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Structural investigations and processing of electronically and protonically conducting polymers

VTT

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Abstract

Various conducting polymers form a special class of materials with the potential for many applications in organic electronics and functional materials. These polymers can be electronically conducting or semiconducting due to a conjugated polymer backbone, or alternatively possess conductivity due to mobile protons or other ions. This thesis discusses such conducting polymers and shows ways how they can be processed by printing and how the nanostructure allows controlling their electrical properties.

The printability of conducting polymers, studied in paper I, has opened up new fields for their use in electronics. We showed that conducting polymers like polyaniline can be printed with industrial printers and high speed (up to 100 m/min) on paper achieving 60 µm resolution.

One of the most promising fields for conducting polymers is sensor applications. Papers II and III show how polyaniline can be utilised to detect changes in temperature and moisture by selecting suitable counter-ions. Melting of the counter-ion side chains was found to induce a reversible change in conductivity. On the other hand, humidity triggered an irreversible change in conductivity due to crystallisation and phase-separation of the counter-ion.

Paper IV studies the effect of polymer microstructure in resistive memory devices. Even though the structure of polymers often has a significant effect on the electrical properties, in this case the polymer-electrode interface was found to be dominating.

Finally, paper V shows that highly self-assembled polymer complexes may be achieved by utilising ionic liquids. The polymer-ionic liquid complex forms a surprisingly well organised nanophase-separated structure that provides pathways for proton conduction.

This thesis takes a step from the laboratory towards applications of conducting polymers and gives insight into utilisation and processing of functional materials to be used in organic electronics components and devices.

Tiivistelmä

Johtavat polymeerit tarjoavat mahdollisuuksia orgaanisen elektroniikan sovelluksiin ja toiminnallisiin materiaaleihin. Polymeeriketjun erityinen konjugoitunut rakenne mahdollistaa niiden toimimisen joko sähköä johtavina materiaaleina tai puolijohteina. Toisaalta polymeerit toimivat ionijohteina, jos niihin voidaan liittää liikkuvia protoneja tai muita ioneja. Tämä väitöskirja käsittelee johtavia polymeerejä ja esittelee, kuinka niitä voidaan käsitellä painomenetelmien avulla sekä kuinka polymeerien rakenne vaikuttaa niiden sähköisiin ominaisuuksiin.

Johdepolymeerien painettavuus, jota tutkittiin artikkelissa I, on mahdollistanut niiden uudenlaisen hyödyntämisen elektroniikassa. Väitöskirjassa osoitetaan, kuinka johtavaa polymeeriä, polyaniliinia, voidaan painaa teollisilla painokoneilla suurella nopeudella (100 m/min) ja saavuttaa 60 µm:n resoluutio.

Yksi lupaavimmista johdepolymeerisovelluksista on anturisovellukset. Artikkelit II ja III osoittavat, kuinka polyaniliinia voidaan hyödyntää lämpötila- ja kosteusantureissa, jos valitaan sille sopivat vastaionit. Vastaionien sivuketjujen sulaminen aiheutti palautuvan johtavuusmuutoksen. Toisaalta kosteus käynnisti palautumattoman johtavuusmuutoksen kiteytyvän ja faasierottuvan vastaionin ansiosta.

Artikkelissa IV tutkitaan, kuinka polymeerin rakenne vaikuttaa muistielementtien toimintaan. Vaikka yleensä polymeerin rakenteella on huomattava vaikutus sähköisiin ominaisuuksiin, tässä tapauksessa polymeerin ja elektrodin rajapinnalla oli hallitsevampi vaikutus.

Artikkeli V esittelee, kuinka ioninesteiden avulla voidaan saavuttaa itsejärjestyneitä polymeerirakenteita. Polymeeri-ioninestekompleksi muodostaa hämmästyttävän hyvin järjestyneen nanomittakaavan rakenteen, joka toimii protonijohteena.

Väitöskirja ottaa askeleen laboratoriosta kohti johtavien polymeerien sovelluksia ja osoittaa, kuinka toiminnallisia materiaaleja ja prosessointia voi hyödyntää orgaanisen elektroniikan komponenttien ja laitteiden valmistuksessa.

Preface

Part of the research for this thesis was carried out with the Molecular Materials group at the Department of Applied Physics at the Aalto University School of Science and Technology, and the rest was done in conjunction with the Printed Functional Solutions group at VTT Technical Research Centre of Finland. Working simultaneously at the university and the research centre has given me a great opportunity to do fundamental research in this area and apply my knowledge to components, production methods and finally, to applications.

Contents

Appendices of this publication are not included in the PDF version. Please order the printed version to get the complete publication (http://www.vtt.fi/publications/index.jsp).

List of abbreviations and symbols

AC = alternating current

ALD = atomic layer deposition

AMPSA = 2-acrylamido-2-methyl-1-propanesulfonic acid

C_{60} = fullerene molecule with 60 carbon atoms

CSA = camphorsulfonic acid

DBSA = dodecylbenzenesulfonic acid

DC = direct current

DCAA = 2,2'-dichloroacetic acid

FFSA = 5-formyl-2-furansulfonic acid

FT-IR spectroscopy = Fourier transform infrared spectroscopy

HOMO = highest occupied molecular orbital

ICP = intrinsically conducting polymer

IL = ionic liquid (a salt that is in a molten state at or near room temperature)

I-V curve = current-voltage curve

LS1 = lattice structure I

LS2 = lattice structure II

LUMO = lowest unoccupied molecular orbital

NDR = negative differential resistance

NMP = *N*-methylpyrrolidone

n-type semiconductor = electron (negative charge) conducting semiconductor

PANI = polyaniline

PANI-EB = polyaniline in emeraldine base form

PANI-LEB = polyaniline in leucoemeraldine base form

PANI-PNB = polyaniline in pernigraniline base form

PCBM = (6,6)-phenyl C_{61}-butyric acid methyl ester

PEDOT = polyethylene dioxythiophene

PEM = polymer electrolyte membrane

PEO = poly(ethylene oxide)

PEOSA = poly(ethylene oxide) sulfonic acid

PLED = polymer light emitting diode

PPV = poly(*p*-phenylene vinylene)

PPY = poly(2,5-pyridine)

PS = polystyrene

PS-PDHF-PS = polystyrene-*block*-poly(9,9-di-*n*-hexyl-2,7-fluorene)-*block*-polystyrene

p-type semiconductor = hole (positive charge) conducting semiconductor

R2R printing = roll-to-roll printing

RFID tag = radio frequency identification tag

RH = relative humidity (%)

SAXS = small angle X-ray scattering

TFSI = bis(trifluoromethane)sulfonimide

TFT = thin film transistor

TNT = trinitrotoluene

UV-Vis-NIR spectroscopy = ultraviolet-visible-near infrared spectroscopy

WAXS = wide angle X-ray scattering

WORM = write-once-read-many-times (a special type of a memory element, which can written once and read many times)

XRD = X-ray diffraction

τ = (here) time scale of a charge transport process (s)

σ = conductivity (S/cm)

μ = chemical potential (J/mol)

b = block

C = capacitance (F)

C_0 = capacitance at time $t = 0$ (F)

eV = 1.602 17653(14) $\cdot$ 10^{-19} C

k = Boltzmann constant 1.380 6504 $\cdot$ 10^{-23} JK^{-1}

n = number of repeating units in a polymer

R = resistance (Ω)

R_{ref} = resistance at a reference temperature (Ω)

R_g = radius of gyration

t = time (s)

T = temperature (°C)

T_{ref} = reference temperature (°C)

x = degree of complexation

2θ = diffraction angle (°)

α = temperature coefficient of resistance

ω = angular frequency (1/s)

List of publications

I: Mäkelä, T., Jussila, S., **Vilkman, M.**, Kosonen, H., and Korhonen, R. *Roll-to-roll method for producing polyaniline patterns on paper*, Synthetic Metals 135–136 (2003), 41–42.

II: **Vilkman, M.**, Kosonen, H., Nykänen, A., Ruokolainen, J., Torkkeli, M., Serimaa, R., and Ikkala, O. *Electrical Conductivity Transitions and Self-Assembly in Comb-Shaped Complexes of Polyaniline Based on Crystallization and Melting of the Supramolecular Side Chains*, Macromolecules 38 (2005), 7793–7797.

III: **Vilkman, M.**, Lehtinen, K., Mäkelä, T., Rannou, P., and Ikkala, O. *Poly(aniline) doped with 5-formyl-2-furansulfonic acid: A humidity memory*, Organic Electronics 11 (2010), 472–478.

IV: **Vilkman, M.**, Solehmainen, K., Laiho, A., Sandberg, H.G.O., and Ikkala, O. *Negative differential resistance in polymeric memory devices containing disordered block copolymers with semiconducting block*, Organic Electronics 10 (2009), 1478–1482.

V: **Vilkman, M.**, Lankinen, A., Volk, N., Kostamo, P., and Ikkala, O. *Self-Assembly of Cationic Rod-Like Poly(2,5-pyridine) by Acidic Bis(trifluoromethane)sulfonimide in the Hydrated State: A Highly-Ordered Self-Assembled Protonic Conductor*, Polymer 51 (2010), 4095–4102.

Author's contribution

Paper I: The author took part in planning the experiments, preparing the samples, measurements and analysis, and in finalising the paper together with the co-authors.

Paper II: The author planned and analysed the experiments together with the co-authors. She performed all the sample preparation, and most of the Fourier transform infrared (FT-IR) and UV-Vis-NIR spectroscopy, differential scanning calorimetry and conductivity measurements, took the optical microscopy pictures, wrote the first version of the manuscript and finalised it together with the co-authors. She also took part in the small angle X-ray scattering measurements.

Paper III: The author planned and analysed the experiments together with the co-authors. She performed all the sample preparation, conductivity, UV-Vis-NIR and FT-IR spectroscopy measurements, took the optical microscopy pictures, wrote the first version of the manuscript and finalised it together with the co-authors. She also took part in measuring the changes in capacitance.

Paper IV: The author planned and analysed the experiments together with the co-authors. She performed all the sample preparation and electrical measurements, wrote the first version of the manuscript and finalised it together with the co-authors.

Paper V: The author planned and analysed the experiments together with the co-authors. She performed all the sample preparation and FT-IR spectroscopy, contact angle and conductivity measurements, wrote the first version of the manuscript and finalised it together with the co-authors. She also took part in the X-ray diffraction measurements.

1. Introduction

Organic electronics is a quickly growing field of research, largely due to the possibilities it offers in terms of flexible, low-cost applications. The low cost is owed to the fact that organic electronics allow for printing on large areas through the use of roll-to-roll (R2R) processes. However, organic electronics may not replace silicon-based electronics since it is difficult to achieve the same performance with organic materials. However, the organic electrical components and devices could be used in applications not accessible to silicon.

Initially, the work related to organic electronics was focused on the development of components. As a result, the first organic electronics products on the market have been quite simple, *e.g.* game cards and packaging applications. However, due to the fast progress and large amount of research, the focus has been moving from components towards devices and more complicated applications.

Polymers are used in many organic electronics applications. They are traditionally thought to be insulating but they can also show semiconducting or conducting properties. Insulating polymers cannot, however, be taken for granted; they have proven challenging in terms of producing a sufficiently thin insulating film (*e.g.* to allow the high capacitance needed in thin film transistors (TFTs) [1]) without pinholes. Despite the importance of dielectrics in many applications, this thesis does not involve studies of polymers as traditional insulators (even though insulating polymers are also used here). Instead, various forms of conducting polymers – being electronically conducting, semiconducting or protonically conducting – are the main topic.

This thesis shows examples of conducting polymers and describes their use in potential applications. The work is focused on modifying the polymer structure, thus changing the electrical or physical properties. Novel processing methods of different forms of conducting polymers are also introduced.

