Stellingen behorende bij het proefschrift:

**Ladingstransport in Polydiacetylenen**

1. De methode om de driftsnelheid van ladingsdralers in een electrisch veld te bepalen in polydiacetylenen zoals gepresenteerd door Donovan et al. is onbetrouwbaar

2. Meting van de stralingsgeinduceerde microgolfgeleiding in verschillende richtingen in anisotrope kristallen opent de mogelijkheid om de bijdrage van geminale recombinatie in de vervalkinetiek te scheiden van die van de relaxatie van de beweeglijkheid van de ladingsdralers.
   (Hoofdstukken 5 en 6 in dit proefschrift)

3. De bereiding van geleidende dunne films van polydiacetylenen met behulp van hoog-energetische straling dient uitgevoerd te worden met een hoge doseringssnelheid en met uitsluiting van zuurstof

4. Dat beweeglijke electronen in vaste stof PPV experimenteel niet zijn aangetoond is niet vanwege het feit dat de electronen niet mobiel zijn, maar het gevolg van beperkingen in de tijdslresolutie van de detectiemethoden.

5. De waarde van $F_{sc} = 0.045$ voor de aan geminale recombinatie ontsnapte fractie ladingen verkregen uit metingen van de stralingsgeinduceerde microgolfgeleiding in monsters van bucky-ballen sluit niet uit dat er een bijdrage in de microgolfgeleiding is ten gevolge van migratie van lading op de afzonderlijke ballen
   (Hoofman *et al.* (1997) Synth. Met. 86, 2355)

6. Bij de uiteindelijke toepassing van geleidende polymeren in all-plastic geïntegreerde schakelingen is van de parameters die de goede werking van het device bepalen de grootte van de beweeglijkheid van de ladingsdralers een minder belangrijke

7. De toekenning van de miljardenclaim door de rechtbank in Miami aan de honderdduizenden rokers in de staat Florida maakt de weg vrij voor 'meerokers' om met succes te procederen tegen rokers

   (Artikel 17; Promotiereglement TU Delft, september 2000)

9. Alcohol kan een positief effect hebben op de rijvaardigheid van gespannen weggebruikers

10. Survival of the fittest is bij de mens geëvolueerd tot survival of the richest

R.J.O.M. Hoofman
Vlaardingen, 24 september 2000
Propositions belonging to the thesis:
Charge Transport in Polydiacetylenes

1. The method of determination of the drift velocity of charge carriers in an electric field in polydiacetylenes as presented by Donovan et al. is inadequate.

2. Measurement of the radiation-induced microwave conductivity in different directions in anisotropic crystals is necessary for the separation of the contribution of the geminate recombination in the decay kinetics from that of the charge carrier mobility relaxation.
   (Chapter 5 and 6 in this thesis)

3. The preparation of conducting thin films of polydiacetylenes by means of high-energy radiation should be carried out with large dose rates and in the absence of oxygen

4. That mobile electrons in solid PPVs have not been observed experimentally thus far is not due to the fact that the electrons are not mobile, but rather to the limitations in the time resolution of the detection techniques.
   (Hoofman et al. (1998) Nature 392, 54)

5. The value of $F_{esc} = 0.045$ for the fraction of charge carriers escaping geminate recombination, obtained from the measurement of the radiation-induced microwave conductivity in samples of bucky-balls does not exclude the possibility that migration of charge on the separate balls contributes to the microwave conductivity
   (Hoofman et al. (1997) Synth. Met. 86, 2355)

6. In the application of conductive polymers in all-plastic integrated circuits the magnitude of the charge carrier mobility is of less importance for the well-functioning of the device than several other parameters.

7. The granting of the billion-dollar claim by the court in Miami to hundred-thousands of smokers in the state of Florida clears the way for 'passive' smokers to sue 'active' smokers successfully.

8. The recent introduction of the regulation in the promotion protocol of the TU Delft that the number of 'playful propositions' should be restricted to two, without stating what is meant with the term 'playful proposition', enhances the playful element of the promotion
   (Clause 17; TU Delft promotion protocol, September 2000)

9. Alcohol can have a positive effect on the driving-skills of nervous drivers.

10. For humans survival of the fittest has evolved to survival of the richest.

R.J.O.M. Hoofman
Vlaardingen, 24 September 2000
Charge Transport in
Polydiacetylenes

Romano J. O.M. Hoofman
The research described in this thesis has been performed at the Radiation Chemistry Department of the Interfaculty Reactor Institute (IRI), Delft University of Technology, Mekelweg 15, 2629 JB, Delft, The Netherlands.
Charge Transport in
Polydiacetylenes

Proefschrift

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voorzitter van het College voor Promoties
in het openbaar te verdedigen op maandag 4 december 2000 om 16:00 uur

door

Romano Julma Oscar Maria HOOFMAN
ingenieur in de moleculaire wetenschappen
geboren te Hulst
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“Polydiacetylenes” Review article
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Chapter 4: R.J.O.M. Hoofman, G.P. van der Laan, L.D.A. Siebbeles, M.P. de Haas, D. Bloor and D.J. Sandman
“Dose Dependence of the Charge Carrier Mobility and Decay Kinetics in Radiation Polymerized Diacetylenes”
Submitted to Macromolecules

"Anisotropy of the charge carrier mobility in polydiacetylene crystals"

R.J.O.M. Hoofman, L.D.A. Siebbeles, M.P. de Haas, M. Szablewski and D. Bloor
“Charge Carrier Dynamics in Polydiacetylene Crystals"
Synthetic Metals (1999) 102 (1-2) pp 1417-1418

“The Influence of Backbone Conformation on the Photoconductivity of Polydiacetylene Chains”
Accepted for publication in Macromolecules
1.1 CONJUGATED POLYMERS AND THEIR APPLICATIONS

Organic polymers are first and foremost used in electrical and electronic applications as insulators, where advantage is taken of their high resistivities and good dielectric performance. In recent years, however, conjugated polymers have proven to be attractive because of their semiconducting properties, which makes them promising candidates for applications in cheap and flexible electronic and opto-electronic materials and devices.

The research field of conductive, conjugated polymers was triggered by the discovery of significant electrical conductivity in thin films of polyyacetylene upon oxidative doping. The study of conductivity in conjugated polymers has expanded to include a wide range of conjugated hydrocarbon and aromatic heterocyclic polymers. The structures of some important conjugated polymers are shown in Figure 1.1. Whereas conventional σ-bonded polymers are readily processed in solution or in the melt, this was in general not possible for conjugated polymers. The delocalized π-electron system makes the molecular chains rigid, with resulting high melting points and low solubilities. It was realized that if conjugated polymers were going to succeed in future applications, the lack of solubility and processability had to be overcome. The solution to this problem appeared to be attachment of flexible alkyl side chains to the conjugated backbone, which allows the polymer to be processed like common plastics. Of essential importance was the fact that the functionalized polymers, because of their solubility, could be highly purified. The possibility that conjugated polymers could be dissolved in organic solvents meant also that they could be coated as a thin film on a substrate. The possibility of coating polymers as thin films has given the proposed commercial application of conductive polymers in electronic devices a further boost.

The real breakthrough came in 1990 with the observation of electroluminescence from poly(p-phenylene vinylene) (PPV). Research into the use of organic conjugated polymers as the active layer in light-emitting diodes (LEDs) has advanced rapidly. The use of conjugated polymers is however not limited to their application in polymer LEDs. Because of their interesting optical and electronic properties, resulting from the extensive π-electron
Charge Transport in Polydiacetylenes

delocalization along the polymer backbone, these polymers can also be applied as the active layer in field-effect transistors for plastic electronics 10-12 and photovoltaic cells for solar energy conversion 13-15. The impressive recent progress on the research of semiconducting polymers shows that π-conjugated polymers constitute an important class of materials for the future.

\[
\begin{align*}
\text{polyacetylene} & \quad \text{polydiacetylene} & \quad \text{polyphenylene vinylene} \\
\text{polyaniline} & \quad \text{polyphenylene sulphide} & \quad \text{polythiophene} \\
\text{polypyrrrole} & \quad \text{polyturan} \\
\end{align*}
\]

Figure 1.1 Molecular structures of different conjugated polymer backbones consisting of n repeat units

1.2 CONDUCTIVITY MEASUREMENTS IN CONJUGATED POLYMERS

The common feature of conjugated polymers is the alternation of single and double or triple bonds along the polymer backbone. The electrons forming the double and triple bonds fully occupy the valence molecular π-orbitals. The empty conduction states have energies that are typically 2 eV higher. This ‘band gap’ of 2 eV is much larger than the thermal energy (k_B T ~ 0.025 eV). Consequently, conjugated polymers exhibit extremely low intrinsic conduction. However, conductivity via the π-electron system can be induced by removing an electron from the valence band or adding an electron to the conduction band. This can be achieved by doping, by charge injection from electrodes or by excitation of an electron from a valence to a conduction band state using light or high-energy radiation.

The conductivity of a material due to a singly-charged carrier is determined by the product of the charge carrier density, \( n \), and the charge carrier mobility, \( \mu \), according to

\[
\sigma = e n \mu \quad (1.1)
\]

where \( e \) is the elementary charge. The conductivities of doped polymers cover the entire
range from insulators to metals, see Figure 1.2. It should be noted however that the high conductivities obtained in the polymers indicated in Figure 1.2 are mainly due to the high charge carrier density achieved by doping. The mobility is usually significantly below \(0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\). Applications in electronic devices require higher values.

![Graph showing conductivity values of different materials](image)

**Figure 1.2.** Comparison of room temperature conductivity values of doped polymers with other materials.

The macroscopic conductivity of conjugated polymers is largely determined by their morphology which is often complex. The complexity is schematically depicted in Figure 1.3. Small domains of crystalline and/or amorphous morphology constitute the polymeric material. The mobility of charge carriers in a crystalline domain is determined by intrachain motion (process 1 in Figure 1.3) and interchain motion (process 2 in Figure 1.3). Transport over domain boundaries (process 3 in Figure 1.3) is much more difficult. In conjugated polymer the intrachain charge transport is usually much faster than interchain charge transport. Structural factors such as chain planarity, degree of crystallinity and cross-links are expected to play a role in interchain transport. To measure one-dimensional transport along the polymer backbone is not an easy task. Conventional DC conductivity techniques always will probe a combination of intra- and interchain charge transport.
Figure 1.3 Schematic representation of the complex morphology of a polycrystalline conjugated polymer. Arrows 1, 2 and 3 represent the intrachain, interchain and interdomain charge transport, respectively.

The interpretation of conductivity measurements in polymeric materials often suffers from complicated such as micro-heterogeneities within the sample, chain end effects, field induced space charge problems, saturation of the drift mobility and electrode contact problems. Recently Blum and Bässler\textsuperscript{16} discussed the problems associated with conductivity measurements in crystalline polymers caused by charge carriers that are blocked when reaching the chain ends. They concluded that a DC conductivity study was rather a study of chain to chain hopping and suggested that an AC conductivity experiment on a GHz scale was needed to study the charge transport process along the backbone itself.

In this work we present results obtained using such an ultra high frequency AC method, the Time-Resolved Microwave Conductivity (TRMC) technique\textsuperscript{17-19}. The charge carriers are produced by pulses of 3 MeV electrons that cause ionizations throughout the sample up to a thickness of several millimeters. Microwaves are then used to monitor the change in conductivity (dielectric loss) of the medium resulting from the formation of mobile charge carriers. The decay kinetics of the radiation-induced conductivity transients is studied from nanoseconds to milliseconds. A detailed description of the TRMC technique is given in Chapter 3.
1.3 CHARGE TRANSPORT MODELS

The charge carrier mobility is defined as the equilibrium drift velocity of a charge carrier in an electric field $E$ divided by the field strength, i.e. $\mu = \frac{v_{eq}}{E}$. For low fields $\mu$ is independent of the field, $E$. When the charge carriers are in thermal equilibrium with the environment the mobility is related to the diffusion coefficient of the charge carriers, $D$, by the Einstein relation,

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

(1.2)

with $k_B$ the Boltzmann constant and $T$ the temperature.

For a charge carrier in an electric field experiencing a frictional force proportional to its momentum, the equation of motion is

$$m \frac{dv}{dt} = eE - \frac{mv}{\tau}$$

(1.3)

$\mu$ can be seen to be related to the mass, $m$, and the momentum relaxation time, $\tau$, via

$$\mu = \frac{v_{eq}}{E} = \frac{e\tau}{m}$$

(1.4)

The reciprocal of $\tau$ is a measure of the frictional force opposing charge motion. Note, that according to band theory the mass $m$ in Eqs. (1.3) and (1.4) corresponds to the effective mass, which can differ significantly from the electron mass for electronic charge carriers.

In the case where charge transport can be considered to be the result of a hopping type motion between equivalent sites at an average distance $d$, the mobility is given by

$$\mu = \frac{ev_J d^2}{2nkT}$$

(1.5)

where $n$ is the dimensionality of the system in which motion occurs and $v_J$ is the jump frequency from the site $j$ to an adjacent site. Note that Eqs. (1.4) and (1.5) are only valid when the diffusion coefficient is time-independent.

Since polymers do not have a perfectly ordered structure, adjacent sites are not necessarily equivalent. Structural disorder can cause the charge carriers to perform a hopping motion in an energy profile with wells of varying depths and/or barriers with
different heights (as schematically shown in Figure 1.4). Also an excess charge carrier in conjugated polymers can deform the lattice around it. The charge carrier together with its structural deformation is referred to as the polaron. Due to energetic disorder and polaronic effects the jump frequencies ($v_j$ in Eq. (1.5)) become temperature- and site-dependent, giving rise to dispersive transport. In that case the mobility depends on time, temperature, and the strength and frequency of the external electric field, in a manner that is determined by the details of the energy profile and the charge transport mechanism.

When an energy barrier between adjacent sites is too high the charge carrier cannot hop over this barrier, but the charge carrier can possibly tunnel through the barrier. To allow tunneling both neighboring sites need to be equal in energy. This is generally not the case in real conjugated polymer chains because of the naturally occurring structural disorder, however the energies of both sites can be matched by thermal vibrations of the lattice.

![Figure 1.4 Schematic representation of charge hopping over and tunneling through energy barriers.](image)

When the energy difference between adjacent sites is so large that it cannot be overcome by either hopping or tunneling, it can be considered a well (see Figure 1.4) in which the charge carriers can become trapped for a long time and then no longer contribute to the conductivity. Trapping may take place at chemical groups, impurities, or physical irregularities.

Random walks of a charge on lattices that include traps have been theoretically studied extensively previously. The presence of shallow or deep traps have a different effect on the decay of the conductivity. When a charge carrier encounters a shallow trap, it will be only temporarily localized and will be released again after a certain time. This trapping and release of charge carriers results in a gradual relaxation of the charge carrier mobility. In this case the charge carrier mobility decreases as a function of time according to an inverse power law.
\[ \mu(t) \propto t^{-\alpha} \]  

where \( \alpha \) is defined as the power factor and is related to the average trap depth.

On the other hand, when a charge carrier encounters a deep trap, it will be entirely immobilized and it will no longer contribute to the conductivity. The decrease in the number of mobile charge carriers by immobilization in deep traps can be described by a stretched exponential decay \(^{33,37,39,41}\)

\[ n(t) \propto e^{\left(\frac{t}{\tau}\right)^{\beta}} \]  

where \( \tau \) is the characteristic decay time, which can be related to the number density of deep traps, and \( \beta \) is defined as \(^{35,41}\)

\[ \beta = \frac{d}{d+2} \]  

with \( d \) the spatial dimensionality. In the case of one-dimensional charge transport in a medium with randomly distributed deep traps, the power \( \beta \) equals 1/3.

1.4 POLYDIACETYLENES, A HIGHLY-CRYSTALLINE CLASS OF CONJUGATED POLYMERS

Polydiacetylenes (PDAs) constitute a class of unusual polymeric materials, since they can be produced as almost perfect single crystals by solid state topochemical polymerization of the monomer crystals \(^{46}\). In perfect crystals the polymer backbones are perfectly aligned over macroscopic distances, thus providing prototypical systems for studying electronic transport in one-dimensional conjugated chains. PDAs are therefore of great importance for the fundamental information they can provide on low dimensional conduction.

The high charge carrier mobility along the perfectly aligned backbone which has been observed is a most interesting property, which could be used in future applications. In order to achieve fast switching times in FETs high charge carrier mobility is a necessity. Another application that exploits a high charge carrier mobility can be found in organic solar cells. Polydiacetylenes that are coupled to an organic dye display properties, such as efficient light absorption, light-induced electron transfer, and efficient charge transport, which are needed for photovoltaic energy conversion \(^{47}\). Several groups have reported on molecules containing dyes such as porphyrins \(^{48}\) and phthalocyanines \(^{49,50}\) bridged to a diacetylene.
Charge Transport in Polydiacetylenes

The almost complete lack of (electro)luminescence in polydiacetylenes rules out the possibility for application in LEDs. However, the non-linear optical NLO properties of polydiacetylenes have emerged as the most potential aspect for possible application, since amongst the variety of polymeric structures, polydiacetylenes possess one of the largest nonlinear responses \(^{51}\) and a fast exciton response time \(^{52}\). For this reason diacetylenes appear to be attractive materials to be used as active elements in devices for optical information storage and processing or photolithography \(^{53-56}\). Xu et al.\(^{57}\) reported a relatively new polydiacetylene, which shows an increasing absorption coefficient with increasing incident light intensity. A material which shows such a kind of optical power-limiting behavior could be used as protective coating for solid state sensors and human eyes.

1.5 SCOPE OF THIS THESIS

In this thesis results are presented of the study of charge transport in polydiacetylenes by TRMC. Charge carriers are produced by pulsed irradiation with high-energy electrons or UV light. The radiation-induced conductivity is measured using the electrodeless time-resolved microwave conductivity (TRMC) technique. The measurements provide insight into the magnitude of the charge carrier mobility and into the decay kinetics of the charges. Attention is paid to the relation between the structure of the polymer and the charge carrier mobility. The technique is applied to bulk powders, single crystals and isolated chains in solution. The technique also enables the measurement of anisotropy of the charge carrier mobility in single crystals.

In Chapter 2 the structure of PDAs and a literature review on conductivity studies of PDAs are presented. In Chapter 3 the basic principles of the microwave conductivity technique and the different set-ups used to measure conductivity in single crystals, polycrystalline powder and dilute solutions are shown and discussed. The application of the TRMC method for the measurement of the anisotropy of the conductivity is analyzed in detail in section 3.5. In Chapter 4 effects of accumulated radiation-dose on the mobility and the decay of the charge carriers in diacetylenes polymerized by high-energy radiation are investigated. Because of the fact that for most PDAs rather high radiation doses are required to reach the maximum monomer to polymer conversion, the conductive paths for charge transport have become far from optimal. In Chapter 5 the radiation-induced conductivity in a variety of polydiacetylene bulk samples is studied. Particular attention is given to difference in both charge carrier mobility and decay kinetics for samples which were prepared by either a different monomer synthesis or a different polymerization route. The observations can be attributed to defects introduced during the synthesis of the monomer material or during the heat- or radiation-induced polymerization of the monomers. In Chapter 6 the anisotropy in the conductivity is investigated for different
polydiacetylene single crystals. For some samples the mobility along the direction of the backbone is found to be up to a factor of 100 larger than in a perpendicular direction. In Chapter 7 the charge carrier mobility along isolated polydiacetylenes chains in solution is investigated. The results provide insight into the effects of the backbone conformation on the opto-electronic properties of PDAs in solution.

REFERENCES

(22) Bässler, H. phys. stat. sol. (B) 1993, 175, 15-56.
Charge Transport in Polydiacetylenes


2.1 INTRODUCTION

Polydiacetylenes (PDAs) constitute a class of unusual polymeric materials, since they can be produced as almost perfect single crystals by solid state topochemical polymerization of the monomer crystals\(^1\), see Figure 2.1. PDAs with a great variety of side groups have been synthesized. Typical examples are shown in Figure 2.2. Depending on the side group the diacetylene derivatives can be polymerized using heat, UV light or high-energy radiation\(^2-4\).

![Figure 2.1 Schematic representation of the solid state polymerization of diacetylenes, where the R's indicate the pendent groups.](image)

In an ideal PDA crystal the polymer chains are perfectly aligned parallel to each other and in the absence of defects the conjugated \(\pi\)-electron system extends over the entire polymer backbone. Because of this, PDAs have received an enormous amount of attention as potential materials for applications in photolithography, nonlinear optics and molecular electronic devices\(^5,6\). One of the barriers to their technical implementation has proven to be the difficulty of large-scale production of PDA thin films. A considerable step forward was made with the synthesis of monomeric diacetylene derivatives which formed soluble polymeric materials. Polymer solutions could then be used to produce thin PDA layers by the Langmuir-Blodgett technique, drop-casting or spin-coating. However, most PDAs are insoluble. Of the diacetylene derivatives shown in Figure 2.2 nBCMU's form readily soluble
Charge Transport in Polycatenylenes

polymers, the remaining PDAs are insoluble. In the case of an insoluble polymer a thin polymer film can sometimes be obtained by polymerisation of a film of the monomer. Monomer films can also be formed using chemical vapour deposition.

\[
\begin{align*}
R & \quad pTS \quad X = \text{CH}_3 \\
& \quad FBS \quad X = \text{F} \\
& \quad DCH \\
& \quad \text{THD} \\
& \quad \text{DQ} \\
& \quad m\text{-AAPB} \\
& \quad -(\text{CH}_2)_n-\text{O-CH}_3 \\
& \quad \text{ETCD} \quad n = 4 \text{ and } X = \text{CH}_2\text{CH}_3 \\
& \quad \text{IPUDO} \quad n = 4 \text{ and } X = \text{CH(CH}_3)_2 \\
& \quad \text{TCDU} \quad n = 4 \text{ and } X = \text{CH}_3 \\
& \quad \text{nBCMU} \quad n = n \text{ and } X = \text{CH}_2\text{CO}_2\text{C}_4\text{H}_9
\end{align*}
\]

Figure 2.2 Chemical structure and acronyms of the pendent groups R of the PDAs used in this work.
2.2 STRUCTURE OF POLYDIACETYLENES

Most PDA derivatives have a monoclinic crystal structure. That of poly-\( p \)TS is shown in Figure 2.3A as a projection of the diacetylene units in a plane perpendicular to the polymer backbone. Thus, the polymer backbones are oriented perpendicular to the plane of the drawing.

![Diagram of polydiacetylene structure]

**Figure 2.3** Crystal structure of bis-\((p\)-toluene sulphonate\) diacetylene polymer (poly-\( p \)TS) according to Kobelt and Paulus\(^7\). Top: projection onto the a-c plane which is perpendicular to the polymer chains, showing the orientation of the plane of the polymer chains. Bottom: polymer chain along the b-direction.
Table 2.1 Lattice parameters and density of different PDA crystals at room temperature.

<table>
<thead>
<tr>
<th>PDA derivative</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (deg)</th>
<th>MW</th>
<th>ρ (g/cm³)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pTS</td>
<td>14.49</td>
<td>4.91</td>
<td>14.94</td>
<td>118</td>
<td>418.5</td>
<td>1.48</td>
<td>[7]</td>
</tr>
<tr>
<td>FBS</td>
<td>13.93</td>
<td>4.90</td>
<td>14.06</td>
<td>113</td>
<td>426.4</td>
<td>1.61</td>
<td>[8]</td>
</tr>
<tr>
<td>DCH</td>
<td>12.87</td>
<td>4.91</td>
<td>17.40</td>
<td>108</td>
<td>408.5</td>
<td>1.30</td>
<td>[9]</td>
</tr>
<tr>
<td>TCDU</td>
<td>19.63</td>
<td>4.95</td>
<td>11.84</td>
<td>95</td>
<td>432.5</td>
<td>1.25</td>
<td>[10]</td>
</tr>
<tr>
<td>THD</td>
<td>9.05</td>
<td>4.87</td>
<td>13.65</td>
<td>109</td>
<td>412.5</td>
<td>1.28</td>
<td>[11]</td>
</tr>
<tr>
<td>ETCD</td>
<td>18.30</td>
<td>4.89</td>
<td>10.78</td>
<td>95</td>
<td>336.4</td>
<td>1.16</td>
<td>[12,13]</td>
</tr>
<tr>
<td>IPUDO*</td>
<td>10.87</td>
<td>4.89</td>
<td>39.19</td>
<td>90</td>
<td>364.5</td>
<td>1.16</td>
<td>[14]</td>
</tr>
<tr>
<td>4BCMU</td>
<td>5.37</td>
<td>4.89</td>
<td>54.15</td>
<td>90</td>
<td>508.6</td>
<td>1.22</td>
<td>[15,16]</td>
</tr>
</tbody>
</table>

*Note that in the case of IPUDO a crystallographic unit cell requires four monomer units instead of two as depicted in Figure 2.3 for poly-TS. Therefore, to compare the lattice parameters of IPUDO with the other derivatives, the c distance of IPUDO should be divided by two.

The length of an individual diacetylene unit within a polymer backbone is denoted as b in Table 2.1. The interchain distances are characterized by a and c and the angle between the directions along which a and c are defined is denoted as β. Some authors\textsuperscript{16,17} prefer an alternative notation, in which b and c are interchanged and consequently c is in the direction of the polymer backbone. Table 2.1. shows that b is very similar for different side groups, as would be expected. The interchain distances characterised by a and c can vary substantially however. Note, that the density of different PDAs calculated on the basis of the crystallographic parameters also varies considerably.

Figure 2.3 shows a perfectly regular arrangement of polymer backbones within a polydiacetylene crystal. However, real diacetylene monomer crystals contain structural imperfections such as dislocations. The concentration of dislocations increases with the rate of crystal growth\textsuperscript{18}. During polymerization these dislocations may result in chain distortions and/or chain ends.

Most polydiacetylene crystals absorb red light at room temperature. This has been attributed to a relatively large effective conjugation length exceeding 30 monomer units\textsuperscript{19,20}. Due to the high extinction coefficient polydiacetylene crystals often appear to be black with a metallic luster. However, sufficiently thin crystals exhibit a blue colour due to their dominant absorption at \textit{ca.} 600 nm. Heating the crystal leads to a blue-shift of the absorption and hence the color of a thin crystal changes from blue to red. This reflects the reduction of the conjugation length due to increasing distortions of the polymer chains at higher temperatures. Some polydiacetylene derivatives, e.g. ETCD and IPUDO, fully regain the original polymer backbone conformation on recooling the crystal. This however is not the case for BCMUs for which the color change is irreversible.
Heat induced changes of the backbone conformation have also been observed for thin films. For instance, the absorption spectrum of a polymerized spin-coated film of 4BCMU shows an absorption maximum near 620 nm, see the dotted-line spectrum in Figure 2.4. The solid-line spectrum in Figure 2.4 shows the room temperature absorption after heating of the film above 100°C. The blue shift of the absorption indicates that a different chain conformation has been introduced by heating.

![Optical Absorption](image)

**Figure 2.4** Optical absorption spectra of poly-4BCMU. The dotted-line spectrum with an absorption maximum at ca. 620 nm shows the data for a blue 4BCMU film. The solid-line spectrum with a maximum at ca. 530 nm is for a red 4BCMU film. The dashed curve is the absorption spectrum of a yellow 4BCMU solution in chloroform.

The blue and red forms are also observed in polydiacetylene solutions. In addition a third yellow phase with an absorption maximum near 460 nm also exists in solution, see the dashed curve in Figure 2.4. The yellow color is due to a much shorter conjugation length, corresponding to a twisted, non-planar and highly disordered conformation. Note, that the exact nature of the backbone conformation is still a point of discussion. In Chapter 7 the effect of the backbone conformation on the intrachain photoconductivity in dilute poly-BCMU solutions will be studied.
2.3 CONDUCTIVE PROPERTIES

2.3.1 Introduction

The large body of research carried out on the conductive properties of PDAs has been reviewed by Bässler in 1985, by Schott and Wegner in 1987, and more recently by Zuilhof et al. Much of the early research on PDAs involved studies of the dark conductivity of samples in which charge carriers were introduced by doping. Later, the interest tended to focus more on the actual mobility of charge carriers, since this is the property which determines important parameters such as the current density and the switching speed of practical device structures.

In PDAs, the ‘band gap’ \( E_g \) is larger than 2 eV. The equilibrium concentration of charge carriers can be calculated according to \( N_p = N_e \exp(-E_g/(2kT)) \). A band gap of 2 eV results in an extremely low concentration of charge carriers at room temperature of less than \( 4 \times 10^3 \) cm\(^{-3} \) taking the density of states \( N_\sigma \) to be on the order of the monomer unit concentration, i.e. ca. \( 10^{21} \) cm\(^{-3} \). Taking as an absolute upper limit for the mobility a value of \( 10^3 \) cm\(^2\) V\(^{-1}\) s\(^{-1} \) as found for a good inorganic semiconductor, results in an estimated dark conductivity of only \( 10^{-12} \) S cm\(^{-1} \) or less.

According to the above, all organic “conducting” polymers should be good insulators in their pure state. This is also found to be the case for PDAs for which dark conductivities in the range \( 10^{-15} \) to \( 10^9 \) S cm\(^{-1} \) have been found depending on the side-chain substituents, method of preparation, morphology and physical treatment. The background conductivities higher than \( 10^{-12} \) S cm\(^{-1} \) can be attributed to spurious chemical impurities or physical defects. In order to study the properties of charge carriers it is therefore necessary to artificially create them in the material. For this purpose several methods have been used. These include chemical doping with strong oxidizing or reducing agents (section 2.3.2), electrode charge injection (section 2.3.3), and ionization with supra-band gap photons (section 2.3.4) or high-energy radiation (section 2.3.5). Results obtained for PDAs using these different methods will be discussed below. The charge carrier mobility and its anisotropy will be discussed in sections 2.3.6 and 2.3.7, respectively.

2.3.2 Chemical Doping

Conjugated polymers can be made conducting by adding dopants, which act as reducing or oxidizing agents and hence introduce an electron in the conduction band or a hole in the valence band, respectively. Dopant levels used to obtain conducting conjugated polymers are typically up to a few tens of percent per monomer unit, whereas in inorganic semiconductors much lower doping levels in the ppm range are used.

Unlike polyacetylene, PDAs cannot be easily doped by exposure to gaseous electron acceptors, e.g. halogen vapors. The main obstacle against doping is the densely packed
crystal structure of PDAs, which does not offer easy diffusion paths for dopant molecules to penetrate the lattice. In spite of this difficulty, there have been many different attempts to make PDAs conducting by doping. Most studies have involved doping of poly-pTS (for its structure see Figure 2.2). In Figure 2.5 the resulting conductivity in doped poly-pTS samples are presented as a function of the concentration of electron spins as determined by EPR, i.e. the concentration of radical sites.

![Graph showing conductivity vs spin density for doped poly-pTS samples](image)

**Figure 2.5** Conductivity plotted versus spin density for different doped poly-pTS samples. ■: poly-pTS with different dopants; ○: 75As+ ion-implanted poly-pTS.

[Reproduced with permission of Sandman *et al.* from reference 54.]

Doping of poly-pTS single crystals with iodine vapor at temperatures below 100°C has yielded a maximum conductivity of $2 \times 10^{-2}$ S cm$^{-1}$ 54. The doping temperature was kept under 100 °C, since PDAs tend to degrade at higher temperatures. Thin crystals (less than 0.5 mm thick) were used to ensure homogeneous doping. Mixing of the monomer crystals with dopant, i.e. doping before polymerization, as well as doping during polymerization did not give rise to higher conductivities than post-polymerization doping of the PDA crystals 44,55. A conductivity of only about $10^{-4}$ S cm$^{-1}$ was obtained by doping with I$_2$ before polymerization, while doping with I$_2$ during polymerization resulted in an even lower conductivity of the order of $10^{-7}$ S cm$^{-1}$. Also, even though SO$_3$ gas has a strong tendency to

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Chapter 2
diffuse into poly-pTS crystals, introduction of this dopant during polymerization did not result in a conductivity exceeding $10^{-4}$ S cm$^{-1}$.

In an attempt to achieve a higher conductivity, Nakanishi et al. used finely powdered $p$TS monomer crystals, which were then polymerized by $\gamma$-irradiation at room temperature. The polymer obtained was mixed with dopant and then pelletized into a thin disk under a pressure of 0.26 GPa. Of the dopants studied under high-pressure conditions only AgClO$_4$ gave a significant conductivity equal to $7 \times 10^{-2}$ S cm$^{-1}$. A higher conductivity of 2 S cm$^{-1}$ was achieved by mixing AgClO$_4$ with monomer crystallites with subsequent polymerization carried out under high-pressure (4.9 GPa). High pressure applied during polymerization may result in smaller sizes of polymer crystallites resulting in a less heterogeneous distribution of dopants throughout the pellet.

![Graph](image)

**Figure 2.6** Semi-logarithmic plots of the conductivity versus exposure time for iodine doping of poly-DCH at different temperatures. [Reproduced with permission of Elsevier Science from reference 37].

