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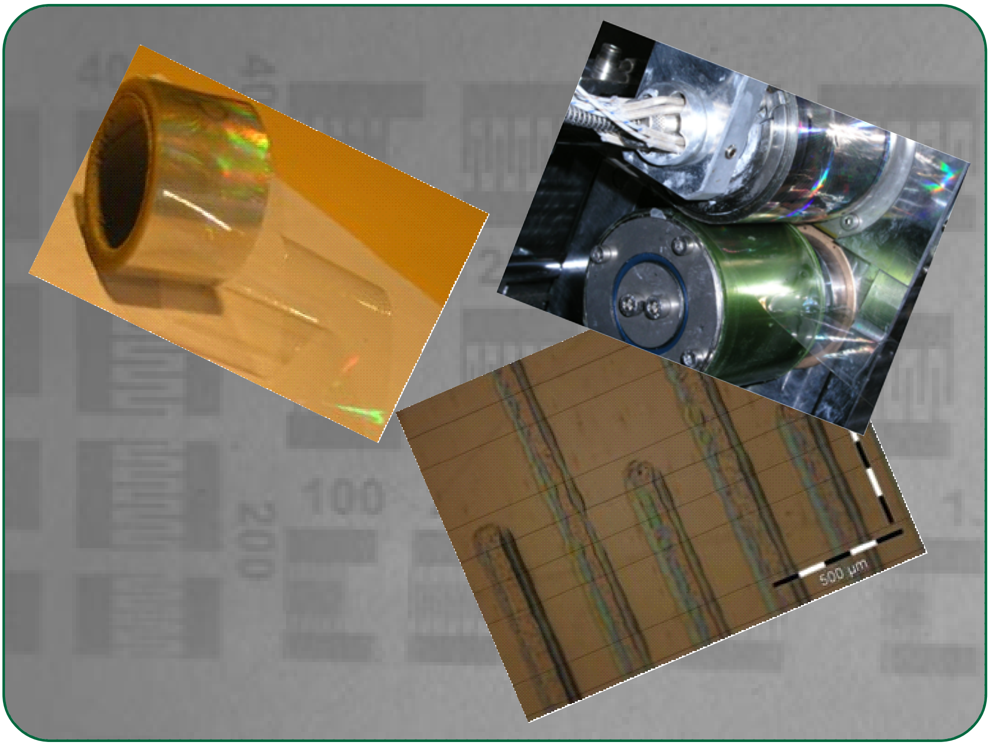

Tapio Mäkelä

Towards printed electronic devices

Large-scale processing methods for conducting polyaniline

Åbo Akademi University

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Large-scale processing methods for conducting polyaniline

Tapio Mäkelä

DOCTORAL DISSERTATION

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Mäkelä, Tapio. Towards printed electronic devices. Large-scale processing methods for conducting polyaniline [Sähköäjohtavan polyaniliinin prosessointi painettavassa elektroniikassa. Prosessering av elektriskt ledande polyanilin för tryckbar elektronik]. Espoo 2008. VTT Publications 674. 61 p. + app. 28 p.

Keywords polyaniline, conducting polymers, nanoimprint lithography, roll-to-roll, flexo, gravure

Abstract

In this work, five different patterning methods were developed to demonstrate the processing possibilities of polyaniline (PANI). Two different dopants, camphorsulfonic acid (CSA) and dodecylbenzenesulfonic acid (DBSA), were used to achieve PANI with high electrical conductivity that was soluble in various solvents. These solutions were used as printing inks in the processing.

PANI was used in step-by-step methods such as UV lithography and nanoimprinting lithography (NIL). The continuous methods used were rotogravure printing (GRAVURE), flexographic printing (FLEXO) and roll-to-roll nanoimprinting lithography (rrNIL). Dimensions from the submicrometre to the millimetre scale were demonstrated in both processing routes. The functionality of PANI within the studied methods is compared and problems in scaling up to high-volume manufacturing are discussed.