2. Electronically and protonically conducting polymers

2.1 Electronically conducting polymers

Electronic conductivity in polymers can be divided roughly into two different categories: i) polymer composites, where the conductivity is achieved by adding conducting (usually metallic) particles to an insulating polymer matrix, forming a percolative network, and ii) intrinsically conducting polymers (ICPs), where the conductivity arises from a special conjugated structure of the polymer backbone. This thesis covers only the ICP type of electronically conducting polymers. Intrinsically conducting polymers are conjugated materials that have a chemical structure with alternating single and double bonds. The most simple and the first conducting polymer to be identified was polyacetylene ($-CH=CH-)_n$. Its discovery in the 1970s and subsequent studies led to a Nobel prize for Heeger, MacDiarmid and Shirakawa in 2000 [2]. Each carbon is sp^2 hybridised in the polyacetylene chain and thus it can be considered as a one-dimensional analogue of graphite, which might - at first sight - be metallically conducting along the chain due to resonance between the possibly equal bonds forming a half-filled π-electron band. The first requirement for metallic conductivity is to have energy levels near the Fermi level (*i.e.* the chemical potential μ) that can be thermally populated. It has been calculated that for polyacetylene, which has ideally equal single and double bond lengths and a chain with 1000 carbon atoms, the separation between the Fermi level and the next highest level would be 0.04 eV, which is comparable to thermal energies. This fulfils the first requirement, but in practice polyacetylene is still not conducting as such due to the following reasons: First, electron mobility along the chain has to be high, *i.e.* scattering of electrons should be low. This is difficult to satisfy with polymers since

any deviation from the planar zigzag conformation will cause scattering. A highly crystalline material can overcome these problems, but the high conductivity level is still not achieved. Therefore, the main reason for the apparently low conductivity arises from differences in the actual bond lengths: C-C and C=C bonds of the polymer are not equivalent i.e. they are alternatively shorter or longer, which is called Peierls distortion. This distortion has a conclusive effect on the electric properties of polyacetylene since it opens a gap between the HOMO (highest occupied molecular orbital) level, which is the fully occupied π-band (valence band), and the LUMO (lowest unoccupied molecular orbital) level, which corresponds to an empty π*-band (conduction band). Thus polyacetylene is an intrinsic semiconductor with a band gap of 1.5 eV and it requires doping in order to be conducting. Conjugated polymers with a narrower band gap have since been synthesised [3,4] but a vanishing band gap has not been reached. [5,6]

Polymers that have π-conjugation over elements other than carbon atoms exist as well. One of the most well-known examples is polyaniline (PANI), which is also studied in this thesis. In the polyaniline structure, p_z orbitals of nitrogen participate in the conjugation as well. In addition, polyaniline differs from the other conjugated polymers due to the special chemical structure of the backbone since polyaniline exists in three different oxidation states, which are presented in Figure 1. The most reduced state, leucoemeraldine, only has aminic nitrogen atoms in the chain. In the fully oxidised state, pernigraniline, all nitrogens are iminic and the ratio of phenylene rings with a benzoid or quinoid structure is 1:1. The half oxidised form, emeraldine, has an iminic/aminic ratio of 1:1 but benzoid and quinoid structures exist as 3:1, respectively. [6]

Pernigraniline base
PANI-PNB

Emeraldine base
PANI-EB

Leucoemeraldine base
PANI-LEB
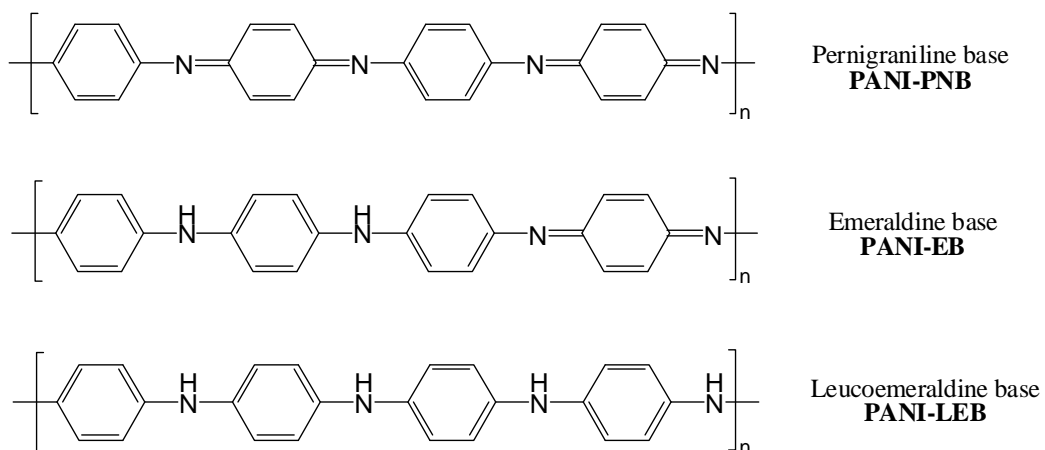
Figure 1. The three existing oxidation states for polyaniline: the fully oxidised pernigrani-line state, the half-oxidised emeraldine state and the fully reduced leucoemeraldine state.

Figure 2 shows some other important conjugated polymer structures, which include polythiophene and its widely used derivatives polyethylene dioxythiophene (PEDOT) and poly(3-alkyl)thiophene, where the alkyl side chain enables processing from melt [7], polypyrrole, polypyridine, which is a photoluminescent polymer and polyphenylene vinylene, which is an electroluminescent polymer.
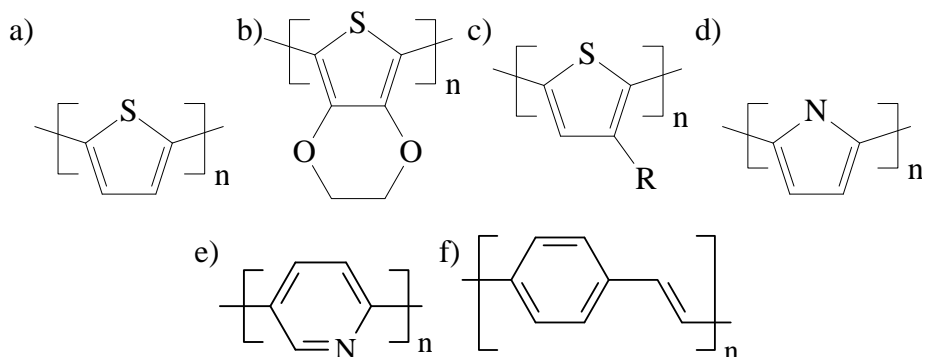
Figure 2. Molecular structures of some conjugated polymers: a) polythiophene, b) polyethylene dioxythiophene (PEDOT), c) poly(3-alkyl)thiophene, d) polypyrrole, e) polypyridine and f) polyphenylene vinylene.

2.1.1 Semiconducting polymers

Conjugated organic polymers are either insulators or semiconductors in the un-
doped state and their conductivity varies from 10^{-10} to 10^{-5} S/cm. Their semicon-
ductivity can be utilised in several applications, which include *e.g.* polymer light
emitting diodes (PLEDs) [8-12], plastic photovoltaic cells [13-20] and field ef-
fect transistors (FETs) [21-25]. PLEDs are electronic devices, which exploit the
phenomenon of electroluminescence, *i.e.* light is generated by electrical excita-
tion. The first electroluminescent polymer, poly(*p*-phenylene vinylene) (PPV),
was discovered in 1990 by Burroughes et al. [26]. On the other hand, a plastic
photovoltaic cell is a device, which transforms solar radiation energy into elec-
tricity, and it can thus be considered as an inverse to a light-emitting diode. The
first polymer photovoltaic cells did resemble single-layer PLEDs but it was soon
discovered that the photo-induced charge generation required for the operation
of the cell was extremely inefficient. Nowadays, the best plastic photovoltaic
cells are based on bulk heterojunction architectures, where the electron donors
(the undoped conjugated polymers) are mixed with electron acceptor molecules
(*e.g.* PCBM = (6,6)-phenyl C61-butyric acid methyl ester, a substituted form of
fullerene C_{60}, which allows better solubility in solvents). Then there are electron
accepting molecules in the close vicinity of the donor material and the charge
can be generated by photo-induced electron transfer. Now a stable charge stor-
age configuration is formed in the polymer backbone in the form of a positive
polaron, which is highly delocalised and mobile. [13,27]

A completely different application of undoped conjugated polymers is a
polymer-based field-effect transistor (FET). Figure 3 shows a simplified struc-
ture of a FET, which consists of a semiconductor deposited on two electrodes,
called 'source' and 'drain'. The semiconducting polymer and the electrodes are
separated from a third electrode, the 'gate', by a thin insulating layer. The opera-
tion is described as follows. If there is no voltage between the source and the
gate electrodes, the FET is in an insulating OFF state. If a voltage is then applied
between these electrodes, charge carriers are generated in the semiconductor, the
device is in its conducting ON state and current flows between the source and
the drain electrodes.
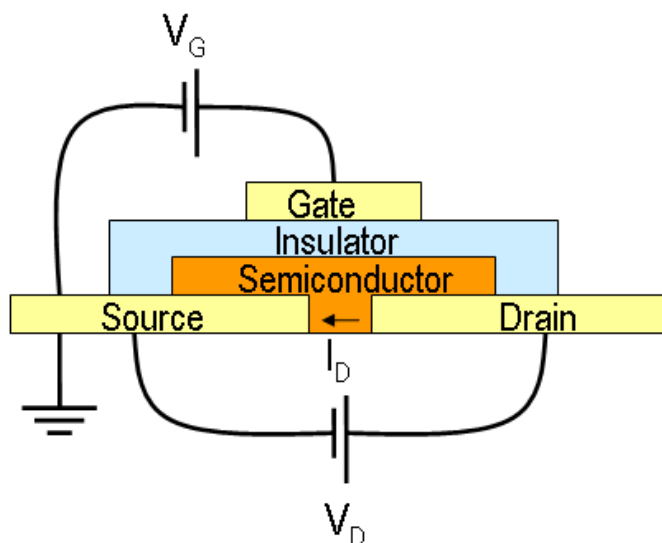
Figure 3. A schematic picture of an organic thin film field effect transistor.

The crucial parameter in FETs is the ON/OFF ratio, which refers to the ratio of the conductivity values between the states when the gate voltage is switched on and off, respectively. Usually this ratio has to exceed 10^6. In polymer FETs, the amount of residual dopant in the system has the strongest effect on the ON/OFF ratio and thus purification of the polymer has to be carried out carefully. The charge carrier mobility and the ON-state concentration also have an effect on the ratio, because conductivity of the polymer in the ON state is proportional to these parameters. [6] The weakest link in the polymer FETs is indeed the low mobility of charge. The best FETs based on p-type (hole conducting) conjugated polymers have carrier mobilities approaching 0.7 cm^2/Vs [28,29], and for n-type (electron conducting) conjugated polymers, the electron mobility has reached the level of 0.45-0.85 cm^2/Vs [30]. This is far from the mobility values in Si single crystal FETs exceeding 1500 cm^2/Vs. However, the advantage of polymeric FETs is their easy solution processing as well as thin film properties (*e.g.* flexibility) and they could be used as large-area and low-cost flexible electronic components. Non-polymeric small molecule organic semiconductors have shown a clearly higher level of mobility than polymeric semiconductors; pentacene has been reported to be able to reach a level of 5.5 cm^2/Vs [31]. However, their inability for solution processing by printing hinders their use in low-cost, large area applications.

