data<sup>21</sup> and calculated results for the shortest oligothiophenes. The polarizabilities for T2 and T3 were calculated to be 3 and 16  $Å^3$ , respectively whereas the experimental values are 4.5 and 11 Å<sup>3</sup>. The experimental results for these triplet states are considerably more reliable than those for the corresponding singlet states because of the very long lifetime of the triplet excited state.



**Figure 9.4**: Schematic energy level diagram and orbital occupation for singlet and triplet states of OPV3.

The large difference in excess polarizability between the triplet and singlet exciton can be understood in terms of the sum-over-states description for the polarizability:

$$\alpha_a = \frac{2}{3} \sum_{\substack{n \\ n \neq a}} \frac{|\mu_{na}|^2}{\Delta E_{na}}$$
(9.8)

where *a* is the state for which the polarizability is calculated and the sum runs over all states other than *a*.  $\Delta E_{na}$  is the energy difference between states *a* and *n* and  $\mu_{na}$  is the transition

dipole moment between these states. The lowest states for both multiplicities are of B<sub>u</sub> symmetry (see Figure 9.4 for energy level diagram of PV2), therefore only excitations to Ag states are allowed. Thus the polarizability of a state of a B<sub>n</sub> exciton arises from mixing with A<sub>g</sub> states. For the lowest triplet states there are only allowed transitions to higher electronic states and therefore all terms in the summation give a positive contribution to the polarizability. In the case of the lowest singlet exciton the most important contributions are also those resulting from mixing with higher lying Ag states, although there are other contributions that can be considered negligible.<sup>45</sup> The large difference between singlet and triplet excess polarizabilities can be explained by considering the transition energies to the closest lying Ag state. As an example, the calculated energies for the lowest five excitations in PV2 are listed in Table 9.3 for both the triplet and the singlet, and are shown schematically in Figure 4. The energy difference between the lowest singlet  $B_u$  state and the lowest  $A_g$  state is 0.24 eV whereas for the triplet this energy difference is 0.79 eV. If it is assumed that the allowed transition with the lowest energy is the main contributor to the polarizability of a certain state it can be understood from Eq. 9.8 that this contribution will be considerably higher for the singlet exciton than for the triplet if the transition dipole moment is similar. Van der Horst et al. have in fact found that in their calculations of exciton polarizabilities of conjugated polymers the main contribution (99%) was due to the mixing with the lowest lying higher state to which a transition was allowed.<sup>25</sup>

nr	Sir	nglet	Triplet		
	Energy	Symmetry	Energy	Symmetry	
1	2.67	Bu	1.83	B <sub>u</sub>	
2	2.91	Ag	2.61	Ag	
3	3.50	Ag	2.88	Ag	
4	3.51	Bu	3.33	Bu	
5	3.65	Ag	3.36	Ag	

Table 9.3: Excitation energy (from ground state) for lowest singlet and triplet states in PV2 in eV.

#### Higher excited states

Table 9.2 also lists the excess polarizability of the singlet and triplet  $A_g$  exciton states. The  ${}^{1}A_{g}$  column in the table shows some very interesting values. For the longer oligomers of all oligomer series the excess polarizability becomes negative, which implies a decrease in polarizability upon excitation. The decrease in polarizability is of the same order of magnitude as the increases found for the  ${}^{1}B_{u}$  state and are much larger (but negative) than the polarizability for the ground state. A TDDFT calculation of the ground state polarizability of PV2 for instance gives a value of 61 Å<sup>3</sup>. Therefore the lowest  ${}^{1}A_{g}$  states of longer conjugated oligomers are expected to have a negative overall polarizability. This can again be understood by using the same arguments as used above in terms of a sum-over-states description. There is a large negative contribution to the polarizability that arises from the mixing of the  ${}^{1}A_{g}$  state with the  ${}^{1}B_{u}$  state lying below it. This negative contribution is counteracted by positive contributions due to mixing with all higher lying  ${}^{1}B_{u}$  states.

The negative contribution to the excess polarizability for the  ${}^{1}A_{g}$  state is the same as the dominant positive contribution to the polarizability for the  ${}^{1}B_{u}$  state described above. This explains why the absolute values of the  ${}^{1}B_{u}$  and  ${}^{1}A_{g}$  excess polarizabilities are so similar. In the short oligomers a positive value is found for the excess polarizability of the  ${}^{1}A_{g}$  state which shows that the negative contribution is not dominant yet in these cases. Upon lengthening of the chains the energy difference between the B<sub>u</sub> and A<sub>g</sub> states decreases, which leads to two states that are located in a gap between the ground state and higher lying excited states that are relatively far away in energy. Therefore the response of both states to an applied electric field is dominated by the interaction between them.

Application of an electric field leads to a Stark splitting<sup>46</sup> of the two strongly coupled states in which the energy of the lower state ( $B_u$ ) decreases quadratically with the applied field, while the energy of the upper state ( $A_g$ ) increases with the field strength. The lowest ( $B_u$ ) state attains a dipole moment which has a negative interaction with the applied field (it is directed parallel to the electric field), hence the excitation energy lowers. The upper state shifts to higher energy since it attains a dipole moment which has a positive interaction with the applied field (the direction of this dipole is anti-parallel to the electric field). This is an example of the well-known quadratic Stark effect where the upper state formally has a negative polarizability.<sup>46,47</sup>

Similar splitting of states was found theoretically in solvent effect studies of ethylene in its twisted geometry.<sup>48</sup> The electric field of the surrounding solvent induces a splitting between the two lowest excited states and the upper one attains a dipole moment opposite to the electric field and therefore has a negative polarizability.

The quadratic Stark effect has been investigated experimentally by Harrison *et al.* for a ladder-type poly-para-phenylene using nonlinear optical techniques.<sup>49</sup> It was concluded that the quadratic Stark effect observed for the lowest excited state ( $B_u$ ) was mainly caused by coupling with the next excited state of  $A_g$  symmetry, which is in agreement with the calculations presented here for similar systems and with the earlier results from quasi-particle calculations.<sup>25</sup>

For the triplet  $A_g$  state negative polarizabilities might have been expected as well since a negative contribution is present here also due to coupling with the lowest  ${}^{3}B_{u}$  state. However the energy gap between these two states is considerably larger than in the case of singlet states as shown above (see Table 9.3) and the negative contribution does not become dominant.

#### 9.4 Summary and conclusions

This chapter describes, for the first time, a method to calculate electrostatic properties of excited states of molecular systems using time-dependent density functional theory in combination with a static electric field. The method is shown to give reliable results for increases in polarizability upon excitation for short conjugated molecules. For longer conjugated chains an overestimate of the excess polarizability is observed similar to the results found earlier for the ground state. The results for short oligomers are in reasonable agreement with the experimental values from both electro-absorption measurements and time-resolved

microwave conductivity measurements (TRMC) for the lowest singlet excited state of  $B_u$  symmetry. Triplet polarizabilities for the lowest  $B_u$  states are found to be considerably smaller than singlet values, in agreement with experimental observations. The triplet polarizabilities for short thiophene oligomers are found to agree nicely with experimental data for these systems, for the longer chains the polarizabilities were obtained. The calculated results indicate that the strong coupling between the lowest  $B_u$  and  $A_g$  states in all oligomers is an important factor which determines the polarizability of both states. The quadratic Stark effect causes a large positive polarizability for the lower state while the higher state ( $A_g$ ) has a negative polarizability.