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Tiivistelmä

Tässä väitöskirjatyössä tutkittiin sähköäjohtavan polymeerin, polyaniliinin (PANI), soveltuvuutta painettavan elektroniikan valmistuksessa. Työn tavoitteena oli kehittää liuosmaisille polymeereille soveltuvia valmistusmenetelmiä. PANI-pohjaisia rakenteita tuotettiin muovi- ja paperisubstraateille viittä erilaista kuviointimenetelmää hyödyntäen. Substraatit valittiin kemiallisten ominaisuuksien, hinnan ja saatavuuden perusteella. Erityistä huomiota on kiinnitetty massatuotantoon soveltuviin menetelmiin, joissa PANIa voidaan hyödyntää painomusteen tavoin. Painetut rakenteet analysoitiin optisella mikroskoopilla, atomivoimamikroskoopilla (AFM) sekä sähköisten mittausten avulla. Menetelmien hyödynnettävyyttä elektroniikan valmistuksessa on vertailtu ja arvioitu.

Kokeissa käytettävät sähköäjohtavat PANI-liuokset aikaansaatiin protonoimalla polyaniliini-emäs substituoidulla hapolla, tässä työssä joko kamfersulfonihapolla (CSA) tai dodekyylibentseenisulfonihapolla (DBSA). Protonointi nostaa polymeerin sähkönjohtokykyä useita kertaluokkia sekä aikaansaa liukenevuuden, joka on perusedellytys vietäessä materiaali tutkittuihin prosessointimenetelmiin. Protonoinnin poistaminen palauttaa polymeerin sähkönjohtavuuden eristeen tasolle. Tätä erityisominaisuutta on hyödynnetty yhdessä prosessointimenetelmässä (UV-litografia). Muut UV-avusteisen litografian lisäksi hyödynnetyt menetelmät ovat nanoimprinttaus (NIL), syväpaino (GRAVURE), flexopaino (FLEXO), sekä rullalta-rullalle-nanoimprinttaus (rrNIL). UV- ja NIL-menetelmissä kuviointi tapahtuu substraatin ollessa paikallaan, kun taas GRAVURE-, FLEXO- ja rrNIL-menetelmät ovat jatkuvia rullalta-rullallemenetelmiä. Edellä mainituilla menetelmillä katetaan viivanleveydet nanometreistä millimetritasolle.

Työssä on osoitettu PANIn hyödynnettävyys em. valmistusmenetelmissä sekä mahdollisuus johdepolymeerien prosessointiin; paitsi osana perinteistä elektroniikan valmistusta esim. UV-tekniikalla, myös uusia menetelmiä hyödyntäen. Painetut sähköiset rakenteet aikaansaavat funktionaalisille polymeereille uusia käyttökohteita tulevaisuudessa. Rullalta-rullallemenetelmät mahdollistavat materiaalien käytön elektroniikan massatuotteissa.

Mäkelä, Tapio. Towards printed electronic devices. Large-scale processing methods for conducting polyaniline [Sähköäjohtavan polyaniliinin prosessointi painettavassa elektroniikassa. Prosessering av elektriskt ledande polyanilin för tryckbar elektronik]. Espoo 2008. VTT Publications 674. 61 s. + bil. 28 s.

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Referat

Doktorsavhandlingen behandlar möjligheterna att använda elektriskt ledande polymerer, speciellt polyanilin (PANI) för att tillverka tryckbar elektronik. Målsättningen var att utveckla tillverkningsmetoder för polymerer i lösning. PANI-baserade strukturer producerades på plast- och papperssubstrat med fem olika mönstringsmetoder. Substraten valdes utifrån kemiska egenskaper, pris och tillgänglighet. Speciellt betonades metoder lämpade för massproduktion, där PANI kan användas som en trycksvärta. De tryckta strukturerna analyserades med optisk mikroskopi, atomkraftmikroskopi (AFM) samt elektriska mätningar. Tillverkningsmetodernas lämplighet för framställning av tryckbar elektronik har utvärderats.