Dopant molecules are expected to diffuse more easily into crystals at high temperatures. Since poly-DCH (for its structure see Figure 2.2) is highly heat-resistant, doping with I$_2$ could be performed at elevated temperatures. In an open system a maximum conductivity of $10^{-3}$ S cm$^{-1}$ was obtained (see Figure 2.6), while a considerably higher value of 0.06 S cm$^{-1}$ was found in a closed system. Using SbF$_5$ as a dopant gave much lower conductivities, in the range $10^{-4}$ to $10^6$ S cm$^{-1}$. This can be understood from the less efficient diffusion of SbF$_5$ into the microscopic defects in the crystals. A disadvantage of poly-DCH, considering the crystal structure, is that the bulky pendent groups prevent the dopant molecules approaching close to the polymer backbone. However, the primary charge transfer interaction has been suggested to occur between the dopant and the pendent
group. The lower ionization potential of the polymer backbone then allows subsequent hole transfer to occur from the pendent group to the polymer backbone.\textsuperscript{45}

Besides the chemical doping of polymer crystals by exposure to oxidizing or reducing agents, ion implantation has also been used to increase the number of charge carriers in a material. Several authors\textsuperscript{42,57-61} have reported that ion implantation into normally insulating organic materials can significantly increase their conductivity. For PDAs, a maximum conductivity of 10 S cm\(^{-1}\) has been attained in poly-DCH by implantation of 150 keV \(^{75}\)As\(^+\) ions with a fluence of \(5 \times 10^{16}\) cm\(^{-2}\).\textsuperscript{42,62,63} In poly-pTS, a much lower conductivity, less than \(10^{-4}\) S cm\(^{-1}\), was obtained under similar implantation conditions.\textsuperscript{54} This difference has been ascribed to the fact that the poly-DCH side groups are more stable towards bond scission than the poly-pTS side groups.\textsuperscript{54} Note that the penetration depth of 150 keV \(^{75}\)As\(^+\) in organic materials is only a few tens of nanometers\textsuperscript{61,64} and consequently doping occurs only very close to the crystal surface.

In general, doping causes destruction of the polydiacetylene crystal structure. For example, the golden metallic luster of the pristine poly-pTS surface turns dull and then black after several hours of exposure to various dopant vapors (e.g., Cs, I\(_2\), SbCl\(_3\), and FeCl\(_3\))\textsuperscript{54,65}. The doped samples also showed many fine cracks, mainly along the polymer chain direction. The SbCl\(_3\)-doped poly-pTS crystals became badly cracked. Even the overall shape of the crystals changed and they disintegrated into fragments.\textsuperscript{54} Ion-implanted poly-pTS showed a color change from metallic gold in the pristine state to shiny black when the fluence of the \(^{75}\)As\(^+\) ions exceeded \(\sim 10^{16}\) cm\(^{-2}\). In the intermediate fluence range, \(10^{14} < \phi < 10^{15}\) cm\(^{-2}\), the color ranged from metallic green to reddish black.\textsuperscript{42,67} All of these observations demonstrate destruction of the crystalline structure by doping, which would be expected to have a negative effect on the charge carrier mobility.

In less crystalline PDA systems, such as multilayers,\textsuperscript{49,66} bilayers,\textsuperscript{67} or solvent cast films,\textsuperscript{38,50,68-72} a higher dopant concentration can be achieved. The higher doping level was expected to compensate for the negative effect on the charge carrier mobility of the lower structural ordering and hence possibly give rise to a higher net conductivity. However, the highest conductivity obtained for CHCl\(_3\) cast films of poly-3BCMU doped with iodine of the order of \(10^{-5}\) S cm\(^{-1}\)\textsuperscript{70-72} is still much smaller than the maximum conductivity obtained for doped poly-TS single crystals.

Poly-nBCMU and other poly-alkylcarbonylmethylurethane are highly soluble in both polar and non-polar solvents\textsuperscript{19,20,73-76}, in contrast to other PDAs. This has made it possible to study the AC conductivity of doped PDA solutions.\textsuperscript{39,40,77} A toluene solution of poly-4BCMU doped with iodine exhibited a conductivity of the order of \(10^{-11}\) S cm\(^{-1}\), which was only one order of magnitude higher than in the absence of the dopant.\textsuperscript{40} Poly-4BCMU solutions can transform into a gel state on changing the temperature or the solvent.
### Table 2.2 Conductivity achieved by doping of PDA crystals and films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dopant</th>
<th>Doping Method</th>
<th>$\sigma_{\text{max}}$ (S cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-$p$TS</td>
<td>I$_2$</td>
<td>a</td>
<td>$2 \times 10^{-2}$</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td></td>
<td>$3 \times 10^{-7}$</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td></td>
<td>$1 \times 10^{-4}$</td>
<td>44</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>a</td>
<td></td>
<td>$6 \times 10^{-5}$</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td></td>
<td>$2 \times 10^{-5}$</td>
<td>44</td>
</tr>
<tr>
<td>SbCl$_3$</td>
<td>a</td>
<td></td>
<td>$1 \times 10^{-4}$</td>
<td>54</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>a*</td>
<td></td>
<td>$2 \times 10^{-8}$</td>
<td>56</td>
</tr>
<tr>
<td>Et$_4$NClO$_4$</td>
<td>a*</td>
<td></td>
<td>$2 \times 10^{-8}$</td>
<td>56</td>
</tr>
<tr>
<td>AgNO$_3$</td>
<td>a*</td>
<td></td>
<td>$7 \times 10^{-9}$</td>
<td>56</td>
</tr>
<tr>
<td>Cs</td>
<td>a</td>
<td></td>
<td>$7 \times 10^{-5}$</td>
<td>54</td>
</tr>
<tr>
<td>AgClO$_4$</td>
<td>a*</td>
<td></td>
<td>$7 \times 10^{-2}$</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>c*</td>
<td></td>
<td>$2 \times 10^{0}$</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td></td>
<td>$3 \times 10^{-4}$</td>
<td>44</td>
</tr>
<tr>
<td>SbF$_3$</td>
<td>d</td>
<td></td>
<td>$5 \times 10^{-5}$</td>
<td>44</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>c</td>
<td></td>
<td>$2 \times 10^{-4}$</td>
<td>44</td>
</tr>
<tr>
<td>$^{75}$As$^+$</td>
<td>e</td>
<td></td>
<td>$7 \times 10^{-5}$</td>
<td>54</td>
</tr>
<tr>
<td>polyDCH</td>
<td>I$_2$</td>
<td>a</td>
<td>$6 \times 10^{-2}$</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td></td>
<td>$6 \times 10^{-7}$</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>SbF$_3$</td>
<td>a</td>
<td>$3 \times 10^{-6}$</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td></td>
<td>$8 \times 10^{-5}$</td>
<td>44</td>
</tr>
<tr>
<td>AgClO$_4$</td>
<td>d</td>
<td></td>
<td>$7 \times 10^{-6}$</td>
<td>44</td>
</tr>
<tr>
<td>TCNQ</td>
<td>d</td>
<td></td>
<td>$2 \times 10^{-7}$</td>
<td>44</td>
</tr>
<tr>
<td>$^{75}$As$^+$</td>
<td>e</td>
<td></td>
<td>$1 \times 10^{1}$</td>
<td>42,54</td>
</tr>
<tr>
<td>Poly-m-AAPB</td>
<td>I$_2$</td>
<td>a</td>
<td>$1 \times 10^{-4}$</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td></td>
<td>$5 \times 10^{-2}$</td>
<td>56</td>
</tr>
<tr>
<td>Poly-3BCMU</td>
<td>I$_2$</td>
<td>b</td>
<td>$5 \times 10^{-5}$</td>
<td>38,39,72</td>
</tr>
<tr>
<td>Poly-4BCMU</td>
<td>I$_2$</td>
<td>a</td>
<td>$4 \times 10^{-7}$</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td></td>
<td>$5 \times 10^{3}$</td>
<td>40,71</td>
</tr>
<tr>
<td>Poly-TCDU</td>
<td>$^{75}$As$^+$</td>
<td>c</td>
<td>$7 \times 10^{-3}$</td>
<td>54</td>
</tr>
<tr>
<td>Poly-THD</td>
<td>I$_2$</td>
<td>a*</td>
<td>$3 \times 10^{-2}$</td>
<td>47,78,79</td>
</tr>
<tr>
<td>Poly-11-8-DA</td>
<td>I$_2$</td>
<td>b</td>
<td>$2 \times 10^{-7}$</td>
<td>49</td>
</tr>
<tr>
<td>Poly-DQ</td>
<td>I$_2$</td>
<td>a</td>
<td>$1 \times 10^{-6}$</td>
<td>80</td>
</tr>
</tbody>
</table>

a) Chemical doping of polymer crystals  
d) Doping during polymerization
b) Chemical doping of polymer film  
e) Ion implantation with $^{75}$As$^+$
c) Doping prior to polymerization  
* doping under high pressure
polarity. The conductivity in I₂-doped gels has been found to be 100 times higher than in solutions of poly-4BCMU and has been attributed to electronic conduction through the interconnected gel network rather than to ionic conduction.

Table 2.2 summarizes the conductivities obtained for doped PDA materials, which have been discussed above. No doped PDA material has been found as yet, which combines a high carrier concentration with a high charge carrier mobility. The maximum conductivity achieved is still three to four orders of magnitude lower than in chemically doped polyacetylenes.

2.3.3 Charge Injection

Electronic charge carriers can be injected into organic materials using electrodes for which the Fermi level is close to or higher in energy than the conduction band or lowest unoccupied molecular orbital of the material. This effect has been used with great success recently to produce light emitting diodes in which a fluorescent conjugated polymer forms the active inter-electrode layer. The near-complete lack of fluorescence of PDA films makes them unsuitable for such applications and consequently little research has been carried out in this area.

![Energy (eV)]

Figure 2.7 Valence band (VB) and conduction band (CB) energies for poly-DCH with respect to the vacuum level together with the work functions of different metals used as electrodes.

[Reprinted with permission of Elsevier Science from reference 89]

A study of electron injection into single crystal poly-DCH was however carried out some time ago by Spanning and Bässler. In these experiments the electrode materials investigated were Mg, Ca, Na and NaK alloy. For Mg, a barrier to electron injection of 0.24 eV was determined, which made it possible to estimate the positions of the energy levels of
the conduction band and valence band of the polymer with respect to vacuum to be $-3.4$ eV and $-5.8$ eV, respectively, as shown in Figure 2.7. Despite the fact that the energy levels of the PDA chains within poly-pTS are expected to be close to those for poly-DCH, no evidence for electron injection could be found for the former compound. This was at the time attributed to a high concentration of surface trapping states for poly-pTS.

When using a negatively biased NaK electrode with poly-DCH, the current density was found to increase with the square of the applied voltage indicating the conductivity to be space charge limited. Under these conditions the charge carrier mobility can be estimated by applying Child’s law,

$$ \mu = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} $$ \hspace{1cm} (2.1)

where $j_{scL}$, $A$, $V$ and $L$ are the space charge-limited current, the surface area of the electrode, the voltage applied over the electrodes and the distance between the electrodes, respectively. The mobility value obtained was $(6 \pm 2) \times 10^1$ cm$^2$ V$^{-1}$ s$^{-1}$.

Subsequent work at the same laboratory using electrolytic contacts has cast serious doubt on this interpretation of the data.$^{5,90}$ It is now thought that the conductivity observed was predominantly caused by intercalation of metal atoms into the poly-DCH lattice resulting in chemical doping of the sample. This could also explain the unexpected difference between poly-DCH and poly-pTS if diffusion into the latter is less efficient. The more recent study$^{5,90}$ showed that doping of poly-DCH with iodine from solution could be field induced, thus indicating the great care with which such “charge injection” measurements should be interpreted.

### 2.3.4 Photoconductivity

Charge carriers can be formed in semiconducting materials by photoexcitation. This can occur directly on irradiation with photons with energies larger than that of the band-gap as was discussed in Chapter 1. Alternatively, an optical transition can occur to a bound exciton state, which subsequently undergoes thermal, or field-induced dissociation into separated charge carriers. An understanding of photo-induced charge carrier formation requires therefore knowledge of the energy level structure of the material. Several techniques have been applied in attempts to elucidate the nature of the upper excited states. These include steady-state measurements of the optical absorption and emission spectra, as well as electro-absorption and reflection studies of the influence of an applied electric field on the optical properties, and measurements of the wavelength dependence of the photoconductivity (the “action spectrum”).

The conductivity measured in an action spectrum is the product of the quantum yield for formation, $\eta$, the sum of the mobilities, $\Sigma \mu$, and the lifetime, $\tau$, of the charge carriers. The
separate determination of these individual parameters requires the application of time-resolved techniques which monitor the transient conductivity of the material induced by a short (usually submicrosecond) flash of light. Results on PDAs obtained using different steady state and time-resolved techniques will be discussed separately below.

2.3.4.1 Steady-State Photoconductivity

Photoconductivity has been detected in all PDAs investigated. While the corresponding DA monomers show no observable photocurrent, measurable photoconductivity is found for samples containing as little as ca. 10% polymer.\textsuperscript{91,92}

Comparison of optical absorption spectra with photoconductivity action spectra makes it possible to distinguish transitions to neutral bound exciton states and charge separated states. Figure 2.8 shows the photoabsorption and the photoconductivity spectra of poly-TCDU (for its structure see Figure 2.2) measured by Lochner \textit{et al.}\textsuperscript{24}. The onset of the photoconductivity occurs at approximately 0.5 eV above the onset of the absorption, which is due to a transition to the lowest singlet exciton. From the absence of fluorescence from this exciton it has been concluded that it is extremely short lived and consequently thermal ionization into free charge carriers is improbable.

![Photoconductivity spectra](image)

Figure 2.8 Absorption spectrum and action spectrum of poly-TCDU.\textsuperscript{[Reproduced from reference 24 with permission of Wiley-VCH and the authors]}

Action spectra have been measured in a variety of PDAs and the photoconductivity
threshold has been found to vary between 2.2 and 2.7 eV \(^{23,24,33-35,40,46,91,93-104}\). Chance et al. \(^{94}\) have measured action spectra for holes and electrons separately and found them to be identical. In a number of PDA samples photoconductivity has been observed at photon energies even lower than the energy of the first absorption band of the polymer. This has been attributed to ionization of interfacial or impurity defects \(^{23,33-35,40,51,91,93,95,96,98,99,102}\). It is now generally accepted that the exciton binding energy for PDAs is approximately 0.5 eV\(^{105}\). This value has also been obtained from electroabsorption and electroreflectance studies on several PDAs \(^{36-38,106-111}\).

The action spectrum of poly-DCH exhibits an additional band at a photon energy near 3.6 eV, which is assigned to excitation of the carbazole group in the side-chain followed by electron transfer to the polymer backbone \(^{46,100,101}\).

At low light intensities the photoconductivity in PDAs increases linearly with the intensity, while at higher intensities it increases sublinearly. This has been attributed to a transition from first-order geminate recombination of charge carrier pairs to second-order homogeneous recombination \(^{35,93,99,112-117}\).

The quantum yield for charge carrier generation in poly-pTS, poly-TCDU and poly-DCH has been found to increase quadratically with photon energy for excitation up to approximately 1 eV above the onset of the photoconductivity and to saturate at higher energies \(^{23,24,93,95}\). The overall quantum yield for charge carrier generation, \(\eta\), is the product of the primary quantum yield, \(\phi\), for formation of a charge carrier pair and the probability that this pair escapes mutual geminate recombination, \(P\), i.e. \(\eta = \phi P\). According to Onsager theory \(^{118-120}\), \(P\) is thermally activated with an activation energy, \(E_A = \frac{\varepsilon^2}{4\pi\varepsilon_0\varepsilon r}\), which depends inversely on the initial separation distance, \(r\), between the electron and the hole. For poly-pTS, Lochner et al. \(^{95}\) found \(E_A = 54\) meV in the temperature range between 100 and 190 K, which gives an initial electron-hole separation of \(r = 116\) Å, assuming \(\varepsilon = 2.3\). However at temperatures above 190 K \(E_A\) was found to increase with temperature which was ascribed to a decrease in the initial separation distance \(r\) with temperature to \(r = 70\) Å at room temperature.

Donovan and Wilson \(^{121}\) found that the overall quantum yield depended only weakly on temperature and on the basis of this concluded that the mechanism of charge carrier production could not be described in terms of the Onsager theory at temperatures below 100 K.

The observation by Lochner et al. that \(E_A\) is independent of the photon energy for temperatures above 100 K \(^{95}\) indicates that the escape probability \(P\) and the initial separation \(r\) do not depend on the photon energy. This is in contrast to results obtained with anthracene \(^{122}\) and selenium \(^{123}\), where \(r\) was found to increase with photon energy. Since \(P\) is independent of the photon energy, the energy dependence of the photoconductivity must be due to the variation of the primary quantum yield \(\phi\). This rules out the direct production
of charge carriers via a valence band to conduction band transition, since in that case the primary quantum yield, \( \phi \), would be independent of wavelength and equal to 1. The energy dependence of \( \phi \) has been attributed to competition between a transition to a neutral exciton state and a transition to the conduction band, which leads to charge carrier pairs that escape from recombination with a probability that is independent of, or only weakly dependent on, the photon energy \(^{24}\). The involvement of excitonic states in the production of charge carriers in the presence of an external electric field has been confirmed by the quadratic increase of the photoconductivity for field strengths above \( 10^7 \) V cm\(^{-1}\)\(^{124}\).

2.3.4.2. Time-Resolved Photoconductivity

In time-resolved photoconductivity experiments, charge carriers are produced by pulsed photo-excitation and the decay of the photocurrent, due to the discharge of charge carriers at the electrodes or by trapping and/or charge recombination, is measured as a function of time. In time-of-flight (TOF) experiments the mobility of charge carriers in a sample is determined from measurement of the transit time, \( t_p \), that charge carriers need to travel over a distance \( L \) in the presence of an external electric field \( E \). The mobility can be obtained from the relation \( \mu = L/(Et_p) \).

In a classical TOF experiment, as introduced by Kepler \(^{125}\) and LeBlanc \(^{126}\), a thin sheet of charge carriers is produced adjacent to one of the electrodes by illumination with strongly absorbed light through one of the electrodes, see Figure 2.9A. Alternatively illumination does not occur through an electrode, but directly on the sample creating a charge carrier sheet near the surface, see Figure 2.9B. An optical mask can be used to produce charges only at a specific distance from one of the electrodes, see Figure 2.9C. In the absence of deep trapping the charges move through the sample and a current can be measured, which vanishes after the transit time, \( t_p \), when the charges have been removed by discharge at an electrode. Besides discharge at the electrodes the photocurrent can also decay due to trapping and/or electron-hole recombination. When a configuration such as that in Figure 2.9A or Figure 2.9C is used, the signals due to electrons and holes can be distinguished by inversion of the applied voltage.

Chance \textit{et al.} \(^{94}\) were the first to perform classical TOF experiments on poly-\( p \)TS using the configuration shown in Figure 2.9A. They observed that electrons and holes became trapped at defect sites on a timescale of approximately 0.5 \( \mu \)s in heat-polymerized samples, while in \( \gamma \)-ray polymerized samples much shorter, unresolvable trapping times were found. In heat polymerized samples Chance \textit{et al.} could place upper and lower limits of 3 and \( 10^{-3} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) on both the electron and hole mobilities. Subsequently, Reimer & Bässler \(^{127}\) obtained a charge carrier mobility of \( 4.8 \pm 1.5 \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in their TOF experiments. The increase of the charge carrier mobility with temperature observed was attributed to shallow traps and/or carrier jumps between polymer chain ends.
Figure 2.9. Different time-of-flight (TOF) configurations.
(A) Classical Kepler-LeBlanc TOF configuration, in which a thin layer of charge carriers are produced by pulsed irradiation through a transparent electrode.
(B) Configuration in which charge carriers are produced over the entire surface between the electrodes.
(C) Configuration using an optical mask, by which charge carriers are produced locally on the sample surface.

Donovan & Wilson\textsuperscript{25,128} performed TOF experiments on thermally polymerized poly-\textit{p}TS samples using a configuration similar to Figure 2.9B. From their results at short times (nanoseconds) they concluded that the carrier drift velocity is saturated at approximately the velocity of sound, down to the lowest field applied, i.e. 10\textsuperscript{4} V cm\textsuperscript{-1}. Based on this, they deduced that the charge carrier mobility must have an extremely high value of at least 2 \times 10\textsuperscript{3} cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}. Donovan and Wilson claimed that the intrinsic charge carrier motion in the short-time region is unaffected by barriers or traps and that a charge carrier can travel over a distance of millimeters before meeting a trap\textsuperscript{129}. In the longer time regime, from 1 \mu s to 1 s, the current was found to decay according to a t\textsuperscript{-\alpha} power-law (with \alpha \approx 0.8 to 0.95 depending on the sample)\textsuperscript{129,130}. This behavior is characteristic for dispersive 1D-charge transport in the presence of traps, defects and barriers\textsuperscript{130,131}.

Blum and Bässler\textsuperscript{132,133} also performed TOF experiments on heat-polymerized poly-\textit{p}TS crystals, using a set-up similar to that of Figure 2.9B. The measured current decay could also be described by a t\textsuperscript{-\alpha} power-law. In contrast to Donovan and Wilson\textsuperscript{25,128-130}, however, a power-law behavior with \alpha = 1.35 \pm 0.05 was observed even at short times (15 ns < t < 1 \mu s). For longer times (t > 1 \mu s) Blum and Bässler found \alpha = 0.8 \pm 0.05 in agreement with the results of Donovan and Wilson and claimed that the dispersive character was due to the limited chain length of the polymer, which was about 1500 Å\textsuperscript{134}. Once created, photocarriers move freely along the polymer chains and need to overcome barriers between
chain ends, which causes dispersion due to a waiting time distribution for motion from one chain to the next. This transport mechanism also explained the weakly field dependent velocity for fields below $5 \times 10^3$ V cm$^{-1}$ and the linear increase of the velocity at fields above $2 \times 10^4$ V cm$^{-1}$.

![Figure 2.10 Transient TOF currents for electrons (-) and holes (+) in poly-$p$TS.](image)

[Reprinted from references 135,136 with permission from the Institute of Physics]

Fisher et al.$^{135-140}$ used TOF configurations based on the principles shown in Figures 2.9B and 2.9C to study the mobility of electrons and holes in poly-$p$TS crystals along the polymer chain direction. Typical transients obtained with their technique are shown in Figure 2.10. In oxygen-free samples they found that electrons are the dominant current carriers and can traverse samples with a length up to 9 mm, while holes drift only over about 60 µm before they become trapped $^{135,136}$. A large carrier drift range of 8 mm has also been found in crystalline poly-4BCMU samples $^{141}$, while a short range of 80 µm was found in Langmuir-Blodgett PDA films $^{142}$. In poly-$p$TS crystals introduction of oxygen causes severe trapping of electrons and also reduces the lifetime of holes $^{139}$. For electric field strengths near $10^2$ V cm$^{-1}$ the transit time for electrons was found to scale linearly with the sample length from which it was concluded that the transport is Gaussian and not dispersive $^{135,137,138}$. At lower field strengths and at lower temperatures a transition to trap-limited dispersive transport occurs, in agreement with the results of Blum and Bässler $^{132}$. However, in the experiments of Fisher and Willock at higher field strengths the electron drift velocity tends to saturate at the speed of sound along the polymer chain direction, in contrast to the results of Blum and Bässler $^{132}$. From their data, Fisher et al. $^{135,137}$ inferred a trap-limited electron mobility at low fields of the order of $1$ cm$^2$ V$^{-1}$ s$^{-1}$, but this interpretation of the experimental data has been criticized by Wintle $^{143}$.

Moses, Sinclair & Heeger $^{144-146}$ achieved picosecond-time-resolution in their transient-photoconductivity measurements on poly-$p$TS by using the Auston microstrip transmission
line switch technique. In these experiments the experimental arrangement corresponds to the configurations shown in Figures 2.9B and 2.9C. Typical photocurrents are shown for poly-pTS at various temperatures and at different electric fields strengths in Figure 2.11. Each transient is characterized by two components, a fast initial decay followed by a slowly decaying tail. The fast initial decay is insensitive to temperature and electric field, while the tail strongly depends on temperature and electric field, which was ascribed to trapped-dominated transport. A single exponent could fit the initial decay of this tail, while for longer times the photocurrent decayed as a power law, as was also found in the TOF studies mentioned above. From the complete disappearance of the tail at certain field strength, a mobility of approximately 5 cm² V⁻¹ s⁻¹ was deduced. Furthermore, Moses et al. concluded that one species of carrier has a substantially higher mobility than the other. However, it could not be decided whether the electron or the hole was the major charge carrier. They also found that the carrier drift velocity was proportional to the external applied field in the time domain below 100 ns.

![Graphs showing transient photocurrents](image)

**Figure 2.11** Transient photocurrents obtained for poly-pTS using the Autson switch technique. (A) For different temperatures; from top to bottom: 300K, 180K, 60K and 15 K. (B) For different electric field strengths; from top to bottom; 10⁵ V cm⁻¹, 3 x 10⁵ V cm⁻¹, 10⁵ V cm⁻¹ and 3 x 10⁴ V cm⁻¹. [Reprinted from reference 146 with permission from Springer Verlag, Heidelberg]

In an attempt to reproduce the results of Moses et al., Donovan & Wilson observed only a "featureless decay of the photocurrent". However, from the current remaining at 300 ps they obtained an acoustic carrier drift velocity, i.e. 2 x 10⁵ cm s⁻¹, as found previously. In a further study, Donovan and Wilson attributed the increase in decay rate of the
photocurrent with increasing electric field solely to an increase in the bimolecular recombination rate. This is in contrast to the interpretation of Moses et al. who ascribed the enhancement of the photocurrent decay with electric field to a linear increase of the drift velocity. Frankevich has presented a critical reaction to the work of Donovan and Wilson, and concluded that their photoconductivity results are consistent with a mobility of about 3 cm²V⁻¹s⁻¹, which is 5 orders of magnitude lower than the value they claimed.

Auston transmission line experiments on poly-pTS samples have also been carried out by Yang et al., who found a saturated carrier drift velocity of 5 x 10⁶ cm s⁻¹ in the field range between 8000 and 15000 V cm⁻¹. This mobility of 500 cm²V⁻¹s⁻¹ was obtained. The fact that the velocity is one order of magnitude higher than obtained by Moses, Blum and Donovan at comparable field strengths was attributed to a better crystal quality.

The work discussed above concerns transient photoconductivity measurements on solid crystalline samples of PDA derivatives, mainly poly-pTS. In solution, both a rod-like polymer chain structure and a coil conformation of the polymer chain can be realized depending on the solvent/non-solvent ratio or the temperature. Hence, information on the effect of the polymer chain conformation on charge transport can be obtained from studies of PDAs in solution. Very recently, Donovan et al. applied the Auston switch technique to a poly-4BCMU solution. Conductivity signals were observable in the red rod phase of a poly-4BCMU-toluene solution at room temperature, while no conductivity at all was observed in the yellow coil phase at elevated temperatures. They obtained a drift velocity of 266 m s⁻¹ on a rod-like molecule, which is a factor of 8 lower than the value obtained for a poly-pTS single crystal. The difference in magnitude is ascribed to more order in PDA crystals as compared to a PDA molecule in solution.

In summary, considerable controversy still exists concerning the motion of photogenerated carriers in PDAs. According to some studies, the velocity of charge carriers is independent of the electric field strength, while in others a field-dependent velocity has been found. In addition estimates of charge carrier mobilities differing by many orders of magnitude have been derived. Agreement is also absent as to whether the electron or hole is the major charge carrier in PDAs.

### 2.3.5 Radiation-Induced Conductivity

The conductivity of PDAs induced by irradiation with 3 MeV electrons was first reported by Van der Laan et al. in 1994 using the pulse radiolysis time-resolved microwave conductivity (PR-TRMC) technique. The conductivity could be measured as a function of the conversion of monomer to polymer. Intermittent measurements of conductivity transients were made as a function of the accumulated radiation dose using the same electron beam beginning with an initially monomeric 4BCMU polycrystalline sample.
Both the mobility and lifetime of the charge carriers were found to decrease at high total doses indicating degradation of the material. Significant negative effects were observed even for doses much lower than those routinely used to produce "polymeric" materials using high energy radiation. This indicates that the production of PDAs via this route could possibly be substantially improved by optimizing the dose conditions. Polymerization with high-energy radiation has been shown to induce chemical defects \(^{68,162,163}\), which are capable of trapping the mobile charge carriers, hence reducing the number of charge carriers which contribute to the conductivity.

**2.3.6 Charge Carrier Mobility**

In the previous sections a variety of methods have been discussed by which estimates have been made of the mobility of charge carriers in PDA materials. The results for poly-pTS single crystals are summarized in Table 2.3. The values can be separated into 2 categories; those close to or in excess of \(10^3\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) and those on the order of or less than \(10\) cm\(^2\)V\(^{-1}\)s\(^{-1}\). The larger values will be discussed first.

The value of \(6 \times 10^2\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) of Spannring and Bässler \(^{89}\) was retracted in a subsequent publication \(^{590}\), on the basis of evidence that spurious doping of the sample by the electrode materials had probably influenced the results in the earlier study. The value of \(500\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) determined by Yang et al. \(^{152,153}\) on a nanosecond timescale in a thin film of poly-pTS has been criticized by Fischer and Willock \(^{135}\) on the basis of the high laser intensities used which could have resulted in severe space charge perturbation of the electric field. Finally, the extremely large value of \(2 \times 10^5\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) estimated by Donovan and Wilson \(^{25,128}\) has been the subject of much discussion \(^5\). Frankevich \(^{151}\) has suggested that the photocurrent at short times in the Donovan and Wilson experiment should be attributed mainly to geminate ion pairs rather than escaped pairs as assumed by the latter authors, and concluded that the results were in fact consistent with a much smaller mobility of approximately \(3\) cm\(^2\)V\(^{-1}\)s\(^{-1}\).

A high charge carrier mobility of \(2.8 \times 10^3\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) was also reported for poly-DCH (not listed in Table 2.3) by Sebastian and Weiser \(^{106}\). This was in fact not a direct measurement, since the mobility was obtained from the relation \(\mu = e \tau/m^*\). From electroreflectance measurements the effective mass, \(m^*\), was found to be \(0.05m_e\), with \(m_e\) the electron mass. The scattering time was estimated to be \(\tau = 8 \times 10^{-14}\) s. Apart from the assumptions involved, the fact that this estimate was derived from optical experiments raises doubts as to the relevance of the data to the relaxed state of the electron and hole observed in charge transport measurements.

At the present time there would appear to be a broad consensus, which would agree with the conclusion reached in Bässler's exhaustive earlier review of mobility values in PDAs that "there is no need to invoke a mobility greater than about \(100\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) for carrier transport along a defect-free PDA chain" \(^5\). The large number of values in the 1 to \(10\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) range...
1 s\(^{-1}\) range listed in Table 2.3 would tend to support this conclusion. The relatively small variations for a given material and from one PDA derivative to another are probably within the limits of the accuracy of the various measurement techniques. Differences due to different methods of preparation and structural variations dependent on side chain composition could however also play a role.

<table>
<thead>
<tr>
<th>Mobility(\times) (cm(^3)V(^{-1})s(^{-1}))</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 2.0(\times)10(^3)</td>
<td>Transient photoconductivity</td>
<td>128,129</td>
</tr>
<tr>
<td>(6±2)(\times)10(^3)</td>
<td>Charge injection</td>
<td>89</td>
</tr>
<tr>
<td>500</td>
<td>Transient photoconductivity</td>
<td>152,153</td>
</tr>
<tr>
<td>8.9</td>
<td>Transient photoconductivity</td>
<td>138</td>
</tr>
<tr>
<td>7.6</td>
<td>PR-TRMC</td>
<td>164</td>
</tr>
<tr>
<td>5.0</td>
<td>Transient photoconductivity</td>
<td>144-146</td>
</tr>
<tr>
<td>4.8±1.5</td>
<td>Transient photoconductivity</td>
<td>127</td>
</tr>
<tr>
<td>4.0</td>
<td>Transient photoconductivity</td>
<td>140</td>
</tr>
<tr>
<td>3.0±2.0</td>
<td>Transient photoconductivity</td>
<td>112,165</td>
</tr>
<tr>
<td>1.0</td>
<td>Transient photoconductivity</td>
<td>137</td>
</tr>
<tr>
<td>0.5-3.0</td>
<td>Dark conductivity</td>
<td>166</td>
</tr>
<tr>
<td>10(^{-3})·3</td>
<td>Transient photoconductivity</td>
<td>94</td>
</tr>
</tbody>
</table>

*parallel to the polymer backbone direction.*

An important issue, which still remains to be categorically addressed, is the relative mobility of holes and electrons in PDAs. While there seems to be little doubt that the electron has a mobility on the order of 1 cm\(^2\)V\(^{-1}\)s\(^{-1}\) or higher, on the basis of the TOF experiments of Fischer and Willock \(^{136}\), the mobility of the hole still remains an unknown quantity. The early work of Chance et al. \(^{94}\) did however indicate that both carriers had approximately the same mobility.

To our knowledge only the work of Kertész et al. \(^{167}\) provides a theoretical prediction of the charge carrier mobility in PDAs. Their band structure calculation on an idealized PDA chain provides effective masses for electrons and holes equal to 0.17 \(m_e\) and 0.19 \(m_e\), respectively. Using the Bardeen-Shockley deformation potential approximation \(^{168}\) and these effective masses, they obtained an electron and hole mobility of 1700 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and
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26 cm$^3$V$^{-1}$s$^{-1}$, respectively. The calculations of Kertész et al. do not include the effect of polaron formation, which would reduce the mobility considerably. From theoretical studies, Cade & Movaghar$^{169}$ concluded that excess holes or electrons on a PDA chain are localized and that the charge transport at room temperature is rather polaronic than bandlike. The effective mass of the polaronic charge carriers was estimated to be 0.6 $m_e$. This value is larger than the values of Kertész et al. and would result in a smaller mobility. Furthermore, the theoretical predictions assume perfect polymer chains without disorder. The inclusion of disorder in the theoretical description would further reduce the calculated mobility and shift its magnitude closer to the lower range of values obtained in experimental studies.