This method for the calculation of excited state properties can be a valuable tool in the study of non-linear optical effects and the nature of electronically excited states in conjugated polymers. The effect of factors such as geometry changes and substituent effects can be studied systematically. This is the subject of chapter 10.

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### Tuning of the Excited State Properties of

### Phenylene vinylene Oligomers<sup>\*</sup>

This chapter discusses a time-dependent density functional theory (TDDFT) study of the effect of molecular structure on the excited state polarizability of conjugated molecules. A short phenylene vinylene oligomer containing three phenyl rings (PV2, distyryl benzene) is taken as a model system. Introduction of methyl substituents is shown to have only a small influence on the increase in polarizability upon excitation (the excess polarizability,  $\Delta \overline{\alpha}$ ). Methoxy groups have a much larger effect but in this case  $\Delta \overline{\alpha}$  depends strongly on the dihedral angle between the side-chain and the backbone of the molecule. If the central phenyl ring of PV2 has a *meta*-configuration rather than *para*, both the optical absorption spectrum and the excess polarizability change considerably.

#### **10.1 Introduction**

Conjugated oligomers and polymers are attractive candidates for application in organic optoelectronic devices because of their low cost and easy processability, compared to crystalline inorganic materials. Examples of such devices include light emitting diodes (LEDs),<sup>1,2</sup> solid state lasers and photovoltaic devices.<sup>3,4</sup> In all of these devices the excited state of the conjugated molecule plays a decisive role. In LEDs the excited electronic state or exciton is formed by combination of an electron and a positive charge ('hole') that are injected from the opposite electrodes. The excited states decay to the ground state by fluorescence, generally the emission is from the lowest singlet state.

In photovoltaic devices this process is reversed. The first step in this case is light absorption, which leads to formation of an exciton. This exciton can dissociate into free electrons and holes, which can be collected at different ends of the absorbing material through electrodes. It may be clear that the nature and properties of the electronically excited state of

<sup>&</sup>lt;sup>\*</sup> This chapter is based on: F.C. Grozema, R. Telesca, J.G. Snijders and L.D.A. Siebbeles, *J. Chem. Phys.*, **118** (2003), 9441-9446.

conjugated molecules play an important role in the performance of photovoltaic and light emitting devices.

Valuable information on the nature of excitons in conjugated molecules can be obtained from studies of the changes in the electronic polarizability ( $\Delta \overline{\alpha}$ ) upon excitation. The polarizability of the exciton can be considered as a measure of the spatial extent of the excited state.<sup>5-7</sup> The 'size' of the exciton may be one of the factors determining the formation probability of an exciton when an electron and a hole approach each other. Furthermore, the exciton polarizability is also a measure of the exciton binding energy, the attraction between the electron and hole. A large polarizability, which implies a small exciton binding energy, is favorable for exciton dissociation in photovoltaic devices.

Experimental information on excited state polarizabilities is available from two techniques. The first is the flash photolysis time-resolved microwave conductivity technique (FP-TRMC) in which the change in dielectric constant (i.e. the macroscopic polarizability) upon excitation of molecules in a solution is monitored using microwaves.<sup>5,8</sup> The excited state on which information is obtained is usually the lowest excited singlet state but in materials with an appreciable triplet yield it is also possible to gain information about the triplet state.<sup>9</sup>

The second method is electro-absorption or -emission spectroscopy,<sup>10,11</sup> where the changes in absorption- or emission-spectra are monitored as a function of an externally applied electric field. In the case of electro-absorption information is obtained for the Franck-Condon (vertical) excited state, while in electro-emission the relaxed fluorescing state is probed.

The first demonstration of a conjugated-polymer light emitting diode was based on an unsubstituted poly(phenylene vinylene) (PPV) which is insoluble and thus precludes processing from common organic solvents.<sup>12</sup> Conjugated polymers can be made soluble introduction of side chains such as alkyl and alkoxy groups. Introduction of electronically active substituents such as alkoxy or cyano groups also offers the opportunity to tune the absorption and emission wavelength. Substituents can also be expected to have a considerable influence on the electronic properties of the excited state, such as the excited state polarizability. This has been shown experimentally by an FP-TRMC study reported recently by Candeias *et al.*<sup>13</sup> who showed that the number and position of alkoxy side-chains influences the excited state polarizability significantly. Similar observations have been made by Lane *et al.* who performed electro-absorption measurements.<sup>14</sup>

In chapter 9 it was shown that the increase in polarizability upon excitation of a molecule (the excess polarizability,  $\Delta \overline{\alpha}$ ) can be obtained by calculating the optical absorption spectrum, using time-dependent density functional theory, as a function of an externally applied electric field.<sup>15</sup> For short conjugated molecules the method was found to give excess state polarizabilities that are in good agreement with experimental data. For more extended linear conjugated molecules the excited state polarizability is considerably overestimated, similar to the well-known overestimation of the polarizability of long linear molecules in the ground state.<sup>16,17</sup>

This chapter describes a detailed computational study of the effects of substituents and other structural modification on the excited state polarizability of conjugated molecules. A

short phenylene vinylene oligomer, PV2, is used as a model system for PPV, one of the materials that is most often used in polymer-based LEDs and photovoltaic cells. The structures of the molecules that were studied are shown in Figure 10.1.



**Figure 10.1**: Structures of the phenylenevinylene derivatives for which calculations have been performed.

#### **10.2 Computational details**

The calculations described below were performed using the Time Dependent Density Functional Theory code as implemented in the Amsterdam Density Functional Program Package (ADF). <sup>18-21</sup> The calculations were performed in the same way as published previously for unsubstituted conjugated oligomers.<sup>15</sup> For the ground state calculations the Local Density Approximation (LDA) for the exchange and correlation functional based on the parameterization of the electron gas data given by Vosko, Wilk and Nusair (VWN)<sup>22</sup> was used, together with the Generalized Gradient Approximation corrections by Becke<sup>23</sup> (exchange) and Perdew<sup>24</sup> (correlation).