De elektriskt ledande PANI-lösningarna som användes vid försöken framställdes genom att protonera en PANI-bas med en substituerad syra, här antingen kamfersulfonsyra (CSA) eller dodecylbenzensulfonsyra (DBSA). Protoneringen höjer polymerens elektriska ledningsförmåga med flera tiopotenser och gör också att polymeren blir löslig, det senare en förutsättning för de undersökta framställningsmetoderna. En deprotonering återför polymeren till en elektrisk isolator. Denna specialegenskap utnyttjades i en processeringsmetod, ultraviolett litografi (UV). Metoderna som användes utöver UV-litografi var nanoimprintning (NIL), djuptryck (GRAVURE), flexotryck (FLEXO), och kontinuerlig (roll-to-roll) nanoimprintning (rrNIL). Vid mönstring med UV- och NIL-metoderna är subtratet stationärt medan GRAVURE-, FLEXO- och rrNIL-metoderna är kontinuerliga metoder. Dessa metoder täcker ett linjebreddsintervall från några nanometer till flere millimeter.

Arbetet påvisade PANIs användbarhet i ovan nämda tillverkningsmetoder. Dessa representerade dels processer som är konventionella vid elektronikproduktion såsom UV-litografi men även helt nya metoder. Tryckta strukturer ger funktionella polymerer helt nya användningsområden i framtiden. Roll-to-roll metoderna möjliggör tillämpningar inom massproducerad elektronik.

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List of publications

Paper I	Mäkelä, T., Pienimaa, S., Jussila, S. and Isotalo, H. Lithographic patterning of conductive polyaniline, Synth. Met. Vol. 101, 705–706 (1999).
Paper II	Mäkelä, T., Haatainen, T., Ahopelto, J. and Isotalo, H. Imprinted electrically conductive patterns from a polyaniline blend, J. Vac. Sci. Technol. B 19 (2), 487–489 (2001).
Paper III	Mäkelä, T., Haatainen, T., Ahopelto, J. and Isotalo, H. Imprinted electrically conductive polyaniline blends, Synth. Met. Vol. 121, 1309–1310 (2001).
Paper IV	Mäkelä, T., Jussila, S., Vilkman, M., Kosonen, H. and Korhonen, R. Roll-to-roll method for producing polyaniline patterns on paper, Synth. Met. Vol. 135–136, 41–42 (2003).
Paper V	Mäkelä, T., Jussila, S., Kosonen, H., Bäcklund, T., Sandberg, H. and Stubb, H. Utilizing roll-to-roll techniques for manufacturing source-drain electrodes for all-polymer field-effect transistors, Synth. Met. Vol. 153, 285–288 (2005).
Paper VI	Mäkelä, T., Haatainen, T., Majander, P. and Ahopelto, J. Continuous roll to roll nanoimprinting of inherently conducting polyaniline, Microelectr. Eng. 84, 877–879 (2007).

Author’s contribution

Paper I	The author participated in the planning of the experiments and did all the experimental work and analysis, and finalized the manuscript with the co-authors.
Papers II–III	The author did all the planning of the experiments and did all the polymer solutions, imprint experiments and conductivity measurements. The reactive ion etching (RIE) and film thickness measurements were done by M.Sc. T. Haatainen. The Si-stamp used in the experiments was prepared by the co-authors, T. Haatainen and J. Ahopelto. The author wrote the first version of the manuscript and finalized it with the co-authors.
Paper IV	The author did all the planning of the experiments, the measurements and analysis together with the co-authors. He wrote the manuscript and finalized it with the co-authors.
Paper V	The author did all the planning of the experiments and all printing experiments and analysis. The OFET device manufacturing and measurements were done together with the co-authors. He wrote the manuscript and finalized it with the co-authors.
Paper VI	The author did all the planning of the experiments, the polymer solutions, the sample manufacturing and the conductivity measurements. The Ni-stamps used in work were done by M.Sc. T. Haatainen and M.Sc. P. Majander. The author wrote the paper and finalized it together with the co-authors.