2.3.7 Anisotropy

Nearly perfect single crystals of PDAs in which the polymer chains are well aligned can be obtained by solid-state topochemical polymerization$^{170,171}$. In such crystals the polymer chains are parallel to each other and well separated. The shortest interchain distance in poly-PTS single crystals along the crystallographic c-axis (see Figure 2.3) is as large as 7.5 Å$^7$. Due to the difference between the conductive pathways along and perpendicular to the polymer chains the mobility of charge carriers is expected to be highly anisotropic and to be favored along the direction of the polymer backbone. The anisotropy here is defined as the ratio of the mobilities parallel and perpendicular to the polymer chain direction. Anisotropy values obtained in different experimental studies are listed in Table 2.4.

Scherman & Wegner$^{33,34}$ were the first to study the anisotropy of the dark conductivity of poly-PTS single crystals and found a surprisingly low value of 6. A comparable anisotropy in poly-PTS of the order of ten was also found from transient photoconductivity measurements by Chance et al.$^{94}$. However, from other studies of the dark conductivity$^{43}$, the photoconductivity$^{91,112,115,116,124,172}$, and the radiation-induced conductivity$^{164}$ much larger anisotropies, exceeding 100, have been found.

Polymerization with γ-rays induces chemical defects$^{68,162,163}$, which can distort the charge motion and reduce the mobility along the polymer chain. The negative effect of γ-ray polymerization on the anisotropy in PDA single crystals could also explain the low value of the anisotropy of 1.5$^{173}$ observed in single crystals of γ-ray polymerized 1,4-bis(3-quinol)-1,3-butadiyne (DQ). However, it should be realized that the monomer-to polymer conversion in these samples was only 25%$^{174}$.

A decrease in the anisotropy of the conductivity has also been observed in fully polymerized TS/FBS mixed crystals with increasing FBS content$^{172}$, which was attributed to a decrease of the average unperturbed chain length.

Since doping has a negative effect on the quality of PDA crystal, it is to be expected that the anisotropy of doped PDA crystals decreases with increasing doping concentration. This has been observed in iodine-doped films of 3BCMU$^{72}$, where the anisotropy was about 3
for low dopant content and gradually decreased with increasing dopant concentration. However, Ohnuma et al.\textsuperscript{21} found a value of 6.5 for the anisotropy independent of the dopant concentration in an iodine-doped 4BCMU single crystal.

<table>
<thead>
<tr>
<th>PDA</th>
<th>$\frac{\mu_\parallel}{\mu_\perp}$</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-pTS</td>
<td>$&gt;10^4$</td>
<td>Steady-State</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photoconductivity</td>
<td></td>
</tr>
<tr>
<td>poly-pTS (a)</td>
<td>$9 \times 10^2$</td>
<td>Dark Conductivity</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>$1.8 \times 10^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly-pTS (a)</td>
<td>$4.0 \times 10^2$</td>
<td>Steady-state</td>
<td>91,92</td>
</tr>
<tr>
<td></td>
<td>$1.0 \times 10^3$</td>
<td>Photoconductivity</td>
<td></td>
</tr>
<tr>
<td>poly-pTS</td>
<td>$(8 \pm 3) \times 10^2$</td>
<td>Steady-state</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photoconductivity</td>
<td></td>
</tr>
<tr>
<td>poly-pTS</td>
<td>220</td>
<td>PR-TRMC</td>
<td>164</td>
</tr>
<tr>
<td>poly-pTS</td>
<td>$10^5$</td>
<td>Steady-state</td>
<td>115,116</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photoconductivity</td>
<td></td>
</tr>
<tr>
<td>poly-pTS</td>
<td>10</td>
<td>TOF</td>
<td>94</td>
</tr>
<tr>
<td>poly-pTS</td>
<td>6</td>
<td>Dark Conductivity</td>
<td>33,34</td>
</tr>
<tr>
<td>I$_2$-doped poly-4BCMU</td>
<td>6.5±0.4</td>
<td>Dark conductivity</td>
<td>71</td>
</tr>
<tr>
<td>I$_2$-doped poly-3BCMU</td>
<td>3</td>
<td>Dark conductivity</td>
<td>72</td>
</tr>
<tr>
<td>poly-DQ</td>
<td>1.5</td>
<td>Steady-state</td>
<td>173</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photoconductivity</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{(a)} values for the two crystallographic directions orthogonal to the polymer backbone

An enhancement of the anisotropy in films of conducting polymers can be obtained by stretching them\textsuperscript{175-177}. This effect has been observed in films of iodine-doped 3BCMU, which is attributed to an increase in the alignment of the polymer backbones with increasing stretching ratio\textsuperscript{72}.

In summary, it has invariably been found that the conductivity in PDAs along the polymer backbone direction exceeds that in a perpendicular direction. The actual magnitude of the anisotropy, however, depends strongly on the order in the sample, which in crystals is related to the method of monomer crystal growth and polymerization.

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3.1 INTRODUCTION

In the Time Resolved Microwave Conductivity (TRMC) technique microwaves are used to measure conductivity changes in materials. The rapid oscillating electric field of the microwaves causes only a small perturbation of the diffusive motion of the charge carriers. The TRMC technique has advantages over conventional DC conductivity methods in solid materials, which suffer from problems with electrode contacts and field-induced space-charge when heterogeneous materials, such as powders are under study. The method is also free from effects due to dielectric polarization and field-induced drift of charge carriers to domain boundaries. Therefore, the TRMC method enables charge carrier dynamics to be studied in amorphous and polycrystalline bulk solids and in thin-layers.

The method of using microwaves for studies of ionic processes was introduced by Margenau, who analyzed the behavior of charged particles in the gas phase under the influence of a microwave field and calculated the conductivity as a function of the electron density, pressure and microwave frequency. This work was extended by Biondi, Brown and Rose, who made time-resolved studies of the diffusion and recombination of electrons and positive ions in gaseous helium. In 1969 the attenuation of microwaves was applied to the study of radiation-induced high-mobility charge carriers in inorganic semiconductors.

In the early seventies Warman and de Haas succeeded in applying the TRMC technique to the study of electrons formed in nanosecond pulse-irradiated liquid hydrocarbons. Since the introduction of this pulse-radiolysis time-resolved microwave conductivity (PRTRMC) technique, it has been applied to study radiation-induced charge carriers in a variety of liquids, gases, and solid materials, including ice, DNA, C60 bucky balls, polymers and columnar aggregates.

In the early eighties the attenuation of microwaves resulting from short-lived changes in the dipole moment of photo-absorbing species in solutions was detected by Warman and de Haas and Fessenden et al. using pulsed laser light as a radiation source. The combination of flash-photolysis and TRMC, FP-TRMC has been intensively used to study
the intramolecular charge separation in donor-acceptor compounds \textsuperscript{60-74}. An extensive review of these donor-acceptor measurements has been published \textsuperscript{75}. This technique has also been applied to study the dynamics of charge carriers in dilute polymer solutions \textsuperscript{76-78} and more recently to study the dynamics of charge carriers in polymer thin films \textsuperscript{79} and bilayer systems \textsuperscript{80}. Recently, it has been used to investigate the polarizability of neutral photo-excitations (excitons) on conjugated polymers and oligomers in dilute solutions \textsuperscript{81,82}.

The experiments described in this thesis concern the time-resolved monitoring of changes in the conductivity due to formation of charge carriers in diacetylene derivatives in the solid state and in solution by irradiation with 3 MeV electrons and by 4 eV photons, respectively. The charge carrier production will be discussed in section 3.2. In section 3.3 the basic equipment for measuring changes in the microwave conductivity of a medium on pulsed irradiation is presented. In section 3.4 the measurement of the conductivity changes in PDA crystalline powders and dilute solutions using the TRMC technique will be discussed. In section 3.5 a new application of the TRMC technique will be presented: the study of the anisotropy of the conductivity in a single crystal. The problems related to the shape of the crystals studied will be discussed. This new application will be used in chapter 6 to study the anisotropy in the charge carrier mobility of a series of polydiacetylene crystals. In section 3.6 it will be analyzed how information about mobilities of the charge carriers can be obtained from the conductivity measurements.

3.2. CHARGE CARRIER PRODUCTION

\textit{Pulse Radiolysis} is the method by which charge carriers are produced using a short pulse of high-energy radiation, while in \textit{Flash Photolysis} a pulsed light beam is used. In the present work either pulses of high-energy electrons (3MeV) from a Van de Graaff accelerator or pulses of UV photons (4 eV) from an XeCl-excimer laser are used.

High energy, "ionizing" radiation differs from UV photons in two important respects: a) it is non-specific, i.e. all optical excitation and ionization levels of the medium are excited, irrespective of its "color" or morphology, and b) it is highly penetrating. The latter property results in close to homogeneous dose distribution in single-crystal or powder samples several millimeters thick for electron energies of a few MeV \textsuperscript{49}.

The dose-depth profile in the flash-photolysis experiment on the other hand is dependent on the optical density of the irradiated material. In optically absorbing materials low-energy photons usually penetrate at most only a few microns. Therefore, flash-photolysis can only be applied to produce charge carriers in thin films or in dilute solutions of the material in a non-absorbing solvent.
3.2.1 Pulse Radiolysis

Pulse-radiolysis studies are most frequently carried out using electron accelerators, which provide short pulses of electrons with kinetic energies in the MeV range. In the pulse radiolysis described in this thesis charge carriers are produced in the material of interest using 3 MeV electron pulses from a Van de Graaff accelerator. The current during the pulse is ca. 4 A. The pulse duration could be varied from 0.3 ns to 50 ns. In this way the radiation dose could be varied over two orders of magnitude. For a detailed description of the pulsed Van de Graaff accelerator the reader is referred to publications of the IRI accelerator group.\textsuperscript{83-87}

The penetration depth of 3 MeV electrons is ca. 15 mm in materials with a density of ca. 1 g cm\(^{-3}\). This is much larger than the PR-TRMC cell-thickness of 3.55 mm (see paragraph 3.4). Energy transfer from a high-energy electron to the medium occurs in discrete events (excitations and ionizations) along the track of the primary electron. The average energy transfer per event is approximately 40 eV for hydrocarbon liquids and solids.\textsuperscript{88} Such events are separated on average by a distance of approximately 200 nm along the track. A large fraction of the energy transfer events results in ionization of molecules with formation of secondary electrons. These secondary electrons, if they have sufficient energy, lose their energy via further excitation of electronic transitions, and ultimately by excitation of molecular vibrations and other modes of the medium until eventually they become thermalized or trapped. For organic materials the average thermalization distance is in the order of 5 to 10 nm.\textsuperscript{88}

The initial yield of ion pairs in saturated hydrocarbons is estimated to be between 4 and 5 (100 eV\(^{-1}\))\textsuperscript{89-91}, which corresponds to an average pair formation energy, \(E_p\), i.e. the average energy needed to form an electron-hole pair, between 20 and 25 eV. Pair formation energies have been measured for high energy radiation for a large variety of materials and a semi-empirical relationship (Eq. 3.2) derived by Alig \textit{et al.}\textsuperscript{94} in terms of the ionization potential or band-gap \(E_g\) has been found to provide a good (\(\pm 20\%\)) approximation for inorganic semiconductors with \(E_g=2\) eV\textsuperscript{94,96}.

\[
E_p = 2.73E_g + 0.55 \quad [\text{eV}]
\]

(3.1)

In conjugated polymers with side chains the ionization events will take place in both the backbone and the side chains. The relative number of ionizations in both moieties is determined by the electron density in these regions. It is assumed that the pair formation energy in the side chains, \(E_p(s)\), is 25 eV, the upper value estimated for non-polar hydrocarbons. Since the electronic structure of the polymer backbone is analogous to that of a semi-conductor with a band gap, \(E_g\), the pair formation energy of the conjugated polymer backbone \(E_p(b)\), can be estimated using Eq. (3.1) and a bandgap of \(E_g=2.5\) eV for
polydiacetylenes (see Chapter 2). According to Eq.(3.1), the pair formation energy for the polymer backbone, $E_p(b)$, is found to be 7.3 eV. The average pair formation energy due to ionizations in the side-chains and on the polymer backbones is calculated according to

$$\langle E_p \rangle = \left( \frac{F(b)}{E_p(b)} + \frac{F(s)}{E_p(s)} \right)^{-1}$$

(3.2)

in which $F(b)$ and $F(s)$ are the electron density fractions in the backbone and the sidechain, respectively. For poly-\(p\)-TS for example the average pair formation energy can be calculated to be 20 eV using Eq.(3.2) and $F(b) = 0.14$ and $F(s) = 0.86$.

If the pair formation energy is known, the concentration of charge carriers formed initially by a high energy radiation pulse, $N_p^0$, can be calculated according to

$$N_p^0 = \frac{D_v}{E_p}$$

(3.3)

where $D_v$ is the amount of energy per unit volume deposited in the sample by the irradiation pulse. The dose per unit volume is related to the more conventional dose parameter $D$, the dose in “Gray” (1 Gy = 1 J/kg), by

$$D_v = D \cdot \rho$$

(3.4)

with $\rho$ the density of the irradiated material.

The energy deposited in the sample was calibrated using thin-film radiochromic dosimeters (Far West Technology Nr. 92) according to the procedure described previously. This was related to the integrated beam charge per pulse, $Q$ (nC), which was monitored routinely during the course of experiments. The relationship between $D$ and $Q$ was found to be $D=1.09 \times Q$ Gy for the conditions used.

For polydiacetylenes, the initial concentration of charge carrier pairs produced using a 5 ns, 4A pulse (i.e. $Q=20$ nC) is therefore $ca. 10$ μM. This corresponds to only approximately $4 \times 10^6$ ionization events per diacetylene monomer unit in a PDA sample (taking 500 Å³ as the volume of a PDA monomer unit).
3.2.2 Flash Photolysis

The average concentration of excited molecules created by a laser pulse will be equal to the concentration of absorbed photons, $N_{abs}$, and can be calculated using Lambert-Beer’s law according to

$$N_{abs} = \frac{I_0 \left(1 - 10^{-OD}\right)}{E_\lambda L}$$  \hspace{1cm} (3.5)

where $I_0$ is the photon-energy flux, $L$ is the optical path length through the solution, $OD$ is the optical density of the solution and $E_\lambda$ is the energy of the absorbed photons corresponding to a wavelength $\lambda$.

In this thesis dilute polydiacetylene solutions were flash photolysed using single 308 nm pulses of 7 ns FWHM from a Lumonics HyperEx 400 excimer laser. The beam power was measured using a Scientech 365 power meter. The energy flux per pulse was determined to be approximately $I_0 = 8$ mJ cm$^{-2}$. Lower pulse energies were achieved by placing calibrated neutral density filters in the laser beam with optical densities between 0.1 and 2.

Since only a fraction of the initial excitations gives rise to ionization in the polymer molecule, the initial concentration of charge carrier pairs produced is related to the concentration of excited molecules as

$$N_{p}^0 = N_{abs} \phi_p$$  \hspace{1cm} (3.6)

where $\phi_p$ is the primary quantum yield for charge carrier generation.
3.3 TRMC EQUIPMENT

The interaction of microwaves with a weakly conducting medium results in a decrease in the amplitude and a change of the phase of the electric field (see Figure 3.1). The resulting attenuation and phase shift can be related to the change in the real component of the conductivity, $\Delta \sigma_R$, and the change in the imaginary component, $\Delta \sigma_i$, respectively. In this thesis, only the changes occurring in the real component of the conductivity will be considered.

![Image of microwave interaction](image)

$\Delta \sigma = \Delta \sigma_R + i\Delta \sigma_i \text{ (S/m)}$

**Figure 3.1** Schematic representation of the propagation of microwaves through a weakly conducting dielectric medium. The full drawn oscillation represents the electric field of the microwaves, while grey-displayed oscillation represent the electric field in the absence of the dielectric medium. The electric field is attenuated and its phase is shifted by the presence of the conducting medium.

The basic requirements of an apparatus for measuring changes in the microwave conductivity of a medium on pulsed irradiation are (1) a microwave source, preferably of variable frequency, (2) a cell for containing the sample and (3) a device for the detection of rapid changes in the microwave power level. Experiments can be carried out in transmission as shown in Figure 3.1, however, in the TRMC experiments reported here a reflection design has been used (Figure 3.2). The use of a reflection design requires the incorporation of a fourth essential component into the microwave circuit, which can separate the incident and reflected wave. This is achieved using a circulator.
3.3.1 Microwave apparatus

A schematic representation of the TRMC setup is shown in Figure 3.2. The microwave circuitry is constructed of rectangular waveguide. The microwave source was a Gunn diode oscillator. After passing through a variable attenuator, the microwaves are directed by the circulator to the microwave measurement cell. In rectangular waveguides, microwaves propagate in the z-direction as polarized Transverse Electric (TE) waves\textsuperscript{97,98}, with the electric field vector parallel to the short axis of the waveguide, as is shown in Figures 3.3 and 3.4.

The microwave cell containing the sample is closed at one end with a metal plate positioned at the end of the waveguide. The probing microwaves are reflected at the metal plate and form a standing wave pattern in the cell. The reflected microwaves are directed by the circulator to a Schottky barrier diode detector, which monitors the microwave power. At the power levels used, the voltage output of this detector, \( V \), is not a linear function of the incident power. However, since the transient changes in the power level, \( P \), are very small the relative change can be obtained from the resulting change in output voltage using the expression

\[
\frac{\Delta P}{P} = N_c \frac{\Delta V}{V}
\]  

(3.7)
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The power proportionality factor, $N_e$, which depends on the microwave frequency as well as the power level, was obtained by calibration of the microwave detector and was between 1.5 and 2.

The output of the microwave detector was connected to a cascade of a home-built impedance matching amplifier, which consisted of two field effect transistors (ATF 21186) and a video amplifier of Comlinear™ type CLC 100. The low noise impedance matching amplifier has a frequency range from 10 Hz to 1 GHz and a total amplification of 3.3. The CLC 100 has a frequency range from DC to 0.5 GHz and an amplification factor of 10. The amplified signal (33 times) could be monitored on a linear timescale using a Tektronix SCD1000 digital oscilloscope or a Tektronix TDS 680B both with a time response of ca. 1 ns or on a logarithmic timescale using a Sony/Tektronix RTD 710 digitizer with a time response of ca. 3 ns.

The active components of the equipment are contained in a Faraday cage to reduce pick-up due to electromagnetic interference caused by the electron or laser pulses. For a more detailed description of the microwave setup the reader is referred to the work of Warman et al. 99,100, Schouten 97 and Schuddeboom 72.

3.3.2 Microwave cells

In the PR-TRMC technique the microwave cell is completely open at one end and therefore can be considered as a single reflection cell. In the case of FP-TRMC, the cell is converted into a resonant cavity by placing at the open end of the cell an additional metal plate with a central, circular hole ("iris"). The sensitivity in the resonant cavity is larger than in the single reflection cell at the expense of an increase of the response time (ca. 6 ns). This cell enables the measurement of very small conductivity changes in dilute solutions. The maximum electric field strength in the PR-TRMC cell was approximately 20 V cm⁻¹ and in the FP-TRMC cavity at the resonance frequency approximately 100 V cm⁻¹.

3.3.2.1 PR-TRMC cell

In the PR-TRMC set-up the waveguide had an internal cross section of 7.1 × 3.55 mm² and microwave frequencies in the Ka-band (27 - 38 GHz) were used. The microwave cell shown on the left in Figure 3.3 was used for conductivity measurements on solid samples, such as powders and single crystals. The cell consists of a 14 mm length of waveguide closed at one end with a metal plate and flanged at the other end. The copper top wall of the cell was reduced to ca. 0.4 mm thickness to minimize attenuation of the electron beam. To make the cells chemically inert, the walls were gold-plated via a redox exchange of copper with gold. The cell and the waveguide circuitry were routinely purged with SF₆ gas to scavenge any highly-mobile electrons that might be formed in the remaining air in the cell.

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volume on irradiation.

Polycrystalline powder samples were compressed by hand into the cell using a close fitting Teflon rod resulting in a sample as shown in the right-hand top of Figure 3.3. When a sufficient amount of sample was available, i.e. approximately 200 mg, the complete irradiated length of the cell, i.e. $d=10$ mm, was filled with sample. When less material was available, the sample was compressed in a rectangular shaped cavity of $2 \times 6 \times 3$ mm$^3$ dimension in a polymethylmethacrylate (PMMA) block. This PMMA block was then inserted into the microwave cell, as shown in Figure 3.3 (middle right).

![Diagram of PR-TRMC Cell](image)

**Figure 3.3** Microwave cell used in PR-TRMC setup. The microwave cell can be filled in three different ways.

1. The cell can be completely filled with material up to a length of 14 mm (of which a maximum length of 10 mm is irradiated) (see top right-hand figure).
2. A PMMA block in which a 36 mm$^3$ volume can be filled with material and can be inserted in the cell (see middle right-hand figure).
3. Configuration allowing rotation of a sample inside the waveguide. The right-hand PMMA block contains a PMMA cylinder. A sample can be positioned on the left-hand end of the cylinder. Rotation of the cylinder changes the orientation of the sample. The length of the left-hand PMMA block is such that the sample is positioned at a maximum of the electric field. See Figure 3.10 in this chapter for a more detailed description.

The microwaves are polarized transverse electric ($\text{TE}_{10}$) waves with the electric field component parallel to the $y$-axis, as shown in Figure 3.3. The linear polarization of the microwaves makes it possible to study anisotropy in aligned polymer samples. The set-up used to study the anisotropy of the conductivity is also shown in Figure 3.3. Two blocks of PMMA were inserted into the microwave cell. One block contains a PMMA cylinder with
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the sample, e.g. the polydiacetylene crystal, mounted on one end. The cylinder can be rotated, which allows the measurement of the mobility as a function of the sample orientation with respect to the microwave electric field. The length of the other PMMA block is such that the sample is positioned at a maximum of the electric field.

The cell is contained in a cryostat in which the temperature could be varied from −100°C to +200°C regulated by a thermocouple which is placed in contact with the cell.

3.3.2.2 FP-TRMC cell

In the FP-TRMC set-up a X-band (8.2-12.4 GHz) waveguide with an internal cross section of 10 × 23 mm² was used. The design of the cell which was used to measure the photo-induced conductivity in dilute polymer solutions is shown in Figure 3.4. The cell was constructed of copper and brass which was gold-plated via a redox exchange of copper with gold. The iris coupling is a 0.5 mm thick copper plate with a circular hole, which is made vacuum tight with a piece of polyimide (Kapton®) attached with two-component cement. The temperature of the cell could be varied between 0 and 100°C using an RL6 Lauda cryostat. Single light pulses from an excimer laser (see paragraph 3.3.2) can enter the cavity via a grating of several 1.5 × 5.0 mm holes in opposite, broadwall sides of the cell. The gratings are covered and sealed with Supracil quartz windows.

![FP-TRMC Cell](image)

**Figure 3.4** Schematic representation of the FP-TRMC cell used for photoconductivity measurements on dilute polymer solutions.
The cell could be filled with a dilute solution through the inlet. UV spectroscopic grade benzene and UV spectroscopic grade dioxane (Fluka) were used as solvents. The dioxane was passed over a column of freshly activated silica gel (activated at 200°C) immediately prior to use in order to remove trace amounts of water. To remove air and scavenge any mobile electrons that might be formed in low-yield multiphoton ionization events in the solvent, the solutions were purged with CO₂.

3.4 CONDUCTIVITY MEASUREMENTS IN HOMOGENEOUS SAMPLES

For small changes in the reflected power, $P$, the relative change $\Delta P$ is directly proportional to the radiation-induced conductivity of the sample, $\Delta \sigma$. The sensitivity factor $A$ relates a change in the reflected power to a change in the conductivity of the sample

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

(3.8)

![Graphs](image.png)

**Figure 3.5** Typical radiation-induced conductivity transient obtained for a solid sample of poly-pTS using the PR-TRMC technique and for a dilute solution of poly-4BCMU using the FP-TRMC technique. In the PR-TRMC experiments the charge carriers were produced by irradiation with a single 0.5 ns pulse of 3 MeV electrons, while in the FP-TRMC a 7 ns FWHM pulse of 308 nm from an excimer laser was used.

The absolute magnitude of the conductivity determined in a PR-TRMC experiment is normalized by the energy absorbed per unit volume in the sample, while the conductivity in a FP-TRMC experiments is normalized by the product of the concentration of absorbed photons and the elementary charge. Examples of a transient conductivity signal observed using the PR-TRMC and the FP-TRMC methods are shown in the left and the right panel of

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Figure 3.5, respectively. It can be seen that the maximum attainable time resolution is in the order of 1 nanosecond for the PR-TRMC technique while in case of the FP-TRMC technique this is about one order of magnitude larger.

The sensitivity factor $A$ (in Eq. (3.8)) takes into account the electric field variation distribution for a succession of media with different dielectric constants along the direction of microwave propagation. The sensitivity factor for the single-reflection cell (PR-TRMC) differs from that in a multiple-reflection cell (FP-TRMC) and these will therefore be discussed separately in sections 3.4.1 and 3.4.2, respectively.

### 3.4.1 Sensitivity factor for the single-reflection cell (PR-TRMC)

In the PR-TRMC reflection cell, interference effects due to the similarity between the wavelength of the probing microwaves and the length of the sample result in a sinusoidal dependence of the fractional microwave absorption ($\Delta P/P$) on the microwave frequency, as is illustrated in Figure 3.6.

![Figure 3.6](image-url)

**Figure 3.6** The frequency dependence of the fractional absorption of the microwave power, $\Delta P/P$, per nanocoulomb beam charge as obtained for 25 mg poly-pTS contained in a PMMA block (see Figure 3.3). The line through the datapoints represents a result of the fitting procedure described in references $^{19,87,99-101}$. From this fit a value of $3 \times 10^3$ S m$^{-1}$ nC$^{-1}$ is obtained for the radiation-induced conductivity in poly-pTS.

The frequency dependence of $\Delta P/P$ can be fitted to an analytic expression using as fitting parameters the geometrical and dielectric properties of the sample, as described in detail previously $^{19,87,99-101}$. 
In case of a homogeneously filled cell over a length $d$ with one dielectric, the sensitivity factor at the maxima of the fractional change in the reflected power can be expressed by the analytical formula

$$A_{\text{max}} = \frac{2\lambda_n f_{\text{max}} d}{\varepsilon_0 c^2}$$  \hspace{1cm} (3.9)$$

in which $\lambda_n$ is the wavelength of the microwaves in air, $c$ the velocity of light and $f_{\text{max}}$ the frequency at which a maximum absorption is observed. Typical $A_{\text{max}}$ values for a cell homogeneous filled with a medium with a low dielectric constant are of the order of 10. In a PMMA container somewhat lower values are found close to 3.

The sensitivity factor $A$ given by Eqs. (3.9) is valid for a microwave cell which is filled with a succession of homogeneous media along the direction of the microwave propagation. In the case of compressed powdered samples, the cell volume is not completely filled with material and it is microheterogeneous in nature. The microwave field strength distribution is strongly affected by the inhomogeneous filling of the cell. Therefore, the observed microwave absorption in such a measurement cannot be directly related to the conductivity of the material itself.

![Graph](image)

**Figure 3.7** The effect of the fill factor, $f$, on the fractional change in absorbed microwave power for the case of a PMMA sample holder filled with 1,1,6,6-tetraphenylhexadiyne diamine (THD) polydiacetylene.

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The correction factor, that will be applied in the case of inhomogeneous filling of the cell, was obtained empirically by a series of measurements in which the fill factor was varied. The fill factor is defined as

\[ f = \frac{m}{\rho abd} \]  \hspace{1cm} (3.10)

where \( m \) is the mass of the material of interest, \( \rho \) is the density of the material and \( abd \) is the volume in which the sample is contained. The change in microwave power, \( \Delta P/P \), as a function of \( f \), is shown in Figure 3.7.

The conductivity results in Figure 3.7 show a rather complex dependence on the fill fraction at low filling. In the experiments on compressed samples reported in this thesis the fill fraction varies between 0.6 and 0.8. In this region the observed conductivity is linearly proportional to \( f \). Therefore, for small changes of the fill fraction in compressed samples, the relative change of the reflected microwave power, \( \Delta P/P \), is taken to be directly proportional to the change in conductivity of the sample \(^{19}\), \( \Delta \sigma \), according to

\[ \frac{\Delta P}{P} = A f \Delta \sigma \]  \hspace{1cm} (3.11)

3.4.2 Sensitivity factor for the multiple-reflection cell (FP-TRMC)

In a multiple-reflection cell, the iris ensures that microwaves can propagate in the solvent only for distinct frequencies. At a resonance frequency there is a node in the standing wave at the position of the iris. The resonance frequency, \( f_0 \), for a homogeneously-filled cavity with a medium with dielectric constant \( \varepsilon_r \), is given to a good approximation by

\[ f_0 = \frac{c}{2 \sqrt{\varepsilon_r}} \left( \frac{m}{d} \right)^2 + \left( \frac{1}{a} \right)^2 \]  \hspace{1cm} (3.12)

where \( m \) is an integer which is equal to the number of half wavelengths in the cavity, \( d \) is the length of the cavity and \( a \) is the width of the waveguide.
Figure 3.8 Frequency dependence of the power reflected by a resonant cavity. The curve is characterized by three parameters: the resonance frequency, $f_0$, the fraction of the power reflected at resonance, $R_0$, and the full width $\Delta f$ between the half-power frequencies, $f_+$ and $f_-$. 

The resonance curve is measured by scanning the power reflected by the resonant cavity containing the solution, $P_r$, over a range of frequencies and dividing this by the incident power, $P_i$, determined using a totally reflecting end-plate. Such a resonance curve is illustrated in Figure 3.8. The normalized reflected power as a function of frequency, $R(f) = P_r / P_i$, is characterized by three parameters: the resonance frequency, $f_0$, which is the frequency at which the minimum normalized reflected power, $R$, is observed, the value of $R$ at the resonance frequency, i.e. $R_0$, and the full width, $\Delta f$, at the "half-power" frequencies. In Figure 3.8 these parameters are indicated together with the upper and lower "half-power" frequencies. The cavity is characterized by its "loaded" quality factor,

$$Q_L = \frac{f_0}{\Delta f}$$  \hspace{1cm} (3.13)

and response time,

$$\tau_{RC} = \frac{Q_L}{\pi f_0}$$  \hspace{1cm} (3.14)

For the cavities used, $Q_L$ and $\tau_{RC}$ have typically values of ca. 200 and ca. 6 ns, respectively.
Figure 3.9 The frequency dependence of the fractional absorption of the microwave power, $\Delta P/P$, as obtained for a dilute solution in the cavity cell (see Figure 3.4). Each datapoint was obtained by irradiation of the solution using an 8 mJ cm$^2$ laser pulse (308 nm).

A small change in the conductivity of the solution in the cavity results in a change in the reflected power, as is illustrated in Figure 3.9. A maximum in the change in the reflected power is observed at the resonance frequency. The sensitivity factor $A$ at the resonance frequency can be calculated from the cavity characteristics and is given by:

$$A = \frac{Q_L \left(1 + \frac{1}{\sqrt{R_0}}\right)}{\pi \varepsilon_0 \varepsilon \varepsilon'}$$

(3.15)

The $A$ values for the X-band cavities used were of the order of 1000. These values are two orders of magnitude larger than in the PR-TRMC experiments for which a cavity design was not used.

3.5 CONDUCTIVITY MEASUREMENTS IN ANISOTROPIC CRYSTALS

In the previous section conductivity measurements in homogeneous conductive media were discussed. The linear polarization of the microwaves makes it possible to study anisotropy in aligned polymer samples. In this section the measurement of conductivity in anisotropic crystals and the experimental problems associated with it will be discussed.