The basis set used for the calculations described below was of Triple Zeta quality including polarization functions (TZP, basis set IV in ADF) consisting of Slater-type functions.<sup>25</sup> The geometries of the molecules studied were completely optimized in the ground state, constraining them to  $C_{2h}$  or  $C_{2v}$  symmetry. Excess polarizabilities of these

systems were calculated using Response theory based on time-dependent density functional Theory (TDDFT) as implemented in the RESPONSE code of ADF,<sup>21,26,27</sup> in combination with a static electric field. The combination of TDDFT with a static uniform electric field makes it possible to analyze the electrostatic properties of molecules in their excited state. The dependence of the excitation energy,  $E_{exc}$ , on a static external electric field depends on the changes in dipole moment and polarizability upon excitation. A change in dipole moment,  $\Delta\mu$ , gives a linear dependence on the applied electric field whereas a change in polarizability,  $\Delta\alpha$ , causes a quadratic field dependence of the excitation energy. For an electric field,  $F_i$ , in direction *i*:

$$E_{exc}(F_i) = E_{exc}(0) - \Delta \mu_i F_i - \frac{1}{2} \Delta \alpha_{ii} F_i^2$$
(10.1)

where  $\Delta \alpha_{ii}$  is the change in the *i*-th diagonal element of the polarizability tensor  $\alpha$ . In the following, the excess polarizabilities are given as average values,  $\Delta \overline{\alpha}$ , defined as

$$\Delta \overline{\alpha} = \frac{1}{3} (\Delta \alpha_{xx} + \Delta \alpha_{yy} + \Delta \alpha_{zz})$$
(10.2)

The excitation energies for the lowest 10 states were calculated for electric fields ranging from 0 a.u. to  $3x10^{-4}$  a.u. in along all three axes. The largest component of the excess polarizability was found to be the one along the main chain of the molecule. The component directed perpendicular to the plane of the molecule was negligible in all cases.

This method for the calculation of the changes in electrostatic properties is analogous to the way in which excited state properties are obtained from electro-absorption measurements. It was shown previously that the calculated excitation energy indeed varies quadratically with the applied electric field.<sup>15</sup> For short conjugated oligomers the calculated increase in polarizability upon excitation was found to be in good agreement with experimental data. For longer oligomers a large overestimation of the excess polarizability was found, similar to the well-known overestimation of ground state polarizabilities when using conventional exchange correlation functionals.<sup>16,17</sup> Recently Van Faassen *et al.* have demonstrated that this problem of over-polarization can be solved by using so-called current-density-functionals for describing non-local exchange-correlation effects in extended conjugated systems.<sup>17,28</sup> It is of considerable interest to examine whether such current-density-functionals also improve the description of the polarizability of the excited state. Such calculations are currently being pursued and will be the subject of a future publication.

The present work is restricted to short oligomers with different molecular structures. It is expected that the overestimation of the polarizability is of minor importance in this case since a good agreement with experimental data was obtained previously for molecules of similar size.<sup>15</sup> Moreover, the main focus in this work is on the effect of substituents on the excess polarizability rather than on the absolute magnitude.

#### **10.3 Results and discussion**

Calculations of the excess polarizability were performed for all structures shown in Figure 10.1 by the method outlined in the previous section. Table 10.1 gives the results obtained for selected excited states of the molecules studied. The results for PV2 from chapter 9 are also given for comparison with the substituted analogues of PV2. The table also gives experimental values where these are available.

Compound	State	E <sub>exc</sub> (eV)	Osc.	$\Delta \overline{\alpha}$ (Å <sup>3</sup> )	$\Delta \overline{lpha}$ (Å <sup>3</sup> )
					exp.
PV2	<sup>1</sup> Bu	2.67	1.58	351	420 <sup>a</sup>
	${}^{1}A_{g}$	2.91	0.00	-273	-
diMe-PV2	<sup>1</sup> B <sub>u</sub>	2.69	1.53	271	-
	${}^{1}A_{g}$	2.97	0.00	-184	-
tetraMe-PV2	<sup>1</sup> B <sub>u</sub>	2.69	1.66	383	300 <sup>b</sup>
	${}^{1}A_{g}$	2.96	0.00	-274	-
PV2-1 <i>da</i>	<sup>1</sup> B <sub>u</sub>	2.47	1.04	91	150 <sup>b</sup> ,
					340 <sup>a</sup>
	${}^{1}A_{g}$	2.90	0.00	362	
	${}^{1}B_{u}$	2.96	0.52	-301	
PV2-3da	<sup>1</sup> B <sub>u</sub>	2.22	1.06	808	311 <sup>a</sup>
	${}^{1}A_{g}$	2.35	0.00	-620	-
PV2-CN	<sup>1</sup> B <sub>u</sub>	2.52	0.52	107	-
	<sup>1</sup> B <sub>u</sub>	2.72	1.00	283	
	${}^{1}A_{g}$	2.89	0.00	-229	
meta-PV2	<sup>1</sup> B <sub>2</sub>	2.83	0.03	1148	-
	<sup>1</sup> A <sub>1</sub>	2.92	0.05	-1084	-
	${}^{1}B_{2}$	3.51	1.80	88	80 <sup>a</sup>

**Table 10.1:** Excitation energy from the ground state, oscillator strength and excess polarizability of PV2 analogues.

Experimental data from:

<sup>a</sup> Electro absorption measurements by Lane et al. ref. 14

<sup>b</sup> FP-TRMC measurements by Gelinck et al. ref. 5

#### Methyl substituents

The first type of substituent considered here are methyl groups, see structures b and c in Figure 10.1. The results for methyl substituents can be considered representative for the effect of alkyl side-chains on the properties of excitons. Conjugated polymers are often substituted with alkyl chains in order to make them (more) soluble. Introduction of two methyl groups on the central phenyl ring of PV2 with C<sub>2h</sub> symmetry, giving *di*-Me-PV2, hardly influences excitation energy and oscillator strength of the lowest allowed absorption band. The calculated excess polarizability of the lowest <sup>1</sup>B<sub>u</sub> state, 271 Å<sup>3</sup>, is somewhat (~20%) lower than that for the unsubstituted PV2, 351 Å<sup>3</sup>. This decrease in excess polarizability can be

related to the energy difference between the lowest  ${}^{1}B_{u}$  state and the next  ${}^{1}A_{g}$  state. The polarizability,  $\alpha_{a}$ , for state *a* in terms of the sum-over-states expression is given by<sup>29</sup>

$$\alpha_a = \frac{2}{3} \sum_{\substack{n \\ n \neq a}} \frac{|\mu_{na}|^2}{\Delta E_{na}}$$
(10.3)

In Eq. 10.3 the summation runs over all states other than *a*.  $\Delta E_{na}$  is the energy difference between states *a* and *n* and  $\mu_{na}$  is the transition dipole moment between these states. In this description, the polarizability of a  ${}^{1}B_{u}$  exciton is due to mixing with all other  ${}^{1}A_{g}$  states, since these are the only states for which  $\mu_{na}$  is non-zero in C<sub>2h</sub> symmetry. The main contribution to the polarizability of the lowest  ${}^{1}B_{u}$  state is in general due to the to the next higher  ${}^{1}A_{g}$  state since the energy difference,  $\Delta E_{na}$ , in the denominator is the smallest for this contribution. This same interaction leads to a negative value for  $\Delta \alpha$  for the lowest  ${}^{1}A_{g}$  state that is of similar magnitude as the positive value for the lowest  ${}^{1}B_{u}$  state, as discussed previously. <sup>15</sup> The difference in excess polarizability for the lowest  ${}^{1}B_{u}$  excited state for *di*-Me-PV2 and PV2 can now be explained by considering the energy difference between the lowest  ${}^{1}A_{g}$  and  ${}^{1}B_{u}$  excited states. This energy difference is somewhat larger for *di*-Me-PV2, causing a decrease in the exciton polarizability.