Related publications

Paper VII Kaihovirta, N., Tobjörk, D., Mäkelä, T. and Österbacka, R. Low-Voltage Organic Transistors Fabricated Using Reverse Gravure Coating on Prepatterned Substrates, Adv. Eng. Mater. (2008), in press.

Paper VIII Sandberg, H., Bäcklund, T., Österbacka, R., Jussila, S., Mäkelä, T. and Stubb, H. Applications of an all-polymer solution-processed high-performance transistor, Synth. Met. Vol. 155, 662–665 (2005).

Paper IX Bäcklund, T., Sandberg, H., Österbacka, R., Mäkelä, T., Jussila, S. and Stubb, H. Towards all-polymer field-effect transistors with solution processable materials, Synth. Met. Vol. 148, 87–91 (2005).

Paper X Tiitu, M., Hiekkataipale, P., Hartikainen, J., Mäkelä, T. and Ikkala, O. Viscoelastic and electrical transitions in gelation of electrically conducting polyaniline, Macromolecules Vol. 35, 5212–5217 (2002).

Paper XI Mäkelä, T., Sten, J., Hujanen, A. and Isotalo, H. High freguency polyaniline shields, Synth. Met. Vol. 101, 707 (1999).

Paper XII Mäkelä, T., Pienimaa, S., Taka, T., Jussila, S. and Isotalo, H. Thin Polyaniline Films in EMI shielding, Synth. Met. Vol. 85, 1335–1336 (1997).

Paper XIII Mäkelä, T. and Kosonen, H. Temperature detector/indicator, FIN Patent 113895 (2004).

Paper XIV Mäkelä, T., Pietilä, M., Jussila, S. and Korhonen, R. Layered structure, sensor and method of producing and using the same, US Patent 7157134 B2 (2007).

Contents

Appendices

Publications I–VI

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List of abbreviations and symbols

AFM	Atomic force microscope
$(CH)_x$	Polyacetylene
CSA	Camphorsulfonic acid
DBSA	Dodecylbenzenesulfonic acid
EB	Emeraldine base
EBeam	Electron beam
EMC	Electromagnetic compatibility
FLEXO	Flexographic printing
GRAVURE	Rotogravure printing
IC	Integrated circuit
ICP	Inherently conducting polymer
	Intrinsically conducting polymer
LEB	Leucoemeraldine base
m-cresol	Meta-cresol
MIMIC	Micromoulding in capillaries
NIL	Nanoimprinting lithography (also hot embossing)
NIP	Place of contact where one roll touches another
OFET	Organic field-effect transistor
OLED	Organic light emitting diode
PANI	Polyaniline
PC	Polycarbonate
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEN	Poly(ethylene-2,6-naphthalate)
PET	Polyethylene terephthalate
PHT	Poly(3-hexylthiophene)

PMMA	Polymethylmethacrylate
PNB	Pernigraniline Base
PP	Polypropylene
PSS	Polystyrenesulfonate
PT	Polythiophene
PVP	Poly(vinylphenol)
RFID	Radiofrequency identification
RIE	Reactive ion etching
RM	Replica moulding
rrNIL	Roll-to-roll nanoimprinting lithography (also roll-to-roll hot embossing)
rrPHT	Regio-regular poly(3-hexylthiophene)
SAMIM	Solvent assisted micromoulding
SFIL	Step-and-flash imprint lithography
T_g	Glass transition temperature
Trans-$(CH)_x$	Trans-polyacetylene
UV	Ultraviolet
wt-%	Percentage of weight
η	Viscosity
μCP	Microcontact printing
μTM	Microtransfer moulding

1 Introduction

Inherently conducting polymers (ICPs) were discovered in 1977 when the first reports on electrical conductivity in doped polyacetylene $(CH)_x$ were published [1, 2]. This discovery revealed new exotic fundamental properties in polymers and a new lively basic research field was born.