2.1.2 Conducting polymers

Doping increases the conductivity of conjugated polymers to high levels, which are typically of the order of $1-10^4$ S/cm. Doping is a reversible phenomenon since doped polymers can be converted back to the original state without any change in the backbone. The conductivity of the polymer can be easily controlled by modifying the degree of doping; otherwise, a fully doped polymer can be blended with a conventional insulating polymer, which enables the mechanical properties to be tailored as well. [32]

Applications of conducting polymers in the doped state cover a large range of different functions and it is beyond the scope of this thesis to provide a thorough introduction to all or even some of them here. However, sensor applications of polyaniline are presented in more detail in chapter 4, since this field is closely related to the studies in this thesis. One study of the applications was presented by Pron et al. [6] who divided them into two general categories. The first category involves utilising the properties that exist after the doping process (organic conductors etc.) while the second category is related to exploiting the changes that take place during the doping/dedoping process (sensors etc.). Organic conductors, which can have conductivity values of several hundred S/cm, can be used as transparent electrodes. One example, which has to be mentioned due to its high annual production, is the use of polymeric conductors as an improving layer in capacitors. Another common use of conductive polymers is charge dissipation, since they are well suited for coating or blending with synthetic highly insulating conventional polymers, which usually have very low conductivity values (below 10^{-12} S/cm).

Since doping is an essential factor in conducting polymer science, I will go into more detail: first we will take a look at a conventional inorganic semiconductor, silicon. Pure silicon is an insulator since all four outer electrons are used to bind silicon atoms together by single covalent bonds in a three-dimensional lattice. The electrons are tightly bound and form a filled valence band. The energy required to move one electron from the valence band to a conduction band is about 1.1 eV and thus much greater than kT at room temperature (0.0256 eV), which indicates the thermal energy available. If a small amount of silicon atoms are replaced with 'impurity' atoms (which have three or five valence electrons), the material becomes semiconducting due to extra holes or electrons in the lattice, which are only loosely bound. This is the traditional doping process. [5,33]

For conducting polymers, the doping process is slightly different. The impurity atoms do not substitute any of the atoms in the polymer chain but are incorporated interstitially, *i.e.* they take up locations between the chains. The polymer in the undoped state can have either a conjugated backbone, like *trans*-$(CH)_x$, or a nonconjugated backbone, like a polyaniline emeraldine base (PANI-EB). Thus there are also two ways of doping: the reduction-oxidation (redox) type and the acid-base one. In the case of *trans*-$(CH)_x$, doping is a redox process and conjugation is retained in a modified form after doping. The number of electrons in the backbone changes and the built up charge is delocalised over 15 CH-units. However, if only a small amount of dopant molecules are used (similar to silicon doping), the charge is not able to travel further since it is connected to its counter-ion by Coulombic interactions. For the extra electron or hole to be able to travel longer distances along the chain, neighbouring dopants are required. This is why conjugated molecules require high doping levels. [2]

As an example of the acid-base doping, PANI-EB becomes conjugated only after protonation with an acid and a subsequent internal redox reaction in the backbone. In the process, the iminic nitrogen atoms are protonated. Oxidative doping is also possible in the case of polyaniline but a leuco-emeraldine base must then be used as a starting material. These two processes of polyaniline doping are presented in Figure 4. Note that both of these processes lead to the same product. In the oxidative doping (I and II in Figure 4), the reaction leads straight to radical cations, *i.e.* polarons. The acid-base doping is a two-stage process where the protonation of basic iminic nitrogens first creates bipolarons (III and IV in Figure 4). Subsequently, charge is distributed as polarons due to an internal redox-reaction, and a so-called polaron lattice is formed (II and III in Figure 4). [6]
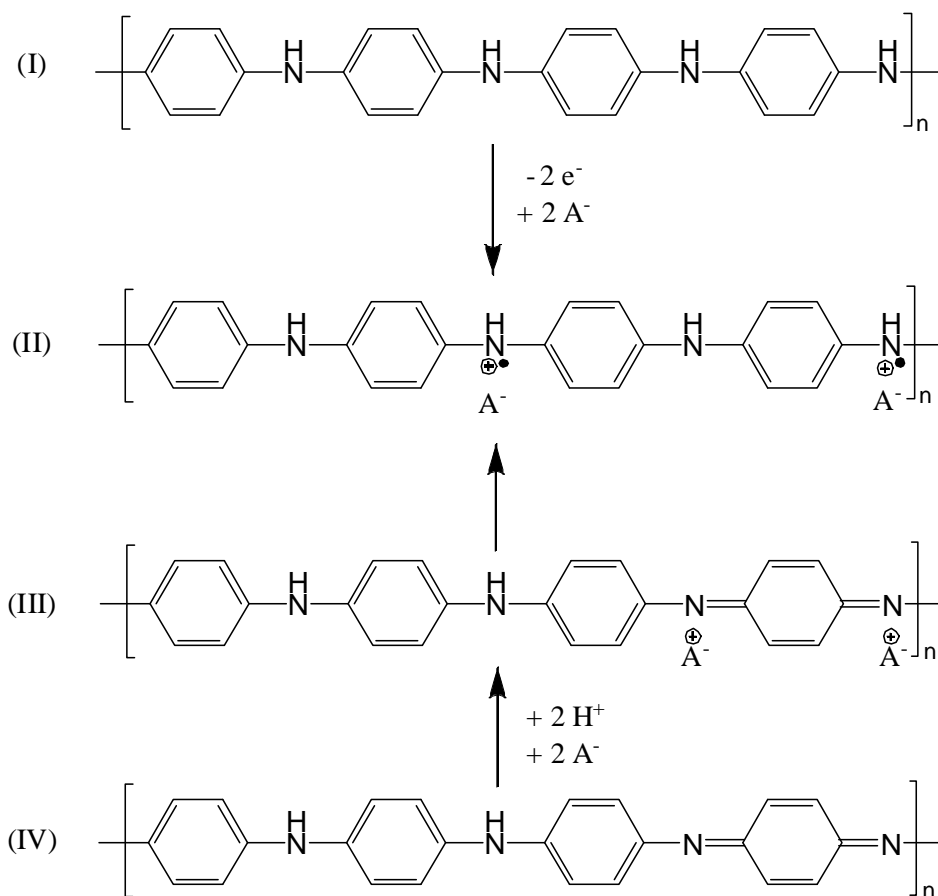
Figure 4. Doping of polyaniline through two routes: oxidative doping (I-II) and protonic acid doping (IV-II). A⁻ denotes the dopant anion.

There is another phenomenon referred to as secondary doping, in which the solvent and solvent vapours affect the structural order and subsequently modify the electrical conductivity of doped conductive polymers. A secondary dopant differs from the primary one in that the properties it may have caused can still persist even after full removal of the secondary dopant. Polyaniline is especially sensitive to solvent vapours: *e.g.* the conductivity of camphorsulfonic acid - doped polyaniline, PANI(CSA), can change by nearly four orders of magnitude when exposed to different solvents. [34]

Counter-ion modification

The dopants, which are also called counter-ions, may also modify the polymer or the polymer solution in other ways beyond the change in conductivity. These kinds of counter-ions are commonly called functional dopants. I use polyaniline here as an example to demonstrate the effect of some functional dopants on both the physical and the electrical properties of the polymer.

The discovery of dopant-induced processability was an important step in polyaniline research. In the past, conducting polyaniline was categorised as an intractable material and it could be dissolved only in the emeraldine base form in strong acids, *N*-methylpyrrolidone (NMP) or in selected amines. When Y. Cao et al. realised that functionalised protonic acids could be used to dope polyaniline, the complex became finally soluble in common nonpolar or weakly polar solvents. This opened up possibilities for the industrial processing of polyaniline; nowadays, this is the basis for printed electronics utilising *e.g.* conjugated polymers. The idea of functionalised solubilising dopants is based on using an acid with *e.g.* a long alkyl tail that is compatible with nonpolar solvents, thus making the whole complex soluble in them. The first examples of functional dopants were dodecylbenzenesulfonic acid (DBSA) and camphorsulfonic acid (CSA) (the molecular formulae are shown in Figure 5). [35-37].

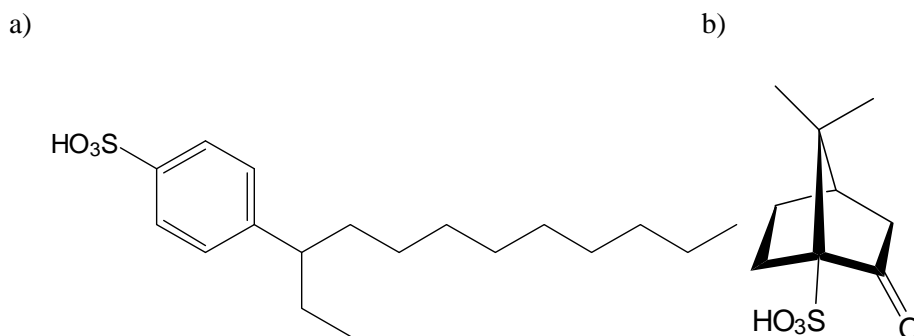a)   b)

Figure 5. The molecular formula of a) dodecylbenzenesulfonic acid (DBSA) and b) camphorsulfonic acid (CSA).

It should be mentioned that solubility or processability can also be achieved in other ways like side chain functionalisation, precursor route chemistry (polyacetylene and PPV) or by aqueous colloidal dispersions created by template synthe-

sis (polythiophene) [7]. However, these are beyond the scope of the thesis and will not be discussed here.

In addition to improved solubility, the mechanical properties of the polyaniline film can also be improved by the use of plasticising dopants. One of the dopants of this type is diesters of sulfophthalic acid [38,39] (molecular formula shown in Figure 6). Esters of *i*-phthalic acid are known industrial plasticisers, and if a sulphonic acid group is added to this structure, they can function as dopants in addition to the plasticising effect.
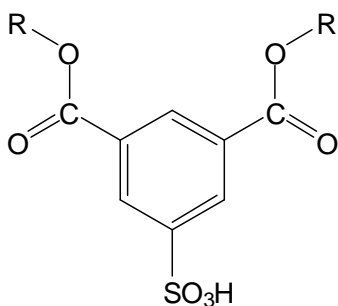
Figure 6. The molecular formula of diester of sulfo-*i*-phthalic acid.

Plasticising dopants that possess spacer-like alkyl chains can lead to self-assembled lamellar or cylindrical self-assemblies, see Figure 7. Self-assemblies are formed taken that the side chains are sufficiently long to allow sufficient repulsion towards the polar backbone. The self-assembly provides order to the material but also causes separation between the polymer chains, and is therefore expected to have a major impact on the electrical properties.
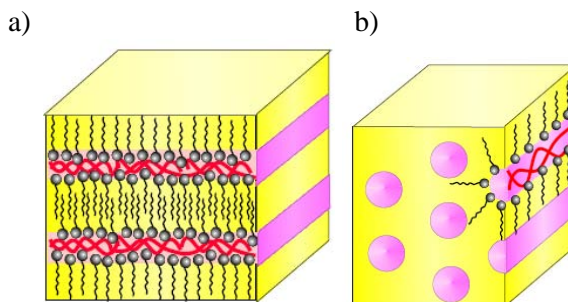
Figure 7. Examples of a) lamellar and b) cylindrical self-assemblies by complexing poly-aniline with protonating and plasticising dopants.

If films of PANI doped with 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(alkyl), or di(alkoxy) esters are cast from 2,2'-dichloroacetic acid (DCAA), they are flexible, can be bent several times without damage and show elongation at break exceeding 45%. The conductivity of these films is also high. [40] A still higher elongation (ca. 200 %) has been attained with a similar system, except sulfosuccinates were used [41] instead of sulfophthalates.

Phosphoric acid diesters are another group of dopants that have plasticising properties. These properties were discovered in 1993. In fact, these diesters are extremely efficient plasticisers since PANI becomes plasticised even at a low doping degree ($x = 0.3$) when di-2-ethylhexyl hydrogen phosphate is used as a dopant [42]. Plasticised PANI can also be thermally processed but in this case, aromatic esters of phosphoric acid are recommended because they have better thermal stability than aliphatic ones [43].