Alternatively, the differences in excess polarizability can be discussed in a more qualitative way in terms of the degree of delocalization or the 'size' of the exciton. The methyl-groups at the central phenyl ring have a localizing effects on the exciton because the energy of an exciton localized on the substituted phenyl ring is lower than that for an unsubstituted phenyl ring. The (fractional) localization of the exciton is reflected in a smaller excess polarizability.

The second methyl-substituted oligomer, *tetra*-Me-PV2 (Figure 10.1c), has two methyl groups on the terminal phenyl rings. The excess polarizability for this molecule (383 Å<sup>3</sup>) was calculated to be somewhat larger than that for the unsubstituted PV2. If the energy difference between the lowest  ${}^{1}B_{u}$  and  ${}^{1}A_{g}$  excited states is compared to that for PV2 in this case, it is found that there is not much difference, the values for *tetra*-Me-PV2 is even somewhat larger. This clearly indicates, that although the largest contribution is due to mixing with the lowest  ${}^{1}A_{g}$  state above the  ${}^{1}B_{u}$  state, the mixing with other states is also important for explaining subtle differences between the excess polarizabilities for *tetra*-Me-PV2 and PV2.

In terms of the degree of delocalization of the exciton it can be said that the methyl groups on the terminal phenyl rings lower the exciton energy at these sites, causing a more delocalized exciton, and consequently a higher excess polarizability.

An experimental value for the excess polarizability is available for PV2 from electroabsorption measurements (420 Å<sup>3</sup>).<sup>14</sup> From FP-TRMC experiments an excess polarizability was measured for a PV2 that has two tertiary butyl groups on both the outer rings, analogous to *tetra*-Me-PV2 in figure 1. From these measurements a value of 300 Å<sup>3</sup> was obtained.<sup>5</sup> These two experimental values cannot be compared directly because of considerable differences between both experiments. In the electro-absorption measurements the vertical excited state of a molecule trapped in a solid matrix is probed while in the FP-TRMC technique the relaxed excited state is studied in dilute solution. Because of these differences, it is difficult to derive the actual effect of the introduction of methyl substituents from the experimental data. It is concluded that the calculated excess polarizabilities for both *tetra*-Me-PV2 and PV2 are in reasonable agreement with the experimental values available.

#### Methoxy substituents

Most poly- and oligo-phenylenevinylenes that are used in experimental work are substituted with solubilizing alkoxy side-chains. It was shown recently in a computational study, that alkoxy groups have a large influence on the degree of delocalization of a positive charge along a phenylenevinylene chain.<sup>30</sup> A similar effect is obtained for the lowest excited <sup>1</sup>B<sub>u</sub> state of PV2. Introduction of two methoxy substituents on the central ring, giving PV2-1da (Figure 10.1d), lowers the excess polarizability from 351 Å<sup>3</sup> (PV2) to only 91 Å<sup>3</sup>. Alkoxy side chains have a much stronger localizing effects than the alkyl groups discussed above. This indicates that atomic orbitals on the oxygen atoms of the methoxy groups contribute significantly to the  $\pi$ -electron system of the phenylene vinylene backbone. If the energy difference between the lowest excited state (of  ${}^{1}B_{u}$  symmetry) and the second excited state for PV2-1*da* is compared to that energy difference for PV2 it is clear that the introduction of two methoxy substituents on the central phenyl ring considerably increases the energy difference. According to the sumover-states description in Eq. 10.3 this increase in the energy difference leads to a considerable lowering of the polarizability of the excited state of PV2-1da compared to that for PV2. Note that in the case of PV2-1da the lowest  ${}^{1}A_{g}$  state has a positive excess polarizability. This can be understood be considering the next <sup>1</sup>B<sub>u</sub> state, included in Table 10.1. The energy difference between the lowest  ${}^{1}A_{g}$  excited state and the second  ${}^{1}B_{u}$  excited state is very small (0.06 eV), which leads to a large positive contribution due to the mixing between these states (see Eq. 10.3) to the polarizability of the lowest  ${}^{1}A_{g}$  excited state. Thus the excess polarizability of the lowest <sup>1</sup>A<sub>g</sub> excited state is dominated by mixing with the higher lying  ${}^{1}B_{u}$  state rather than with the lower lying  ${}^{1}B_{u}$ .

From experimental work there are two sets of data. The first are from electro-absorption measurements where the excess polarizability decreases from 420 Å<sup>3</sup> for PV2 to 340 Å<sup>3</sup> for PV2-1da, a decrease of only 20%.<sup>14</sup> From FP-TRMC measurements a considerably larger decrease from 300 Å<sup>3</sup> for *tetra-t*-butyl-PV2 to 150 Å<sup>3</sup> for PV2-1*da* was obtained.<sup>5</sup> The large differences between these experimental values and the trends in them may be caused by differences in the surrounding medium. In the electro-absorption measurements by Lane et al.<sup>14</sup> measurements were performed in a solid PMMA matrix at 77 K, whereas in the FP-TRMC experiments by Gelinck et al. the oligomers were studied in benzene solution at room temperature.<sup>5</sup> These very different environments can cause considerable differences in the geometry of the PV oligomer. Another source of the differences can be a more fundamental difference between FP-TRMC and electro-absorption. In electro-absorption it is the vertical (Franck-Condon) excited state that is probed, which means that the excess polarizability that is obtained is the difference between the ground state polarizability (in the ground state geometry) and the excited state polarizability in the ground state geometry. In contrast FP-TRMC measurements are performed on the relaxed excited state. If there are large differences between the ground state and excited state geometries the results from both techniques may

exhibit considerable differences. Conformational differences may also be a source of differences between calculated and experimental values.

One of the structural changes that can affect the excess polarizability is the dihedral angle between the PV backbone and the methoxy side-chain. In all calculations presented in Table 10.1 for methoxy substituted PVs the carbon atoms in the methoxy groups are in the plane of the PV backbone, defined here as the dihedral angle equal to zero. Figure 10.2 shows the dependence of the excess polarizability for PV2-1da on the dihedral angle between the PV backbone and the methoxy side-chain (the rotation is around the bond between the backbone C-atom and the methoxy O-atom). The excess polarizability is minimal (91 Å<sup>3</sup>) for an angle equal to zero and increases up to 264  $Å^3$  for the geometry where both side-chains are perpendicular to the PV plane. This indicates that there is indeed a strong mixing between the  $\pi$ -electron system on the PV backbone and a  $\pi$ -type orbital on the oxygen of the methoxygroup. Inspection of the highest occupied and lowest unoccupied Kohn-Sham orbitals for a zero dihedral angle revealed that there is indeed a p-type orbital on the methoxy groups that contributes to this orbital. The mixing of the  $\pi$ -orbitals on the methoxy group and the PV backbone depends strongly on the dihedral angle, as reflected in the excess polarizability. Other geometry deformations that may affect the excess polarizability are rotations around bonds in the PV backbone. Such rotations will decrease the electronic coupling along the backbone and are therefore expected to lower the excess polarizability.