3.5.1 Background

Microwave absorption results from in-phase charge carrier motion in the direction of the oscillating microwave electric field. Components of motion of charge carriers
The microwave absorption is proportional to the conductivity, which can be described by the Kubo-Greenwood formula\(^{102-105}\)

\[
\Delta \sigma = \frac{2\pi e^2}{m^2 \omega \Omega} \sum_{i(occ)}^{j(unocc)} \left| \langle f | e \cdot p | i \rangle \right|^2 \delta(E_f - E_i - \hbar \omega)
\]  
(3.16)

where \(e\) is the elementary charge, \(m\) the electron mass, \(\Omega\) the volume of the system, \(\omega\) the radian frequency of the microwaves, \(\langle f | e \cdot p | i \rangle = p_{fi} \cdot e\) is the inner product of the transition matrix element of the momentum vector operator \(p\) and the direction of the microwave field \(e\). The summation in Eq. (3.16) runs over all occupied lower charge carrier states \(|i\rangle\) with energy \(E_i\) and all unoccupied higher states \(|f\rangle\) with energy \(E_f\), to which excitation by microwave absorption occurs. The Dirac \(\delta\)-function in Eq. (3.16) accounts for the conservation of energy. The inner product in Eq. (3.16) shows that the conductivity is determined by the induced motion of the charge carriers along the direction of the microwave field. The relative magnitudes and orientations of the transition matrix elements \(p_{fi}\) determine the anisotropy in the conductivity. Note, that Eq. (3.16) can readily be written in terms of the transition dipole moments, that are usually used to describe the absorption of electromagnetic radiation, by using the velocity dipole relation\(^{106}\)

\(\langle f | p | i \rangle = -(j \hbar \omega / e) \langle f | u | i \rangle\), with \(u\) the dipole operator and \(j^2 = 1\). The direction of the transition matrix element \(p_{fi}\) can be specified by an azimuthal angle \(\phi_{fi}\) and a colatitudeinal angle \(\theta_{fi}\) with respect to the electric field direction \(e\). For rotation of the sample through an angle \(\alpha\) around the propagation direction of the microwaves,

\[
\Delta \sigma(\alpha) = \frac{2\pi e^2}{m^2 \omega \Omega} \sum_{i(occ)}^{j(unocc)} \left| p_{fi} \right|^2 \delta(E_f - E_i - \hbar \omega) \times
\]

\[
\left[ \cos^2 \alpha (\cos^2 \theta_{fi}) + \sin^2 \alpha (\sin^2 \phi_{fi} \sin^2 \theta_{fi}) + \sin 2\alpha (\sin \phi_{fi} \sin \theta_{fi} \cos \theta_{fi}) \right]
\]

which can be simplified to

\[
\Delta \sigma(\alpha) = C_0 \cos^2 \alpha + C_1 \sin^2 \alpha + C_2 \sin 2\alpha.
\]  
(3.18)
The coefficients $C_i$ in Eq. (3.18) are determined by the magnitude and orientations of the transition matrix elements of the momentum operator (or equivalently the dipole operator) and describe the anisotropy of the conductivity. If the angle $\alpha$ is chosen such that for $\alpha=0$ the polymer chains in the sample are parallel to $e$ then $C_0$ corresponds to the conductivity along the polymer backbone. $C_1$ is the component of the conductivity perpendicular to the polymer backbone and perpendicular to the microwave propagation direction. The third term on the right-hand side of Eq. (3.18), containing the constant $C_2$, is due to conductivity in a direction neither parallel nor perpendicular to the polymer backbone. In section 3.6 the relationship between the anisotropy of the conductivity and the anisotropy in the charge carrier mobility will be discussed.

3.5.2 Experimental set-up

The experimental set-up used to study the anisotropy in the conductivity of crystals is shown in configuration 3 of Figure 3.3. This configuration is shown in more detail in Figure 3.10. PMMA block II contains a PMMA cylinder of a 2.55-mm diameter. On the back-end of this cylinder a sample can be attached, while the front-side contains a small groove with a depth of 1 mm, which allows rotation of the rod with a screw-driver. Rotation of the rod allows the measurement of the radiation-induced conductivity as a function of the angle between the polymer backbones and the electric field direction. Initially the orientation of the crystals (corresponding to $0^\circ$) was with the backbones parallel to the microwave electric field within an estimated accuracy of $5^\circ$. 
Figure 3.10 Experimental set-up allowing rotation of a sample (with dimensions w x h, represented by the rectangle) inside the microwaveguide. E is the direction of the electric field component of the microwaves (in the y-direction). PMMA block II contains a PMMA cylinder. A sample can be positioned on the left side of the cylinder. Rotation of the cylinder changes the orientation of the sample. The length (b) of the PMMA block I is such that the sample is positioned at a maximum of the standing microwave field. Dimensions: a=7.1 mm, b=5.5 mm, c=2.45 mm, d=3.55 mm, and e=13 mm.

In these experiments the relationship between the observed microwave absorption and the radiation-induced conductivity in the crystal is more complex than in cases where the cross section of the microwave cell was homogeneously filled, as discussed in section 3.4. The microwave field strength distribution is strongly affected by the inhomogeneity in the filling of the waveguide. This is illustrated in Figure 3.11, where the radiation-induced microwave absorption is shown for different-shaped samples of silicon as a function of the angle of rotation around the z-direction (which is perpendicular to the electric field component in the cell). The conductivity in silicon is known to be isotropic, which means that the variation in the microwave absorption as a function of the orientation is solely due to the non-uniform shape of the sample. In the case of a circularly-shaped sample the filling of the waveguide does not change for different rotation angles of the sample and the measured microwave absorption is therefore independent of the orientation.
Figure 3.11 The dose-normalized radiation-induced microwave absorption as a function of the angle of rotation for flat silicon samples of different shape, mounted on the PMMA cylinder as shown in Figure 3.10. The shapes of the silicon samples are illustrated at the bottom of each corresponding graph.

3.5.3 Effect of crystal shape

In order to relate the observed microwave absorption to the conductivity in the crystal, information about the electric field strength distribution is needed. The field strength distribution not only depends on the filling of the waveguide, but also on the dielectric constant of the sample in the direction of the electric field. In polydiacetylenes the dielectric constant along the polymer backbone is larger than in the direction perpendicular to it \(^1\) and the effect of this difference on the field strength distribution must be
considered. The electric field strength distribution can be calculated for a given crystal shape in a given position in the waveguide using numerical methods based on the finite element method \(^{112-115}\). Application of these methods is rather complicated. Therefore an approximate treatment is used to obtain the conductivity from the absorbed microwave power.

For small changes of the conductivity, the relative change of the reflected microwave power, \(\frac{\Delta P}{P}\), is directly proportional to the change in conductivity of the sample \(^{16}\), \(\Delta \sigma\), according to

\[
\frac{\Delta P}{P} = AB \Delta \sigma
\]  

(3.19)

where \(A\) and \(B\) are sensitivity factors, which depend on the microwave frequency and the geometry and the dielectric constants of the materials in the microwave cell. The sensitivity factor \(A\) (see Eq. 3.9) accounts for the effect on the electric field strength distribution of the presence of a succession of media with different dielectric constant along the microwave propagation direction (z-axis). The factor \(B\) accounts for the differences in the electric field strength distribution in case of a succession of media with different dielectric constant along the electric field direction (y-axis). For the TE\(_{10}\) mode used the electric field direction is perpendicular to the propagation direction of the microwaves. If the cross sections of the microwave guide are filled homogeneously the factor \(B\) is equal to 1.

![Figure 3.12](image)

**Figure 3.12** (a) Cross-section of the waveguide as shown in Figure 3.3 (bottom). (b) Schematic representation of the filling of the waveguide as presented in (a). Layer 1 is composed of PMMA, layer 2 contains PMMA and air, while layer 3 contains PMMA, air and sample.

The factor \(B\) can be approximated by an analytical method, which has been used previously for a waveguide filled inhomogeneously perpendicular to the propagation direction \(^{116}\). The present set-up, as shown schematically bottom-left of Figure 3.3, can be approximated as a three-layered laminate, see Figure 3.11.

The response of a heterogeneous system to an alternating voltage, or equivalently to a microwave field, is known as the Maxwell-Wagner effect. The overall dielectric properties
of the multi-component laminated structure in which the electric field is perpendicular to the layers can be described in terms of a complex dielectric constant, given by \(^{(117)}\)

\[
\varepsilon^* = \varepsilon'_* - j\varepsilon''_* = d \left[ \sum_i \frac{d_i}{\varepsilon'_i - j\varepsilon''_i} \right]^{-1}
\]

(3.20)

in which \(d\) is the total height of the laminated structure and \(d_i\) is the height of the \(i\)-th layer. \(\varepsilon'_i\) and \(\varepsilon''_i\) are the real and the imaginary part of the permittivity of the \(i\)-th layer, respectively. The conductivity is proportional to the imaginary part of the permittivity (the dielectric loss)

\[
\sigma = \omega\varepsilon_0\varepsilon^*_v
\]

(3.21)

where \(\varepsilon_0\) is the permittivity in vacuum and \(\omega\) is the radian frequency of the microwaves.

For a three-layered laminate in which only one layer \((i=3)\) produces a dielectric loss \((\varepsilon^*_3 \neq 0 \text{ and } \varepsilon^*_1 = \varepsilon^*_2 = 0)\), as is the case in our experimentalists where only the sample gives rise to a dielectric loss, Eq. (3.20) transforms to

\[
\varepsilon^*_v = \frac{d\varepsilon''_3(\varepsilon'_1\varepsilon'_2)^2d_3}{(d_1\varepsilon'_2\varepsilon'_3 + d_2\varepsilon'_1\varepsilon'_3 + d_3\varepsilon'_1\varepsilon'_2)^2 + (\varepsilon''_3)^2(d_1\varepsilon'_2 + d_2\varepsilon'_1)^2}
\]

(3.22)

If \(\varepsilon''_3\) is small in comparison with the real parts of the dielectric constants, the second term in the denominator can be neglected and the effective dielectric loss can, to a good approximation, be written as

\[
\varepsilon^*_v = B\varepsilon''_3
\]

(3.23)

with

\[
B = -\frac{d(\varepsilon'_1\varepsilon'_2)^2d_3}{(d_1\varepsilon'_2\varepsilon'_3 + d_2\varepsilon'_1\varepsilon'_3 + d_3\varepsilon'_1\varepsilon'_2)^2}
\]

(3.24)

As can be seen in Eq. (3.24), the factor \(B\) is independent of the dielectric loss in the sample, \(\varepsilon''_3\).

In the measurements, rotation of a rectangular shaped sample with dimensions \(w \times h\) is assumed to correspond to changes in the thickness of the layers 2 and 3 with thicknesses \(d_2\) and \(d_3\). For instance, in the situation of a rectangular shaped sample with the longest axis
vertical (schematically shown in Figure 3.12), the thickness of the layers are given by \( d_1 = d - c, d_2 = c - h \) and \( d_3 = h \). When the sample is rotated over 90°, the thicknesses correspond to: \( d_1 = d - c, d_2 = c - w \) and \( d_3 = w \).

The effective dielectric constant within a layer is taken to be the weighted sum of the dielectric constants of the different materials with the volume fractions, \( V \), as weighting factors. For the three layers this gives \( \varepsilon'_1 = \varepsilon'_{PMMA}, \varepsilon'_2 = V_{PMMA}\varepsilon'_{PMMA} + V_{air}\varepsilon'_{air} \) and \( \varepsilon'_3 = V_{PMMA}\varepsilon'_{PMMA} + V_{air}\varepsilon'_{air} + V_{\text{sample}}\varepsilon'_{\text{sample}} \).

For the system presented in Figure 3.12, the ratio of \( B \) at 0° and 90° equals

\[
S_{\text{calc}} = \frac{B(0°)}{B(90°)} = \frac{\hbar [\varepsilon'_2(0°)]^2 [(d - c)\varepsilon'_2(90°)\varepsilon'_3(90°) + (c - w)\varepsilon'_1\varepsilon'_3(90°) + w\varepsilon'_1\varepsilon'_2(90°)]^2}{w[\varepsilon'_2(90°)]^2 [(d - c)\varepsilon'_2(0°)\varepsilon'_3(0°) + (c - h)\varepsilon'_1\varepsilon'_3(0°) + h\varepsilon'_1\varepsilon'_2(0°)]^2}
\]

(3.25)

Note, that the anisotropy in the dielectric constant of the sample is taken into account in the expression of the correction factor, \( S_{\text{calc}} \) in Eq. (3.25). Combination of Eqs. (3.25) and (3.19) gives for the anisotropy in the radiation-induced conductivity

\[
R = \frac{\Delta \sigma(0°)}{\Delta \sigma(90°)} = \frac{\Delta P(0°)/B(0°)}{\Delta P(90°)/B(90°)} = \frac{\Delta P(0°)/\Delta P(90°)}{S}
\]

(3.26)

In order to gain insight into the applicability of this analytical treatment, the anisotropy of the radiation-induced microwave absorption, \( \Delta P(0°)/\Delta P(90°) \), was measured for rectangularly shaped silicon samples of different dimensions. The experimental data can be compared with results obtained from the analytical equation (3.25). In these experiments, n-doped silicon with a background conductivity of 10 S m\(^{-1}\) was used. Since the radiation-induced conductivity in silicon is isotropic, the observed change in the microwave absorption as a function of the orientation of the sample in the waveguide is solely due to changes in the electric field distribution.

Measurements with samples with a rectangular cross section with dimensions 0.2x2.0 mm\(^2\), 0.5x2.0 mm\(^2\), 0.75x2.0 mm\(^2\), 1.0x2.0 mm\(^2\), 1.3x2.0 mm\(^2\), 1.7x2.0 mm\(^2\) and 2.0x2.0 mm\(^2\) and a thickness of 0.5 mm were found to give anisotropic microwave absorption. The dimension of the silicon samples were taken such that they are close to those of the polydiacetylene crystals studied in Chapter 6. The measured anisotropy in the microwave absorption for these samples, \( \Delta P(0°)/\Delta P(90°) \), is presented in Figure 3.13. An orientation of 0° corresponds to the orientation in which the long axis of the sample is parallel to the electric field. It is seen that the anisotropy decreases as the width approaches the length of the sample. In the case of a square sample the anisotropy is equal to 1. The dashed curve in Figure 3.13 represents results of the calculated anisotropy in the microwave absorption.
absorption, i.e. the value of $S_{\text{calc}}$, obtained with Eq. (3.25). The calculated results are seen to overestimate the anisotropy in the microwave absorption by less than a factor of two. Use of Eq. (3.25) is therefore assumed to give an upper limit to $S$ in Eq. (3.26).

![Graph showing induced anisotropy in microwave absorption](image)

**Figure 3.13** Induced anisotropy in the microwave absorption, $\Delta P(0^\circ)/\Delta P(90^\circ)$, for a series of rectangular-shaped silicon samples (indicated by dots with error bars) as a function of the width to length ratio ($w/h$). The dashed curve represents the result for $S_{\text{calc}}$ calculated using Eq. (3.25), which can be seen to be an upper limit to the experimentally measured anisotropy. The full line in grey represents a fit (using Eq. 3.27) through the data points ($S_{\text{exp}}$), which will be regarded as a lower limit to the experimentally measured anisotropy.

The data shown in Figure 3.13 can also be fitted to an empirical equation given by

$$S_{\text{exp}} = C_1 \exp \left( C_2 \frac{w}{h} \right) + C_3 \exp \left( C_4 \frac{w}{h} \right)$$  \hspace{1cm} (3.27)

with $C_1=4$, $C_2=-1.412$, $C_3=62$ and $C_4=-9.136$. The result of the fit is shown as the grey line in Figure 3.13. This expression will be used to obtain a lower limit to the factor of $S$.

In the case of polydiacetylene crystals the value of $h$ corresponds to the projection of the sample dimension on an axis parallel to the polymer backbones, while $w$ is the projection in a perpendicular direction. If $h$ is larger than $w$, Eq. (3.27) can be used to obtain $S_{\text{exp}}$. If $h$ is smaller than $w$, the correction factor $S$ in Eq.(3.26) converts to

$$S_{\text{exp}} = \left( C_1 \exp \left( C_2 \frac{h}{w} \right) + C_3 \exp \left( C_4 \frac{h}{w} \right) \right)^{-1}$$  \hspace{1cm} (3.28)
3.6 CHARGE CARRIER MOBILITY AND ANISOTROPY

In section 3.2 the production of mobile charge carriers was discussed. The concentration of charge carrier pairs produced at time \( t=0 \) was called \( N_p^0 \). Due to geminate and homogeneous recombination the concentration of pairs of positive and negative charge carriers will be reduced. Also trapping of charged species will take place. We now distinguish mobile and immobile (trapped) charge carriers, i.e. charge carriers that do and do not contribute to the conductivity, respectively. The concentration of mobile positive and negative charge carriers can be written as

\[
N_+(t) = F_+(t)N_p^0 \tag{3.29}
\]

and

\[
N_-(t) = F_-(t)N_p^0 \tag{3.30}
\]

where \( F_+(t) \) and \( F_-(t) \) are the fractions of the initially formed positive and negative charge carriers that are mobile and present at time \( t \).

The conductivity due to these mobile charge carriers at time \( t \) is now

\[
\Delta \sigma = e\left[ N_+(t)\mu_+ + N_-(t)\mu_- \right] \tag{3.31}
\]

where \( \mu_+ \) and \( \mu_- \) are the average mobilities of positive and negative species, respectively, present at \( t=t \). After substitution of Eqs. (3.29) and (3.30) in Eq. (3.31)

\[
\Delta \sigma = eN_p^0\left[ F_+(t)\mu_+ + F_-(t)\mu_- \right] \tag{3.32}
\]

Substituting Eq.(3.3) or Eq.(3.6) in Eq.(3.32) gives rise to the expression for the dose-normalized conductivity at time \( t \), \( \Delta \sigma(t)/D_v \) and \( \Delta \sigma(t)/eN_{obs} \), determined in a PR-TRMC and FP-TRMC experiment, respectively,

\[
\frac{\Delta \sigma(t)}{D_v} = \frac{e}{E_p}\left[ F_+(t)\mu_+ + F_-(t)\mu_- \right] \tag{3.33a}
\]

\[
\frac{\Delta \sigma(t)}{eN_{obs}} = \left[ F_+(t)\phi_p\mu_+ + F_-(t)\phi_p\mu_- \right] \tag{3.33b}
\]
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It can be seen from Eq. (3.33a) that since $F_+$(t) and $F_-(t)$ have unity as an upper limit, from the PR-TRMC experiment a lower limit of the sum of the charge carrier mobilities can be obtained

$$\Sigma \mu_{\text{min}} = \frac{E_p \Delta \sigma(t)}{e D_v} \quad (3.34a)$$

Analogously, from the FP-TRMC experiment, we find, with Eq. (3.33b), for the product of the sum of the mobilities and the quantum yield for pair formation

$$\phi_p \Sigma \mu_{\text{min}} = \frac{\Delta \sigma(t)}{e N_{abs}} \quad (3.34b)$$

In liquids, using the PR-TRMC method, it has been found possible to discriminate between the positive and negative charge carriers and to determine their contributions separately. By adding additives (charge scavengers) which immobilize the positive or negatives charges selectively, it is possible to determine the conductivity contribution of the counter charge. Using additional information about the concentration of charge carriers from other experiments (e.g. charge collection with a large DC field), the mobilities can be determined. It has been shown possible to study the mobility of charges on isolated polymer chains. For example in polyphenylenvinylene (PPV) chains dissolved in benzene the charge carrier mobility of holes and electrons has been determined using the PR-TRMC method. The charge carriers produced in the benzene solution react with the PPV chains. Once on the PPV chain both the electron and hole are found to be highly mobile. By adding selective scavengers it was found to be possible to measure the mobility of the hole or electron on the PPV separately. It has been attempted to also investigate the intrachain mobility in PDA chains in solution. Unfortunately however, no significant conductivity signal was observed from which a charge carrier mobility could be determined. This absence of radiation induced conductivity could be attributed to the relatively small mobility on the PDA chains. The smaller mobility could be caused by the fact that in solution a PDA chain is more flexible than a PPV chain.

Time-of-flight experiments in PDAs have shown no experimental evidence for a contribution of holes to the conductivity. If the electrons are considered to be the major charge carriers and it may be assumed that $F_+(t) \mu_+ << F_-(t) \mu_-$, thus Eqs. (3.33a-b) simplify to

$$\frac{\Delta \sigma(t)}{D_v} = \frac{e}{E_p} F_-(t) \mu_- \quad (3.35a)$$
\[ \frac{\Delta \sigma(t)}{eN_{abs}} = F_-(t) \phi_p \mu_- \]  

(3.35b)

Since \( F(t) \leq 1 \), in this case the conductivity measurements enable us to determine a lower limit of the charge carrier mobility, \( \mu_{min} \) or \( \phi_p \mu_{min} \).

Thus far in this section, an isotropic medium is assumed, where \( \sigma \) and \( \mu_- \) are independent of the field directions. A sample of a pulverized anisotropic crystal may still be considered as an isotropic medium in the TRMC experiment. The conductivity observed will now be an average over all relative field directions and the mobilities for each of the charge carriers in the above equations represents the average over all directions.

\[ \langle \mu \rangle = \frac{1}{3} [\mu_\| + \mu_\perp + \bar{\mu}_\perp] \]  

(3.36)

in which \( \mu_\| \) represents the charge carrier mobility along the polymer backbones and \( \mu_\perp \) and \( \bar{\mu}_\perp \) the mobilities in two directions perpendicular to it. It may be remarked here that detailed analysis of the general case of more than one positive and negative species shows that \( \Sigma \mu_{min} \) as defined above is equal to the sum of the average mobilities of positive and negative species present at the time of measurement, each of which averaged over the different directions.

The measurement of the anisotropy in the conductivity of single crystals, \( R = \frac{\Delta \sigma_\|}{\Delta \sigma_\perp} \), has been discussed in section 3.5. Using the same notation as used above, we can write

\[ R = \frac{\Delta \sigma_\|}{\Delta \sigma_\perp} = \frac{F_+(t) \mu_\| (+) + F_-(t) \mu_\| (-)}{F_+(t) \mu_\perp (+) + F_-(t) \mu_\perp (-)} \]  

(3.37)

If it is assumed as above that \( F_+(t) \mu_\| (+) << F_-(t) \mu_\| (-) \), Eq. (3.37) reduces to

\[ \frac{\Delta \sigma_\|}{\Delta \sigma_\perp} = \frac{F_-(t) \mu_\| (-)}{F_+(t) \mu_\perp (+) + F_-(t) \mu_\perp (-)} \]  

(3.38)

which can be rewritten as

\[ \frac{\Delta \sigma_\|}{\Delta \sigma_\perp} = \frac{\mu_\| (-)}{\mu_\perp (-)} \frac{\mu_\perp (+)}{F_+(t) \mu_\perp (+) + 1} \]  

(3.39)
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Since the denominator is equal to or larger than unity, a lower limit of the anisotropy in the charge carrier mobility can be obtained from the present experiments. If \( F_+(t)\mu_+(+) << F_-(t)\mu_-(+) \) the denominator equals unity and

\[
\frac{\Delta\sigma_\parallel}{\Delta\sigma_\perp} = \frac{\mu_+(\cdot)}{\mu_-(\cdot)} = \left( \frac{\mu_+(\cdot)}{\mu_-(\cdot)} \right)_{\min}
\]  

(3.40)

REFERENCES:


Chapter 3
Charge Transport in Polydiacetylenes


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(101) de Haas, M. P. "The measurement of electrical conductance in irradiated dielectric liquids with nanosecond time resolution", Thesis PhD, University of Leiden, 1977


Chapter 4

Radiation-induced In-situ Polymerization of Diacetylenes

4.1 INTRODUCTION

Most polymers are amorphous solids and where crystallinity exists, it is usually over small regions of space of a few microns or less. Polydiacetylenes, however, are distinct from most polymers in that they can be produced as large single crystals by solid state polymerization of the crystalline monomer \(^{12}\). The polymerization of the monomer crystals can be initiated by heat \(^{1,3-9}\), by exposure to UV- or high-energy radiation \(^{6,7,9-20}\) or by applying high pressure \(^{21}\). The majority of diacetylenes will only polymerize completely when exposed to high-energy radiation. However, some diacetylene monomers do not polymerize (easily) by high-energy radiation and must be polymerized thermally \(^{22}\). Radiation-induced polymerization of diacetylenes is usually carried out by using \(\gamma\)-radiation from a \(^{60}\)Co source \(^{10,13-15,19,20,23,24}\).

In a diacetylene crystal the monomers are stacked in a ladder-like fashion. The monomer packing can be described by two parameters, the stacking distance \(d_s\) between the monomers and the angle \(\phi\) between the diacetylene group and the stacking axis (see Figure 4.1). The optimal packing conditions for solid state polymerization of the diacetylene monomers have been derived empirically from experimental data for a large number of diacetylene derivatives by Baughman \(^{2}\) and were found to be \(d_s = 4.9\) Å and \(\phi = 45^\circ\). Quantitative data on crystal structures and details of the reaction mechanisms are now available from a large number of studies \(^{2-6,8,11,25-42}\).

The initiation of the diacetylene polymerization involves the formation of a diradical or dicarbene. Such a radical can react with an adjacent monomer to form a covalent bond. During this process the monomers undergo a crank rotation and join together by a 1,4-addition reaction, as shown in Figure 4.1. This reaction propagates down a row of diacetylene units until halted by a defect or internal stress in the lattice. High-energy radiation produce radicals throughout the monomer matrix and consequently homogeneous polymerization occurs, while UV light initiation in crystals is effective only at the surface. In the case of thermal polymerization the propagation is initiated at defect sites in the
crystals, such as internal cracks, surfaces and grain boundaries. These defect sites are heterogeneously distributed in the monomer matrix and consequently the thermal polymerization of diacetylenes is mainly heterogeneous. Since thermal polymerization starts at defect sites, it can be understood that the thermal polymerization proceeds faster in regions with high dislocation content. An example of heterogeneous thermal polymerization is DCH with the product being of poor quality compared to radiation. However, pTS is an example of a homogeneous polymerization where the presence of defects results in local variation in the rate of polymerization and the existence of non-uniform strain in partially polymerized crystals.

Figure 4.1 Schematic representation of the topochemical polymerization of diacetylenes: transformation of a single crystal of monomers into a single crystal of polymers by formation of bonds between C1 and C4 atoms.
The macroscopic properties of a diacylene compound change completely during the course of polymerization. The monomer crystals are colorless. As a result of increasing degree of polymerization the crystals become colored and finally exhibit a metallic luster. In the polymer chain direction the tensile strength reaches values comparable to those of steel. The polymer chains in a single crystal are perfectly aligned and fully conjugated over large distances, allowing high charge carrier mobilities along the chains.

Polymerization of diacylenes by high-energy radiation is usually carried out using γ-rays from a $^{60}$Co source with an accumulated dose of typically $10^3$ to $10^6$ Gy. Although such a dose can lead to complete conversion of the monomer to polymer, it is not known to what extent the polymer chains are degraded by the radiation and the nature of the degradation products is unknown. Degradation of the polymer chains is expected to have a negative effect on the mobility of charge carriers.

The aim of the work described in this chapter is to obtain an insight into the effect of accumulated radiation-dose on the radiation-induced conductivity in the polymerized diacylenes. High-energy (3 MeV) electron pulses with a dose of typically 2 Gy per pulse are used, which makes it possible to study the radiation-induced conductivity after small increments of the accumulated radiation-dose. Polymerization with high-energy electrons is similar to that with a $^{60}$Co source, since the γ-rays produce high-energy electrons in the sample, mainly by Compton scattering. The mobility and the decay of the charge carriers on polymer chains diluted in a monomer matrix can be studied by means of the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique. Previously, Van der Laan et al. employing this technique, observed that charge transport in nBCMU diacylenes is rather sensitive to radiation-induced defects. In the present work this technique is applied to an extensive study of the radiation-induced polymerization and degradation of 4BCMU and three other diacylene derivatives, ETCD, IPUDO and DCH.

4.2 EXPERIMENTAL SECTION

4.2.1 Materials

Four diacylene monomers were investigated (for their molecular structure see Chapter 2). The synthesis of the different diacylene monomers was carried out by the groups of Prof. David Bloor at the University of Durham (UK) and Prof. Daniel Sandman at the University of Massachusetts (USA) and is briefly described below.

4.2.1.1 ETCD: 1,12-diol-bis (ethylurethane)-5,7-dodecadiyne

The ETCD monomer was synthesized by Hay coupling of monoacetylenes as described elsewhere. Single crystals of the monomer were grown from ethyl acetate solution by slow cooling. The single crystals had a rectangular shape and a pale purple color, indicating
a few percent of monomer conversion.

4.2.1.2 4BCMU: 1,12-bis(n-butoxy carbonyl methyl urethane) 5,7-dodecadiyne

The monomer was synthesized by reaction of an isocyanate with a diacetylene diol. The detailed procedure for synthesis of the monomer has been described elsewhere 52. The monomer was recrystallized twice from acetone-hexane mixtures after which a crystalline powder was obtained. The monomer crystals of 4BCMU were pale blue in color, indicating that polymerization has occurred to a certain extent. However, the conversion of monomer into polymer was only a few percent 52.

4.2.1.3 IPUDO: 1,12-diol-bis (isopropylurethane)-5,7-dodecadiyne

The IPUDO monomer samples were prepared by a reaction of 5,7-dodecadiyne-1,12-diol with isopropylisocyanate using triethylamine and dibutyltin-di-(2-ethylhexanoate) as catalysts 33. Single crystals were grown from a solution in ethylacetate. The single crystals were rectangular and colorless, which indicated that the extent of polymerization was negligible.

4.2.1.4 DCH: 1,6-bis (9-carbazolyl)-2,4-hexadiyne

The DCH monomer was prepared following the general method of Yee and Chance 10. However, the precursor 3-(9-carbazolyl)-1-propyne was prepared using butyllithium as reagent for ease of purifying the product. Fine needle-like crystals were grown by rapid cooling of a hot acetone solution, while larger, chunky crystals were grown by very slow evaporation of an acetone solution. Their very pale color indicated only a small (<1%) initial polymer content.

4.2.2 Radiation-induced Polymerization

The samples were irradiated in a microwave cell, which consisted of a 14 mm length of rectangular, 7.1x3.55 mm², copper waveguide closed at one end with a metal plate and flanged at the other end (see Figure 3.3). Both 4BCMU and DCH were available in sufficient amounts (ca. 200 mg) to fill the microwave cell over a length of ca. 10 mm. The available amounts of ETCD and IPUDO (ca. 30 mg) were too small to fill the microwave cell and therefore a perspex block of 20 × 7.1 × 3.5 mm³, with a small cavity of 2 × 6 × 3 mm³ (length × width × depth) was used to contain the sample. The filled perspex block was inserted into the microwave cell (see Figure 3.3).

The microwave cell containing the monomer sample was irradiated using 4 A pulses of 3 MeV electrons from the Van de Graaff accelerator. The integrated beam charge per pulse was monitored. The energy deposition is close to uniform throughout the sample and equal to 1.09 Gy per nanocoulomb beam charge (1 Gy =1 J/kg), measured using thin film
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radiochromic dosimeters (Far West technology Nr. 92) \(^{34}\). Hence, the dose rate is \(4 \times 10^6\) Gy s\(^{-1}\) during the pulse. To reach a total accumulated dose of 10 kGy series of pulses of 0.5 ns were used. To obtain higher accumulated doses series of 2 or 5 ns pulses were applied.

In the case of 4BCMU the monomer-to-polymer conversion could be determined by removing a few mg of the material from the microwave cell after reaching certain levels of accumulated dose. The polymer of 4BCMU was dissolved in chloroform and the absorption of the polymer at 468 nm was measured using a Uvikon 940 UV/Vis spectrophotometer. At this wavelength the extinction coefficient of the polymer in chloroform was taken to be 17,500 dm\(^3\)mol\(^{-1}\)cm\(^{-1}\)\(^{13}\). This procedure was not possible for ETCD, IPUDO and DCH, since the corresponding polymers are insoluble.

4.2.3 Radiation-induced conductivity

During the polymerization with a series of electron pulses, intermittent measurements of the conductivity induced by a single electron pulse were carried out. The transient change in conductivity due to such a single electron pulse was monitored by measuring the change in the microwave power reflected by the sample using the time resolved microwave conductivity, TRMC, technique \(^{35-58}\). In the present experiment microwaves in the Ka band (26.5-38 GHz) were used. For small changes the relative change in absorbed microwave power \(\Delta P/P\) is proportional to the change in conductivity of the sample, \(\Delta \sigma\). The quantitative relation between the microwave loss and \(\Delta \sigma\) was determined using computational and data fitting procedures described previously \(^{35}\) (see also Chapter 3). In order to obtain radiation-induced conductivity changes in the range \(10^{-4}\) and \(10^{-3}\) S/m, electron pulses with a duration from 0.5 to 20 ns had to be used. To prevent spurious conductivity signals due to electrons produced in the irradiated air inside the waveguide, the waveguide was flushed with sulfur hexafluoride.

Changes in the output of the microwave detector diode were monitored using either a Tektronix TDS680B digital oscilloscope or a Sony/Tektronix RTD 710 digitizer. Using the former, the time response is approximately 1 ns. The latter has a rise time of 5 ns, but is capable of registering the data using a pseudo logarithmic time base\(^{59}\). This allowed recording of transient data from 10 ns to 5 milliseconds using a single electron pulse.

4.2.4 Relation between radiation-induced conductivity and charge carrier mobility

The radiation-induced conductivity is proportional to the product of the sum of the mobilities of the (positive and negative) charge carriers, \(\Sigma \mu\), and the number of mobile electron-hole pairs present per unit volume. Assuming that only those charge carriers that are produced in the polymer regions are mobile the radiation-induced conductivity induced
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is given by

$$\Delta \sigma = e N_{pol} \Sigma \mu$$  \hspace{1cm} (4.1)

where $N_{pol}$ is the concentration of charge carrier pairs in the polymer regions.