Conductivity of doped polyaniline

In addition to the processability-related discoveries, numerous dopants with different functions have been used to achieve the desired properties of the polyaniline complex. One of the main goals continues to be preparing polyaniline with high, metallic conductivity. There are specific cases when polyaniline, as well as other conducting polymers, shows metallic type conductivity, which is described (in addition to high conductivity values) as a positive temperature coefficient of resistivity [44]. The temperature coefficient of resistivity is defined by the following formula:

$$R = R_{ref}\left[1 + \alpha\left(T - T_{ref}\right)\right],$$

where R = resistance at temperature T, R_{ref} = resistance at a reference temperature (usually 20 °C), α = temperature coefficient of resistance, T = conductor temperature (°C) and T_{ref} = reference temperature (°C). For pure metals, α is a positive number, meaning that resistance increases as temperature rises and thus polymers with the same behaviour are referred to as metallic. However, a sample with true metallic conductivity should show a positive temperature coefficient of resistivity within the whole temperature range down to zero temperature, which is usually not the case with conducting polymers. More frequently, thermally activated behaviour is observed up to a finite turning point temperature, above which the metallic-like conductivity is perceived [40,41,44]. For carbon, silicon,

germanium and most of the conducting polymers, α is negative, *i.e.* resistance decreases with increasing temperature.

Choosing the right dopant is crucial if metallic conductivity is the goal, but it is not enough alone because processing conditions, like solvent and additives, could have a significant effect on the transport properties. Before I go into details, I offer a brief introduction to the basic phenomena behind the conductivity in conjugated polymers. When conductivity (σ) is measured, the DC (direct current) conductivity denotes the weakest link in the conductivity path. Thus $\sigma_{dc}(T)$ gives insight into the slowest relevant transport process in the system. AC (alternating current) conductivity provides information about the processes at the time scales of $\tau \approx \omega^{-1}$ (ω being the angular frequency). At low frequencies, transport between the chains can be studied, and at high frequencies, intrachain transport dominates. Thus $\sigma(\omega)$ helps to clarify charge transport in conjugated polymers since the intrachain and interchain transitions may vary significantly.

Even though it is not completely understood, the charge transport in conjugated polymers has usually been described by the following model. Conjugated polymers consist of two types of regions: the ordered ones have metallic conductivity and the disordered ones exhibit hopping type conductivity. In such a model, the charge carriers travel successively over macroscopic distances across both regions in the sample. Thus, the conductivity can be described as a sum of two terms: the first originates from a contribution of the hopping process and the second is related to the metallic regions. [40,45,46]

The role of the dopant in the conducting system has been demonstrated many times. One known example of a complex showing metallic conductivity is PANI doped with camphorsulfonic acid (CSA) and dissolved in *m*-cresol. The high conductivity is often attributed to the ability of *m*-cresol to interact with PANI rings through van der Waals forces and form hydrogen bonds with CSA; according to this hypothesis, the PANI rings are twisted into a more planar conformation, which leads to an increased conjugation length. [47]

Even though PANI doped with CSA and dissolved in *m*-cresol shows metallic conductivity, researchers have also been seeking other systems due to the high toxicity of *m*-cresol. Dufour et al. have used several 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(alkyl), or di(alkoxy) esters to dope PANI and they have been shown to produce metallic-like complexes. The reason behind the metallic conductivity is the dopant-induced flexibility, which allows the PANI backbone to arrange in a crystalline order (proven with wide-angle X-ray scattering (WAXS)). In this case, the changes in conductivity were found to be strongly

related to the hopping transport. The main effect of the plasticising dopants on the conductivity was thus suggested to be due to the variations in the disordered area. They have also added external plasticisers in the system leading to increased crystallinity of PANI, but the conductivity of the complex has still decreased. This, however, is only due to the decrease in the amount of the electrically active component in the system. [40]

Metallic-like conductivity has also been observed in complexes of polyaniline and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA). Very high conductivities were obtained in stretched fibres and films of AMPSA-doped PANI when dissolved in dichloroacetic acid [44]. On the other hand, when hydrogen bonded resorcinols are added to the system, the conductivity of the complex gradually increases by up to four orders of magnitude until it saturates to the value of 6 S/cm when the molar ratio of the PANI repeat unit to resorcinol reaches 1.0. The increase in conductivity is clearly due to the stretching of the PANI chains, as further supported by the X-ray measurements. However, the high conductivity values are not reached without orienting the PANI chains by pressing the film between glass slides in the melt state. [48]

2.2 Protonically conducting polymers

In addition to electronic conductivity, polymers can exhibit ionic conductivity. This group can be divided into two categories: protonically conducting polymers and polymers that can transport larger ions. The latter category contains materials for *e.g.* lithium batteries, where the polymer electrolyte may consist of *e.g.* polyethylene oxide mixed with a lithium salt [49,50]. However, this group of conducting polymers is beyond the scope of this thesis and they are not discussed here in detail. Instead, the protonically conducting polymers are introduced.

The most common use of protonically conducting polymers has been as polymer electrolyte membranes (PEMs) in fuel cells; for comprehensive reviews, see refs [51,52]. A fuel cell can be described as a device that converts the chemical energy of a fuel into electrical energy, and it consists of an ionically conducting electrolyte and a separator layer sandwiched between two electronically conducting gas diffusion electrodes [53]. The best proton-conducting membranes for fuel cells at the moment are phase-separated polymer electrolyte membranes, which consist of hydrophilic and hydrophobic domains. They are based on percolating aqueous networks inside the membrane, where the hydrophobic poly-

mer phase usually forms a stable membrane matrix and the hydrophilic phase consists of solvent, mobile protons and fixed acid groups as the pathways for protons. The proton conductivity depends on both the connectivity of the aqueous network and the ability of each pathway to conduct protons. [54]

The most well-known example of a polymer electrolyte membrane is Nafion®, which consists of a perfluorinated backbone that has sulfonic acid group (-SO$_3$H) terminated vinyl ether groups as side chains. Figure 8 shows the molecular formula of Nafion and presents one suggestion as to how the narrow water channels, which also contain the protonic charge carriers and the sulfonic acid groups, are formed [55]. However, despite the numerous studies on Nafion morphology, the exact organisation in the Nafion membrane is still not totally understood. In any case, researchers concur on the following: the morphology of Nafion is quite complex, the hydrophobic-hydrophilic phases have no well-defined boundaries and the interfaces are "rough". [56]
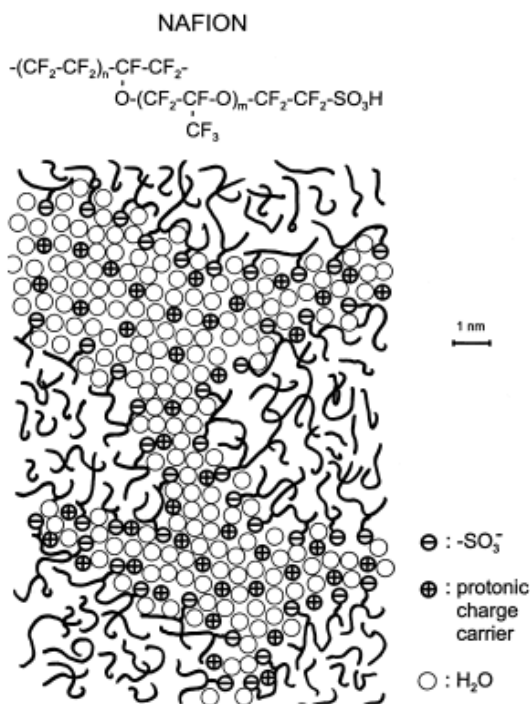

Figure 8. A schematic representation of the microstructure of Nafion [55].

Although Nafion can be considered a standard material for PEMs, it has some disadvantages. Firstly, the price of Nafion is relatively high for large-scale applications. In addition, the operation temperature can not exceed 80 °C due to dehydration. Finally, the recycling of the fluorine-containing membrane is a concern. [54] Thus many efforts have been made to find other alternatives for Nafion; these are often based on self-assembly to allow for a rational design of the percolative water channels and transport properties [57-64]. The importance of the morphology has been demonstrated with comb-shaped architectures with [65] or without [66] fluorination, to give a few examples. The papers showed that the proton conductivity is enhanced if the self-assembly leads to efficiently phase-separated nanochannels for the protons. In their review of the process, Yang et al. [67] (who concentrated on the structural and morphological features of acid-bearing polymers) also concluded that the enhancement of the phase-separation may be of great importance in the design of next-generation membranes. These needs motivated us to study how to control the self-assembly in protonic conductors. The results are presented in chapter 6 and in paper V.

3. Solution processing (paper I)

One of the main advantages of materials used in organic or polymer electronics is their ability to be printed. Printing offers entirely new fields for organic electronics applications when compared to traditional silicon-based microelectronics. In the optimal case, the organic components and devices are flexible, and can be processed in large quantities with industrial printing machines and low cost. The first applications for printed electronics have been simple game cards and packaging applications, but the field of applications has broadened year by year towards more complicated devices, like printed solar cells [68] or memory devices [69]. For reviews and books about printed electronics, see *e.g.* [70-72].

Within this thesis, polyaniline's ability to be printed was demonstrated in paper I (2003). The results showed that polyaniline can be printed at a high speed (up to 100 m/min) on paper, resulting in 60 µm wide conducting patterns. The effect of printing speed and pressure was also studied. Since printing is an essential factor in polymer electronics, I will introduce the main printing methods in this chapter and describe some of their features and challenges in detail. The specifications, however, depend largely on the equipment and printed materials. Thus only approximate values for resolution and film thickness can be given. The printing methods in polymer electronics include gravure, flexographic, screen and inkjet printing, to name a few. All of these methods offer unique advantages, though they also have their limitations. Gravure printing offers relatively high resolution (typically 50 µm [72] but recently a resolution of ca. 20 µm has been demonstrated [73]), and allows also inks with a large viscosity range to be printed due to the possibilities in printing cylinder design (*e.g.* the cup size and geometry can be varied). However, the printing cylinders or plates are quite expensive, since the printed pattern is engraved onto the metallic cylinder. On the other hand, flexographic printing has the advantage of economical printing rubbers where the printed design is patterned. The disadvantage of flexographic printing is poorer

resolution (a minimum line resolution of 76 µm; however, lower values should be possible [72]) mainly due to the deformations of the soft printing rubber during printing. The specific features of screen printing are the ability to print thick layers (usually more than 1 µm), but at the same time, it lacks usually the ability to produce thin layers (however, recently ca. 100 nm thick screen printed layers have been presented [74]). The resolution in screen printing is poorer when compared to gravure and flexographic printing, but the patterned screens are again cheap. Inkjet printing can be used to print low-viscosity solutions (but not high viscosity) and the resolution (usually 20-50 µm) depends *e.g.* on the droplet size. However, hydrophilic/hydrophobic pre-patterning of the substrate enables printing of high-resolution (sub-micron to few microns) patterns with inkjet [75,76]. Inkjet printing is the most flexible method when the printed pattern has to be altered, since the pattern can be designed digitally without any direct costs. However, it lacks the ability for high-speed printing [74]. Based on these features and limitations, it is clear that more than one printing method often has to be used when a complete multilayer component or device is printed.

I will use gravure printing here as an example of the demands and specific features in printed electronics, when compared to traditional graphical printing. Figure 9 shows a close-up of two different table top gravure printers that are used for printing materials on a small scale; the required ink volume is between 0.3 and 2.0 ml with these devices. The printed pattern can be engraved either on a plate (Figure 9a) or on a cylinder (Figure 9b).
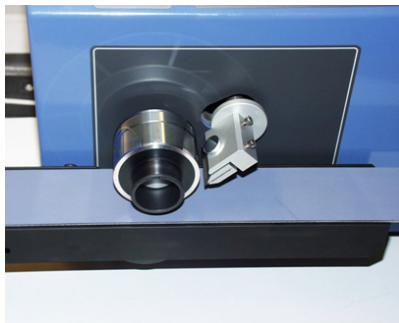
a)   b)

Figure 9. Pictures of two laboratory-scale gravure printing machines that have a) a printing plate (Norbert Schläfli Maschinen/Labratester) or b) a printing cylinder (IGT Testing Systems/IGT G1).