**Figure 10.2**: Dependence of the excess polarizability for the lowest  ${}^{1}B_{u}$  excited state in PV2-1da on the dihedral angle between the methoxy side chains and the plane of the conjugated backbone

The second alkoxy substituted PV2 in Table 10.1, PV2-3*da* (Figure 10.1e), contains two methoxy substituents on all phenyl rings. The excess polarizability for the lowest  ${}^{1}B_{u}$  state in PV2-3*da* was calculated to be 808 Å<sup>3</sup>. This is much larger than the experimental value from electro-absorption measurements (311 Å<sup>3</sup>).<sup>14</sup> Furthermore, the calculated trend in the excess polarizability for the series PV2, PV2-1*da* and PV2-3*da* differs considerably from the results from electro-absorption measurements. The calculations show that introduction of two

methoxy groups on the central phenyl ring localizes the exciton. When all phenyl ring are dialkoxy substituted the excess polarizability becomes larger again, even considerably larger than for the unsubstituted PV2.

In the electro-absorption experiments the introduction of alkoxy side chains on all phenyl rings does not recover the excess polarizability, in fact it was found that it is lowered even more. It is not unlikely that this is caused by geometry deformations in the case of the experiment since the compounds used contain rather long (decyl) side chains. Steric interactions between these chains may force geometry deformations to occur.

FP-TRMC experiments have been performed for an analogous series of PVs containing five phenyl rings.<sup>13</sup> It was found that introduction of two alkoxy groups on the central phenyl ring reduces the excess polarizability by circa 30 %. When all phenyl rings are dialkoxy substituted, the exciton was completely delocalized again and the excess polarizability was even slightly higher than for the unsubstituted oligomer. These FP-TRMC data qualitatively follow of the calculated trends in the excess polarizability for oligomers containing 3 phenyl rings as considered here.

The comparison of experimental data with calculations is somewhat difficult for oligomers that are substituted with rather flexible alkoxy side-chains. The exact nature of the side chains may also play a role here. In the calculations a methoxy substituent is taken, whereas experiments have been performed with considerably longer (branched) alkoxy-chains. The electronic effect of these longer side-chains is expected to be similar to that for a methoxy group. There may, however, be effects due to steric interaction between side-chains on different units that cause structural changes. In the case of alkoxy substituted PV oligomers there are already considerable (quantitative and qualitative) differences between experimental results from different methods, which makes it rather difficult to establish the accuracy of the computational method used for these cases. It should be noted that this is especially the case for oligomers containing flexible alkoxy side-chains. For relatively rigid molecules such as unsubstituted or methyl-substituted PVs there is a very reasonable agreement between experimental data from different techniques and with the calculated values presented here. The same is true for *meta*-PV2, discussed below.

#### Cyano substituents

The third type of substituents considered here are cyano groups. The calculated excess polarizability for CN-PV2 (Figure 10.1f), containing two cyano groups on the central phenyl ring, was found to be 107 Å<sup>3</sup> for the lowest <sup>1</sup>B<sub>u</sub> state. This shows that cyano-groups have a similar exciton-localizing effect as alkoxy side chains. There is a strong coupling between orbitals on the cyano groups and the  $\pi$ -system of the PV backbone. This also causes a second allowed transition (to a <sup>1</sup>B<sub>u</sub> state) to appear, 0.2 eV above the lowest, with an excess polarizability of 283 Å<sup>3</sup>. The higher polarizability of this second <sup>1</sup>B<sub>u</sub> state can easily be related the lower energy difference with the higher lying <sup>1</sup>A<sub>g</sub> state.

There is no experimental information for the cyano substituted PV2 considered here. FP-TRMC experiments have been performed on a PV oligomer of 5 phenyl rings that contained, apart from alkoxy chains on the central ring, a single cyano group on each of the vinyl moieties neighboring the central ring.<sup>13</sup> It was found that the presence of these two cyano groups considerably lowers the excess polarizability, in agreement with the calculations presented here.

#### Meta-PV2

Finally, a PV2 oligomer is discussed that has a backbone that differs from the standard PV2 structure, rather than modifications in the side-chains. In meta-PV2 the two styryl groups are connected to the central ring in a *meta*-configuration rather than the *para*-configuration leading to  $C_{2v}$  symmetry rather than  $C_{2h}$  (see Figure 10.1g). In contrast to the situation for all other PV2 derivatives considered in this work the calculations show that the transition to the lowest excited state is only weakly allowed. The first strongly allowed transition, with an oscillator strength of 1.8, was found to be due to an excitation to the third excited state. Table 1 gives the excess polarizability for the lowest three excited states of meta-PV2. The lowest excited state, of  ${}^{1}B_{2}$  symmetry, has a very large excess polarizability (1148 Å<sup>3</sup>) compared to that for PV2. This large value can be attributed to mixing with the next, close lying, excited state of  ${}^{1}A_{1}$  symmetry to which a strongly allowed transition is expected to exist. Accordingly, the second excited state has a negative excess polarizability of similar absolute magnitude which indicates that the excess polarizabilities of these two states are mainly determined by mutual coupling between them. For the third excited state, which dominates the absorption spectrum of *meta*-PV2, the calculated excess polarizability is rather low (88  $Å^3$ ) compared to that for PV2. This value can be compared to experimental data from electroabsorption measurements,<sup>14</sup> since in this technique the excess polarizability of excited states to which allowed transition exists is probed. An experimental value of 80 Å<sup>3</sup> was obtained from such measurements by Lane *et al.*<sup>14</sup> which in good agreement with the calculated value. It would be of interest to perform FP-TRMC measurements on meta-PV2 since in this technique the lowest (electrically and vibrationally) relaxed excited state is probed. This would make it possible to establish whether there is indeed a lower lying excited state with a high excess polarizability as predicted by the calculations presented here.

#### **10.4 Summary and conclusions**

This chapter discusses a time-dependent density functional theory study of the effect of structural modifications on the excited state polarizability of conjugated molecules. A short phenylenevinylene oligomer containing three phenyl-rings (distyrylbenzene, PV2) is taken as a model system. Introduction of alkyl substituents (methyl) was found to have only a small effect on the excess polarizability. If methyl groups are present only on the central phenyl ring the excess polarizability is slightly reduced compared to that for the unsubstituted PV2, which indicates that the presence of methyl groups slightly localizes the exciton. If the outer rings are methyl-substituted there is a slight increase in excess polarizability.

Introduction of alkoxy (methoxy) side-chains has a much larger effect on the excess polarizability. If two methoxy groups are present on the central phenyl ring the excess polarizability is strongly reduced. This reduction depends on the dihedral angle between the methoxy group and the PV backbone. The maximum reduction (a factor of four) is reached if the methoxy-carbon atom is in the same plane as the backbone. If all phenyl rings are dialkoxy substituted the excess polarizability increases again, to a value even higher than for the unsubstituted oligomer. Cyano substituents were found to have a similar localizing effect on the excited state as methoxy groups.

If the central phenyl ring is connected to the outer styryl moieties in a *meta*-configuration rather than *para*, the properties and nature of the excited states change considerably. A low-lying excited state to which only a weak optical transition exists was found with a much larger excess polarizability than that of PV2. A higher lying state to which a strongly allowed transition exists was found to have a much lower excess polarizability.

The calculated values for relatively rigid oligomers (PV2, Me-PV2s and meta-PV2) were found to be in good agreement with the experimental data available. For molecules containing more flexible groups (e.g. methoxy) the comparison with experimental data is more difficult since conformational changes can have a large effect on the excess polarizability. In these cases there are also significant differences between experimental data from different techniques. It was found, however, that the qualitative trends in the experimental are reproduced in most cases.