The initial concentration of charge carrier pairs in the polymer regions is assumed to be given by

$$N_{pol} = \frac{D_v}{E_p} X$$  \hspace{1cm} (4.2)

in which $D_v$ is the dose per unit volume deposited in the sample, $E_p$ is the average energy to form an electron-hole pair and X is the fraction of monomers that have been converted to polymer. For polydiacetylenes, $E_p$ is estimated to be approximately 20 eV$^{50}$. Note, that $D_v$ (J m$^{-3}$) is the dose per unit volume, which is applied to obtain a single radiation-induced conductivity transient. To relate the dose per unit mass, $D$ (Gy), as obtained from dosimetry measurements using thin film radio chromic dosimeters to the dose per unit volume, knowledge of the density of the sample is needed. Assuming the densities of a monomer sample to be equal to that of a polymer sample the densities were taken to be: $\rho$(poly-ETCD)$=1.16$ g/cm$^3$$^{61}$, $\rho$(poly-4BCMU)$=1.22$ g/cm$^3$$^{62}$, $\rho$(poly-IPUDO)$=1.16$ g/cm$^3$$^{53}$, and $\rho$(poly-DCH)$=1.30$ g/cm$^3$$. (Note that the BCMU results in this work differ from the results published earlier$^{49,50}$ in the sense that in the earlier work the density was assumed to be unity.)

4.3 RESULTS AND DISCUSSION

4.3.1 Dose dependence of Radiation-Induced Conductivity

In Figure 4.2 conductivity transients induced by a single 3 MeV electron pulse are shown for samples of ETCD, 4BCMU, IPUDO and DCH. The transients were normalized to the dose per unit volume deposited by each pulse and were monitored after accumulated radiation doses as indicated. The conductivity at the maximum increases with accumulated dose, which is due to conversion of monomers into polymers. Clearly, the mobility of charge carriers in a monomer region is much smaller than on a polymer chain.

The conductivity shows a fast increase on a timescale of a few nanoseconds due to the production of charge carriers during the pulse and the 1 ns time-resolution of the TRMC technique. For low accumulated dose a slower increase is observed after the fast rise. This is most clearly visible in the transient obtained in ETCD after irradiation with an accumulated dose of 200 Gy. This could be due to transfer of charge carriers from
monomer regions, where the mobility is low, to polymer chains on which the mobility is much higher. This effect decreases with accumulated dose since for high doses most of the monomers have become polymerized.

![Graphs showing dose-normalized radiation-induced conductivity transients](image)

**Figure 4.2** Dose-normalized radiation-induced conductivity transients induced by 0.5 ns pulses in ETCD, 4BCMU and IPUDO for accumulated doses indicated. The results for DCH were obtained using 5 or 20 ns pulses.

The dose-normalised conductivity in ETCD, 4BCMU, IPUDO and DCH, at the end of the pulse, is presented as a function of accumulated dose in Figure 4.3. The left and the right panel of Figure 4.3 contain the same data on a linear and a logarithmic scale,
Figure 4.3 The dose-normalized conductivity directly after the pulse for ETCD, 4BCMU, IPUDO and DCH as a function of accumulated dose. The dashed lines through the data points are the result of fitting Eq (4.6) to the experimental data. The graphs on the left-hand side show the data on a linear accumulated dose scale, while those on the right-hand side show the data on a logarithmic scale.

respectively. It can be seen in the left panel that the conductivity in ETCD, 4BCMU and IPUDO increases proportionally with dose, while in DCH the conductivity is observed to increase only after a dose of 100 kGy. In the dose range between 100 and 300 kGy the conductivity in DCH exhibits a rapid increase. Such autocatalytic behavior has been observed previously for the thermal and radiation-induced polymerization of DCH\textsuperscript{9,10,14} and
for the thermal-polymerization of pTS \(^3,6,9,21\). DCH is distinct from the urethane-substituted derivatives in the sense that the DCH monomer does not exhibit an ideal crystal packing conformation required for solid-state polymerization (i.e. suitable parameters for \(d\), and \(\eta\)). It was demonstrated by Enkelmann \(^{14}\) that in the early stage of polymerization only very short chains are formed. At a conversion of approximately 25% the crystals were found to undergo a phase transition as is evidenced by a sudden change of the lattice parameters. The monoclinic angle abruptly changes by 14° during the transition, while the stacking distance between the carbazole rings is retained \(^9\). The autocatalytic behavior is observed for a dose of ca. 2x10^5 Gy, which agrees with other studies \(^9,10,14\).

The data in the right panel of Figure 4.3 show that the accumulated dose at which the conductivity is at a maximum increases in the order ETCD, 4BCMU, IPUDO and DCH. The decrease of the conductivity at higher accumulated doses can be attributed to a decrease of the charge carrier mobility due to degradation of the polymer chains by radiation as will be discussed below.

4.3.2 Dose Dependence of the Decay Kinetics of the Radiation-Induced Conductivity

In Figure 4.4 the radiation-induced conductivity transients obtained for ETCD, 4BCMU, IPUDO and DCH are shown for different values of the accumulated dose. In order to compare the decay kinetics the transients have been vertically scaled to coincide at short times. At higher accumulated dose the decay of the conductivity becomes faster. The faster decay is most likely due to the introduction of defects by radiation. High-energy radiation induces scission of the polymer backbones \(^{15}\) or chemical changes in the side chains of the polymer \(^{13,64}\). These radiation-induced defects may act as trapping sites at which the charge carriers can become localized.

The conductivity in DCH decays much faster than in the three urethane-substituted samples. The average polymer chain-length of poly-DCH is significantly shorter than that of the urethane substituted polydiacetylenes \(^{14,27}\). Thus the faster decay in poly-DCH could possibly be due to faster trapping of electrons on polymer chain ends. In addition an ionized carbazole could crosslink with an adjacent chain \(^{66}\), making interchain transport more likely, which in turn could lead to a faster encounter of a trap by a charge carrier.
Figure 4.4. Effect of accumulated dose on the decay of the conductivity. To facilitate comparison of the decay kinetics the conductivity transients were scaled with the factors between brackets. For ETCD, 4BCMU and IPUDO 0.5 ns pulses were used and the results for DCH were obtained using 5 or 20 ns pulses.

In Figure 4.5 the time at which the conductivity has decreased to half of the value at the end of the pulse is shown as a function of accumulated dose. This half-life decreases considerably with accumulated dose. Of the three urethane-substituted diacetylenes, 4BCMU exhibits the longest half-life. This could be due to the fact that this compound has the longest pendant group and hence the longest distance between the polymer chains, which leads to the slowest rate of interchain charge recombination.

For accumulated radiation doses between $10^5$ and $10^6$ Gy, which are typically used to produce polydiacetylenes, the half-life of the conductivity in the urethane-substituted polydiacetylenes has decreased by several orders of magnitude as compared to the half-life at low accumulated dose.

In DCH the half-life for accumulated doses below $10^5$ Gy is only about 20 ns. In this dose range the radiation-induced conductivity is at least two orders of magnitude smaller than the maximum conductivity attained, see Figure 4.3. The low conductivity at low doses in DCH could be due to the charge transport on relatively short chains $^{14,27}$ or due to motion 

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of holes along the carbazole stacks. At an accumulated dose near $10^5$ Gy, where the conductivity starts to increase due to charge transport along the polymer chains, see Figure 4.3, the half-life of the conductivity decreases. This decrease is probably due to trapping of charge carriers in deep traps resulting from radiation damage.

![Graph showing half-lives of conductivity as a function of accumulated dose](image)

**Figure 4.5** First half-lives of the conductivity as a function of accumulated dose in ETCD, 4BCMU, IPUDO and DCH. The dashed lines are a guide to the eye.

### 4.3.3 Monomer-to-polymer Conversion in 4BCMU

Since poly4BCMU can be dissolved in chloroform, the monomer conversion as a function of the accumulated dose could be determined from optical absorption, as described in the section 4.2.2. The results are shown in Figure 4.6. As can be seen from the inset, the conversion, $X$, increases proportionally with dose for low dose, i.e. the conversion per unit dose ($X/D$) is constant. At higher accumulated dose, as can be seen in Figure 4.6, the conversion efficiency decreases. The efficiency decreases with the degree of polymerization since the polymer chains already formed can block the polymerization of new chains \(^{34}\).

It has been suggested by Bloor \(^ {66}\) that the conversion can be described by the general Avrami equation

$$X = X_{\text{max}} \left[1 - \exp(-k \ D^n)\right]$$

(4.3)
in which $X_{\text{max}}$ is the maximum conversion, and $k$ and $n$ are empirical constants. The good fit of Eq. (3) to the experimental data in Figure 4.6 shows that the present conversion data for 4BCMU can be described quite well by the Avrami equation. The optimal values of the fitting parameters were found to be $X_{\text{max}} = 0.65$, $k = 0.01 \text{ Gy}^{-0.5}$ and $n = 0.5$. The conversion maximum is considerably lower than the value of 0.92 reported by Patel 32 for an accumulated dose of 500 kGy. Note that in the present study the dose rate during the high-energy electron pulse is $4 \times 10^4 \text{ Gy s}^{-1}$ which is 9 orders of magnitude larger than in the work of Patel, who used a $^{60}$Co source.

![Graph showing conversion as a function of accumulated dose](image)

**Figure 4.6** Monomer-to-polymer conversion for a 4BCMU sample as a function of the total accumulated dose. The inset shows the conversion for low accumulated dose on a linear scale. The drawn line represents a fit of the Avrami equation to the experimental data. The dashed line represents the linear fit as shown in the inset.

### 4.3.4 Dose dependence of the charge carrier mobility

It can be seen in Figure 4.3 that the conductivity in 4BCMU decreases at accumulated doses exceeding $10^4 \text{ Gy}$, while the monomer to polymer conversion, $X$, still increases (see Figure 4.6). The decrease of the conductivity with accumulated radiation dose could be due to a decrease in the mobility resulting from increasing structural disorder. For instance in ETCD and IPUDO mechanical strains are known to result from the mismatch between the monomer lattice and the growing polymer chains 67.
Using Eqs. (4.1) and (4.2), the lower limit of the charge carrier mobilities as a function of the accumulated dose, $\Sigma \mu_{\text{min}}(D)$, is given by

$$
\Sigma \mu_{\text{min}}(D) = \frac{E_p}{e} \left[ \frac{\Delta \sigma(D)}{D_v} \right] \frac{1}{[X(D)]}
$$

The lower limit of the sum of the charge carrier mobilities in 4BCMU was obtained using Eq. (4.4) with the dose normalised conductivity values, $[\Delta \sigma(D)/D_v]$, from Figure 4.3 and the conversion values, $[X(D)]$, from Figure 4.6. The results are shown in Figure 4.7.

The lower limit of the mobility of the charge carriers found in this way is approximately 2.7 cm$^2$ V$^{-1}$ s$^{-1}$ for accumulated doses below 200 Gy and decreases at higher doses. For doses between $10^5$ and $10^6$ Gy, which are conventionally used to produce polydiacetylenes, the mobility has decreased by an order of magnitude.

The line in Figure 4.7 was calculated using the empirical expression

$$
\Sigma \mu_{\text{min}}(D) = \frac{\Sigma \mu(0)}{1 + (\beta D)^\alpha}
$$

The parameters used were $\Sigma \mu_{\text{min}}(0)=2.7$ cm$^2$ V$^{-1}$ s$^{-1}$, $\beta=1.1 \times 10^4$ Gy$^{-1}$ and $\alpha=0.65$. Note that
\( \Sigma \mu_{\text{min}}(0) \) corresponds to the charge carrier mobility on non-degraded polymer backbones diluted in a monomer matrix.

The value obtained for \( \Sigma \mu_{\text{min}}(0) \) is dependent on the assumption that only the charge carriers that are produced in the polymer regions will contribute to the conductivity and that the fraction of the charge carriers arriving in the polymer regions is proportional to \( X \). It could be possible however, that charge carriers that are produced in the monomer regions in the vicinity of a polymer may migrate to the polymer and thus may contribute to the transient conductivity. Such an effect could explain the slow 10-25% increase of the conductivity after the pulse, which is observed at low accumulated dose in 4BCMU and ETCD, respectively. Such an effect would reduce the value of \( \Sigma \mu_{\text{min}}(0) \). Also, no correction has been made for the eventual loss of mobile charge carriers due to charge recombination and/or trapping during to the pulse. Such a correction would increase the value of \( \Sigma \mu_{\text{min}}(0) \).

From the present work it is not possible to give an accurate estimate of the uncertainty in the value of \( \Sigma \mu_{\text{min}}(0) \), the charge carrier mobility on the non-degraded polymer backbones which are diluted in the monomer matrix. The value of \( \Sigma \mu_{\text{min}}(0) = 2.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) as determined for 4BCMU in this work is comparable to the values found in polydiacetylene single crystals from Time-of-Flight measurements \( \text{^{68-75}} \).

Since ETCD, IPUDO and DCH are insoluble, the polymer fraction could not be determined by the method used for 4BCMU. Assuming that the polymerization of these compounds can also be described by the general Avrami equation, Eq. (4.3), and that the charge carrier mobility depends on the accumulated dose in a manner similar to 4BCMU, Eq. (4.5), the dose-normalized conductivity data of Figure 4.3 can be described by

\[
\frac{\Delta \sigma(D)}{D_c} = \frac{X_{\text{max}} \Sigma \mu_{\text{min}}(0)}{1 + (\beta D)^\alpha} \frac{e}{E_p} \left[ 1 - \exp(-k D^n) \right] \tag{4.6}
\]

Equation (4.6) could be fitted to the dose-normalized conductivity in DCH, see Figure 4.3. The optimal values of the fitting parameters were found to be \( X_{\text{max}} \Sigma \mu_{\text{min}}(0) = 0.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), \( \beta = 1.65 \times 10^{-6} \text{ Gy}^{-1.2} \), \( \alpha = 1.2 \), \( k = 2.3 \times 10^{28} \text{ Gy}^{-5} \) and \( n = 5 \).

The experimental data of ETCD and IPUDO could also be reproduced by Eq. (4.6), however, the uncertainty in the values of the fitting parameters was large. Since the molecular structure of ETCD and IPUDO is comparable to that of 4BCMU, it is assumed that the distortion of the polymer backbones by high-energy radiation is comparable. The latter would lead to a comparable reduction of the charge carrier mobility as a function of the accumulated dose. Therefore, the values of \( \alpha \) and \( \beta \) for ETCD and IPUDO were fixed to those found for 4BCMU. The results of fitting the remaining parameters in Eq. (4.6) to the experimental data for ETCD and IPUDO are presented in Figure 4.3 by the dashed lines. These fits yielded a value close to 1 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for the product \( X_{\text{max}} \Sigma \mu_{\text{min}}(0) \) for both ETCD.
and IPUDO. It has been reported by Sandman et al.\textsuperscript{76} that the maximum monomer conversion in both ETCD and IPUDO single crystals is close to 1. Using this value of $X_{\text{max}}$ results in a lower limit of the charge carrier mobility for both compounds close to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. For the parameters $k$ and $n$ in Eq. (4.6), values of 0.02 Gy$^{0.75}$ and 0.75 were found for ETCD, while values of $2.8 \times 10^{-5}$ Gy$^{-1.2}$ and 1.2 were obtained for IPUDO.

### 4.4 CONCLUSIONS

In this work ETCD, 4BCMU, IPUDO and DCH diacylenes were polymerized using high-energy (3 MeV) electrons. The radiation-induced conductivity after a single electron pulse was monitored as a function of the accumulated dose. While the polymer fraction in the urethane-substituted diacylenes (ETCD, 4BCMU and IPUDO) increases proportionally with dose at low dose, the polymerization of DCH shows a threshold behavior. At high accumulated dose the radiation-induced conductivity decreases for all diacylenes investigated. This is attributed to the introduction of defect sites by high-energy radiation, which reduces both the mobility and the lifetime of the charge carriers. An important result is that the reduction of the mobility and the lifetime starts at an accumulated dose, which is substantially lower than those used conventionally for the production of polydiacylene crystals.

For low accumulated dose, lower limits of the charge carrier mobility on the polydiacylene backbone of the order of $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ are found. For a dose between $10^5$ and $10^6$ Gy the mobility of the charge carriers in ETCD, 4BCMU and IPUDO is about one order magnitude lower than at low accumulated dose. Although such doses are required to reach the maximum monomer to polymer conversion, the present results indicate the conductive paths for charge transport have become far from optimal.

### REFERENCES:

1979, 17, 899-903.


Chapter 4


5.1 INTRODUCTION

In the crystalline state polydiacetylenes exhibit a fully conjugated and planar backbone. Such a conjugated backbone provides an ideal system for charge transport, which is reflected by rather high charge carrier mobilities. The charge transport is determined mainly by the structure of the polydiacetylene backbone. Pendent groups, crystallinity, and the presence of defects may however distort the polymer backbone from its most ideal conformation.

Many conductivity studies have been performed on bulk polydiacetylenes. Most of these studies involve conventional DC conductivity measurements of the polymer of the $p$-toluene sulphonate ($p$TS) derivative. Chance et al. were the first to perform classical time-of-flight (TOF) experiments on poly-$p$TS. In heat polymerized samples they could place upper and lower limits of 3 and $10^{-3}$ cm² V⁻¹ s⁻¹ on the charge carrier mobilities. They observed that the charge carriers became trapped at defect sites on a timescale of approximately 0.5 μs in their heat-polymerized most perfect single crystals. This carrier lifetime was assigned to a deep trap density of approximately $10^{14}$ cm⁻³. In γ-ray polymerized samples the carrier lifetimes were much shorter, which made it impossible to derive a charge carrier mobility from these TOF transients. Subsequently, Reimer & Bässler obtained a charge carrier mobility of 5 cm² V⁻¹ s⁻¹ in their TOF experiments at room temperature. An increase of the charge carrier mobility with temperature was observed which was attributed to thermally activated jumps of charges from shallow traps and/or between polymer chain ends.

DC measurements are affected by microheterogenities within the sample, chain end effects, field induced space charge problems, saturation of drift mobility at large field strength and electrode problems. Blum and Bässler discussed the problems associated with conductivity measurements in crystalline polydiacetylenes caused by charge carriers that are blocked when reaching a chain end. They concluded that a DC conductivity study was a study of chain to chain hopping rather than intrachain conduction and suggested that an AC experiment was needed to study specifically charge transport along the backbone.
Charge Transport in Polydiacetylenes

itself.

In the work presented in this Chapter, the radiation-induced conductivity in a variety of bulk samples of polydiacetylenes was studied using the PR-TRMC technique. The radiation-induced conductivity at room temperature will be discussed in section 5.3. The temperature dependence of the radiation-induced conductivity will be presented in section 5.4. The radiation-induced conductivity transients provide information on the charge carrier mobility and charge carrier decay kinetics. Attention will be given to differences in the observations in polymer samples prepared in a different way and which show that the method of monomer synthesis and polymerization route are very critical.

5.2 EXPERIMENTAL

5.2.1. Materials

The syntheses and morphological characterization of the different polydiacetylene derivatives were carried out by the groups of Prof. David Bloor at the University of Durham (UK) and Prof. Daniel Sandman at the University of Massachusetts (USA) and they are briefly described below. All derivatives were obtained as single crystals with the exception of the nBCMU polydiacetylenes which were amorphous powders.

5.2.1.1. Poly-pTS : Poly (1,6-bis(p-toluenesulphonate)-2,4-hexadiyne)

The synthesis of the bis-(p-toluene sulphonate) ester of 2,4-hexadiyne-1,6-diol (monomer units of pTS) followed the route used by Wegner 19, but was modified to ensure high chemical purity as described in the literature 20. This involved the use of high purity solvents and a one-step recrystallisation of the monomer. The single-crystal monomers were dichroic with a pale red color. This deepened with time due to polymerization which proceeded slowly when the monomer was stored at 0°C or rapidly when it was heated above 50°C 21. During this process the crystals darkened and became black before a bronze metallic luster appeared. The polymer crystal exhibited a fibre-like structure in the polymer backbone direction.

The poly-pTS crystals studied in this work were obtained from differently grown monomer crystals and by different methods of polymerization, see Table 5.1. In all cases, the monomer crystals were grown from acetone solutions (chromatography grade solvent). The most perfect crystals, crystals 1 and 4 in Table 5.1, were grown by slow evaporation in which the acetone solution was degassed to remove oxygen. The latter was realized by freezing and thawing the acetone solutions several times under vacuum. When the acetone solvent was less pure and not degassed, slow evaporation resulted in samples typical of many of those reported in the literature 22 with a truncated diamond morphology, crystal 2 in Table 5.1. These crystals contain both dislocations and stacking faults. The flakes,
crystals 3 in Table 5.1, were grown by rapid evaporation under nitrogen atmosphere.

Monomer crystals 1, 2 and 3 were polymerized by heat, while 4 was polymerized using 200 kGy γ-irradiation from a \(^{60}\)Co-source.

<table>
<thead>
<tr>
<th>Crystal No.</th>
<th>Growth method</th>
<th>Polymerization route</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>slow evaporation, degassed</td>
<td>heat, 60°C</td>
<td>small, perfect crystals with gold facets</td>
</tr>
<tr>
<td>2.</td>
<td>slow evaporation, air</td>
<td>heat, 60°C</td>
<td>larger, truncated, less perfect crystals with diamond shaped facets</td>
</tr>
<tr>
<td>3.</td>
<td>fast evaporation, N(_2)</td>
<td>heat, 60°C</td>
<td>rapidly grown flakes least perfect</td>
</tr>
<tr>
<td>4.</td>
<td>slow evaporation, degassed</td>
<td>γ-rays, 200 kGy</td>
<td>small, perfect crystals with gold facets</td>
</tr>
</tbody>
</table>

5.2.1.2. Poly-FBS: Poly (1,6-bis (p-fluorobenzene sulphonate)-2,4-hexadiyne)

The diacetylene monomer FBS was synthesized by reacting p-fluorobenzenesulfonyl chloride with 2,4-hexadiyne-1,6-diol according to the method of Wegner \(^9\) with slight modifications. Single crystals of the monomer with lateral dimensions larger than 1 cm were grown by slow evaporation of an acetone solution.

The single monomer crystals were polymerized by heating at 60°C for an appropriate time \(^{23,24}\) or by 200 kGy γ-irradiation using a \(^{60}\)Co-source. The resulting poly-FBS crystals had practically the same shape as the monomer crystals and were metallic gold in color. As is well known, the morphology and appearance of the poly-pTS and poly-FBS crystals can be similar \(^{24}\). The crystal structures are isomorphous and the crystals can have diamond, hexagonal or platelike forms.

5.2.1.3. Co-polymer of pTS and FBS

The close similarity of shapes and sizes of pTS and FBS molecules and identical symmetries of unit cells of their crystals makes it possible to obtain mixed pTS-FBS crystals. A co-polymer, which contains equal amounts of both monomers, pTS and FBS, randomly distributed along the backbone has been synthesized \(^{23}\). Mixed monomer crystals were obtained by dissolving equimolar amounts of pTS and FBS in acetone and slowly evaporating the solvent at room temperature \(^{25}\). The single crystals were polymerized by heating at 60°C.
5.2.1.4. Poly-DCH: Poly(1,6-bis (9-carbazoly)-2,4-hexadiyne)

The synthesis of the monomer crystals has already been described in paragraph 4.2.1.4. Fine needles of DCH were grown by rapid cooling of a hot acetone solution, while chunky crystals were grown by very slow evaporation of an acetone solution. Both types of crystals were polymerized by either γ-radiation or heat.

Solid-state polymerization using γ-radiation was achieved in a 60Co γ-source with a dose rate of 1 kGy h⁻¹. Almost complete monomer-to-polymer conversion was attained using a total accumulated dose of 500 kGy. The resulting DCH polymer crystals showed the typical metallic luster characteristic of polydiacetylenes.

Polymerization by heat was realized by placing the DCH monomer crystals in a vacuum oven for 6 days at 140°C. Cracking of the crystals occurs in the course of thermal polymerization and the surfaces of the polymer are quite rough in appearance.

5.2.1.5. Poly-THD: Poly(1,1,6,6-tetraphenyl-2,4-hexadiyne diamine)

THD monomers were synthesized by Hay coupling of propargyldiphenylamine. THD monomer crystals were grown in a 4:1 methylene chloride-ether mixture and were either thermally polymerized at a temperature of 80°C for 14 days or polymerized using 500 kGy γ-irradiation from a 60Co-source. The resultant needle-like crystals were red in color with a bright green reflection. THD is exceptional since complete conversion to polymer can be reached at relatively low temperatures.

5.2.1.6. Poly-TCDU: Poly(1,12-diol-bis (phenylurethane)-5,7-dodecadiyne)

The TCDU monomer was prepared by a reaction of phenylisocyanate with 5,7-dodecadiyne-1,12-diol. The monomer crystals were grown as needles by slow evaporation of a dimethylformamide (DMF) solution. The needles were elongated along the b-axis. The monomer crystals were polymerized using 500 kGy γ-irradiation in a 60Co-source. The resulting crystals consisted for 85 % of polymer and had a dark red color.

5.2.1.7. Poly-nBCMU: Poly(n-butoxycarbonylmethylurethanes)

The poly(n-butoxycarbonylmethylurethanes) comprise a whole class of polydiacetylenes with n indicating the number of methylene groups in the intervening alkyl chain. The monomers were synthesized by reacting an isocyanate with a diacetylene diol. The synthesis of 4BCMU (1,12-bis(n-butoxy carbonyl methyl urethane)-5,7-dodecadiyne) was already described in paragraph 4.2.1.2. The synthesis of 3BCMU (1,10-bis(n-butoxy carbonyl methyl urethane)-4,6-decadiyne) has been described in Ref. while that of 6BCMU (1,16-bis(n-butoxy carbonyl methyl urethane)-7,9-hexadecadiyne) and 9BCMU (1,22-bis(n-butoxy carbonyl methyl urethane)-10,12-docosadiyne) can be found in Ref.

All monomers were recrystallized twice from acetone-hexane mixtures. The monomers
were polymerized in the crystalline solid state using 500 kGy γ-irradiation from a 60Co-source. As the polymer conversion increased the samples turned darker blue and above 15 percent they acquired a metallic green-gold luster 30. Unreacted monomer was removed by extraction with acetone. The monomer-extracted polymer thus obtained was dissolved in chloroform and precipitated with hexane. The precipitates were filtered and dried under vacuum. Poly-nBCMUs are highly amorphous as revealed by X-ray diffraction studies 32.

The molecular weights of the polymers were determined in an earlier study 33 and were found to correspond to 1000, 2400 and 4700 monomer units for the 3BCMU, 4BCMU and 9BCMU, respectively. The molecular weight of the 6BCMU is not known, but is expected to be in-between the values for 4BCMU and 9BCMU i.e. approximately 3000 monomer units.

5.2.2. Experimental set-up

The experimental procedures are described in Chapter 3. The Ka-band microwave cell containing the sample was irradiated using 4A pulses of 3 MeV electrons from the Van de Graaff accelerator with a pulse length between 0.5 and 50 ns. For each pulse the transient change in the microwave conductivity was monitored. Detailed information about the determination of the charge carrier mobility from the measured radiation-induced conductivity can be found in Chapter 3.

In most cases the polydiacetylene derivatives were available in sufficient amounts (ca. 200 mg) to fill the microwave cell over a length of ca. 10 mm. The available amount of poly-THD and the poly-nBCMUs were too small to fill the entire microwave cell and therefore a PMMA block with a small cavity to contain the sample was used (see Chapter 3).

In the experiments in this chapter, the single crystals of the polydiacetylene were pulverized. In pulverized samples the polymer backbones are isotropically oriented with respect to the microwave field. Conductivity measurements on pulverized samples yield therefore an average of the charge carrier mobility along and perpendicular to the polymer backbone. As will be discussed in Chapter 6 the mobilities parallel and perpendicular to the backbones can be derived from the average mobility and the anisotropy in the charge carrier mobility. In this chapter only the average mobility will be considered. See Chapter 6 for measurements of the anisotropy using single crystal samples.
5.3 RESULTS AND DISCUSSION

5.3.1 End-of-pulse conductivity at room temperature

In Figure 5.1 typical room temperature radiation-induced conductivity transients are shown as obtained for three differently grown poly-pTS single crystals which have been polymerized by heat (1,2,3) and one poly-pTS crystal polymerized using γ-radiation (4). The transients show an increase in the conductivity during the pulse, which is due to the creation of mobile charges in the material. After the pulse, the conductivity decays due to trapping and/or recombination of the charge carriers. As can be seen from this figure, there are differences in the radiation-induced conductivity transients obtained from the three differently grown heat-polymerized pTS single crystals. The results for the radiation polymerized sample are again different. The specific differences will be discussed later on in this chapter.

![Figure 5.1 Radiation-induced time-resolved microwave conductivity transients for heat- and γ-radiation polymerized pTS polydiacetylenes at room temperature. Number 1 and 4 indicate the most perfect crystal, while 2 and 3 are crystals which contain a substantial amount of defects. Crystals 1 to 3 were polymerized using heat, while in the case of crystal 4 γ-radiation was used. All transients were obtained using a 2 ns electron pulse.](image)

The end-of-pulse conductivity and a characteristic decay time (e.g. the half-life) are the two parameters which characterize the conductivity transients. As pointed out in Chapter 3, the conductivity per unit dose absorbed in the sample, \( \Delta \sigma(t)/D_e \), can be related to the sum of the mobilities of the charge carriers present. Using the end-of-pulse conductivity a lower
limit to the sum of the charge carrier mobilities is obtained according to

\[
\frac{\Delta \sigma_{eop}}{D_v} = \frac{e}{E_p} \Sigma \mu_{\text{min}}
\]

(5.1)

where \(E_p\) is the pair formation energy. The pair formation energy, i.e. the average energy absorbed per initial ionization event, \(E_p\), is taken to be \(3.2 \times 10^{18}\) J (i.e. 20 eV) for all PDA derivatives.

<table>
<thead>
<tr>
<th>PDA derivative</th>
<th>polym. route</th>
<th>(\Delta \sigma_{eop}/D_v) ((\times 10^5 \text{S m}^2\text{J}^{-1}))</th>
<th>(\Sigma \mu_{\text{min}}) ((\text{cm}^2\text{V}^{-1}\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-pTS [1]</td>
<td>heat</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>poly-pTS [2]</td>
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<td>0.4</td>
</tr>
<tr>
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<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>poly-pTS [4]</td>
<td>γ-radiation</td>
<td>0.06</td>
<td>0.12</td>
</tr>
<tr>
<td>poly-THD [1]</td>
<td>heat</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>poly-THD [2]</td>
<td>γ-radiation</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>poly-FBS [1]</td>
<td>heat</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>poly-FBS [2]</td>
<td>γ-radiation</td>
<td>0.06</td>
<td>0.12</td>
</tr>
<tr>
<td>Poly-(50% FBS / 50% TS)</td>
<td>heat</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>poly-TCDU</td>
<td>γ-radiation</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>poly-DCH [1]</td>
<td>heat</td>
<td>0.09</td>
<td>0.18</td>
</tr>
<tr>
<td>poly-DCH [2]</td>
<td>γ-radiation</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>poly-3BCM [U]</td>
<td>γ-radiation</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>poly-4BCM [U]</td>
<td>γ-radiation</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>poly-6BCM [U]</td>
<td>γ-radiation</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>poly-9BCM [U]</td>
<td>γ-radiation</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*different sample preparations, see section 5.2.1.

In Table 5.2 the values of the dose-normalized end-of-pulse conductivity, \(\Delta \sigma_{eop}/D_v\), found at room temperature are listed for the different PDA derivatives studied together with the values obtained for the lower limit of the sum of the charge carrier mobilities, \(\Sigma \mu_{\text{min}}\). It can be seen that there is a difference of almost two orders of magnitude in the values obtained for \(\Sigma \mu_{\text{min}}\) for the different samples. The values are between 0.02 and 1.2 cm²V⁻¹s⁻¹. The values for the poly-BCMUs are at the lower end of this range. The absolute value of
the sum of the charge carrier mobilities can not be determined from these measurements, since the concentration of charge carrier pairs which escape from each other’s Coulomb field is not known in these samples (see also section 3.6).

The vast majority of the pairs of positive and negative species are formed initially in each other’s Coulomb field. If at least one of the species is mobile in all directions, movement due to drift in the mutual field will cause of decrease of the separation of the pair, while diffusion will be the driving force for escape from the Coulomb field. While in a perfect crystal with non-zero mobilities in all directions in general eventually all pairs except a small fraction will be expected to recombine, in practice the recombination will be retarded due to barriers originating from imperfections in the crystal. In this case the microwaves may probe the mobility of the charge carriers in the perfect regions of the crystal, while escape of these carriers from these regions is hindered. The fraction of the initially formed number of pairs that is probed may therefore be considerably larger than the escape fraction in a perfect crystal. On the basis of what is known about thermalization distances in liquids and saturated hydrocarbon solids, it is expected that PDA’s thermalization distances are on the order of 5 to 10 nm, which result in escape fractions on the order of a few percent. A good estimate of a lower limit of the escape fraction would be 2 %, which results in an upper limit for the sum of the charge carrier mobilities, a factor of 50 larger than the lower limits shown in Table 5.2. In this way for poly-pTS[1] an upper limit for the sum of the average charge carrier mobilities is found to be 60 cm²V⁻¹s⁻¹. For imperfect crystals the fractions of charged species not having recombined that are observed in the present experiments at the shortest times after the pulse may be several times larger, and consequently a lower charge carrier mobility compared to the upper limit will be found. It should be noted that the upper limit of the charge carrier mobilities found by TRMC is still considerably lower than the extremely high values found by Donovan et al.¹

In case of the most perfect PDA crystals, such as the heat-polymerized poly-pTS [1], the highest charge carrier mobility has been observed. For less perfect crystals, such as poly-pTS [2], poly-pTS [3] the charge carrier mobilities are lower. The magnitude of the charge carrier mobility depends on the conformation of the polymer backbone and the defect concentration. Distortion of the polymer backbone may affect the mobility along the chain due to very shallow traps. Defects may also cause trapping in much deeper traps. These effects may cause the differences in the four poly-pTS samples shown in Figure 5.1. In the γ-radiation polymerized sample, poly-pTS [4], an even lower charge carrier mobility is observed. The differences in the conductivity transients between heat- and γ-radiation polymerized samples will be discussed further below.
5.3.1.1 Comparison between heat- and γ-radiation polymerized samples

In Figure 5.2 typical room temperature radiation-induced conductivity transients are shown as obtained for several PDA derivatives which have been polymerized by either heat (shown as full-drawn transients) or γ-radiation (shown as dotted transients). The conductivity in the heat-polymerized PDAs differs from the conductivity in the γ-radiation polymerized equivalents. Apart from DCH, PDAs which are produced using γ-radiation show end-of-pulse conductivities lower than their heat-polymerized equivalents. The heat polymerization of DCH is not possible under mild conditions and the polymerization at 140°C for 6 days may well have caused some deterioration of the crystal and disruption of the conduction pathways in the poly-DCH crystal 34. Furthermore, it is known that poly-DCH shows very little chemical degradation on high-energy radiation 35.