The pattern in the printing cylinder or plate consists of small cups, which usually have a depth of 5-50 µm. During the printing process, the cups are filled with the printing ink, the excess ink is removed with a doctor blade, and the ink is then transferred from these cups to the substrate. The most common shape of the cup is pyramidal. Figure 10 shows optical microscopy pictures of two different cup sizes as an example, where the line density has remained the same, *i.e.* the distance between the centre points is the same in both figures. However, the line density of the cups can also be varied.
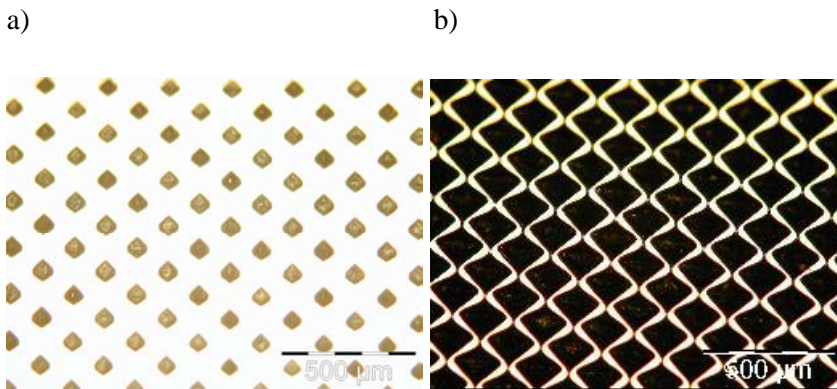
a)   b)

Figure 10. Optical microscopy pictures of cups in a printing cylinder with a depth of a) 11 µm and b) 33 µm. The scale bar in both pictures is 500 µm.

One of the challenges in printed electronics arises from this cup-shaped design of the printing cylinder. Whereas the goal of traditional graphical printing usually involves producing the exact cup-shaped patterns on the substrate, printed electronics requires smooth printed films. In graphical printing, pixel-like patterns are suffice when printing since the pixels are so small (100 µm or less) that they are not visible to the eye. Thus the printed pattern looks continuous, even though it in fact contains pixels. Figure 11 clarifies this difference by showing an optical microscopy picture of a gravure-printed magazine page. The upper part looks smooth green and the lower part looks smooth yellow, despite the pixel-like pattern at the micrometre scale. Naturally, for printed electronics, the pattern cannot contain pixels. Especially the insulating layers have to be homogeneous and pinhole-free in order to avoid dielectric breakdown. Thus it is a challenge to be able to print smooth films with sharp boundaries when using printing devices that were not originally designed for such requirements. Finely

tuned ink formulations (*e.g.* a mixture of high and low boiling solvents and optimal viscosity [77]) and a careful design of the engraved printing pattern (*e.g.* optimised cup shape and volume) will help to overcome this challenge.
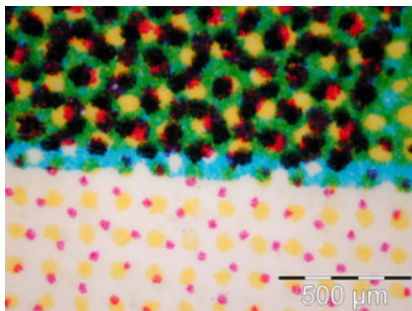

Figure 11. An optical microscopy picture of a gravure-printed magazine page showing the pixel-like printing patterns. The green section along the upper part of the picture and the yellow part at the bottom appear smooth to the eye, even though the actual pattern consists of pixels.

Other challenges in printed electronics involve up-scaling and multilayer printing. Even though it is possible to demonstrate printed components on a laboratory-scale, there is still a long way to go before pilot-printing and finally industrial-scale printing. The main problems I have encountered when moving from laboratory-scale to pilot-scale printing and the printing of multilayer components relate to i) the drying time of the printed layer, ii) the registration (*i.e.* alignment) between successive layers, and iii) the compatibility of solubilities between successive layers. First, since printing at the pilot scale is a roll-to-roll process, the drying time of the ink has to be relatively short. Otherwise the printed layer will stick to the substrate when the sheet is rolled again. The substrate can be run through heating units to speed up the drying process but usually this step cannot last more than a few minutes to avoid overlong heating units. Note that if the printing speed is *e.g.* 5 m/min, the heating unit has to be 10 metres long to achieve 2 min drying time. In addition, the plastic substrate cannot usually stand high temperatures without stretching and thus the drying temperature has to be kept relatively low (usually below 150 °C). The boiling point of the solvent cannot be too low either, in order to keep the ink from drying on the printing cylinder before it is transferred to the substrate.

Secondly, registration between successive printed layers is challenging and requires online optical measurements and continuous alignment during the print-

ing process. The substrate might also stretch during drying or rolling and generate additional difficulties. In the case of flexographic printing, the patterned printing rubber is flexible, which may also make the registration difficult since the diameter of the printing cylinder varies with the applied printing pressure. This has an effect on the registration if long runs (tens of metres) are performed. Finally, the successive layers should not have similar solubility since the bottom layer might be partly dissolved and incorporated into the following layer during multilayer printing. This problem can be avoided by using *e.g.* cross-linkable bottom layers if suitable solvents are not found.

4. Sensors based on electronically conducting polymers

Sensors for specific molecules or environmental conditions represent one of the most promising applications of conducting polymers, enabling detection and monitoring of *e.g.* carbon dioxide gas [78], TNT *i.e.* trinitrotoluene vapour [79], moisture [80-83], and biological moieties, like antigens [84], glucose [85] or DNA [86]. Functionalisation of the counter-ions provides one general strategy to construct efficient, reliable, specific, and yet simple sensors based on conducting polymers. The two conditions that are studied in this thesis include moisture and temperature; these topics will be introduced in the following chapters (4.1 and 4.2) using polyaniline as an example.

4.1 Temperature (paper II)

The usual response of polyaniline to temperature was described in chapter 2.1.2: there is a smooth increase or decrease of conductivity as a function of temperature, which can be called thermochromism, since the optical spectrum also changes as a function of temperature. The characteristics of the conductivity - metallic or otherwise - depend on the dopant and processing conditions, and sometimes the behaviour changes from non-metallic to metallic at a certain temperature.

Some polyaniline complexes show strong thermochromic behaviour at sub-zero temperatures. This can be seen in complexes where polyaniline is doped with a dopant that goes through a glass transition in that temperature range [87]. We have shown that the crystallinity of the dopant chains can also be utilised to induce a rapid change in the conductivity of a polyaniline complex during heating/cooling (paper II). Polyaniline was doped with sulfonated poly(ethylene oxide) (PEOSA) (see Figure 12 for the molecular formula). The PEOSA as such melts at around 55 °C and the complex with PANI melts at a temperature a few

degrees higher (see paper II). When the complex is heated, conductivity drops stepwise at the melting temperature while the opposite occurs during cooling (see Figure 13). Note that this differs from the results of Rannou et al. [87] regarding plasticised dopants, where the conductivity of the complex was low at low temperatures and high at higher temperatures. This was the result of PANI's ability to crystalline better when the side chains became flexible during heating. In our PANI(PEOSA) system, the crystallinity of the side chains seems to improve the overall conductivity, which suggests that the particular crystalline structure of PEO might encourage greater order within the PANI backbone than in the molten state. Figure 14 schematically shows the change in PANI and PEOSA conformations and the alterations observed in the long period (measured with small angle X-ray scattering (SAXS), see paper II).
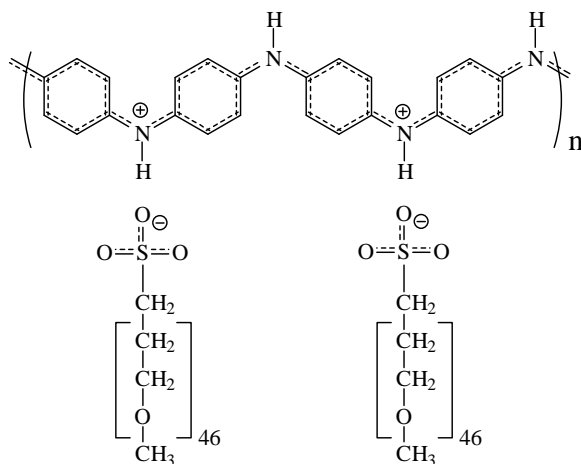

Figure 12. Molecular formula of poly(ethylene oxide) sulfonic acid doped polyaniline, PANI(PEOSA). [Paper II]
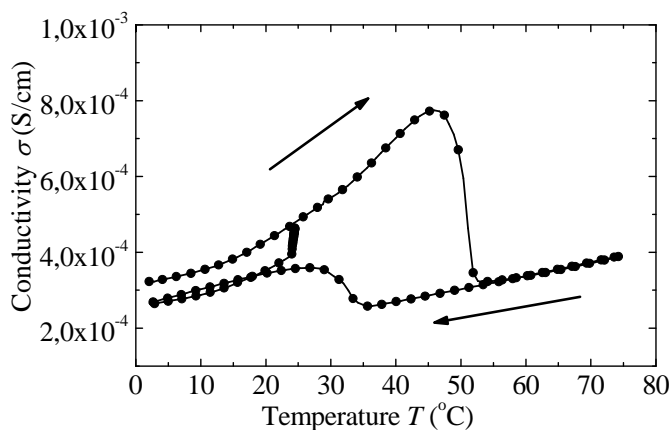
Figure 13. The conductivity of PANI(PEOSA)$_{0.5}$ as a function of temperature. [Paper II]
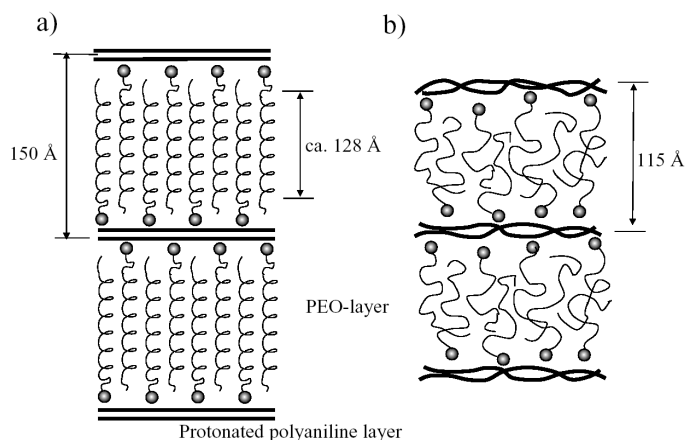
Figure 14. A schematic of the structure of PANI(PEOSA)$_{0.5}$. (a) When the PEO side chains are crystalline, the long period is ca. 150 Å and the self-assembled structure is relatively well-ordered. (b) When the side chains melt, the long period is reduced to ca. 115 Å and the disorder increases. [Paper II]

This kind of step-like change in conductivity might be suitable *e.g.* for flexible temperature sensors, which would set off an alarm if the temperature passes an upper or lower limit. Since the material and processing costs of PANI(PEOSA) are low, the complex would be appropriate for packaging applications where the traditional temperature sensors would be too expensive. Optimising the side chain

length could still help to control the switching ratio, and the switching temperature could be tuned by selecting different crystalline sulphonic acids as the dopants.