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## Summary

Conjugated polymers are of considerable current interest because of their semiconducting and light-emitting properties. These properties, combined with their relatively low cost and good processability as compared to inorganic semiconductors, make them attractive candidates for application in plastic electronic devices. Conjugated polymers are being considered for application as the semi-conducting layer in low-cost field-effect transistors (FETs) for the fabrication of flexible or disposable electronic devices. A second application using the light-emitting properties of conjugated polymers is as an emissive layer in light emitting diodes (LEDs) and large area displays. The third application that is being considered is the use of conjugated polymers as the light absorbing layer in photovoltaic devices. Finally, the fourth possible application is the use of conjugated polymers is as molecular wires in single molecule electronics.

All of these applications critically rely on the ability of the conjugated polymers to transport charges. A thorough understanding of the properties of charge carriers and their mobility is therefore of obvious importance. Some of the applications involve electronically excited states of conjugated polymers. In LEDs the lowest singlet excited state is the emissive state, while in photovoltaic devices the excited state is the primarily formed species. Therefore it is also of interest to study the properties of conjugated polymers or oligomers in their electronically excited state.

This thesis describes a combined experimental and theoretical study of the optoelectronic properties of isolated conjugated polymers in dilute solution. Chapter 1 gives a brief introduction into the history and applications of conjugated polymers. In the introductory chapter some of the models used to describe the transport of charges in disordered materials and methods to measure the mobility of charges are discussed.

The experimental methods used to study the mobility and optical properties of charged conjugated polymers and oligomers are described in chapter 2. Charge carriers are generated by pulse radiolysis (PR). With this technique a polymer solution is irradiated with electrons with a kinetic energy of 3 MeV, which causes ionizations in the sample. The change in conductivity caused by the generation of the charges is monitored using the electrode-less

time-resolved microwave conductivity (TRMC) technique. The change in the optical absorption spectrum of the solution, due to the production of charge carriers is monitored by time-resolved optical absorption spectroscopy.

Theoretical studies of conjugated oligomers in their ionized and electronically excited states have been performed using quantum chemical electronic structure calculations. Chapter 3 briefly discusses the computational methods used in this thesis. The discussion includes Hartree-Fock theory, configuration interaction methods and density functional theory.

In chapter 4 the kinetics of formation and decay of positively charged poly(phenylene vinylene) (PPV) chains in benzene solution is discussed. Pulse radiolysis of oxygen saturated benzene solutions results initially in the formation of benzene radical cations  $Bz^+$  and excess electrons. The excess electrons rapidly undergo attachment to oxygen. The  $Bz^+$  ions diffuse through the solvent and react with the dissolved conjugated polymer chains via electron abstraction, leading to the formation of positively charged polymer chains. This results in a large increase of the conductivity as measured by TRMC, demonstrating that the mobility of positive charges on the polymer chains is much higher than the mobility of  $Bz^+$  in the solvent. The diffusion controlled reaction of  $Bz^+$  with PPV is characterized by a large reaction radius of ca. 400 Å. Comparison of this reaction radius with the radius expected for a densely packed PPV chain (40 Å) shows that the polymer chain in solution possesses a rather open structure, in agreement with light scattering studies. The detailed description of the kinetics of formation and decay of PPV<sup>+</sup> makes it possible to derive a reliable value for the pseudo-one-dimensional mobility of positive charges along the polymer charges along the polymer back bone. A value 0.46 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> was found for MEH-PPV.

In chapter 5 the results of optical absorption and TRMC measurements on positively charged MEH-PPV chains with broken conjugation is described. The mobility of positive charges on the PPV chains was measured using the methods described in chapter 4. It was shown that disruption of the  $\pi$ -conjugated pathway has a large effect on the charge carrier mobility. The mobility is shown to decrease from 0.46 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the fully conjugated MEH-PPV to 0.04 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for MEH-PPV with a conjugation fraction of 85%. The absorption spectrum of positively charged MEH-PPV chains exhibits a maximum at 1.32 eV. This maximum shifts to higher energies with decreasing conjugation fraction. The distribution of charges over conjugated segments over different lengths is consistent with a thermal equilibration; *i.e.* the charges are preferentially localized on the longest conjugated segments.

The effect of the nature of the conjugated polymer backbone on the mobility of charges along polymer chains is discussed in chapter 6. Results of PR-TRMC measurements on pibond-conjugated polymers and on sigma-conjugated polymers (polysilanes) are discussed. For the  $\pi$ -conjugated polymers it was found that the one-dimensional mobility depends strongly on the nature of the backbone. Values ranging from 0.74 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for polyfluorene to 0.02 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for polythiophene have been found. Measurements on a series of polysilanes only differing in the type of side-chains attached to the backbone show that the side chains have a large effect on the one-dimensional mobility. This effect is attributed to the effect of the packing of the side chains on the conformation of the backbone.

The large difference in the one-dimensional mobility of holes along P3HT and MEH-PPV chains obtained from the measurements in chapter 6 is explained theoretically in chapter 7. Quantum chemical calculations show that the deviations from a planar geometry are much larger for P3HT than they are for MEH-PPV. The effect of such torsional disorder on the charge carrier mobility is studied using a model based on the tight-binding approximation. The calculated ratio of the hole mobilities is in agreement with the experimental findings for MEH-PPV and P3HT, however the calculated absolute values are considerably higher. If polymerization defects and chain-end effects are included in the calculations the results become consistent with experimental mobilities.

In chapter 8 the results of a combined experimental and theoretical study of the optoelectronic properties of positively charged oligo(phenylene vinylene)s is presented. The optical absorption spectra for PV cations with different chain lengths and substitution patterns were measured using pulse radiolysis with time-resolved spectrophotometric detection from 1380 to 500 nm (0.9 to 2.5 eV). The geometries of the PV's studied were optimized using density functional theory (DFT) for both the neutral and singly charged molecule. The spectra for the PV radical cations were then calculated using singly excited configuration interaction with an intermediate neglect of differential overlap reference wavefunction (INDO/s-CIS) method together with the DFT geometry. The agreement between experimental and theoretical absorption energies is excellent; most of the calculated radical cation absorption energies are within 0.15 eV of the experimental values. The pattern of dialkoxy-substitution is found to have a large effect on the optical absorption spectrum of the cation. Using the calculated charge distribution it is shown that the degree of delocalization of the charge correlates with the energy of the lowest absorption band. If alkoxy side chains are present only on some of the phenyl-rings, the positive charge tends to localize at those sites.