![Graphs showing conductivity transients for pTS, FBS, THD, and DCH](image)

**Figure 5.2** Dose-normalized radiation-induced conductivity transients for pTS, FBS, THD and DCH polydiacetylene at room temperature. The radiation-induced conductivity transients obtained for heat-polymerized samples are shown as full-drawn lines, while the dotted transients represent the radiation-induced conductivity for γ-radiation polymerized samples. The numbers between brackets correspond to the samples as indicated in Table 5.2.
5.3.1.2 Comparison between homo- and co-polymers

As can be seen in Table 5.2, the mobility in the co-polymer of pTS and FBS is significantly lower than in poly-pTS and poly-FBS alone. It has been reported that the structure of the backbone can be perturbed by a chemical change in the side chain regions\(^{33,36}\), e.g. the substitution of a fluorine atom by a methylene group. This could decrease the charge carrier mobility.

The co-polymer of pTS and FBS is known to have a large number of chain end defects,\(^{23}\) which have been claimed to act as trapping sites.\(^{25,37}\) If the charge carrier mobility in the co-polymer would be equal to that of the pure compounds, then a larger concentration of traps would be expected to give rise to a faster decay of the radiation-induced conductivity. Surprisingly however, the measured decay kinetics for the co-polymer is slower than that of pTS and pFBS (as can be seen in the next section). Apparently, the chain ends do not act as deep trapping sites, but rather as as shallow traps or as reflecting boundaries.

5.3.2 Conductivity Decay Kinetics at room temperature

In addition to the fact that for most PDAs the radiation-induced conductivity in \(\gamma\)-radiation-polymerized samples is lower than in their heat-polymerized equivalents (section 5.3.1.1), the decay is significantly faster, as can be seen from Figure 5.1. The decay of the conductivity is governed by a combination of charge trapping and charge recombination.

5.3.2.1 Homogeneous charge recombination

Homogeneous recombinations results from recombination between ion pairs from different regions of the fast electron track or from different tracks, in contrast to geminate recombination between ion pairs formed close together initially in the so-called spurs. For such homogeneous recombination to be possible it is necessary that two or more charge pairs originating from different spurs of the same or different fast electron tracks are formed within a single domain of the sample in which unhindered mutual diffusion can take place. The contribution of charge recombination due to homogeneous recombination to the decay of the conductivity transients can be investigated by varying the initial concentration of charge carriers. The concentration of charge carriers in the PR-TRMC experiment could be varied over two orders of magnitude by changing the duration of the electron pulse (thus equivalently the radiation dose, see Chapter 3).

In Figure 5.3 radiation-induced transients are shown for different electron pulse lengths for both heat- and \(\gamma\)-radiation polymerized poly-pTS and poly-THD samples. Changing the pulse length from 0.5 to 50 ns with an accompanied change in the dose from \(\text{ca. } 3\) to \(\text{ca. } 300\) \(\text{kJ m}^{-3}\) is seen to have no appreciable effect on the charge carrier decay for the \(\gamma\)-radiation polymerized samples. However, for the heat-polymerized samples the charge carrier decay becomes considerably faster with increasing initial charge carrier...
concentrations. The latter effect can be explained by homogeneous recombination.

![Graphs showing conductivity transients for heat-polymerized and \( \gamma \)-radiation polymerized samples.](image)

Figure 5.3 Effect of increasing radiation dose \((D_r)\) in the pulse on the decay kinetics of dose-normalized radiation-induced conductivity transients for heat-polymerized poly-pTS (pTS[1]) and poly-THD (THD[1]) and \( \gamma \)-radiation polymerized poly-pTS (pTS[4]) and poly-THD (THD[2]). By varying the pulse length (0.5, 2, 5, 10, 20 and 50 ns, the dose deposited in the sample was varied between 3 kJ m\(^{-3}\) (black line) and 250 kJ m\(^{-3}\), corresponding to 1.6 \( \mu \)mol l\(^{-1}\) and 130 \( \mu \)mol l\(^{-1}\) of initially formed electron-hole pairs, respectively. The arrows in the plots on the left indicate the direction in which the transients change with increasing dose.

The highest pulse length \((L_p)\) at which for the different polydiacetylene derivatives no difference in decay is observed within the experimental accuracy is listed in Table 5.3. From the values of \(L_p\) it can be seen that homogeneous recombination plays a more important role in the most perfect crystals, which were heat-polymerized. The latter observation can be explained by the presence of larger domains in heat-polymerized samples. The size of organized domains in the \( \gamma \)-radiation-polymerized samples is expected to be much smaller, which will restrict diffusion throughout the sample and hence reduce
the possibility of homogeneous recombination.

Since the dose-normalized conductivity transients do not change on varying the pulse from a 0.5 to a 2 ns duration, as can be seen for Table 5.3, the homogeneous recombination processes can be neglected for the lowest charge carrier concentration (i.e. using a 0.5 ns pulse). Poly-THD [1] is an exception, since the transients obtained with 0.5 ns and 2 ns pulses differ, showing that homogeneous recombination for these pulses still plays a role. In the following, transients obtained using 0.5 ns pulses will be used to investigate the trapping processes occurring in polydiacetylene derivatives.

5.3.2.3 Charge Trapping Processes

Only a few studies \(^{38,39,40,41}\) can be found in the literature that deal with the decay of the conductivity in polydiacetylenes. In these studies the conductivity decay is attributed to charge trapping. Hunt et al.\(^{38,39}\) reported observations of the decay of photocurrents in thin polydiacetylene films, which followed an \(\exp(-bt^{1/3})\) law over four decades of time. Such a stretched-exponential law follows from the theory of deep trapping in a one-dimensional system \(^{40,41}\). For sufficiently large times the conductivity decay due to the immobilization of charge carriers on a lattice with a certain trap concentration can be described by

\[
\sigma(t) \approx \exp\left[-3\left(\frac{t}{\tau}\right)^{1/2}\right]
\]  

(5.2)

where the characteristic decay time is defined as

\[
\tau = \frac{4}{\pi^2 \chi^4 \nu}
\]  

(5.3)

in which \(x\) is the fraction of lattice sites that corresponds to a trap and \(\nu\) is the jump frequency of a charge carrier.

In some cases conductivity decay can be described by an inverse power law, according to

\[
\sigma(t) \approx t^{-\alpha}
\]  

(5.4)

An inverse power law describing the charge carrier decay is well known from work on amorphous systems. This behavior is found for trapping and release of charge carriers having an exponential trap distribution \(^{42,45}\). An inverse power law with a power \(\alpha\) close to unity is considered a universal characteristic of dispersive photocurrent transients measured in conjugated polymers, reflecting the relaxation of both the charge carrier mobility and the
The analysis of the decay data is complicated by the possible contribution of geminate decay. Ries and Bässler [47,48] have analyzed the conductivity decay due to geminate recombination and trapping by computer simulations, applied to amorphous inorganic semiconductors. Because of lack of quantitative information about the geminate contribution in our case, as working hypothesis it is assumed that this can be neglected at times $t > 10$ ns. The conductivity transients for the polydiacetylenes studied could be fitted over a wide time range by either a stretched exponential (SE) or by an inverse power law (IP), i.e. Eq. (5.2) or Eq. (5.4) respectively. In Table 5.3 the results of fitting the conductivity data to Eq. (5.2) or Eq. (5.4) are shown. On a double-logarithmic plot as in Figure 5.2, the stretched exponential decay gives a curved line (i.e. poly-$p$TS [1]), while the inverse powerlaw is a straight line (i.e. poly-$p$TS [4]).

In most perfect polydiacetylene crystals, such as poly-$p$TS [1], the decay of the

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**Table 5.3** Parameters found from fitting Eq. (5.2) i.e. the stretched exponential (SE), or Eq. (5.4), i.e. the inverse power law (IP), to the measured conductivity transients at long times. In the last column the pulse length at which homogeneous recombination begins to play a role. $L_p$ is listed (together with its corresponding radiation dose $D_r$). All parameters were obtained at room temperature.

<table>
<thead>
<tr>
<th>PDA derivative</th>
<th>Polym.</th>
<th>$t_{1/2}$ (ns)</th>
<th>Time dependence</th>
<th>$\alpha$</th>
<th>$\tau$ (ns)</th>
<th>$L_p$ (ns)</th>
<th>$(D_r)$ (kJ/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$TS [1]</td>
<td>heat</td>
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<td>SE</td>
<td></td>
<td>230</td>
<td>2</td>
<td>13</td>
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<tr>
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<td>heat</td>
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<td>IP</td>
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<td>120</td>
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<td>$p$TS [3]</td>
<td>heat</td>
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<td>IP</td>
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<td>60</td>
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<td>$p$TS [4]</td>
<td>$\gamma$-radiation</td>
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<td>IP</td>
<td>1</td>
<td>50</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>THD [1]</td>
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<td>SE</td>
<td></td>
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<td>0.5</td>
<td>3</td>
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<tr>
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<td>$\gamma$-radiation</td>
<td>2.3</td>
<td>IP</td>
<td>1</td>
<td>50</td>
<td>210</td>
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<td>FBS [1]</td>
<td>heat</td>
<td>6.6</td>
<td>IP</td>
<td>1</td>
<td>20</td>
<td>130</td>
<td></td>
</tr>
<tr>
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<td>$\gamma$-radiation</td>
<td>6.5</td>
<td>IP</td>
<td>1</td>
<td>20</td>
<td>130</td>
<td></td>
</tr>
<tr>
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<td>heat</td>
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<td>SE</td>
<td></td>
<td>860</td>
<td>2</td>
<td>13</td>
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<td>IP</td>
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<td>200</td>
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</tr>
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<td>DCH [1]</td>
<td>heat</td>
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<td>SE</td>
<td></td>
<td>57</td>
<td>50</td>
<td>210</td>
</tr>
<tr>
<td>DCH [2]</td>
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<td>1.8</td>
<td>IP</td>
<td>1</td>
<td>50</td>
<td>210</td>
<td></td>
</tr>
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<td>3BCMU</td>
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<td>IP</td>
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<td>$\gamma$-radiation</td>
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<td>IP</td>
<td>0.63</td>
<td>50</td>
<td>200</td>
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</tbody>
</table>

Chapter 5
conductivity can be best described by a stretched exponential, while in the less pure synthesized crystals of poly-pTS ([2] and [3]) an inverse power is more appropriate. An inverse powerlaw conductivity decay was reported earlier for a poly-pTS crystal with $\alpha$ close to unity (0.8 to 0.95, depending on the crystal)\(^{18,49}\).

In the heat-polymerized crystals of poly-DCH, poly-THD and the co-polymer of pTS and FBS a stretched-exponential decay is observed as in poly-pTS [1]. In contrast to these heat-polymerized crystals, all $\gamma$-polymerized diacetylenes show a conductivity which can best be described by an inverse powerlaw.

In the heat-polymerized materials with the stretched-exponential decay (Eq. (5.2)), assuming that geminate recombination does not interfere in the time region considered, the trap concentrations can be calculated from Eq. (5.3) using the characteristic decay time, $\tau$. For a hopping motion of charge carriers between monomer units at a distance d, the jump frequency, $v$, can be estimated from the charge carrier mobility $\mu = (ed^2/2kT)v$, with $d = 5 \text{ Å}$. For the polydiacetylenes which can be described by Eq.(5.2) a lower limit of the charge carrier mobility on the order of 1 cm$^2$V$^{-1}$s$^{-1}$ is found, which gives rise to a jump frequency of the order of $10^{13}$ s$^{-1}$. Using this jump frequency in Eq. (5.3), the fraction of traps is found to be between $x = 4 \times 10^{-4}$ and $x = 1 \times 10^{-5}$. Knowing that an average poly-pTS chain contains ca. 300 monomer units\(^{50}\), the values found for $x$ correspond to 0.04 to 0.3 defects per poly-pTS chain. If the model is applicable, this shows that the chain ends do not represent the deep trapping sites.

As could be seen from Table 5.3, for a number of cases the decay of the conductivity is best described by an inverse power law, however, with a significant variation of the value of the power $\alpha$. The value of $\alpha$ which can be correlated to the average trap depth\(^{45,51}\). The value found for the power $\alpha$ for the polydiacetylenes is close to unity with the exception of the poly-nBCMU\(\text{s. According to the work of Berlin and Siebbeles}\(^{45,51}\), a value of $\alpha$ close to unity suggests an average trap depth which is much larger than thermal energy. However, the charge carrier mobility is found to be of the order of 1 cm$^2$V$^{-1}$s$^{-1}$, which suggests a relatively small trap depth. This model therefore does not offer an explanation for our observations, however our results may be affected by the neglect of geminate recombination.

The decay of the conductivity in poly-nBCMU\(\text{s (see Figure 5.4) is distinct from that in other $\gamma$-polymerized polydiacetylenes in the sense that the value of $\alpha$ in the inverse power law is considerably smaller. This would be in agreement with a model where the charge carriers move in a disordered energy landscape with a relaxation of the charge carrier mobility\(^{42-45}\). The charge carrier mobilities in the $\gamma$-radiation-polymerized BCMUs are lower than in all other PDAs studied. It should be noted that the poly-nBCMU\(\text{s are amorphous powders while the other PDAs studied are pulverized single crystals. Most
likely, the charge carrier mobility in a single crystal is larger than in an amorphous powder, where the polymer backbones are distorted.

![Graphs](image)

*Figure 5.4* Radiation-induced conductivity transients obtained for different nBCMU polydiacetylenes. The conductivity was induced in the samples using a 0.5 ns high-energy electron pulse and monitored using the PR-TRMC technique.

### 5.3.3 Temperature Dependence of the Conductivity

In the left-side plots of Figure 5.5, dose-normalized radiation-induced conductivity transients are shown for temperatures in the range between -100°C and +100°C for poly-pTS [1], poly-TCDU and the co-polymer of TS and FBS. The conductivity transients show that both the end-of-pulse conductivity and the decay vary significantly with temperature. In order to compare the decay kinetics of the conductivity, the transients have been scaled to coincide at short times using the room-temperature transient as a reference, see the right-side plots of Figure 5.4. First attention will be given to the end-of-pulse conductivity (section 5.3.3.1) and in section 5.3.3.2 further attention will be given to the decay kinetics at different temperatures.
Figure 5.5 Left: dose-normalized radiation-induced conductivity transients obtained at different temperatures for three different polydiacetylene derivatives; PTS, (PTS/FBS) co-polymer and TCDU. Right: conductivity transients shown in the left plots scaled to coincide at short times using the room-temperature transient as a reference. The room-temperature transients are indicated by the thick solid lines. The arrows indicate the direction in which the transients change on heating from −100 to +100°C.
5.3.3.1 End-of-pulse conductivity

As can be seen in the left-side plots of Figure 5.5, the end-of-pulse conductivity increases with increasing temperature. This increase may be due to an increase of the charge carrier mobility, to an increase in the number of charge carriers present at the end of the pulse or to a combination of both. The initial number of charge carriers formed is expected to be independent of temperature, however the actual fraction of mobile charge carriers which contributes to the conductivity might change with temperature. Since the conductivity decay kinetics of poly-pTS does not change much on varying the temperature, it is plausible to assume that the number of charge carriers contributing to the conductivity also does not change much with temperature. Therefore, the increase in the conductivity at elevated temperature is attributed to a thermally activated charge carrier mobility.

In the plots on the left of Figure 5.6 the lower limit of the charge carrier mobility is shown as a function of temperature for poly-pTS [1], poly-TCDU, the co-polymer of pTS and FBS and poly-6BCMU. For poly-pTS [1], poly-TCDU and the co-polymer of pTS and FBS the heating and the cooling curves shown on the left of Figure 5.6 coincide. As can be seen from this figure, all compounds display a gradual increase in $\Sigma \mu_{\text{min}}$ on heating and a decrease on subsequent cooling. The extent to which the charge carrier mobility depends on temperature differs between the compounds with that for poly-6BCMU being extremely weak.

In the right-hand plots of Figure 5.6 the temperature dependence of the charge carrier mobility is plotted in an Arrhenius fashion (ln $\mu$ versus $T^{-1}$). Since all polydiacetylenes studied show an increase in $\Sigma \mu_{\text{min}}$ with increasing temperature, the charge transport is thermally activated. Bässler reported a $T^{-2}$ dependence of charge carrier mobility (ln $\mu$ versus $T^{-2}$) for disordered systems. In the present experiments the mobility data is clearly better described by the Arrhenius relation.

The charge carrier transport in poly-pTS is seen to be thermally-activated with an activation energy of 40 meV. This value agrees with the activation energies found by Blum and Bässler and by Donovan et al. The pTS/FBS co-polymer and poly-TCDU show temperature activated conductivity behavior with activation energies of 80 and 40 meV, respectively.

Poly-6BCMU is only thermally-activated in the high-temperature range between 60 and 100°C, however the temperature dependence is very small. At approximately 100°C $\Sigma \mu_{\text{min}}$ in poly-6BCMU shows a sudden decrease on heating which is irreversible on cooling. This can be explained in terms of a backbone conformational change, evidenced by a metallic-to-red color change observed for all poly-nCMUs. This transition corresponds to irreversible intermolecular melting. It is likely that this conformational change also causes the change in conductivity behavior observed. At even higher temperatures, a second reversible red-to-yellow color change has been reported for these derivatives.
Figure 5.6 Left: The temperature dependence of the lower limit of the charge carrier mobility for poly-pTS, (50:50 TS/FBS)-copolymer, poly-TCDU and poly-6BCMU.
Right: Identical mobility data as shown on the left plotted in an Arrhenius fashion.
The solid circles indicate the charge carrier mobility on heating and the open circles on cooling beginning with heating of the freshly synthesized samples.
5.3.3.2 Decay kinetics

In order to compare the decay kinetics, the conductivity transients have been scaled to coincide at short times using the room-temperature transient as a reference, see the right panel of Figure 5.5. Three examples are selected to illustrate that the decay of the radiation-induced conductivity can differ significantly as a function of temperature and can be quite different in different polydiacetylene derivatives.

Poly-\(\text{pTS}\) [11] is an example for which the conductivity decay can be described by a stretched exponential for a wide time range. The decay kinetics does not change in the temperature range between 0 and 100°C, so that the characteristic trapping time \(\tau\) obtained is constant in this temperature regime. For temperatures below 0°C the conductivity decay becomes faster with decreasing temperature (decreasing \(\tau\)).

The TS/FBS co-polymer shows a stretched-exponential decay similar to poly-\(\text{pTS}\) in the temperature range between 0 and +100°C. The decay does not change significantly with temperature. The long characteristic trapping time \(\tau\) suggests a low concentration of deep traps (see section 5.3.2.3). As was already mentioned in section 5.3.1.2, the number of chain ends in this co-polymer is relatively large. These chain ends may act as barriers which however can be overcome at high temperatures (\(T > 0^\circ\text{C}\)). At temperatures below 0°C the decay of the conductivity gradually changes from a stretched exponential-type behavior to an inverse power law behavior. At a temperature of −100°C the conductivity can be described by an inverse power law with \(\alpha = 0.5\).

Poly-\(\text{TCDU}\)'s conductivity decay behavior can be described by an inverse powerlaw over the entire temperature range of −100°C to +100°C, with the power \(\alpha\) changing from 0.45 to 0.90. On raising the temperature the conductivity decay becomes faster in poly-\(\text{TCDU}\), which is opposite to the temperature dependence of the decay observed in poly-\(\text{pTS}\) and the co-polymer, discussed above. The inverse power law dependence with \(\alpha=0.45\) would suggest trapping of charge carriers in shallow traps, however, the faster decay at elevated temperature suggests also charge trapping in deep traps. A possible explanation might be that at low temperatures the charge carrier is reflected even at relatively low barriers, while at higher temperatures low barriers can be overcome [56,58]. Therefore, the charge carriers probe a larger domain at higher temperatures, which in turn increases the probability of meeting deeper traps.

Poly-\(\text{nBCMU}\)s exhibit an irreversible phase transition at approximately 100°C, which affects the radiation-induced conductivity in these compounds As was shown in the previous section. In Figure 5.7 room temperature conductivity transients are displayed before and after annealing at 140°C. The charge carrier decay in poly-\(\text{4BCMU}\) becomes irreversibly faster after annealing at 140°C. The decay kinetics in the fresh material can be described by an inverse power law with \(\alpha = 0.18\), while after annealing at 140°C the \(\alpha\) is increased to 0.36. This change in decay kinetics is accompanied with the irreversible
chromic transition\textsuperscript{54,55}. When the temperature is increased beyond the melt-temperature (120°C for 4BCMU\textsuperscript{54}), the hydrogen bonds in the material collapse and only half of these bonds are recovered on recrystallization, which results in a strong disorder in the backbone conformation\textsuperscript{59,60}. This introduces traps that reduce both the charge carrier mobility and the lifetime.

![Graph](image)

\textbf{Figure 5.7} Room temperature TRMC transients of fresh and 140°C annealed 4BCMU.

\section*{5.4 CONCLUSIONS}

The transient conductivity resulting from nanosecond pulsed ionization of different polydiacetylenes has been studied using the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique. The polydiacetylene derivatives studied in this work show minimum values of the charge carrier mobility (averaged over all directions) between 0.02 and 1.2 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} at room temperature. The most perfect crystals exhibit mobilities at the upper end of this range, while for less perfect crystals the charge carrier mobilities are significantly lower. Most polydiacetylenes produced by \(\gamma\)-radiation show lower charge carrier mobilities than their heat-polymerized equivalents.

The charge carrier decay in all polydiacetylene derivatives could be described by either an inverse power law or a stretched exponential over a wide time range. In heat-polymerized polydiacetylenes where the backbones contain a high degree of order and a low concentration of defects, which can act as deep traps, the conductivity is best described by a stretched exponential. The conductivity in the majority of \(\gamma\)-polymerized polydiacetylenes is best described by an inverse power law with a power close to 1. In the nBCMU polydiacetylenes however lower powers are found.
The radiation-induced end-of-pulse conductivity was found to vary significantly with changing temperature. The observed increase in the conductivity with temperature is attributed to an increase in the charge carrier mobility (thermally-activated charge transport). The extent to which the conductivity is thermally activated differs between the different derivatives with that of the poly-nBCMUs being extremely weak. For all polydiacetylenes studied with the exception of poly-TCDU, the decay of the conductivity becomes faster with decreasing temperature. TCDU is an exceptional case since the conductivity decay rate decreases with decreasing temperature. In this case the charge carrier decay could be described by an inverse power law over the entire temperature range between $-100$ and $+100^\circ$C, with the power increasing from 0.45 to 0.90.

The end-of-pulse conductivity of the poly-nBCMUs displays an irreversible decrease at approximately $100^\circ$C on heating. The charge carrier mobility in these compounds decreased by a factor of 5 after annealing at $140^\circ$C. The latter effect is associated with a conformational change of the polymer backbone which is also evidenced by a metallic-to-red color change in these compounds. The red phase is the more disordered phase, which explains the lower charge carrier mobility and a faster charge carrier decay found in this phase.

REFERENCES

(20) Stevens, G. C.; Ando, D. J.; Bloor, D.; Ghotra, J. S. *Polymer* 1976, 17, 623-626.
(52) Bässler, H. *phys. stat. sol. (B)* 1993, 175, 15-56.
6.1 INTRODUCTION

The macroscopic conductivity in polymers is determined by both charge transport along a polymer chain (intrachain transport) and charge transport from one polymer chain to another (interchain transport). The mobility of charge carriers along a polymer backbone is usually much higher than in a perpendicular direction involving chain to chain charge transfer. Anisotropic charge transport has been observed in oriented samples of polyacetylene, polypyrroles, polyanilines, polythiophenes, polysilanes, and polydiacetylenes. In certain cases extremely high values of the anisotropy have been found with factors close to or in excess of 100 favoring charge transport along the direction of the conjugated polymer backbones. Bleier et al. measured a photocurrent along the direction of the polymer backbones in oriented samples of trans-polyacetylene a factor 50 higher than in a perpendicular direction, a value which is close to the anisotropy in the conductivity found by Schimmel et al. Results of anisotropy measurements on polydiacetylene derivatives have been reviewed in Chapter 2.

In the work described in this Chapter the PR-TRMC technique was used to study the mobility of charge carriers for continuously variable orientation of the polymer backbones with respect to the microwave electric field vector. In previous DC studies of polydiacetylene crystals only the ratio of the mobility parallel and perpendicular to the polymer backbones could be measured.
6.2. EXPERIMENTAL

6.2.1. Materials

The synthesis and the general properties of the polydiacetylene crystals used are described in Chapter 5. Photographs of typical polymer crystals used are shown in Figure 6.1. The poly-\( pTS \) crystal shown in Figure 6.1 was cleaved from a high quality diamond shaped crystal. The two other crystals are sections obtained by fracture of hexagonal monomer crystals of poly-FBS and the 50:50 \( pTS/FBS \) co-polymer. The irregular facets in the latter two reflect the less perfect cleavage of the monomer crystals. The hexagonal morphology is indicative of a slightly higher density of crystallographic defects, which is confirmed by the somewhat irregular cleavage visible on the surface of the 50:50 \( pTS/FBS \) crystal. More details about the different kinds of crystallographic defects can be found in Chapter 2.

Figure 6.1 From left to right: pictures of the poly-\( pTS[1] \), poly-FBS[1] and the 50:50 \( pTS/FBS \) co-polymer crystal. The \( h \)-axis indicates the direction of the polymer backbones in the crystals, while the \( k \)- and \( w \)-axis represent perpendicular directions.

The polydiacetylene crystals used are characterized by the parameters \( h \), \( w \) and \( k \) in Table 6.1. The value of \( h \) corresponds to the maximum dimension along the axis parallel to the polymer backbones. \( w \) and \( k \) are maximum dimensions perpendicular to the polymer backbones.
Table 6.1 Characteristics of the polydiacetylene crystals used and values of the factors $S_{\text{calc}}$ and $S_{\text{exp}}$.

<table>
<thead>
<tr>
<th>PDA</th>
<th>$h$ (mm)</th>
<th>$w$ (mm)</th>
<th>$k$ (mm)</th>
<th>crystal shape$^*$</th>
<th>$S_{\text{calc}}$</th>
<th>$S_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-pTS [1]</td>
<td>1.8</td>
<td>2.05</td>
<td>0.5</td>
<td>triangle</td>
<td>0.60</td>
<td>0.85</td>
</tr>
<tr>
<td>poly-pTS [2]</td>
<td>2.2</td>
<td>1.65</td>
<td>0.3</td>
<td>rectangle</td>
<td>1.23</td>
<td>1.44</td>
</tr>
<tr>
<td>poly-pTS [3]</td>
<td>2.05</td>
<td>2.4</td>
<td>0.3</td>
<td>rectangle</td>
<td>0.54</td>
<td>0.82</td>
</tr>
<tr>
<td>poly-pTS [4]</td>
<td>1.0</td>
<td>2.2</td>
<td>0.5</td>
<td>triangle</td>
<td>0.25</td>
<td>0.33</td>
</tr>
<tr>
<td>poly-THD [1]</td>
<td>1.15</td>
<td>1.85</td>
<td>0.3</td>
<td>rectangle</td>
<td>0.40</td>
<td>0.54</td>
</tr>
<tr>
<td>poly-THD [2]</td>
<td>1.80</td>
<td>1.30</td>
<td>0.3</td>
<td>rectangle</td>
<td>1.31</td>
<td>1.52</td>
</tr>
<tr>
<td>poly-FBS [1]</td>
<td>2.3</td>
<td>1.35</td>
<td>0.3</td>
<td>parallelogram</td>
<td>1.87</td>
<td>2.01</td>
</tr>
<tr>
<td>poly-FBS [2]</td>
<td>2.3</td>
<td>1.9</td>
<td>0.3</td>
<td>parallelogram</td>
<td>1.03</td>
<td>1.27</td>
</tr>
<tr>
<td>poly-(50% FBS/50% TS)</td>
<td>2.0</td>
<td>1.4</td>
<td>0.3</td>
<td>trapezium</td>
<td>1.38</td>
<td>1.58</td>
</tr>
<tr>
<td>poly-TCDU</td>
<td>1.30</td>
<td>1.85</td>
<td>0.2</td>
<td>rectangle</td>
<td>0.46</td>
<td>0.64</td>
</tr>
<tr>
<td>poly-DCH [1]</td>
<td>2.1</td>
<td>1.3</td>
<td>0.5</td>
<td>rectangle</td>
<td>1.68</td>
<td>1.86</td>
</tr>
<tr>
<td>poly-DCH [2]</td>
<td>1.85</td>
<td>2.1</td>
<td>0.4</td>
<td>rectangle</td>
<td>0.60</td>
<td>0.85</td>
</tr>
<tr>
<td>poly-4BCMU$^*$</td>
<td>2.0</td>
<td>1.2</td>
<td>0.1</td>
<td>rectangle</td>
<td>1.76</td>
<td>1.95</td>
</tr>
<tr>
<td>poly-4BCMU$^{**}$</td>
<td>1.5</td>
<td>1.7</td>
<td>0.1</td>
<td>rectangle</td>
<td>0.65</td>
<td>0.85</td>
</tr>
</tbody>
</table>

$^*$ projected along the direction of propagation of the microwaves
$^{**}$ γ-polymerized crystal (300 kGy 60Co radiation)
$^{**}$ UV-polymerized crystal (flux 3300 mJ cm$^{-2}$ 250 nm photons)

6.2.2. Experimental set-up

The configuration which has been used to measure the anisotropy in the microwave conductivity was shown in configuration 3 of Figure 3.3 and in more detail in Figure 3.10. The polydiacetylene crystal was attached to the end of a rod that can be rotated in the microwave cell. The sample was irradiated with pulses of 3 MeV electrons from the Van de Graaff accelerator. For most measurements 2 or 5 ns pulses were used. For orientations in which the polymer backbones are close to perpendicular to the electric field direction the radiation-induced microwave absorption signals were found to be small. To obtain a satisfactory signal to noise ratio in these cases 10 or 20 ns pulses were used.

As was discussed in section 3.5.3 of Chapter 3 the non-uniform shape of the polydiacetylene crystals causes variation in the microwave absorption as a function of the angle of rotation in the microwave electric field. The anisotropy in the conductivity is obtained from the measured anisotropy in the microwave absorption by

$$R = \frac{\Delta \sigma_\parallel}{\Delta \sigma_\perp} = \frac{\Delta P(0^\circ)}{\Delta P(90^\circ)} \frac{1}{S}$$

(3.26)
using for $S$ the empirical correction factors, $S_{\text{calc}}$ and $S_{\text{exp}}$, see Eqs. (3.25) and (3.27-28) respectively. To calculate the factor $S_{\text{calc}}$ the dielectric constants in the polydiacetylenes were assumed to be equal to those for poly-pTS, which have been reported to be $\varepsilon_{||}=7$ and $\varepsilon_{\perp}=4^{22-24}$. The values of $S_{\text{exp}}$ were obtained from the experimental results for silicon samples, see Figure 3.13. Note, that the dimensions of the silicon samples were taken such that they were close to those of the polydiacetylene crystals studied. The values of the correction factors $S_{\text{calc}}$ and $S_{\text{exp}}$ are shown in Table 6.1.

6.3 RESULTS AND DISCUSSION

The anisotropy of the charge carrier mobility is discussed in section 6.3.1. The effect of the method of monomer crystal growth and polymerization route on the anisotropy are the subject of section 6.3.2.