4.2 Moisture (paper III)

Polyaniline is known to interact with moisture from air. The usual response to moisture is an increase in conductivity in a humid environment [80,88-91]. This is a reversible phenomenon and pumping under vacuum can lead to a decrease in conductivity by an order of magnitude. The rise in conductivity is believed to result from the increased crystallinity of the PANI backbone when moisture is present. The metallic islands then increase in size and some localised polarons are transformed into either delocalised polarons or bipolarons. The amount of absorbed water in polyaniline is quite large: PANI-EB is known to absorb water over 16 wt% but doped polyaniline might absorb as much as 40 % of the polymer's weight in water [92].

Polyaniline has been utilised in many kinds of humidity sensors due to this reversible response to water vapour in air [81,82]. It is easy to observe the change in the polymer electrically with either resistive or capacitive measurements. These sensors provide information on the prevailing moisture level of the surroundings but cannot show the past levels if the electrical information is not saved in any form; saving the information, however, always involves additional costs. Thus there is need for simple and cheap sensors that can provide information on the past moisture content, *i.e.* cumulative or irreversible moisture sensors. This sensor type is an analogue of an electrical write-once-read-many-times memory (WORM) [93-95], and can thus be called a humidity memory. Only a few of these sensors exist, for example, a polybutadiene-$MgSO_4$ composite sensor, which is based on water absorption leading to an increase in capacitance [96], or a colour-changing sensor based on the aggregation of dye molecules [97].

Encouraged by the increasing need of the packaging industry to follow the transportation and storage history of sensitive products, we studied the use of polyaniline as a humidity memory. Paper III shows that if the counter-ion for polyaniline is a crystalline, polar acid, it crystallises and phase-separates in humid conditions. This phase-separation leads to a permanent loss in conductivity, which can be detected with resistive or capacitive measurements even without direct electric contacts through the package. The counter-ion in paper III was chosen as 5-formyl-2-furansulfonic acid (FFSA) (see Figure 15 for the molecular formula), and several doping ratios x were used to produce PANI(FFSA)$_x$ complexes.
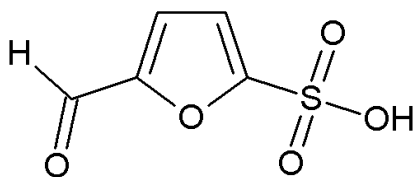
Figure 15. The molecular formula of 5-formyl-2-furansulfonic acid (FFSA).

After studying the change in conductivity in humid conditions with doping ratios that are also lower or higher than the nominally fully doped state ($x = 0.5$), we found that in this case we should select an underdoped sample to achieve a large, easily detectable change in conductivity. In addition, the doping ratio should be reasonable in order to keep the conductivity at a sufficient level. Thus we chose PANI(FFSA)$_{0.3}$ for the detailed studies.

Figure 16 demonstrates that the dopant actually phase-separates from the film as crystals by showing the optical microscopy pictures of PANI(FFSA)$_{0.3}$ films, spin-coated on a glass substrate. In Figure 16a, the film has been exposed to humid air (50 % RH, 25 °C) in a controlled humidity chamber resulting in the appearance of small crystals separating from the matrix. Figure 16b shows an optical microscopy picture of a similar film, but in this case we have placed a water drop on the PANI(FFSA)$_{0.3}$ film. This has led to a phase-separation of larger crystals leaving a blue (*i.e.* dedoped) PANI film behind.

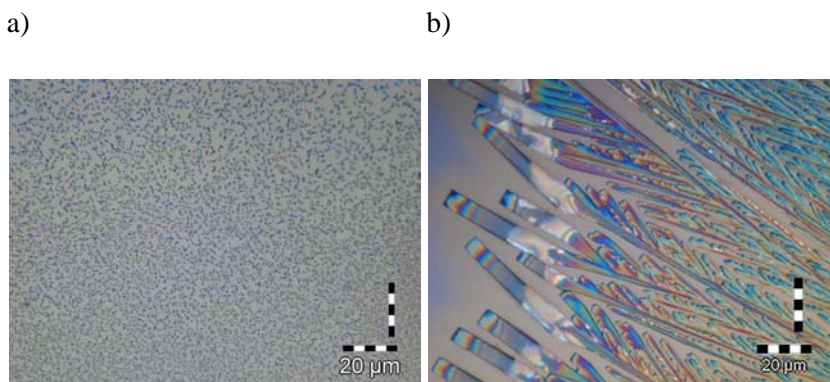a)   b)

Figure 16. Optical micrographs of a PANI(FFSA)$_{0.3}$ thin film spin-coated on a glass sub-strate showing how phase-separated hydrated FFSA crystals formed after (a) a few days humidity treatment in a humidity chamber (50 % RH at 25 °C) or (b) water was deposited on top of its free surface. [Paper III]

The resulting change in electrical properties was measured with direct resistance measurements and with capacitive measurements through a substrate. The resistance measurements (see paper III) showed that the change from a conducting state to a poorly conducting state was indeed irreversible, since the conductivity of the film did not recover after the film was placed in dry air. In addition, we demonstrated that the change can be detected with capacitive measurements even through the substrate without any direct electric contacts with the sensor (see Figure 17). This would be optimal for packaging applications where the contents have to be protected from moisture. The sensor can also be used in applications where it is important to identify if the package has been opened at any stage during transportation or storage (see paper III for details).
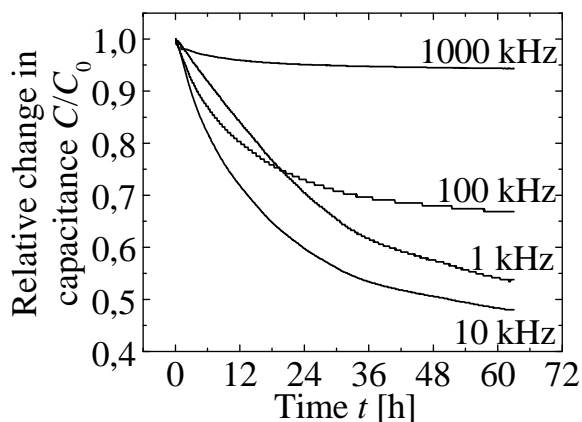

Figure 17. Evolution of the reduced capacitance C/C_0 of the PANI(FFSA)$_{0.3}$-based sensor (at four different frequencies) as a function of the elapsed time after it is in contact with the ca. 20 % RH atmosphere of the VTT laboratory, in which the ca. 2.5 days tests were performed. Note that C_0 indicates the capacitance value before the activation of this humidity sensor. [Paper III]

5. Memory devices based on semiconducting polymers (paper IV)

An electronic memory is a fundamental part of all modern computers. They are components that can store retrievable digital data over time, *i.e.* they can be both read and written. The operation of an electronic memory can be divided into two groups: volatile and non-volatile memories. A volatile memory loses the stored information if the power is switched off and thus requires constant power or periodic refreshing. In comparison, the non-volatile memory can store the information if the power is turned off as well. Memories are needed in applications other than computers as well. If the aim is for the application to be printed and flexible, the memory portion has to fulfil the same requirements. One example where flexibility is often desired is a radio frequency identification (RFID) tag. [98,99]

A polymeric memory can help with the demand for thin, flexible memories, which can be integrated with the other potentially organic counterparts and optimally can also be printed. Different types of polymeric memory devices exist, *e.g.* ferroelectric and resistive ones. An industrial-scale printed and flexible ferroelectric memory device has already been presented by Thin Film Electronics [69,100], but no other examples of fully printed memory devices yet exist. The mechanism behind a ferroelectric memory device is relatively well known [101], but the operation of resistive memory devices remains the subject of debate. However, due to recent developments, the mechanism behind a resistive memory is also becoming clearer. The following text describes the observations related to resistive memories.

The resistive memory elements are based on switching between at least two metastable states, the ON and OFF states, which have high or low conductivity (respectively). The elements usually consist of a sandwich structure, where a thin layer is placed between two coplanar electrodes. The middle layer can consist of a wide variety of materials, *e.g.* conducting or semiconducting particles in

an organic matrix [99,102-106], a mixture of electron acceptors and donors [107,108], conjugated polymers [109], and even just thin insulating layers [102,110,111]. The variety of the working materials is large; thus it is possible that the switching mechanism might also differ from case to case. One of the suggested working mechanisms is based on the formation of conducting filaments, which are formed inside the middle layer due to electroformation. The hypothesis is supported by experimental data, showing *e.g.* localised hot spots to form on the electrodes during filament formation [110,112]. As another example, if the active layer consists of a polymer film containing small conjugated organic compounds and metal nanoparticles, the experimental data does not support the filament formation mechanism. Instead, it is suggested that an electric-field-induced charge transfer model explains the observed electronic transitions. [108]

In the case of filamentary conduction, both dispersion of semiconducting fullerenes within an insulating polymer matrix [113], and electrode surface engineering or patterning [114-116] have been successfully used to control the filament growth. Since stable and predictable filament formation is a prerequisite for reliable operation, we wanted to determine if block copolymers with a semiconducting middle block could be used to control the filament growth. Therein the logic was the following: In multicomponent materials, *e.g.* dispersing semiconductors, such as fullerenes, in polymers there is always a danger that the high electric field causes local structural changes due to phase separation that in turn promotes filament growth. In this sense, block copolymers having semiconducting blocks allowing permanent connectivity to the other blocks forming the matrix could be interesting. Typically, block copolymers are pursued to allow self-assembled structures, where the classic structures are the lamellar, gyroidal, cylindrical and spherical structures of diblock copolymers [117]. Therein the self-assembled domain size is typically tens of nm. In this work, we expected that smaller sizes of semiconducting material within insulating matrices would be preferred. This could be achieved by selecting block copolymers in the disordered state, *i.e.* where the microphase separation does not take place due to the small length of the blocks. In this case, each individual semiconducting polymer would be ideally dispersed separately within the matrix, where the size of the semiconducting polymer is specified only by its radius of gyration. Thus we compared two polymers as the middle layer: a purely insulating polymer, polystyrene (PS), and a block copolymer polystyrene-*block*-poly(9,9-di-*n*-hexyl-2,7-fluorene)-*block*-polystyrene (PS-PDHF-PS), where the fluorine part forms con-

jugated and semiconducting regions inside the polymer film. The molecular formula of the block copolymer is shown in Figure 18. The approximated radii of gyration (R_g) for the blocks in the PS-PDHF-PS block copolymer are also shown.
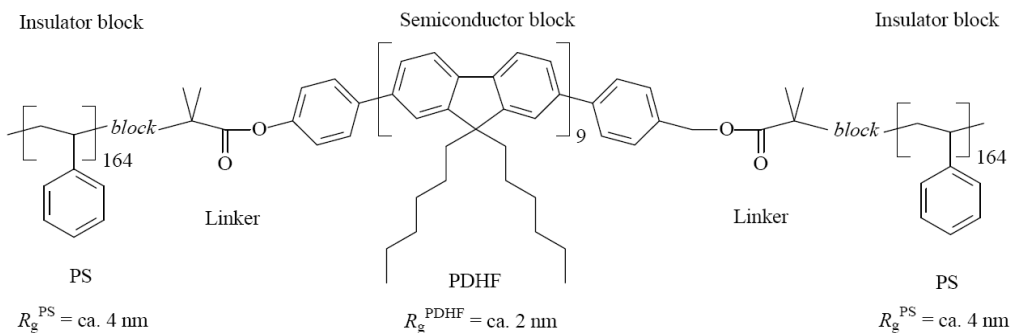

Figure 18. The molecular formula of polystyrene–block-poly(9,9-di-n-hexyl-2,7-fluorene)–block-polystyrene (PS–*b*-PDHF–*b*-PS). The approximated radii of gyration (R_g) are given for the block lengths used, indicating the sizes of the dispersed PDHF chains [118] as separated by the insulating PS chains. Note that the length of the PDHF is small, leading to a disordered phase. [Paper IV]