In chapter 9 a time-dependent density functional theory study of the excited state polarizabilities of conjugated oligomers is presented. The increase in polarizability upon excitation (the excess polarizability,  $\Delta \overline{\alpha}$ ) was obtained by evaluating the dependence of the excitation energy on an external static electric field. The excitation energy was found to vary quadratically with the field strength. The excess polarizabilities obtained for singlet excited states are in reasonable agreement with the experimental results for the shorter oligomers, particularly if the experimental uncertainties are considered. For longer oligomers the excess polarizabilities. Excess polarizabilities of triplet states were found to be smaller than those for the corresponding singlet state, which agrees with experimental results that are available for triplet polarizabilities. Negative polarizabilities are obtained for the lowest singlet Ag states of longer oligomers. The polarizability of the lowest Bu and Ag excited states of the conjugated molecules studied here are determined mainly by the interaction between these two states. Upon application of a static electric field a quadratic Stark effect is observed in which the lower Bu state has a positive excess polarizability while that of the upper Ag state is negative.

The calculated excess polarizabilities discussed in chapter 9 involve unsubstituted conjugated oligomers. In chapter 10 the method presented in chapter 9 is used to study the effect of molecular structure on the excited state polarizability of conjugated molecules. A short phenylenevinylene oligomer containing three phenyl rings (PV2, distyryl benzene) is

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taken as a model system. Introduction of methyl substituents is shown to have only a small influence on the increase in polarizability upon excitation. Methoxy groups have a much larger effect but in this case the excess polarizability depends strongly on the dihedral angle between the side-chain and the backbone of the molecule. If the central phenyl ring of PV2 has a *meta*-configuration rather than *para*, both the optical absorption spectrum and the excess polarizability change considerably.

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# Samenvatting

Op het moment is er veel interesse in geconjugeerde polymeren vanwege hun halfgeleidende en lichtuitzendende eigenschappen. Deze eigenschappen, gecombineerd met hun relatief lage prijs en goede bewerkbaarheid vergeleken met anorganische halfgeleiders, maken geconjugeerde polymeren aantrekkelijke kandidaten voor toepassing in plastic elektronica. Een van de toepassingen waar het gebruik van geconjugeerde polymeren wordt overwogen is hun gebruik als halfgeleidende laag in goedkope veldeffect transistoren (FETs) voor het construeren van wegwerp elektronica. Een tweede toepassing is het gebruik van geconjugeerde polymeren als de lichtuitzendende laag in lichtuitzendende diodes (LEDs). De derde toepassing van geconjugeerde is hun gebruik als de licht absorberende laag in zonnecellen. De laatste (mogelijke) toepassing van geconjugeerde polymeren is hun gebruik als moleculaire draden in elektronica gebaseerd op enkele moleculen.

Het vermogen van geconjugeerde polymeren om ladingen te transporteren is in al deze toepassingen van groot belang. Een goed begrip van de eigenschappen van ladingsdragers in deze materialen en informatie over hun mobiliteit is daarom erg belangrijk. In enkele van de bovengenoemde toepassingen spelen aangeslagen elektronische toestanden een belangrijke rol. In LEDs is de laagste singlet aangeslagen toestand de lichtuitzendende toestand. In zonnecellen zijn het de aangeslagen toestanden die initieel gevormd worden. Het bestuderen van de eigenschappen geconjugeerde polymeren of oligomeren in hun elektronisch aangeslagen toestand is daarom ook interessant.

Dit proefschrift beschrijft een gecombineerd experimenteel en theoretisch onderzoek naar de opto-elektronische eigenschappen van geïsoleerde geconjugeerde polymeren en oligomeren in verdunde oplossingen. Hoofdstuk 1 geeft een kort overzicht van de geschiedenis en toepassingen van geconjugeerde polymeren. Hoofdstuk 1 beschrijft ook enkele modellen die gebruikt worden voor de beschrijving van ladingstransport in wanordelijke materialen en er worden er een aantal methoden voor het meten van de mobiliteit van ladingdragers besproken.

De experimentele methoden die gebruikt zijn voor het bestuderen van de mobiliteit en optische eigenschappen van geladen geconjugeerde polymeren worden beschreven in hoofdstuk 2. Ladingsdragers worden gegenereerd door middel van puls radiolyse. Bij deze techniek wordt een oplossing bestraald met elektronen die een kinetische energie van 3 MeV hebben. Dit leidt tot ionisaties in de bestudeerde oplossing. De verandering in het geleidingsvermogen van de oplossing veroorzaakt door generatie van ladingsdragers kan gemeten worden door gebruikt te maken van tijdsopgeloste microgolfgeleidingsmetingen (TRMC). Verandering van het optische absorptie spectrum van een oplossing kan worden bestudeerd door gebruik te maken van tijdsopgeloste optische absorptie metingen.

Theoretisch onderzoek aan geconjugeerde oligomeren in hun geïoniseerde en elektronisch aangeslagen toestand is uitgevoerd door gebruik te maken van kwantum chemische elektronen structuur berekeningen. In hoofdstuk 3 worden de rekenmethoden die gebruikt zijn in dit proefschrift kort beschreven. Het hoofdstuk beschrijft onder ander de Hartree-Fock theorie, de configuratie interactie methode en dichtheidsfunktionaal theorie.

In hoofdstuk 4 wordt de vormings- en recombinatie kinetiek van positief geladen poly(phenylene vinylene) (PPV) ketens opgelost in benzeen beschreven. Puls radiolyse van een zuurstof verzadigde oplossing in benzeen resulteert initieel in de vorming van benzeen radicaal kationen,  $Bz^+$  en overtollige elektronen in oplossing. De overtollige elektronen verdwijnen erg snel doordat ze worden opgenomen door zuurstof. De  $Bz^+$  ionen diffunderen door de oplossing en kunnen reageren met de opgeloste polymeer ketens door een elektron over te nemen van het polymeer. Deze reactie gaat vergezeld van een grote toename in het geleidingsvermogen van de oplossing, zoals blijkt uit TRMC metingen. Dit laat zien dat de mobiliteit van positieve ladingen op de polymeer ketens veel hoger is dan de mobiliteit van Bz<sup>+</sup> ionen in oplossing. De diffusie-gecontroleerde reactie van Bz<sup>+</sup> met PPV wordt gekarakteriseerd door een grote reactie straal van ongeveer 400 Å. Vergelijking van deze straal met de verwachte straal van dicht opeen gepakte PPV keten (40 Å) laat zien dat de polymeer ketens in oplossing een vrij open structuur hebben. Dit is in overeenstemming met de resultaten van lichtverstrooiingsexperimenten. De gedetailleerde beschrijving van de vormings- en recombinatie kinetiek van PPV<sup>+</sup> maakte het mogelijk om een betrouwbare waarde af te leiden voor de mobiliteit van ladingen langs polymeer ketens. Voor MEH-PPV is een waarde van  $0.46 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  gevonden.

Hoofdstuk 5 beschrijft optische absorptie en TRMC experimenten aan positief geladen MEH-PPV ketens waarin een bepaald percentage van de vinyl groepen verzadigd is. De mobiliteit van positieve ladingen langs de PPV ketens werd gemeten volgens de methode beschreven in hoofdstuk 4. Het opbreken van het  $\pi$ -geconjugeerde. pad heeft een groot effect op de gemeten mobiliteit. De mobiliteit neemt af van 0.46 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> voor volledig geconjugeerd MEH-PPV naar 0.04 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> voor MEH-PPV met een conjugatie fractie van 85%. Het absorptie spectrum van volledig geconjugeerd MEH-PPV vertoont een maximum bij 1.32 eV. Dit maximum schuift naar hogere energieën als de hoeveelheid brekingen in conjugatie toeneemt. De verdeling van ladingen over geconjugeerde ketensegmenten van verschillende lengte komt overeen met een verdeling verwacht voor een thermisch evenwicht. De ladingen zitten bij voorkeur op de langste geconjugeerde segmenten.