6.3.1 Anisotropy of the charge carrier mobility

In Figure 6.2 the dose-normalized radiation-induced microwave absorption at the end of the high-energy electron pulse is given as a function of the angle $\alpha$ between the polydiacetylene backbones and the microwave electric field. The data were obtained with the samples poly-pTS[1], poly-FBS[1] and their 50:50 co-polymer. The data have been normalized such that the fractional absorption per nanocoulomb beam charge $\Delta P/PQ$ is unity at $\alpha=0^\circ$. As can be seen in Figure 6.2 the microwave absorption at angles of $90^\circ$ and $270^\circ$ is approximately two orders of magnitude lower than at angles of $0^\circ$ and $180^\circ$. The lines drawn in Figure 6.2 are the results of fitting Eq.(3.19) to the experimental data with the coefficients $C_i$ as fitting parameters. This gives

$$\frac{C_1}{C_0} = \frac{[\Delta P/PQ](0^\circ)}{[\Delta P/PQ](90^\circ)}$$  \hspace{1cm} (6.1)

Since $\Delta P$ is proportional to the incident power $P$ and the beam charge $Q$,

$$\frac{[\Delta P/PQ](0^\circ)}{[\Delta P/PQ](90^\circ)} = \frac{\Delta P(0^\circ)}{\Delta P(90^\circ)}$$  \hspace{1cm} (6.2)

with $\Delta P(0^\circ)/\Delta P(90^\circ)$ in the previous notation (Eq. 3.27) where it was silently assumed that $\Delta P(0^\circ)$ and $\Delta P(90^\circ)$ were measured with the same power $P$ and the beam charge $Q$. The anisotropy of the microwave conductivity can now be obtained from the anisotropy of the microwave absorption, using Eq. (3.27) and this gives
Anisotropic Charge Carrier Transport in Polydiacetylene Single Crystals

\[
\frac{\Delta \sigma_1}{\Delta \sigma_\perp} = C_1 \frac{1}{C_0 S}
\]  

(6.3)

The results are presented in Table 6.2. The two values of \(\Delta \sigma_1/\Delta \sigma_\perp\) given were obtained using \(S_{\text{calc}}\) and \(S_{\text{exp}}\) from Table 6.1. For all crystals investigated \(\Delta \sigma_1/\Delta \sigma_\perp\) was greater than unity as expected, since in polydiacetylenes the intrachain mobility is expected to be larger than the interchain mobility.

![Graphs showing orientation vs. microwave absorption for pTS, FBS, and 50:50 pTS/FBS](image)

**Figure 6.2** The radiation-induced beam charge-normalized microwave absorption as a function of the angle between the polymer backbones and the microwave electric field vector for pTS, FBS and their 50:50 co-polymer.
Charge Transport in Polydiacetylenes

Since the structure of polydiacetylenes differs in different directions perpendicular to the backbones the conductivity in different directions perpendicular to the backbones is not necessarily the same. Within the accuracy of the experiments the conductivity perpendicular to the backbones in a poly-\textit{p}TS [1] crystal was found not to change upon rotation of the crystal by 90° around the direction of the polymer backbones however.

<table>
<thead>
<tr>
<th>PDA derivative</th>
<th>Polymerization route</th>
<th>$\frac{C_1}{C_0}$</th>
<th>$\Delta \sigma / \Delta \sigma_1$</th>
<th>$\langle \mu \rangle_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-\textit{p}TS [1]</td>
<td>heat</td>
<td>82</td>
<td>136</td>
<td>96</td>
</tr>
<tr>
<td>poly-\textit{p}TS [2]</td>
<td>heat</td>
<td>17</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>poly-\textit{p}TS [3]</td>
<td>heat</td>
<td>20</td>
<td>37</td>
<td>24</td>
</tr>
<tr>
<td>poly-\textit{p}TS [4]</td>
<td>\gamma-radiation</td>
<td>1.8</td>
<td>7.2</td>
<td>5.4</td>
</tr>
<tr>
<td>poly-THD [1]</td>
<td>heat</td>
<td>16</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>poly-THD [2]</td>
<td>\gamma-radiation</td>
<td>1.5</td>
<td>11</td>
<td>1.0</td>
</tr>
<tr>
<td>poly-FBS [1]</td>
<td>heat</td>
<td>40</td>
<td>21</td>
<td>20</td>
</tr>
<tr>
<td>poly-FBS [2]</td>
<td>\gamma-radiation</td>
<td>3.2</td>
<td>3.1</td>
<td>2.5</td>
</tr>
<tr>
<td>poly-(50% FBS / 50% TS)</td>
<td>heat</td>
<td>167</td>
<td>121</td>
<td>106</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PDA derivative</th>
<th>Polymerization route</th>
<th>$\frac{C_1}{C_0}$</th>
<th>$\Delta \sigma / \Delta \sigma_1$</th>
<th>$\langle \mu \rangle_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-TCUD</td>
<td>\gamma-radiation</td>
<td>2.0</td>
<td>4.3</td>
<td>3.1</td>
</tr>
<tr>
<td>poly-DCH [1]</td>
<td>heat</td>
<td>13</td>
<td>7.7</td>
<td>7.0</td>
</tr>
<tr>
<td>poly-DCH [2]</td>
<td>\gamma-radiation</td>
<td>2.4</td>
<td>4</td>
<td>2.8</td>
</tr>
<tr>
<td>poly-4BCMU*</td>
<td>\gamma-radiation</td>
<td>4.0</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>poly-4BCMU**</td>
<td>UV</td>
<td>18</td>
<td>28</td>
<td>21</td>
</tr>
</tbody>
</table>

* \gamma-polymerized crystal (300 kGy 60Co radiation)
** UV-polymerized crystal (flux 3300 mJ cm$^{-2}$ 250 nm photons)

The present anisotropy measurements on polydiacetylene single crystals could not be used to derive the values of $\Delta \sigma_1$ and $\Delta \sigma_2$ separately, because of the large uncertainty in the factor $B$ in Eq. (3.24) which leads to a corresponding uncertainty in the conductivity value. As discussed in Chapter 5 (see Table 5.2) for the same compounds as used in the present anisotropy measurements, the lower limit of the sum of the average charge carrier mobilities could be obtained from measurements using a microwave cell that was fully filled with a pulverized polydiacetylene crystal.

Assuming that the charge carrier mobilities in the two perpendicular directions of a PDA crystal are equal, which seemed to be true for poly-\textit{p}TS[1], the average charge carrier mobility is
Anisotropic Charge Carrier Transport in Polydiacetylene Single Crystals

\[ \langle \mu \rangle = \frac{\mu_\parallel + \mu_\perp}{3} \quad (6.4) \]

It is assumed that holes do not contribute to the conductivity at the time scale of our measurement. In this case the anisotropy in the microwave conductivity, \( \Delta \sigma_\parallel / \Delta \sigma_\perp \), gives rise to a lower limit of the anisotropy in the charge carrier mobility, \( <\mu_\parallel / \mu_\perp> \) (see Section 3.6), i.e.

\[ \frac{\Delta \sigma_\parallel}{\Delta \sigma_\perp} = \left( \frac{\mu_\parallel}{\mu_\perp} \right)_\text{min} \quad (6.5) \]

Combination of the minimum mobility values in Table 5.2 with the average of the two values for \( \Delta \sigma_\parallel / \Delta \sigma_\perp \) in Table 6.2 yields the lower limit value of the intrachain mobility \( \mu_\parallel \) using Eqs. (6.4) and (6.5).

As can be seen in Table 6.2 an anisotropy of approximately 100 has been found for poly-pTS[1]. In a preliminary PR-TRMC study of Van der Laan et al.\(^3\) the anisotropy of the charge carrier mobility in a poly-pTS[1] crystal was determined to be 220. However, in that work effects of the sample shape and the anisotropy of the dielectric constants on the measured microwave absorption were not taken into account. Taking these effects into account and using the correct experimental parameters the anisotropy in the charge carrier mobility found by van der Laan et al. reduces to 90, which is close to the lowest value (\( \mu_{\exp} \)) for poly-pTS[1] in Table 6.2.

In previous DC studies by other workers\(^6,9,20\) the anisotropy of the conductivity in poly-pTS was found to be in the order of 10\(^2\) to 10\(^3\). The value found in the present study for poly-pTS[1] is at the lower end of this range.

The anisotropy in poly-pTS[1] is approximately a factor five larger than in poly-FBS[1]. This has also been observed in photoconductivity experiments by Sworakowski et al.\(^25\). This could possibly be due to the fluorine atom in the pendant groups facilitating the interchain transport. The anisotropy in the photoconductivity in the co-polymer found by Sworakowski et al.\(^25\) has a value between that found for poly-pTS[1] and poly-FBS[1]. According to the present results, however, the anisotropy in the co-polymer is closer to that in poly-pTS[1].
In the left panel of Figure 6.3 the anisotropy in the microwave conductivity in perfect PTS crystals is shown as a function of temperature. The anisotropy was calculated from the differences in fractional absorption per nanocoulomb beam charge using $S_{\text{calc}}$ as correction. In obtaining the anisotropy values in Figure 6.3 the effect of the eventual variation of the dielectric constants with temperature on the factor $S_{\text{calc}}$ was neglected. The anisotropy increases from a value of 35 at $-80^\circ$C to a value close to 200 at $+80^\circ$C. Experimentally it was found that the conductivity perpendicular to the polymer backbones remained fairly constant on changing the temperature. This might suggests that the chain-to-chain charge transport occurs via a temperature-independent charge transfer process, such as long-distance tunneling. The increase in the anisotropy with temperature can then be attributed to an increase in the intrachain charge carrier mobility.

From the results presented in Chapter 5 on $\Sigma \mu_{\text{m\text{a}}}$ for different temperatures (Figure 5.6) a lower limit of the intrachain charge carrier mobility could be obtained as a function of temperature from the results, in the way discussed above for the room temperature value. The results are shown in the right panel of Figure 6.3. The temperature dependence of the intrachain mobility (right panel) resembles the temperature dependence of the anisotropy of the conductivity (left panel) within 20%, from which it can also be concluded that the activation of the anisotropy with temperature is mainly due to the intrachain mobility.

**Figure 6.3** Left panel: Anisotropy of the microwave conductivity in poly-$p$TS [1] as a function of temperature. The arrows indicate the direction of the heating and cooling cycles. Right panel: the lower limit of the intrachain mobility as a function of temperature obtained from the temperature dependence of the average of the sum of charge carrier mobilities (see Chapter 5).
6.3.2. Effect of crystal morphology and polymerization route

The data for the crystals poly-$p$TS[1], poly-$p$TS[2] and poly-$p$TS[3] which were obtained by heat polymerization of three differently grown monomer crystals, indicate that the anisotropy of the charge carrier mobility is sensitive to the crystal quality. The most perfect $p$TS crystal, poly-$p$TS [1], shows the highest intrachain mobility, see Table 6.2. The perfect faceting on the poly-$p$TS[1] crystal shown in Figure 6.1 indicates a low defect density 26. In the crystals of poly-$p$TS[2] and poly-$p$TS[3] the lower intrachain mobility is attributed to the presence of defects and/or less perfect chain conformations. Such a decrease of the intrachain mobility would lower the anisotropy as is observed. In poly-$p$TS[2] dislocations grow out from the center into the irregular truncated ends. Hence, the dislocation axes will be normal to the polymer axis, producing misalignment, which might facilitate interchain transport. This effect would again decrease the anisotropy.

As Figure 6.1 shows, the morphology of the poly-FBS[1] and the co-polymer samples reflects a higher density of monomer growth defects, e.g. dislocations and stacking faults, as compared to the poly-$p$TS[1] crystal. The dislocations and stacking faults will reduce intrachain transport and therefore decrease the anisotropy.

It is evident from Table 6.2 that the polymerization route (thermal polymerization or polymerization using high-energy radiation) has an important effect on the anisotropy. The anisotropy in the $\gamma$-ray polymerized polydiacetylene crystals is at least one order of magnitude smaller than in the thermally-polymerized crystals with the exception of poly-DCH. Also the values of $\mu_{//\text{min}}$ for the $\gamma$-ray polymerized crystals are found to be much smaller than for the heat-polymerized crystals, again with poly-DCH as an exception. The lower values found for $\mu_{//\text{min}}$ for the $\gamma$-ray polymerized crystals are most likely due to defects that cause structural and/or chemical defects on the polymer backbone. A decrease of the intrachain mobility has a lowering effect on the anisotropy, which is observed for the $\gamma$-irradiated samples. A lowering of the anisotropy would also result from an increase in the interchain motion. It is not unlikely that some defects also facilitate such interchain transport.

Poly-DCH is an exceptional case, which shows a higher intrachain mobility in the $\gamma$-ray polymerized crystal. The intrachain mobility in the heat-polymerized sample is lowered due to the extended heat treatment, as was already noted in Chapter 5. In DCH there is a bulky aromatic carbazole ring and no saturated alkane chain in the pendent group, as in most other polydiacetylene derivatives. It was suggested by Sakamoto et al. 27 that the conductive path formation through the extension of the aromatic $\pi$ electron systems by cross-linking and condensation of aromatic rings would be easier in DCH. The latter would result in enhanced interchain transport.
In Table 6.2 the anisotropy in the conductivity of a UV-polymerized 4BCMU crystal is also listed. The maximum anisotropy was found to be 28, which is larger than the maximum anisotropy obtained in a γ-radiation polymerized sample, see Table 6.2. The much smaller anisotropy in γ-radiation polymerized 4BCMU as compared to a UV-polymerized sample suggests that the damage induced in the polymer regions by UV light is much less than for γ-radiation from a ⁶⁰Co source.

6.4 CONCLUSIONS

The anisotropy in the conductivity of polydiacetylene single crystals was studied using the PR-TRMC technique. The anisotropy could be measured for different orientations of the single crystal in the microwave field. The conductivity along the direction of the polymer backbones was found to be larger than in a perpendicular direction by up to a factor in excess of 100 for some samples.

The increase of anisotropy with temperature for a polydiacetylene single crystal is mainly attributed to an increase of the intrachain charge carrier mobility with temperature. The interchain charge carrier mobility remained fairly constant on changing temperature, which suggests that the chain-to-chain charge transport occurs via a temperature-independent charge transfer process, such as tunneling.

The anisotropy has been shown to be strongly dependent on the method of monomer crystal preparation and the way of polymerizing the single crystal. In the most perfect polydiacetylene crystals the highest anisotropy has been found and the highest mobility along the polymer backbones. Defects lower the intrachain mobility and decrease the anisotropy in the conductivity. High-energy radiation (such as γ-radiation from a ⁶⁰Co source) decreases substantially the anisotropy of the conductivity in polydiacetylene single crystals. The lower anisotropy in the γ-radiation polymerized samples is attributed to the introduction of defects that in turn reduces the intrachain charge carrier mobility. From comparison between a UV polymerized and γ-radiation polymerized 4BCMU sample it could be concluded that the former method of polymerization gives rise to a larger anisotropy in the charge carrier mobility.
REFERENCES


Chapter 7

Photoconductivity of Isolated Polydiacetylene Chains in Solution

7.1 INTRODUCTION

Polydiacetylenes (PDAs) have been extensively studied for their unique opto-electronic properties, such as dramatic thermochromic and solvatochromic changes \textsuperscript{1-5} and large nonlinear optical susceptibilities \textsuperscript{6-8} with ultrafast response times \textsuperscript{7}. The one-dimensional conjugated backbone combined with the structures of the sidegroups is responsible for these unique characteristics, which make PDAs potential candidates for photonic \textsuperscript{6} and electronic applications \textsuperscript{9,10}.

Since most of the early polydiacetylene derivatives were quite insoluble, the properties of their solutions received very little attention until a new class of PDAs was synthesized which showed relatively high solubility in both aqueous \textsuperscript{11,12} and non-aqueous solvents \textsuperscript{13-16}, the n-butoxycarbonylmethylurethane-PDAs or nBCMU derivatives (see Chapter 2). Poly-nBCMU solutions are found to exhibit dramatic color changes, from red to yellow or from blue to yellow, when the solvent / non-solvent ratio or the temperature is increased \textsuperscript{15,17}. In the majority of cases, formation of the blue or red solutions (or suspensions) is followed by precipitation or gel formation \textsuperscript{17-19}. These solvatochromic \textsuperscript{16,18,20-25} and thermochromic \textsuperscript{15,26} transitions have been extensively studied. Additional information on the chromatic properties in conjugated polymers can be found in reference [27].

The origin of the color change of poly-nBCMUs has been a point of considerable debate. At the heart of the debate is the fundamental question; is the chromatic transition a purely intramolecular effect or is it an intermolecular effect induced by aggregation of the PDA chains. In the former case, it has been argued that the color change is a result of a backbone conformational change; either a rod-to-coil \textsuperscript{18,20} or planar-to-nonplanar transition \textsuperscript{16}. Advocates of the intermolecular process, such as Wegner \textit{et al.} \textsuperscript{21} and Hsu \textit{et al.} \textsuperscript{22} suggested that the solvatochromic shift was the consequence of aggregation of the wormlike coils present in the yellow solution. Kim \textit{et al.} \textsuperscript{28} claimed that the chromatic transitions are primarily a result of changes in the conformational ordering of the polymer backbone and that aggregation only occurs as a secondary consequence of the conformational change. Baughman \textit{et al.} \textsuperscript{29} have proposed a different explanation in which
the polydiacetylene backbone can adopt an acetylenic or a butatrienic structure, shifting
towards the former as the backbone becomes more planar and ordered and the level of
electron delocalization increases. However, this explanation was based on the
thermochromic transitions of solid materials and not solutions. It was subsequently applied
to solutions but discredited by the NMR study of Babbit and Patel\textsuperscript{30} who saw no evidence
for a cumulenic structure in yellow solutions. This was confirmed later by others\textsuperscript{23,31}.

The exact nature of the structure and conformation of the backbone and sidegroups in
the yellow, blue and red solutions and what drives the transition between them still remains
unknown. However, evidence exists that the structure and packing of the sidegroups play
an important role in inducing the chromic change. For example, most solutions of poly-
nBCMU\textsubscript{s} having an odd number of methylene groups adjacent to the polymer backbone
undergo a change from blue to yellow, while those having an even number of methylenes
undergo red to yellow transitions\textsuperscript{15,17,22,32,33}. Poly-IBC\textsubscript{M}U is an exception to this odd-even
relationship, since it exhibits a red phase at low temperatures\textsuperscript{16}. Poly-nBCMU\textsubscript{s} with an odd
number of methylene groups can readily adopt a strain-free planar conformation with
intramolecular hydrogen bonds between adjacent sidegroups in the blue phase. In contrast,
poly-nBCMU\textsubscript{s} having an even number of methylene groups can form intramolecular
hydrogen bonds only in a slightly twisted, non-planar conformation\textsuperscript{33,34}. This results in a
shorter effective conjugation length than in the planar conformation of the blue form. It has
been suggested that in the yellow solutions the intramolecular hydrogen bonds are
completely broken\textsuperscript{13,15,17}. However, alternative explanations have been presented\textsuperscript{35,36} and
the rupture of hydrogen bonds in the yellow solutions should be considered to be unproven.
There is little doubt that the effective conjugation length is substantially smaller in the
yellow solutions as a result of static and/or dynamic disorder in the polymer backbone.

The effective average conjugation length of the blue-colored compounds, having the
lowest-energy optical transition with a wavelength maximum, $\lambda_{\text{max}}$, between 600 and 700
nm, has been estimated to be larger than 30 repeat units. The red-colored compounds (500
nm $<\lambda_{\text{max}}< 600$ nm) have an effective conjugation length between 10 and 20 repeat units,
while the yellow structures (400 nm $<\lambda_{\text{max}}< 500$ nm) have a conjugation length shorter
than 6 repeat units\textsuperscript{16}.

Recently, Donovan \textit{et al.}\textsuperscript{37} have observed ultrafast intramolecular photocurrents on
isolated rod-like poly-4BCMU chains in toluene at room temperature, while no
 photocurrent was observed in the coil-state at higher temperatures. In the present work,
flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements were
performed on poly-nBCMU solutions. The thermotropic behavior of the n-BCM\textsubscript{U}-solutions
could be followed both optically and by the photoconductivity measurements. The results
provide new insights into the opto-electronic properties of these PDAs in the rod and the
coil states.
7.2 EXPERIMENTAL

7.2.1 Materials

The synthesis and the general properties of the nBCMU polydiacetylene samples were previously described in Chapter 5. In this Chapter, polymer solutions of nBCMUs were prepared by adding several milligrams to the UV spectroscopic grade solvents (Fluka) in a 20-ml vessel and placing the vessel in an oven at 70°C for several hours. The solutions were always stored in the dark, in order to avoid photodegradation 38.

All nBCMU polydiacetylenes studied were found to be readily soluble in dioxane, resulting in clear, yellow solutions which did not change color on cooling to room temperature. On standing for several days in a refrigerator at ca. 5°C the poly-4BCMU and the poly-6BCMU solutions remained clear and yellow. In contrast, the poly-3BCMU and poly-9BCMU solutions changed to blue and aggregates consisting of small rectangular grains started to form. After several days these aggregates separated from the solution. In the case of poly-3BCMU the liquid phase became clear and colorless, while for poly-9BCMU it remained blue. After filtering off the aggregates in the latter case, the optical density at 308 nm was less than 0.03, which was too low to carry out quantitative TRMC measurements.

The 4, 6, and 9BCMU polymers could be dissolved at 70 °C to give clear yellow solutions in benzene. Poly-3BCMU could however not be readily dissolved in benzene even at 70 °C. During cooling to room temperature the 4 and 6 BCMU polymer solutions became red. On standing for several days these solutions changed to a red gel phase, which eventually separated from an upper layer of colorless solvent. The poly-9BCMU solution remained clear and yellow on cooling to room temperature. However, after standing at 5°C it changed to purple and started to form clearly visible aggregates.

When the solutions, which formed a red gel or blue solid phase on standing at 5°C for several days, were shaken they formed suspensions, which were optically clear and appeared to be homogeneous to the eye. These red and blue suspensions were relatively stable at room temperature, i.e. they did not revert to yellow solutions and they showed no signs of phase separation for several hours. These suspensions were the room temperature starting points for the heating and cooling trajectories in the optical absorption and FP-TRMC studies. While their method of preparation clearly indicates that a certain degree of aggregation of the polymer chains almost certainly occurs in the suspensions, they will be loosely referred to as red and blue solutions in the remainder of the text.

Absorption spectra were recorded using a Uvikon 940 UV/Vis spectrophotometer. The concentrations were determined, using an extinction coefficient of 17,500 l mol⁻¹ cm⁻¹ found for yellow solutions of both 3 and 4BCMU in chloroform at 468 nm 39. In the present work concentrations between 1 and 50 μM monomer units were used. Absorption spectra
were subsequently measured on heating and cooling the solutions in a thermostatted cuvette.

7.2.2 Time-resolved FP-TRMC measurements

The solutions were flash photolyzed using 7 ns FWHM pulses of 308-nm light from a Lumonics HyperEX 400 excimer laser (see Chapter 3). The maximum power flux per pulse in the cell was approximately 8 mJ/cm². This corresponds to approximately 1 absorbed photon per 25 monomer units for the concentrations used.

For flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements, the solutions are usually purged with CO₂, in order to remove air and scavenge any mobile electrons that might be formed in low-yield multiphoton ionization events.

In this Chapter, all photoconductivity measurements were obtained by measuring the change in the reflected power at the resonance frequency of a microwave resonant cavity. This can be directly related to a change in the real, or dielectric loss, component of the conductivity of the solution. The effect of varying the microwave power from ca 1 to ca 40 mW (field strengths from ca 10 to ca 70 V/cm) for solutions of 4-BCM U and 6-BCM U in benzene has been investigated. No effect was found on the value of the magnitude or the decay kinetics of the conductivity transients. The microwave circuitry, its operation and the procedure of data analysis have been described in Chapter 3.

7.3 RESULTS

Before presenting the results of the photo- and radiation-induced conductivity measurements, information on the optical properties of the nBCM U solutions will be given.

7.3.1 Optical Absorption

In dioxane the odd and even BCMUs have very different optical absorption spectra initially, see Figure 7.1. The spectra of the 4 and 6BCM U solutions are characterized by a single unstructured absorption band with a maximum at 465 nm (yellow). The slight shift to shorter wavelengths with increasing temperature can be attributed to the decrease of the dielectric constant of the solvent. The spectra for the 3 and 9 BCM U solutions are characterized by two absorption bands: one at high temperatures, which is very similar to the 465 nm band found for the even BCMUs and a broad structured band at low temperatures, which extends to ca. 680 nm. An important observation is the well-defined isosbestic points at ca. 500 nm. This indicates that the two bands correspond to two distinctly separate structures of the polymer chains, which are in thermal equilibrium. These are simply denoted as B (for blue) and Y (for yellow)
Figure 7.1 Thermochromic behavior of different n-BCMUS PDAs in dioxane. The arrows indicate the direction in which the spectra shift on heating from room temperature (thick solid line). The temperatures used were:
3BCMUs: 20, 26, 33, 39, 45, 50, 57, 63 and 70°C
4BCMUs: 20, 30, 41, 47, 55 and 65°C
6BCMU: 20, 26, 33, 39, 45, 54, 60 and 66°C
9BCMU: 20, 25, 29, 34, 39, 42, 47, 54, 64 and 73°C

From the heights of the long-wavelength spectra, the equilibrium constant, K=[Y]/[B], can be determined. In Figure 7.2 these values are plotted as ln K against 1/T for 3 and 9BCMUs. From the slopes the values of the enthalpy difference between the two structures, ΔH, can be determined and these values are listed in Table 7.1. The values of ca. 2.2 eV are in good agreement with the previous estimate made by Lim et al. 18.

Table 7.1 The enthalpy and entropy differences between the coil and rod states

<table>
<thead>
<tr>
<th>solvent</th>
<th>ΔH_{heating} (eV)</th>
<th>ΔS_{heating} (10^{-3} eV K^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3BCMUs</td>
<td>Dioxane (Y/B)</td>
<td>2.1</td>
</tr>
<tr>
<td>9BCMUs</td>
<td>Dioxane (Y/B)</td>
<td>2.3</td>
</tr>
<tr>
<td>4BCMUs</td>
<td>Benzene (Y/R)</td>
<td>1.8</td>
</tr>
<tr>
<td>6BCMUs</td>
<td>Benzene (Y/R)</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Figure 7.2 The equilibrium constant, K, plotted logarithmically versus the inverse of the temperature for 3BCMU (circles) and 9BCMU (squares) in dioxane. The dashed lines are best linear fits through the data points.

For the benzene solutions, the results are somewhat more complicated in that the even BCMUs also display a strong thermochromic effect. The optical absorption spectra of the even BCMUs show two absorption bands one at high temperatures with a maximum at 465 nm (yellow) very similar to that observed in dioxane solutions and one at 540 nm (red), see Figure 7.3. Similar to the absorption spectra for 3 and 9BCMU in dioxane, the shortest wavelength band increases with increasing temperature at the expense of the longer wavelength band. Also a well-defined isosbestic point is observed indicating the presence of rod-like and coil-like states in thermal equilibrium. The enthalpy differences obtained as for 3 and 9 BCMU in dioxane are listed in Table 7.1.

The thermochromic behavior of the 9BCMU solution in benzene is seen to be more complex than that for the even BCMUs presented above. Thus, the initial room temperature spectrum appears to consist of two separate components, one with a sharp maximum at 540 nm very similar to that for 4 and 6BCMU, and a much broader band extending to approximately 670 nm, i.e. similar to 9BCMU at room temperature in dioxane. The former, red band is seen to decrease more rapidly with increasing temperature than the latter. We conclude that two different structures contribute to the initial absorption of the 9BCMU. Because of this the transition to the ultimate high temperature yellow form does not display a well-defined isosbestic point. The initial room temperature spectrum of 9BCMU in benzene is identical with that obtained in a 60:40 hexane:chloroform mixture by Bloor et al. 40
Figure 7.3 Thermochromic behavior of different n-BCMU PDAs in benzene. The arrows indicate the direction in which the spectra shift on heating from room temperature (thick solid line). The temperatures used were:

4BCMU: 20, 26, 31, 39, 43, 48, 52, 61 and 66°C
6BCMU: 20, 26, 30, 34, 39, 43, 48, 52, 58 and 66°C
9BCMU: 20, 26, 32, 35, 39, 44, 49, 58, 63, 68 and 72°C
Figure 7.4 The thermo chromic behavior of 4, 6 and 9 BCMU in benzene. The filled circles indicate the absorption at 550 nm for a heating cycle and the open circles for a cooling cycle.

Figure 7.4 shows the optical density at 550 nm for the different BCMUs in benzene as a function of temperature. As can be seen, a considerable hysteresis is observed.

7.3.2 Photoconductivity

In Figure 7.5 photoconductivity transients are shown for the n-BCMУ solutions in dioxane at room temperature. A marked difference can be seen between the odd and even BCMU solutions. Photoexcitation of the blue solutions of 3 and 9 BCMU yields readily measurable, long-lived conductivity transients, while flash-photolysis of the yellow solutions of 4 and 6 BCMU results in a very small short-lived change in the photoconductivity. Yellow solutions of 3 and 9 BCMU could be prepared at room temperature by cooling an initially hot solution. These solutions also displayed no significant photoinduced conductivity transients as was also found for the yellow 4 and 6 BCMU solutions.
Figure 7.5 Transient changes in the photoconductivity on flash photolysis of n-BCMU solutions in dioxane at room temperature.

The results obtained for the 4, 6 and 9BCMU solutions at room temperature in benzene are presented in Figure 7.6. All three solutions are seen to yield readily measurable long-lived photoconductivity transients.

Figure 7.6 Transient changes in the photoconductivity on flash photolysis of n–BCMU solutions in benzene.
Figure 7.7 Photoconductivity transients for 4BCMU in benzene upon heating. The arrow indicates the heating cycle going from room temperature to higher temperatures. The upper solid line was recorded at room temperature (24°C); the other transients were measured at 33, 41, 46, 52, 56 and 60°C.

In Figure 7.7 the temperature dependence of the photoconductivity is presented for a solution of 4BCMU in benzene. The measured conductivity decreases upon heating and at approximately 60°C it has practically vanished.

Figure 7.8 Temperature dependence of the photoconductivity on heating (▲) and cooling (▼) starting with 4BCMU in benzene. The dashed and dotted curves represent the optical absorption at 545 nm on heating and cooling, respectively (analogous to data in Figure 7.3).
Photoconductivity of Isolated Polydiacetylene Chains in Solution

In Figure 7.8 the maxima of the conductivity transients from Figure 7.7 are shown at different temperatures together with the optical absorption of the same solution at 545 nm. The decrease in photoconductivity on heating and increase on cooling are seen to closely follow the changes in the 545 nm absorption corresponding to the red form of the polymer. Similar results were found for the 6 and 9BCMU in benzene and the 3 and 9BCMU in dioxane.

**Table 7.2** $\phi_p \Sigma \mu_{\text{run}}$ (product of the quantum yield for charge carrier generation and the lower limit of sum of the charge carrier mobilities) determined at the end of the laser pulse for different BCMU dioxane or benzene solutions at room temperature

<table>
<thead>
<tr>
<th>PDA-derivatives</th>
<th>dioxane</th>
<th>benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>color</td>
<td>$\phi_p \Sigma \mu_{\text{run}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($\times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$)</td>
</tr>
<tr>
<td>3BCMU</td>
<td>B</td>
<td>3.0 $\pm$ 0.5</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.05 $\pm$ 0.02</td>
</tr>
<tr>
<td>4BCMU</td>
<td>Y</td>
<td>0.07 $\pm$ 0.03</td>
</tr>
<tr>
<td>6BCMU</td>
<td>Y</td>
<td>0.07 $\pm$ 0.03</td>
</tr>
<tr>
<td>9BCMU</td>
<td>B</td>
<td>0.8 $\pm$ 0.2</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.05 $\pm$ 0.02</td>
</tr>
</tbody>
</table>

As mentioned in the experimental section the transient change in the conductivity is given by $\Delta \sigma = eN(t) \Sigma \mu(t)$. The charge carrier concentration is equal to $N(t) = N_{\text{abs}} \phi_p P(t)$, with $N_{\text{abs}}$ the number of absorbed photons per unit volume, $\phi_p$ the quantum efficiency for charge carrier generation and $P(t)$ the fraction of charge carriers that has survived recombination at time $t$. Since $P(t) \leq 1$ and $\Sigma \mu(t) \leq \Sigma \mu(0)$ the value of $\Delta \sigma/eN_{\text{abs}}$ at the end of the laser pulse provides a lower limit of $\phi_p \Sigma \mu$ at zero time. In Table 7.2 the values of $\phi_p \Sigma \mu_{\text{run}}$ obtained from the conductivity in Figures 7.5 and 7.6 at the end of the laser pulse are given for the different BCMUs in dioxane and benzene at room temperature.

To obtain a more detailed insight into the decay kinetics of the photoconductivity the measurements on 4BCMU solutions in benzene were extended to longer timescales and lower light intensities. The light-intensity normalized photoconductivity transients are plotted double logarithmically in Figure 7.9. The decay of the conductivity transients after the initial growth during the pulse is seen to be approximately linear on this double logarithmic representation indicating an inverse power-law time dependence, i.e. $\Delta \sigma \propto 1/t^\alpha$. The dashed straight line in Figure 7.9 corresponds to $\alpha = 0.4$.  

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Figure 7.9 Light-intensity normalized photoconductivity transients for a 4BCMU solution in benzene plotted double logarithmically for five different excitation energy fluxes. The initial rise below 10 ns is due simply to the increase in conductivity occurring during the laser pulse. The dashed line corresponds to an inverse power law time dependence of the decay.

7.4 DISCUSSION

7.4.1 Optical Absorption of BCMU solutions

The thermochromic behavior of n-BCMUs in dioxane and benzene shown in Figures 7.1 and 7.3 is similar to results obtained in other solvents \(^{15,18,21}\) and solvent mixtures \(^{22}\). Three states can be distinguished, characterized by yellow, red and blue colors. The enthalpies of formation of the blue and red forms from the yellow form of \(-2.2\) eV and \(-1.8\) eV respectively indicate that the blue form is energetically the most stable of the three. The broad structureless spectrum of the yellow form is attributed to a coil-like configuration of the polymer backbones with relatively short conjugation lengths. The red and blue forms are considered to result from the adoption of a more planar backbone structure with a higher degree of conjugation. Both long-wavelength forms display well-defined structure in their absorption bands indicative of strong coupling with the vibrational modes of the polymer backbone and only a narrow distribution of conjugation lengths.