Thus when compared to nanoparticles inside an insulating matrix, the block copolymer provides the advantage of evenly distributed semiconducting domains inside the insulating polystyrene matrix, whereas the nanoparticles are prone to aggregation. The PS-PDHF-PS block copolymer forms a layer in which the semiconducting blocks do not have an aggregation tendency or even form a self-assembled structure due to the relatively short middle block. This kind of simple one-component solution would be optimal, especially for printing. Figure 19 illustrates this idea by showing the local enhanced electric fields that might control the filament growth in the nanoparticle and block copolymer films.

a) Dispersion
Nanoscale additives, such as fullerenes and nanoparticles, in insulating matrix

b) Disordered block copolymers
Semiconducting middle blocks of length scale R_g^{PDHF} separated by PS of length scale R_g^{PS}

c) Purely insulating homopolymer

Enhanced local electric field to promote filament formation

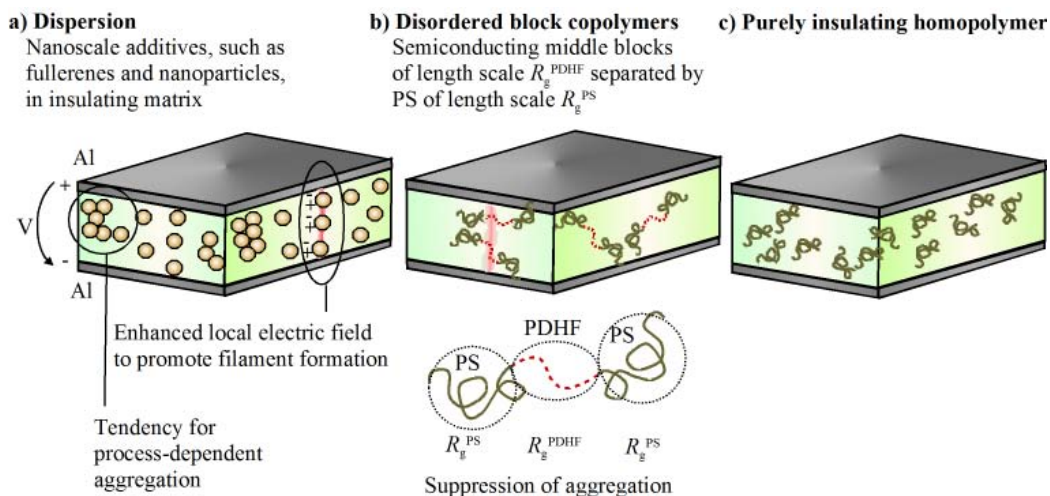Tendency for process-dependent aggregation

Suppression of aggregation

Figure 19. Suggested schemes for the effect of dispersions. (a) Dispersion of fullerenes or nanoparticles in an inert matrix. A local enhanced electric field in the dielectric constituents is also illustrated, which might control filament formation. (b) Semiconducting polymer chains (PDHF) form the middle block of a block copolymer with insulating end blocks (PS). In the disordered state, the PDHF chains of average sizes $R_g^{PDHF} \approx 2$ nm are separated by the PS chains (radius of gyration $R_g^{PS} \approx 4$ nm). (c) Purely insulating polymer film, where the formation of the filaments is suggested to be controlled solely by the electrode surface structures and device inhomogeneities. [Paper IV]

To our surprise, the semiconducting blocks did not present any advantage over the pure insulating polystyrene layer when the electrical properties of these two devices were compared. The polystyrene-based memory element was working as well as the block copolymer one, and both showed negative differential resistance (NDR) when thin films (below 100 nm) were used. The negative differential resistance can be utilised in non-volatile memory elements by unipolar switching [119]. There the memory element is switched between two metastable states with a short voltage pulse. The magnitude of the applied voltage pulse determines the achieved current level. We were able to switch both of the tested memory elements between the ON state (high current) and the OFF state (low current) and we found no differences in the stability or reliability in the performance. For both materials, PS and PS-PDHF-PS, NDR was relatively easy to achieve but switching between the ON and OFF states remained challenging. Figure 20 shows the best programming cycle that these materials were able to achieve using PS-DHF-PS as an example. However, the switching was stable only in random devices.
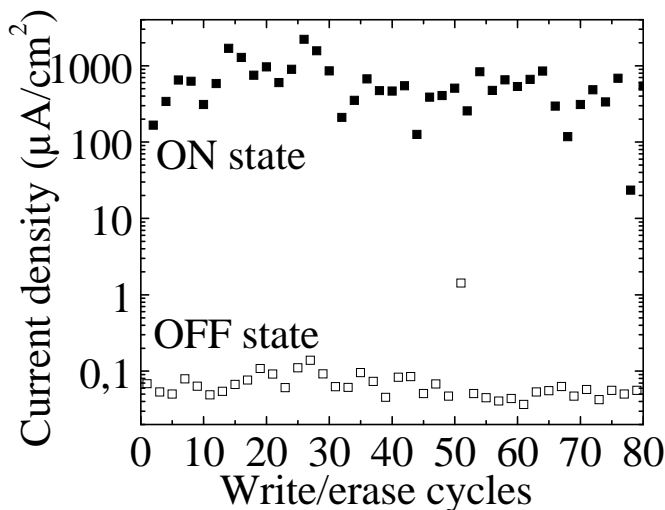
Figure 20. Programming results showing consistent switching and ON–OFF current ratios greater than three orders of magnitude for PS-*b*-PDHF-*b*-PS (85 nm), utilising a 4.7 mm^2 device area and native oxide on the bottom aluminium electrode. [Paper IV]

In addition to only changing the middle layer, we altered the properties of the bottom aluminium electrode through oxygen plasma treatment, which increased the thickness of the aluminium oxide layer on the electrode in comparison to that of the native oxide. Previous studies by Verbakel et al. [114] have shown that an evaporated Al_2O_3 layer on the bottom electrode improves the reliability of organic memory elements. However, in our case, the additional oxide had an adverse effect since the surface properties (roughness and/or morphology) of the Al_2O_3 layer may differ from the evaporated material. Even the NDR phenomenon was not optimal for plasma treated samples, *i.e.* the *I-V* curve showed no clear maximum.

In conclusion, this study supported the idea that the polymer layer is not the most important part of the memory element. It was also encouraging to discover that inexpensive insulating polymers can serve as the middle layer as well. Thus efforts should be guided towards surface conditioning of the substrate or the electrodes to trigger the filament formation. Promising, R2R-compatible methods for surface treatment could include *e.g.* structuring a polymer substrate by hot embossing (or nanoimprinting) and providing an additional oxide layer on the electrodes through R2R atomic layer deposition [120] (ALD), if needed.

6. Self-assembled structures of protonic conductors (paper V)

As emphasised recently in literature, the operation of protonically conducting polymer membranes seems to be highly dependent on the micro- or nanoscale structure of the phase-separated polymer system. It has been suggested that control over the self-assembled structure would lead to clearly nano- or microphase-separated domains; this would be essential for achieving efficient fuel cell membranes with high protonic conductivity. [65-67]

This encouraged us to study if bis(trifluoromethane)sulfonimide (TFSI) - an ionic liquid (IL) material - could assist the self-assembly of a rigid rod polymer complex and simultaneously enable protonic conductivity. Ionic liquids are salts that are in a molten state at or near room temperature [121]. If the ionic liquid formed a complex with the rigid polymer, the IL-induced softening of the complex could allow for efficient self-assembly. In addition, as TFSI is known to form efficient protonic conductors as salts with oligomeric compounds [122-126], the polymer complex should also function as a protonic conductor. And finally, ILs might even help with the problem of dehydration at temperatures above 100 °C, based on the observations of notable protonic conductivity of IL salts at high temperatures and non-humidified conditions [123].

We chose to use poly(2,5-pyridine) (PPY) as the polymer, especially since aromatic polymers usually offer better chemical and thermal stability than aliphatic polymers [67]. On the other hand, the rigidity of the polymer backbone could allow formation of nanochannels for proton transport if a well-organised self-assembled structure was achieved. The molecular formulae of PPY and TFSI are shown in Figure 21. We tested PPY(TFSI)$_x$ complexes with different protonating ratios x. Fourier transform infrared (FT-IR) spectroscopy was used to assure the complex formation (see paper V for details). The spectra of dry

films showed that at low complexing ratios, the TFSI molecules are bound with ionic bonds, and at higher ratios hydrogen bonding is also present.
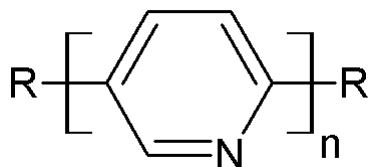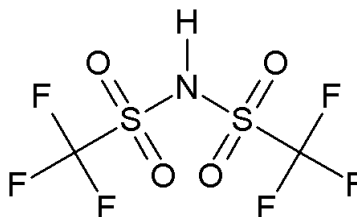
a)   b)

Figure 21. Molecular formulae of a) poly(2,5-pyridine) (PPY) and b) bis(trifluoromethane) sulfonimide (TFSI).

The self-assembly of the $PPY(TFSI)_x$ complexes as thin films was studied with X-ray diffraction (XRD) and we soon found that the material has different properties when dried (sample preparation in a nitrogen glove box and drying in vacuum) than when wet (after a controlled humidity treatment or storage in air). The dry state is highly unnatural for the complex and it was in fact very difficult to avoid water absorption from air. However, with XRD, we managed to determine that the complex does not form a self-assembled structure without the presence of moisture. Instead, when exposed to humid air, the thin films of PPY(TFSI) form a surprisingly well-organised structure. Figure 22 demonstrates this by showing an X-ray diffraction curve for $PPY(TFSI)_{0.25}$. At first, there is no structure in a dry state or after a short 17-hour humidity treatment. After a long 150-hour humidity treatment, however, the spin-coated film has formed an extremely well-organised lamellar structure where the peaks are sharp and even the 7th order peak is visible. The long period of the lamellar structure is 13.08 Å, and is denoted as lattice structure I (LS1) in the figure.

Figure 22. XRD curves of PPY(TFSI)$_{0.25}$ stored in a dry atmosphere after deposition (black curve), after a short 17-hour water vapour treatment (red curve), and after a long 150-hour water vapour treatment (blue curve) at 80 % RH. LS1 (lattice structure I) denotes the periodic structure with a lattice constant of 13.08 Å. [Paper V]