Het effect van de structuur van de hoofdketen van geconjugeerde polymeren op de mobiliteit van ladingen langs de ketens word beschreven in hoofdstuk 6. Dit hoofdstuk beschrijft PR-TRMC metingen aan zowel  $\pi$ -geconjugeerde polymeren als aan  $\sigma$ -

geconjugeerde polymeren (polysilanen). De resultaten laten zien dat de structuur van de hoofdketen een grote invloed heeft op de 1-dimensionale mobiliteit van ladingsdragers. Er warden gevonden van  $0.74 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  voor polyfluoreen tot  $0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  voor polythiofeen. Metingen aan een serie polysilanen die alleen verschillen in de zijketens laten zien dat het type zijketen een grote invloed kan hebben op de mobiliteit. Dit effect wordt toegeschreven aan het effect dat de pakking van de zijketens heeft of de conformatie van de hoofdketen van het polymeer.

Het grote verschil tussen de 1-dimensionale mobiliteit langs P3HT en MEH-PPV gevonden in de metingen beschreven in hoofdstuk 6 word theoretisch verklaard in hoofdstuk 7. Kwantum chemische berekeningen laten zien dat de afwijkingen van een volledig vlakke structuur veel groter zijn voor P3HT dan voor MEH-PPV. Het effect van deze torsionele wanorde wordt bestudeerd met een model gebaseerd op de zogenaamde tight-binding benadering. De berekende ratio van de mobiliteiten is in overeenstemming met experimentele resultaten voor MEH-PPV en P3HT, echter de absolute waarden zijn behoorlijk wat te hoog. Als polymerisatie defecten en effecten veroorzaakt door ketenuiteinden worden meegenomen zijn de berekende resultaten wel in overeenstemming met de experimenteel bepaalde mobiliteiten.

In hoofstuk 8 worden de resultaten beschreven van een gecombineerd experimenteel en theoretisch onderzoek naar de opto-elektronische eigenschappen van positief geladen oligo(phenylene vinylene)n beschreven. Het optische absorptie spectrum van PV kationen, variërend in ketenlengte en positie van de zijketens, werd gemeten met behulp van puls radiolyse gecombineerd met tijdsopgeloste optische absorptie detectie voor golflengtes tussen 1380 nm en 500 nm (0.9 tot 2.5 eV). De geometrieën van de bestudeerde PVs werden geoptimaliseerd door gebruik te maken van dichtheids functionaal theorie berekeningen, zowel voor het neutrale als voor het positief geladen molecuul. De spectra voor de PV radicaal cationen werden uitgerekend door het uitvoeren configuratie interactie berekeningen waarbij alleen enkel geëxciteerde toestanden werden meegenomen. De overeenstemming tussen de berekende en gemeten absorptie energieën is erg goed; voor de meeste gevallen ligt het berekende absorptie maximum binnen 0.15 eV van de experimentele waarde. Er werd ook gevonden dat de posities van de alkoxy zijketens een grote invloed heeft op het optische absorptie spectrum van het cation. De berekende ladingsverdelingen laten zien dat er een relatie is tussen de uitgebreidheid van de lading en de elektronische overgang met de laagste energie. De lading is bij voorkeur gelokaliseerd op plekken waar de alkoxy zijketens zich bevinden.

Hoofdstuk 9 beschrijft een onderzoek naar aangeslagentoestandspolarizeerbaarheden van geconjugeerde moleculen waarbij gebruik gemaakt word van tijdsafhankelijke dichtheidsfunctionaal theorie berekeningen. De toename in polarizeerbaarheid door over te gaan naar een elektronisch aangeslagen toestand ( $\Delta \overline{\alpha}$ ) werd berekend door de excitatie energie te berekenen als functie van een extern aangelegd statisch elektrisch veld. De excitatie energie vertoond een kwadratisch afhankelijkheid van de veldsterkte. De berekende toenames in de polarizeerbaarheid voor singlet toestanden van korte oligomeren zijn in redelijke overeenstemming met experimentele resultaten. Voor langere oligomeren wordt de toename in polariseerbaarheid behoorlijk overschat. Soortgelijke resultaten zijn eerder ook gevonden

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voor grondtoestandspolarizeerbaarheden. Voor triplet toestanden is de toename in polariseerbaarheid na excitatie een stuk kleiner dan voor singlet toestanden. Dit is in overeenstemming met de beschikbare experimentele informatie. Voor de laagste  $A_g$  aangeslagen toestand van langere oligomeren werden negatieve waarden gevonden. De toename in polarizeerbaarheid voor de laagste  $B_u$  and  $A_g$  aangeslagen toestanden van de hier bestudeerde moleculen wordt voornamelijk bepaald door de interactie tussen deze twee toestanden. Het aanleggen van een statisch elektrisch veld veroorzaakt een Stark effect waarbij de polarizeerbaarheid van lagere  $B_u$  toestand toeneemt bij excitatie en de polarizeerbaarheid van de hogere  $A_g$  toestand afneemt.

In hoofdstuk 9 werden de toenames in polarizeerbaarheid als gevolg van optische excitatie besproken voor moleculen zonder zijketens. In hoofdstuk 10 word de methode beschreven in hoofdstuk 9 gebruikt om het effect van de moleculaire structuur op  $\Delta \overline{\alpha}$  te bestuderen. Hierbij word een kort phenylene vinylene oligomeer genomen als modelsysteem. Introductie van methyl zijketens heeft een erg klein effect op  $\Delta \overline{\alpha}$ . Methoxy-groepen hebben een veel groter effect. In dit geval is  $\Delta \overline{\alpha}$  echter wel sterk afhankelijk van de tweevlakshoek tussen de zij- en hoofdketen van het molecuul. Als de centrale phenyl ring in plaats van een *para*-configuratie een *meta*-configuratie heeft, treden er grote veranderingen op in zowel het optische absorptie spectrum als het in de aangeslagentoestandspolarizeerbaarheid.

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Ferdinand Grozema

Delft, mei 2003

# **Curriculum Vitae**

Ferdinand Cornelius Grozema was born in Scheemda on the 4<sup>th</sup> of November 1973. He started secondary school at the "Winschoter Scholen Gemeenschap" in Winschoten, where he obtained his VWO-diploma in 1992. In that same year he started his study in chemistry at the Rijksuniversiteit Groningen. He specialized in Computational Chemistry under supervision of Dr. P.Th. van Duijnen. In the group of Dr. Van Duijnen he performed his undergraduate research on intermolecular interactions and solvent effects.

From October 1998 to April 2003 he was a PhD student in the Radiation Chemistry Department at the Interfaculty Reactor Institute at the Delft University of Technology. In this group he performed a combined experimental and theoretical study of the opto-electronic properties of conjugated molecular wires, under the supervision of Prof. dr. L.D.A. Siebbeles and Dr. J.M. Warman.
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List of publications