In the case of the yellow forms there is little doubt that true solutions are formed with the polymer chains isolated from each other. The blue and red forms however form solid precipitates and gels, respectively, on standing and their method of preparation in the present work makes it almost certain that these are suspensions of at least partially
aggregated polymer chains rather than solutions of isolated polymer chains. The overall spectral characteristics, thermodynamics, and type of aggregation (i.e. solid versus gel) indicate that the planarity of the backbone and the conjugation length, are greater in the blue form. Both red and blue forms do however appear to have a very regular, rod-like backbone structure as evidenced by the sharpness of the vibrational bands in both cases. The appearance of both blue and red states together in 9BCMU has been found previously in a 60:40 hexane:chloroform mixture by Bloor et al. The latter work also shows solutions with the 'pure' blue and red forms and discussed the dependence of the polymer structure on solvent. The blue form shows distinct Raman spectra close to those of the initial crystalline materials, which agrees with the observation of crystallites in the blue BCMU solutions. The red form has been found to have Raman spectra with very similar frequencies for the double and triple stretching modes for a variety of polydiacetylenes. Thus, the backbone structures would appear to be very similar despite differences in sidegroup structure.

7.4.2 Photoconductivity of dilute BCMU solutions

The most prominent characteristic of the photoconductivity of the BCMU solutions studied is the complete contrast between the yellow solutions, which display an extremely small, short-lived conductivity, and the red and blue solutions for which large, long-lived conductivity transients are observed. This is in agreement with the observations of Donovan et al. who studied the photoconductivity of a toluene solution of 4BCMU using the Austin switch technique. The differences observed could be ascribed to the influence of the backbone conformation on the mobility of the charge carriers formed. Thus the static and dynamic backbone disorder of the yellow form, as evidenced by its broad structureless absorption spectrum, would be expected to result in a considerably lower mobility than the more extended backbone conjugation and rigidity associated with the red and blue forms.

However, the possibility cannot be completely dismissed that the difference is a result of aggregation which undoubtedly (eventually) occurs in the case of the longer wavelength forms but is definitely absent in the case of the yellow solutions. The readily observable transients observed in the former "solutions" could then be ascribed to the occurrence of interchain exciton dissociation within aggregated chain segments resulting in an electron and hole on separate polymer chains. This could retard the rapid geminate recombination of charges which would take place on isolated chains.

Donovan et al. purported that in their experiments the chains were isolated even for the red solutions of 4BCMU. In our case it is quite certain that aggregation must be present in the initial red and blue solutions investigated because of the method of preparation. However, in the temperature study of 4BCMU shown in Figure 7.8, the conductivity signal was found to return precisely to the level found for the initial solution when it was cooled.
down. Since the cooling took place over a period of minutes while visual evidence of gel formation, even on standing at 5°C, takes several hours, it is presumed that much less chain aggregation was present in the freshly cooled solution while the photoconductivity was unchanged. This would therefore suggest that the large conductivity transients observed for the red form are in fact mainly due to the higher mobility of the charge carriers rather than to an interchain mechanism of formation. It has however been clearly demonstrated, in identical TRMC experiments on a benzene solution of a phenylene-vinylene polymer, that chain aggregation can result in an order of magnitude larger photoconductivity transients as a result of interchain exciton dissociation\textsuperscript{43,44}.

Differentiation between the red and the blue forms of the present BCMUs is more difficult since the values of $\phi_{p}\Sigma\mu_{mm}$ all lie within the range $0.8 \times 10^{-4}$ to $3 \times 10^{-4}$ cm$^2$/Vs with the two blue solutions of 9 BCMU lying at the bottom of the range and the blue solution of 3 BCMU in dioxane at the top. On comparing the optical spectra it is apparent that the vibrational fine structure for 9 BCMU is substantially broader than for 3 BCMU. This is taken to indicate that the polymer backbone in the latter case has a more uniform structure. Therefore, the higher value of $3 \times 10^{-4}$ cm$^2$/Vs for $\phi_{p}\Sigma\mu_{mn}$ is considered to be associated with a well-defined planar, all-trans configuration. The vibrational bands in the red solution spectra of 4 BCMU and 6 BCMU in benzene are very similar to each other and also similar in width to that for the blue 3 BCMU solution in dioxane. The somewhat lower values of $\phi_{p}\Sigma\mu_{mm}$ for the "red" compounds, i.e. $1.4 \times 10^{-4}$ and $1.1 \times 10^{-4}$ cm$^2$/Vs are therefore considered to be a result of the shorter conjugation length resulting from a lack of perfect coplanarity in what is otherwise a well defined, all-trans backbone structure. In agreement with this, the photoconductivity in thin films is also found to be lower in red as opposed to blue forms of diacetylenes, which can be interconverted from blue to red in the solid state by high-temperature annealing. Similar results on a thin film of another polydiacetylene derivative were reported recently by Savenije et al.\textsuperscript{45}.

As can be seen from Figure 7.6, a substantial decay of the photoconductivity transients occurs over a timescale of tens of nanoseconds following the laser pulse. This is still much longer however than the very rapid, nanosecond decay time found in the recent DC flash-photoconductivity study of 4-BCMU in toluene by Donovan et al.\textsuperscript{37}. However, the laser pulse width in our measurements was 7 ns, i.e. much longer than the 25 ps used in reference \textsuperscript{37}. In addition the risetime of detection was an order of magnitude longer than the 700 ps of the previous work. These two facts combined help to explain, at least in part, why we were unable to observe the very rapid decay process observed in that work. Another factor which might contribute to a difference between the decay kinetics is the much higher intensity (in photons/cm$^2$/s) used in the work of Donovan et al.\textsuperscript{37}. In Figure 7.9 the gradual decrease in the magnitude of the transients and increase in the decay rate with increasing laser pulse
intensity indicates that charge recombination becomes more important as the initial charge carrier concentration increases. However, for the two lowest intensities used, the difference in the decay is not very large and therefore at these intensities it can be assumed that homogeneous charge recombination does not play a dominant role. Because of lack of quantitative information about the geminate recombination, it is assumed that this contribution to the decay can be neglected at long times.

The decay kinetics at long times can be well described by a t\(^{\alpha}\) law (with \(\alpha=0.34\pm0.04\)). Note, that this value of \(\alpha\) is much lower than the value close to unity found by Movaghari et al.\(^{46}\) in PTS crystals. Alternatively, Hunt et al.\(^{47}\) and Rughooputh et al.\(^{48}\) found that the charge carrier decay in PDA-10H crystals could well be described by an exp(-bt\(^{1/3}\)) law, which is characteristic of deep trapping in a one-dimensional system.

A power-law dependence of the decay of the mobility is characteristic for a thermally activated hopping motion in a disordered energy landscape with shallow traps with an exponential distribution of their depths \(^{49-52}\). In such an energy landscape each localisation site of the charge carrier can act as a temporary trap. The dwell time in a trap increases with the depth. As time proceeds it becomes more likely that a charge carrier has encountered a deeper trap and consequently the mobility of the charge carrier decreases with time.

For times exceeding the inverse of the average frequency for hopping between adjacent traps and for a sufficiently small external electric field the relaxation of the charge carrier mobility in an energy landscape with an exponential trap distribution can be described by the inverse powerlaw (see Eq. (22) in \(^{52}\))

\[
\mu(t) = \frac{e w_0 a^2 A}{(w_0 t)^\alpha} \tag{7.1}
\]

with

\[
\alpha = \frac{T_0 - T}{T_0 + T} \tag{7.2}
\]

In Eqs. (7.1) and (7.2) \(e\) is the electronic charge, \(w_0\) is the attempt frequency for hopping, \(a\) is the jump distance between adjacent traps, \(T\) is the temperature and \(k_B T_0\) is the average trap depth with \(k_B\) the Boltzmann constant. The factor \(A\) in Eq. (7.1) depends on the average trap depth and the temperature, see \(^{52}\). Note, that Eq. (7.1) is only valid for an electric field strength \(E \leq k_B T(ea)\). As discussed in the experimental section the maximum electric field strength in the experiments is \(E=10^4\) V/m. This field strength is sufficiently low for Eq. (7.1) to be applicable for jump distances less than 2.5 \(\mu\)m, which corresponds to 5000 monomer units. According to Eq. (7.1) the slope of the decay of the conductivity in Fig. 7.9 (i.e. the value of \(\alpha\)) is entirely determined by the average trap depth \(k_B T_0\). As discussed
above the experimental results yield $\alpha = 0.34 \pm 0.04$, which corresponds to an average trap depth of $0.05 \pm 0.005$ eV.

7.5 CONCLUSIONS

n-Butoxycarbonylmethylurethane-polydiacetylenes, nBCMU-PDAs, undergo thermo- and solvatochromic transitions in solution. Odd BCMUs undergo a rod-to-coil transition visualized as a blue to yellow color change, while the even BCMUs change from red to yellow. The isolated rod state (blue or red) is metastable and reverts to a gel-like form in the case of the red state, while the blue state forms crystallites, which eventually precipitate. The rod-to-coil transitions can be followed as changes in the optical absorption spectra of the solutions. The observation of the co-existence of both a blue and a red form for 9BCMU in benzene is exceptional.

Photoexcitation of BCMU solutions in the rod state results in a large transient change in the photo conductivity as monitored using the time-resolved microwave conductivity (TRMC) technique, while hardly any signal can be observed in the coil-state (in dioxane). The thermochromic shift going from the rod state at room temperature to the coil state at $65^\circ$C could be followed by measuring the conductivity, which showed a gradual decrease with temperature close to that found for the long-wavelength optical absorption. It can not be conclusively ruled out that the large conductivities found for the rod state do not arise from interchain exciton dissociation in aggregated segments. The lower limit of the product of the quantum efficiency for charge carrier formation, $\phi_p$, and the sum of the charge carrier mobilities, $\Sigma \mu_{\text{max}}$, is found to be $\phi_p\Sigma \mu_{\text{max}} = 1.2 \pm 0.2 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ for the red state, while a slightly larger value of $3.0 \pm 0.5 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ was found for the blue state.

The conductivity signal eventually decays during time according to a power law with a power $\alpha = 0.34 \pm 0.04$. This observation suggests a decay of the charge carrier mobility as a consequence of their motion in a disordered energy landscape with shallow traps. The experimental decay could be described assuming an exponential distribution of trap depths with an average depth of $0.05 \pm 0.005$ eV.

REFERENCES

(6) Sauteret, C.; Hermann, J. P.; Frey, R.; Pradère, F.; Ducuing, J.; Baughman, R. H.; Chance, R. R.
Photoconductivity of Isolated Polydiacetylene Chains in Solution


(42) Bloor, D. Polymer 1999, 40, 3901 ff.


Charge Transport in Polydiacetylenes


Summary

Polydiacetylenes constitute a class of unusual polymeric materials, since they can be produced as almost perfect single crystals by solid state polymerization of the monomer crystals. In an ideal polydiacetylene crystal the polymer backbones are straight and parallel to each other. The pendant groups determine the spacing between the backbones. Polydiacetylenes have semiconducting properties and each polydiacetylene backbone may therefore be considered to function as a one-dimensional wire. Polydiacetylenes received much attention because of their potential as materials for applications in photolithography, nonlinear optics and molecular electronic devices.

In reality, the charge carrier transport in polydiacetylenes is perturbed due to various effects. Defects in the structure, introduced in the polydiacetylene crystals during the monomer synthesis or during the solid-state polymerization, can deform the polymer backbones and act as charge carrier traps. Static and dynamic disorder can distort the planarity of the polymer backbone. It has been argued that in some cases the pendant groups can distort the backbone conformation by means of polarity or steric hindrance effects. Distortion of the polymer backbone lowers the effective conjugation length and hinders the charge carrier transport.

In this thesis, results are presented of charge transport studies in polydiacetylene crystals and polydiacetylenes in solution. Charge carriers are produced by pulsed irradiation with high-energy electrons or UV light. The radiation-induced conductivity is measured using the electrodeless time-resolved microwave conductivity (TRMC) technique. This technique is applied to bulk powdered samples, single crystals and isolated PDA chains in solution. The measurements provide results on the magnitude of the charge carrier mobility and the decay kinetics of the charges in these systems. The results presented in this thesis may help to understand the effect of defects, backbone conformation and pendant groups on both the charge carrier mobility and charge decay kinetics. This information can be used to design new polydiacetylenes with high charge carrier mobilities and long lifetimes for future applications.

In the first chapter a short introduction on charge transport in conjugated polymers is given and the chapter is concluded with an outline of this thesis. Chapter 2 provides a
literature review on the structure of polydiacetylenes and the charge transport in these materials. The crystal structure of the different polydiacetylenes and the backbone conformation are topics which are briefly addressed in the first part of this chapter. The last part comprises an extensive review on the research carried out on the conductive properties of polydiacetylenes. The earliest research on polydiacetylenes involved studies of the dark conductivity of samples in which charge carriers were introduced by doping. Later, the interest has focussed more on the charge carrier mobility. This is the property which determines important practical parameters such as the switching speed of device structures.

Chapter 3 is the experimental section, in which the basic concepts of the Time-Resolved Microwave Conductivity (TRMC) technique used in this work are explained. The TRMC technique is a contactless, high-frequency conductivity technique. Changes in the conductivity due to the formation of charges in diacetylene derivatives can be monitored time resolved. Short pulses of light (4 eV) from a laser or high-energy electrons (3 MeV) from an electron accelerator were used to produce the free charge carriers. Particular attention is given to the application of this technique to the study of the charge transport in polydiacetylene systems in different forms, such as polycrystalline powders, single crystals and dilute solutions and the charge transport in different directions in single crystals.

The radiation-induced in-situ polymerization of four diacetylene derivatives has been investigated in Chapter 4. The aim of the work described in this chapter is to obtain insight into the effect of accumulated radiation dose on the mobility and the decay of the charge carriers in polymerized diacetylenes. The radiation-induced conductivity after a single electron pulse was monitored as a function of the accumulated dose. The radiation-induced conductivity was found to be very different for the different derivatives. While the polymerization in the urethane-substituted diacetylenes (ETCD, 4BCMU and IPUDO) immediately starts at low accumulated dose, the polymerization of DCH shows a threshold behavior. At high accumulated dose the radiation-induced conductivity decreases for all diacetylenes investigated, which is attributed to the introduction of defect sites by high energy radiation. For low accumulated doses the minimum value of the charge carrier mobility is of the order of 1 cm²V⁻¹s⁻¹. For doses which are conventionally used for the polymerization of polydiacetylene crystals the charge carrier mobility is about one order of magnitude lower than for low accumulated doses. Although full polymer conversion is attained at these high doses, the conductive paths for charge transport have become far from optimal.

In Chapter 5 the pulse-radiolysis TRMC technique has been applied to bulk samples. Differences in both charge carrier mobility and decay kinetics have been found for samples which were either prepared by different monomer synthesis and/or a different polymerization route. The polydiacetylene derivatives studied show minimum values of the charge carrier mobility between 0.02 and 1.2 cm²V⁻¹s⁻¹. The most perfect crystals exhibit
mobilities at the upper limit of this range, while for less perfect crystals the mobilities are significantly reduced. Most polydiacetylenes produced using γ-radiation show lower charge carrier mobilities than their heat-polymerized equivalents. The domains in which the charge carriers can move freely are smaller in the γ-polymerized samples as is evidenced by the contribution of homogeneous recombination to the conductivity decay. The conductivity decay in the heat-polymerized polydiacetylenes is found to be best described by a stretched exponential law. The conductivity decay in the majority of γ-radiation polymerization polydiacetylenes is best described by an inverse power law with a power close to 1. At present it is not clear which charge transport mechanism might explain such a behavior. In the poly-nBCMU's the powers found are much lower, which may suggest that the charge carriers in these compounds move in a disordered energy landscape, giving rise to a relaxation of the charge carrier mobility.

The radiation-induced conductivity was found to depend significantly on temperature. The observed increase in the conductivity with temperature is attributed to thermally-activated charge transport. The extent to which the charge carrier mobility is thermally activated differs between the different derivatives, the temperature dependence for the poly-nBCMU's being extremely weakly. For most polydiacetylenes studied, the decay of the radiation-induced conductivity becomes faster with decreasing temperature. Poly-TCDU was found to be an exceptional case since the conductivity decay increased with temperature. The radiation-induced conductivity observed in poly-BCMU's shows an irreversible decrease around +100°C on heating, accompanied with a faster decay after the transition. In these compounds a metallic-to-red transition was observed, with a more disordered phase at the higher temperature. The greater disorder explains the lower charge carrier mobility and the faster charge carrier decay.

The conductivity measurements on pulverized samples in Chapter 5 yield an average of the charge carrier mobility in the directions along and perpendicular to the polymer backbone. In Chapter 6 the PR-TRMC technique was used to study the mobility of charge carriers for different orientations of the polymer backbones with respect to the electric field direction. The mobility along the direction of the polydiacetylene backbones is larger than in a perpendicular direction. The anisotropy is strongly dependent on the method of monomer crystal preparation and the way of polymerization the monomer crystals. The lower anisotropy observed in γ-radiation polymerized polydiacetylenes is mainly attributed to the introduction of defects which reduce the intrachain charge carrier mobility. It can however not be ruled out that the intrachain mobility is reduced due to a distorted polymer backbone. From comparison between a UV polymerized and γ-radiation polymerized 4BCMU sample it could also been concluded that polymerization of a diacetylene single crystal using high dose rate UV laser pulses gives rise to a larger anisotropy in the charge carrier mobility.

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In Chapter 7 the effect of backbone conformation on the conductivity is studied in dilute solutions of the poly-(n-butoxycarbonylmethylurethane) diacetylenes, which show the order-disorder (rod-to-coil) transitions. The conformational changes in solution are accompanied by large spectroscopic changes indicative of a major modification of the polymer electronic structure at the transition. In this thesis, three different phases (evidenced by a blue, red and yellow color) could be observed. The blue and red phase are thought to exhibit a planar backbone conformation. In the red phase the conjugation on the polymer backbone is more disrupted than in the blue phase, due to conformational kinks. The main chain conformation in the yellow (coil) phase is even more deformed, which leads to a further reduction of electronic delocalization. This reduction in the electronic delocalization along the polymer backbone has a large effect on the conductivity in these different states. The solvato- and thermochromic behavior of dilute poly-(n-butoxycarbonylmethyl-urethane) diacetylene solutions were studied both optically and by photoconductivity measurements. For both blue and red solutions large, long-lived photoconductivity transients are observed, while the yellow solutions display an extremely small, short-lived conductivity. It is not possible to distinguish whether this difference in photoconductivity is due to a difference in charge carrier mobility or to a difference in charge carrier formation. It seems reasonable to assume that this difference is due to a difference in charge carrier mobility, since the static and dynamic backbone disorder of the yellow form is much larger than in the red or blue forms. A difference in the photoconductivity between the blue and red phases in solution was less prominent. The somewhat lower conductivity values obtained for the red solutions tend to support the suggested lower conjugation length in this red phase.
Samenvatting

Polydiacetylenen vormen een uitzonderlijke klasse van polymeren, omdat ze gemaakt kunnen worden als bijna perfecte één-kristallen via vaste stof polymerisatie van de monomeer-kristallen. In een ideaal polydiacetylen kristal zijn de polymeer-hoofdketens recht en liggen ze parallel ten opzichte van elkaar. De zijketens bepalen de afstand tussen de hoofdketens. Polydiacetylenen hebben half-geleidende eigenschappen en elke polydiacetylen hoofdketens kan daarom beschouwd worden als een 1-dimensionaal stroomdraadje. Polydiacetylenen hebben veel belangstelling gekregen vanwege de mogelijke toepassing als materiaal in de foto-lithografie, niet-lineaire optica en microelectronica.

In werkelijkheid is het ladingstransport in polydiacetylenen verstoord. Structuur-defecten, geïntroduceerd in de polydiacetylen kristallen tijdens de monomeer synthese of tijdens de vaste stof polymerisatie, kunnen de polymeer hoofdketens vervormen en optreden als ‘trap’ voor ladingsdragers. Statische en dynamische wanorde in het kristal kunnen de rechtheid van de hoofdketens ook verstoren. Er is verondersteld dat in sommige gevallen de zijketens de vorm en ligging van de hoofdketens kunnen verstoren door polariteitseffecten en sterische hinder. Verstoring van de polymeer hoofdketens verkleint de effectieve conjugatielengte en belemmert het ladingstransport op de ketens.

In dit proefschrift worden resulten gepresenteerd van een studie van het ladingstransport in polydiacetylen één-kristallen en in polydiacetylenen in oplossing. Ladingsdragers worden aangemaakt door gepulste bestraling met hoog-energetische electronen of UV licht. De stralingsgeïnduceerde geleiding werd gemeten met behulp van de contactloze tijdsopgeloste microgolfgeleidings (TRMC) techniek. Deze techniek is toegepast op bulk gepoederde samples, één-kristallen en geïsoleerde PDA ketens in de oplossing. Tevens is de geleiding in verschillende richtingen in één-kristallen gemeten. De resultaten van deze metingen geven informatie over de grootte van de ladingsdragersbeweeglijkheid en de vervalkinetiek van de ladingen in deze systemen. De resultaten die in dit proefschrift gepresenteerd zijn vergroten het inzicht in de effecten van defecten, hoofdketen conformatie en zijketens op zowel de ladingsdragersbeweeglijkheid als de vervalkinetiek van de ladingen. Deze informatie kan gebruikt worden om nieuwe polydiacetylen
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materialen met hoge beweeglijkheden en lange levensduur te ontwerpen voor toekomstige toepassingen.

In het eerste hoofdstuk wordt een korte inleiding over het ladingstransport in geconjugeerde polymeren gegeven en het hoofdstuk wordt afgesloten met een overzicht van de inhoud van dit proefschrift.

Hoofdstuk 2 geeft een overzicht van de literatuur over de structuur van polydiacetylenen en het ladingstransport in deze materialen. De kristalstructuur van de verschillende polydiacetylenen en de hoefdketen conformatie zijn onderwerpen die kort worden behandeld in het eerste gedeelte van dit hoofdstuk. Het laatste gedeelte bevat een overzicht van de grote hoeveelheid onderzoek aan de geleidende eigenschappen van polydiacetylenen. In het begin was het onderzoek voornamelijk gericht op de intrinsieke geleiding van polydiacetylenen, waarin de ladingsdragers werden geïntroduceerd door doping. Later is de interesse meer verschoven naar de metingen van de ladingsdragersbeweeglijkheid. Dit is de grootteid die belangrijke praktische parameters bepaalt, zoals de schakelsnelheid van een transistor.

Hoofdstuk 3 is het experimentele gedeelte, waarin de basisconcepten van de tijdsopgeloste microgolfgeleidingstechniek (TRMC) worden uitgelegd. De TRMC techniek is een hoogfrequente geleidingstechniek, waarin geen electrode-contacten nodig zijn. Veranderingen in de geleiding, veroorzaakt door de vorming van ladingsdragers in de polydiacetylenen, kunnen in de tijd gevolgd worden. Korte lichtpulsen (4 eV) van een laser of korte pulsen hoog-energetische electronen (3 MeV) van een elektronenversneller werden gebruikt om 'vrije' ladingsdragers in het materiaal aan te maken. Speciale aandacht worden besteed aan de toepassing van de TRMC techniek voor de bestudering van ladingstransport in polydiacetylenen systemen in verschillende vormen, zoals polykrystallijne poeders, één-kristallen een verdunde oplossingen.

De stralingsgeïnduceerde in-situ polymerisatie van vier verschillende polydiacetylenen wordt besproken in hoofdstuk 4. Het doel van het onderzoek, dat in dit hoofdstuk beschreven staat, is inzicht krijgen in het effect van de totale stralingsdosis op de beweeglijkheid en het verval van de ladingsdragers in de gepolymeriseerde diacetylenen. De stralingsgeïnduceerde geleiding na een enkele electron puls werd gevolgd als functie van de totale dosis. De stralingsgeïnduceerde geleiding was verschillend in de verschillende polydiacetylenen. De polymerisatie in de urethaan-gesubstitueerde diacetylenen (ETCD, 4BCMU and IPUDO) begint onmiddellijk bij lage dosis, terwijl de polymerisatie van DCH een drempeldosis vertoont. Bij hoge dosis neemt de stralingsgeïnduceerde geleiding af voor alle bestudeerde diacetylenen, wat wordt toegeschreven aan defecten die worden aangemaakt door de hoog-energetische straling. Voor lage dosis werd voor de beweeglijkheid een minimum waarde gevonden in de orde van 1 cm²V⁻¹s⁻¹. Voor stralingsdosissen die normaal gebruikt worden om polydiacetyleen kristallen te
polymeriseren is de beweeglijkheid ongeveer een orde van grootte kleiner dan voor lage dosis. Alhoewel met deze hoge dosissen volledige polymerisatie wordt verkregen, is het geleidingpad voor ladingstransport ernstig verstoord.

In hoofdstuk 5 werden gepoederde monsters bestudeerd. Verschillen in de beweeglijkheid en de verval kinetiek van de ladingsdragers zijn gevonden voor polydiacetylenen gemaakt via verschillende monomeer synthese en/of verschillende polymerisatie routes. Voor de bestudeerde polydiacetylenen werden minimum waarden tussen 0.02 en 1.2 cm²V⁻¹s⁻¹ gevonden voor de ladingsdragersbeweeglijkheid. De meest perfecte kristallen hebben beweegelijkheden met waarden aan de bovenkant van deze range, terwijl de beweegelijkheid in de minder perfecte kristallen aanzienlijk lager is. De meeste polydiacetylenen, die met γ-straling gemaakt zijn, hebben lagere beweegelijkheden dan hun thermisch-gepolymerizeerde equivalenten. Ook zijn de domeinen waarin de ladingsdragers vrij kunnen bewegen veel kleiner, wat blijkt uit de kleine bijdrage van homogene recombinaat tot de vervalkinetiek van de geleiding. De vervalkinetiek in de thermisch-gepolymeriseerde polydiacetylenen kan het beste beschreven worden door een 'stretched-exponentieel' gedrag. De kinetiek in de meerderheid van de γ-gepolymeriseerde polydiacetylenen wordt het beste beschreven door een ‘inverse-power’ gedrag met een macht dichtbij 1. Tot op heden is het niet duidelijk welk transport mechanisme zo’n gedrag zou kunnen verklaren. In de poly-nBCMU’s zijn de machten echter veel lager, wat zou kunnen duiden op een transport van ladingsdragers in een wanordelijk energielandschap, waardoor de ladingsdrager beweeglijkheid afneemt in de loop van de tijd.

De stralingsgeïnduceerde geleiding is afhankelijk van de temperatuur. De waargenomen toename van de geleiding met de temperatuur kan worden toeschreven aan thermisch-geactiveerd ladingstransport. De mate waarin de beweeglijkheid thermisch geactiveerd is verschilt voor verschillende polydiacetylenen. Voor de meeste polydiacetylenen die bestudeerd zijn, wordt het verval van de stralingsgeïnduceerde geleiding sneller bij verlaging van de temperatuur. Poly-TCDU is hierop echter een uitzondering omdat hierin het verval juist sneller wordt bij verhoging van de temperatuur. De stralingsgeïnduceerde geleiding in de poly-nBCMU's vertoont tijdens het verhitten een irreversibele verlaging rond +100°C, wat vergezeld gaat met een sneller verval van de geleiding na deze overgang. In deze stoffen treedt een fase-overgang op, waarbij de kleur verandert van metallic naar rood en waarbij een meer wanordelijke fase wordt verkregen na verhitting. De toename van de wanorde verklaart de lagere beweeglijkheid en het snellere verval van de geleiding.

De geleidingsmetingen aan verpulverde polydiacetylene kristallen leveren een gemiddelde van de beweegelijkheden in de richting van en loodrecht op de polymeerketens op. In hoofdstuk 6 werd geleidbaarheid bestudeerd in één-kristallen voor verschillende orientaties van de polymeerketens in het elektrische veld. De beweeglijkheid in de richting van de polymeerketens is groter dan in een richting loodrecht erop. De grootte van

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anisotropie in de beweeglijkheid hangt sterk van de wijze waarop het monomeer kristal bereid en gepolymeriseerd wordt. De lagere anisotropie in γ-gepolymeriseerde polydiacetylenen wordt voornamelijk toegeschreven aan geïntroduceerde defecten, die de beweeglijkheid langs de keten verlagen. Het kan echter niet worden uitgesloten dat de beweeglijkheid langs de keten lager is door een verstoring van de polymeerketen. Door een UV-gepolymeriseerd en een γ-gepolymeriseerd 4BCMU polydiacyleen te vergelijken bleek dat de polymerisatie van een polydiacyleen één-kristal met hoge dosis UV laser pulsen leidt tot een grotere anisotropie in de beweeglijkheid.

In hoofdstuk 7 wordt het effect bestudeerd van de keten conformatie op de geleiding in poly-(n-butoxycarbonylmethylurethaan) diacetylenen in verdunde oplossingen. De veranderingen in ketenconformatie bij de orde-wanorde overgangen worden gevisualiseerd door grote spectroscope veranderingen, welke uiten op een belangrijke verandering in de electronische structuur van het polymeer. In dit proefschrift werden drie verschillende fases waargenomen (aangeduid door een blauwe, rode en gele kleur). Aan de blauwe en aan de rode fase worden een rechte ketenconformatie toegeschreven. Door knikken in de polymeerketen in de rode fase is de conjugatie van de polymeerketen echter meer verbroken dan in de blauwe. De ketenconformatie in de gele vorm is nog meer vervormd, wat leidt tot een verdere afname van de electronische delocalisatie op deze ketens. Deze afname van de electronische delocalisatie langs de polymeerketen heeft een groot effect op de geleiding in deze verschillende fases. Het solvato- en thermochromische gedrag van de verdure poly-(n-butoxycarbonylmethylurethaan) diacyleen oplossing werd bestudeerd zowel door gebruik te maken van optische als van fotogeleidings-experimenten. Voor zowel de blauwe als voor de rode oplossing worden grote, lange-levende fotogeleidingssignalen gemeten, terwijl deze in de gele oplossingen juist extreem klein en kort levend zijn. Het lijkt redelijk om aan te nemen dat het verschil is toe te schrijven aan een verschil in beweeglijkheid, omdat de statische en dynamische wanorde in de gele vorm veel groter is dan in de rode of blauwe vormen. Het verschil in fotogeleiding tussen de blauwe en rode fase in oplossing is niet zo duidelijk. De iets lagere fotogeleiding in de rode oplossing leidt echter wel te kloppen met de lagere conjugatie lengte in deze fase.
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Dankwoord
Romano Julma Oscar Maria Hoofman was born in Hulst on the 14th of March 1971. He started secondary school at the "Jansenius Scholengemeenschap" in Hulst, where he obtained his diploma atheneum-β in May 1989. In September of that same year he started the study "Molecular Sciences" at Wageningen Agricultural University. He performed research projects in Experimental Physics (under supervision of dr.ir. C.A. Vriezinga) and in Molecular Physics (under supervision of Prof. dr. T.J. Schaafsma). He obtained his MSc degree in chemistry in November 1995. From September 1995 to September 2000 he carried out postgraduate research in the Radiation Chemistry Department of the Interfaculty Reactor Institute at the Delft University of Technology. His research topic was "one-dimensional charge transport in isolated and bulk conjugated polymers". The results of this research are presented in this thesis and in a number of publications. Since September 2000 he has been employed as a senior scientist Semiconductor Process Modules at Philips Research in Leuven, Belgium.
List of Publications

(1) "Charge Migration in Pulse-Irradiated Undoped C60 powder Studied with the Time-Resolved Microwave Conductivity Technique"
R.J.O.M. Hoofman, G.P. van der Laan, M.P. de Haas and K. Tanigaki

(2) "Anisotropy of the charge-carrier mobility in polydiacetylene crystals"
R.J.O.M. Hoofman, L.D.A. Siebbeles, M.P. de Haas, A. Hummel and D. Bloor

(3) "Highly mobile electrons and holes on isolated chains of the semiconducting polymer poly(phenylene vinylene)"
Nature (1998) 392, March 5, pp 54-56

(4) "De Bewegelijkheden van Elektronen en Gaten langs Afzonderlijke Polymeerketen"
Nederlands Tijdschrift voor de Natuurkunde (1998) 64 (8) pp 214-217

(5) "Charge Carrier Dynamics in para-Toluene Sulphonate Polydiacetylene Crystals"
R.J.O.M. Hoofman, L.D.A. Siebbeles, M.P. de Haas, M. Szablewski and D. Bloor
Synthetic Metals (1999) 102 () pp 1417-1418

(6) "Polydiacetylenes"
In Supramolecular Photosensitive and Electro-active Materials, edited by Nalwa, H.S.
accepted by Academic Press

"The Influence of Backbone Conformation on the Photoconductivity of Polydiacetylene Chains"
Accepted for publication in Macromolecules

"Dose Dependence of the Charge Carrier Mobility and Decay Kinetics in Radiation Polymerized Diacetylenes"
Submitted