The amount of hydrophilicity depends on the amount of TFSI in the complex. For low loading of TFSI, the film needs a long time to absorb the amount of water required to enable the self-assembly. In comparison, if the amount of TFSI increases, the water molecules are absorbed from the air quite quickly. Figure 23 shows the XRD curve for PPY(TFSI)$_{1.00}$, where the self-assembled structure already exists after the short 17-hour humidity treatment.
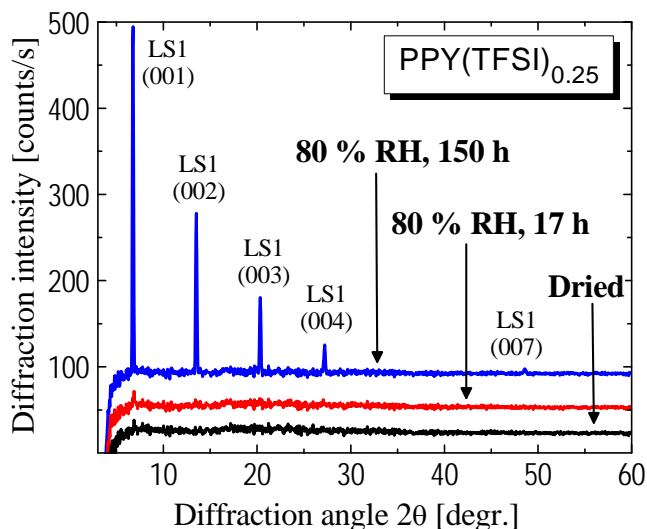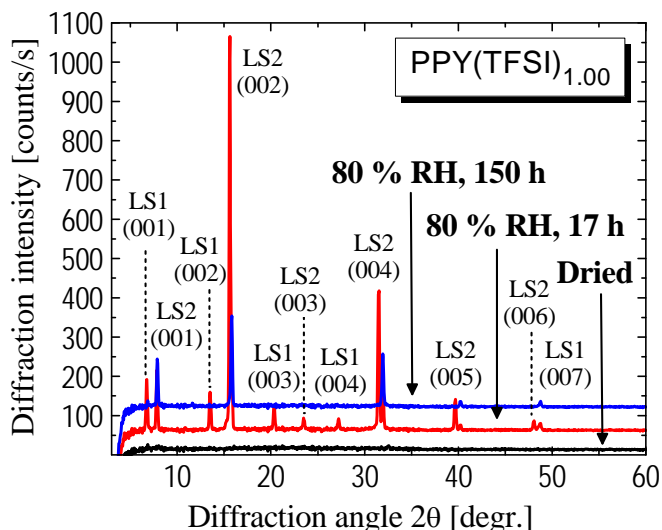
Figure 23. XRD curve PPY(TFSI)$_{1.00}$ stored in a dry atmosphere after deposition (black curve), after a short 17-hour water vapour treatment (red curve), and after a long 150-hour water vapour treatment (blue curve) at 80 % RH. LS1 (lattice structure I) and LS2 (lattice structure II) denote the two distinct periodic structures with lattice constants of 13.08 Å and 11.31 Å, respectively. [Paper V]

In addition to the LS1 structure, Figure 23 shows also another set of peaks, called lattice structure II (LS2) with a lattice constant of 11.31 Å. We recognised this structure be the same as that for pure TFSI without PPY. It is thus clear that if the amount of TFSI exceeds a certain limit (located between $x = 0.25$ and $x = 0.50$), part of the TFSI molecules detach from the PPY and form a separate phase, probably with water. This was also supported by the FT-IR measurements, which indicate that the hydrogen bonds are broken if x is high and the films are wetted. Figure 24 shows a schematic picture of the suggested self-assembled structures with low and high loading of TFSI.
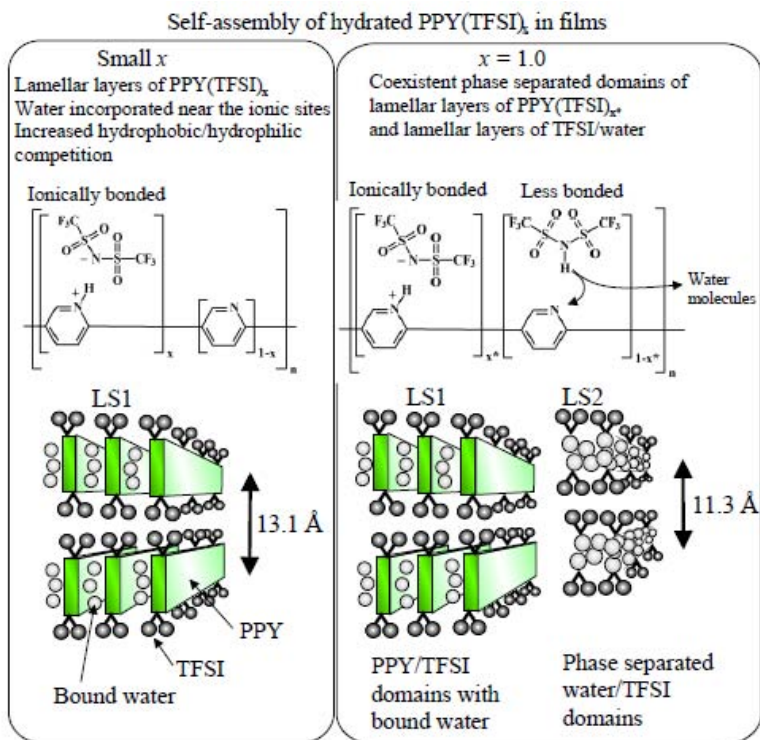
Figure 24. The suggested schematic presentation of PPY(TFSI)$_x$ in the hydrated state in thin films on a glass substrate. For low nominal degrees of complexation (up to a limiting value x^* which is between 0.25 and 0.50), there is only lamellar self-assembly due to the fact that PPY/TFSI complexes incorporate the absorbed water within the structure. For higher nominal degrees of complexation, the added TFSI further increases the hygroscopicity to cause phase separation of additional water which binds with the highly acidic amphiphilic TFSI-molecules. [Paper V]

Thus we showed that ionic liquids can really be used to induce a highly organised self-assembled structure when complexed with a rigid rod polymer. In addition, the complexes showed reasonable high protonic conductivity values in the order of 10^{-4} S/cm (see paper V) at room atmosphere. However, this is just a first step towards working fuel cell membranes. It would be interesting to determine whether the PPY(TFSI) complex could maintain the conductivity level at elevated temperatures. It would also be important to determine if similar highly ordered structures could be achieved through printing. Finally, since the material is soft, it should be possible to orient the films by shearing. This could lead to *e.g.* anisotropic or improved conductivity values.

7. Summary

This thesis concentrated on how the structural design of different conducting polymers could be exploited to prepare materials with a specific function. In addition, the ability to fabricate thin films of these polymers was demonstrated by printing.

Polyaniline was used as a model material for high-speed gravure printing with an industrial-scale pilot printer. The special features and limitations of gravure, flexographic, screen and inkjet printing were also presented. Gravure printing was used as an example to introduce the challenges in the printing of conjugated polymers in more detail.

Conducting polymer sensors that are able to detect changes in temperature and humidity were presented. These sensors were based on polyaniline complexes that utilise functional counter-ions. The changes in temperature were followed with the help of a crystalline counter-ion, which has a different conformation below and above its melting temperature, inducing a detectable and reversible change in conductivity. The presence of humidity was detected with the help of a hygroscopic counter-ion, which crystallises and phase-separates in humid conditions, inducing a detectable and irreversible effect on the conductivity.

Polymers were also used as a middle layer in resistive memory elements, which were based on filamentary conduction inside the polymer film. We wanted to determine whether a semiconducting block between insulating blocks has any effect on the filament formation. The results showed that in this case, the polymer structure does not have a significant effect; instead the interface between the bottom electrode and the polymer was found to contribute to the electrical properties substantially.

A highly ordered protonically conducting polymer complex was achieved by combining a rigid rod polymer, poly(2,5-pyridine), with an ionic liquid material, bis(trifluoromethane)sulfonimide (TFSI), through ionic and hydrogen bonds.

Their complex showed extremely well-organised structures with reasonable protonic conductivity, demonstrating that the self-assembly of polymers can be improved with ionic liquids and that these materials might be utilised as membranes for proton-conducting fuel cells.

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Title
Structural investigations and processing of electronically and protonically conducting polymers

Abstract

Different conducting polymers form a special class of materials with the potential for many applications in organic electronics and functional materials. These polymers can be electronically conducting or semiconducting due to a conjugated polymer backbone, or alternatively possess conductivity due to mobile protons or other ions. This thesis discusses such conducting polymers and shows ways how they can be processed by printing and how the nanostructure allows controlling their electrical properties.

The printability of conducting polymers, studied in paper I, has opened up new fields for their use in electronics. We showed that conducting polymers like polyaniline can be printed with industrial printers and high speed (up to 100 m/min) on paper achieving 60 µm resolution.

One of the most promising fields for conducting polymers is sensor applications. Papers II and III show how polyaniline can be utilised to detect changes in temperature and moisture by selecting suitable counter-ions. Melting of the counter-ion side chains was found to induce a reversible change in conductivity. On the other hand, humidity triggered an irreversible change in conductivity due to crystallisation and phase-separation of the counter-ion.

Paper IV studies the effect of polymer microstructure in resistive memory de-vices. Even though the structure of polymers often has a significant effect on the electrical properties, in this case the polymer-electrode interface was found to be dominating.

Finally, paper V shows that highly self-assembled polymer complexes may be achieved by utilising ionic liquids. The polymer-ionic liquid complex forms a surprisingly well organised nanophase-separated structure that provides path-ways for proton conduction.

This thesis takes a step from the laboratory towards applications of conducting polymers and gives insight into utilisation and processing of functional materials to be used in organic electronics components and devices.

Tekijä(t)
Marja Vilkman

Nimeke

Tutkimuksia sähköisesti johtavien polymeerien rakenteista ja prosessoinnista

Tiivistelmä

Johtavat polymeerit tarjoavat mahdollisuuksia orgaanisen elektroniikan sovelluksiin ja toiminnallisiin materiaaleihin. Polymeeriketjun erityinen konjugoitunut rakenne mahdollistaa niiden toimimisen joko sähköä johtavina materiaaleina tai puolijohteina. Toisaalta polymeerit toimivat ionijohteina, jos niihin voidaan liittää liikkuvia protoneja tai muita ioneja. Tämä väitöskirja käsittelee johtavia polymeerejä ja esittelee, kuinka niitä voidaan käsitellä painomenetelmien avulla sekä kuinka polymeerien rakenne vaikuttaa niiden sähköisiin ominaisuuksiin.

Johdepolymeerien painettavuus, jota tutkittiin artikkelissa I, on mahdollistanut niiden uudenlaisen hyödyntämisen elektroniikassa. Väitöskirjassa osoitetaan, kuinka johtavaa polymeeriä, polyaniliinia, voidaan painaa teollisilla painokoneilla suurella nopeudella (100 m/min) ja saavuttaa 60 µm:n resoluutio.

Yksi lupaavimmista johdepolymeerisovelluksista on anturisovellukset. Artikkelit II ja III osoittavat, kuinka polyaniliinia voidaan hyödyntää lämpötila- ja kosteusantureissa, jos valitaan sille sopivat vastaionit. Vastaionien sivuketjujen sulaminen aiheutti palautuvan johtavuusmuutoksen. Toisaalta kosteus käynnisti palautumattoman johtavuusmuutoksen kiteytyvän ja faasierottuvan vastaionin ansiosta.

Artikkelissa IV tutkitaan, kuinka polymeerin rakenne vaikuttaa muistielementtien toimintaan. Vaikka yleensä polymeerin rakenteella on huomattava vaikutus sähköisiin ominaisuuksiin, tässä tapauksessa polymeerin ja elektrodin rajapinnalla oli hallitsevampi vaikutus.

Artikkeli V esittelee, kuinka ioninesteiden avulla voidaan saavuttaa itsejärjestyneitä polymeerirakenteita. Polymeeri-ioninestekompleksi muodostaa hämmästyttävän hyvin järjestyneen nanomittakaavan rakenteen, joka toimii protonijohteena.

Väitöskirja ottaa askeleen laboratoriosta kohti johtavien polymeerien sovelluksia ja osoittaa, kuinka toiminnallisia materiaaleja ja prosessointia voi hyödyntää orgaanisen elektroniikan komponenttien ja laitteiden valmistuksessa.

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Conducting polymers have been studied since their discovery in 1970s. They have shown potential to be used in many organic electronics applications like solar cells, displays and RFID tags. The applications of conducting polymers have the advantage of flexibility and low cost when compared to traditional silicon-based electronics.

However, often the polymers seem to have a life of their own and it might be difficult to predict their electrical properties. This thesis aims at taking control over the electrical properties of conducting polymers by modifying their structural order. A few methods for structural control are presented in the thesis.

To be able to lower the fabrication costs, an important field of research in organic electronics is large-scale production. Also this aspect is studied in this thesis and novel printing methods for conducting polymers are presented.

As an outcome, this thesis takes a step from the laboratory towards applications of conducting polymers. It shows how we can control the electrical properties of polymers by structural control and how the polymers can be processed by printing.