The new research activities on ICPs were also stimulated by the novel applications that were foreseen. The combination of electrical conductivity and the properties and processability of polymers was tempting. Most of the early proposed applications were based on replacing inorganic materials in various products.

A special focus was on highly conducting polymers. Soon, lower conductivities, and especially the semi-conducting regime, became equally interesting. The semiconductor properties of ICPs were giving rise to new electronic device concepts. Today, the processability properties are highly stressed when looking for low-cost large-scale production. ICPs in polymer blends and inks are in focus for plastics processing and printing techniques.

The applications realised so far [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17] include high conductivity materials for conductors, electromagnetic shieldings (EMC), batteries, capacitors, resistors, etc. Lower conductivities are applied in antistatic applications or anticorrosion coatings.

In the semiconductor state, ICPs have launched applications such as organic light emitting diodes (OLEDs) [18, 19, 20, 21], organic field-effect transistors (OFETs) [22, 23, 24, 25], solar cells [26] – some including efficiency enhancing blend concepts – and electrochromic displays [27]. All these organic electronic devices can be based on molecules, oligomers, polymers or blends. The most studied organic devices are OLEDs, OFETs, solar cells and, most recently, plastic memory concepts [28]. Various interactions with humidity, temperature, ultraviolet (UV) light and biological environments are also proposed for sensor concepts. On a system basis, including large-scale processing, these can form complex information systems.

Today, one talks about printable electronics and paper-based intelligence. Obviously, this calls for polymer resins for all electronic materials, including metals, semiconductors and insulators. In this work some concepts for large-scale polymer electronics are developed. In particular, the focus lies on the problems connected with scaling up the processing. One then looks for suitable printing techniques, ultimately roll-to-roll manufacturing. This calls for special properties in the various electronic materials.

Highly conducting polyaniline (PANI) processed from solution or as a blend is in focus in this work. A number of processing and printing techniques have been developed: step-by-step methods such as UV lithography, thermal nanoimprinting lithography (NIL) and continuous methods such as rotogravure printing (GRAVURE), flexographic printing (FLEXO) and roll-to-roll nanoimprinting lithography (rrNIL), which will be described using PANI as a case material. Various substrate materials, such as plastics, paper and glass has been used. These have been chosen and developed only to a stage where they fulfil their purpose, without further development efforts.

The processing of conjugated polymers has been difficult, but nowadays the solubility and stability of PANI at room atmosphere is sufficient, thereby allowing ink formulations and repeatable processing parameters. In industrial-scale applications, low material costs, availability, different solvents, non-toxicity, high conductivity and processing by printing give increased possibilities to use PANI.

This work starts with an introduction part covering the basic properties of ICPs, especially PANI, followed by a presentation of the various processing and printing methods, including both step-by-step and continuous processing methods, again with special emphasis on PANI. The following experimental section covers techniques and equipment. All papers included in this thesis are related to the processing and possible applications of PANI. The results and discussion part will cover the findings, key problems and future possibilities.

1.1 Conducting polymers and PANI

The molecular structures of some typical ICPs – $(CH)_x$, polythiophene (PT), polypyrrole and PANI – are shown in Figure 1 [29]. The general demand for electrical conductivity in polymers is a conjugated backbone structure where single and double bonds alternate. In conjugated polymers (unlike in insulating polymers), sp^2p_z hybridization leads to one unpaired electron per carbon atom; therefore, all four valence electrons are not tied up. Electronically, the conjugated backbone leads to a semiconductor-like energy band structure where the valence band is separated from the conduction band by a forbidden energy gap. The magnitude of the energy gap ranges from 1.5 eV to several eV, making these materials electrical insulators or semiconductors.

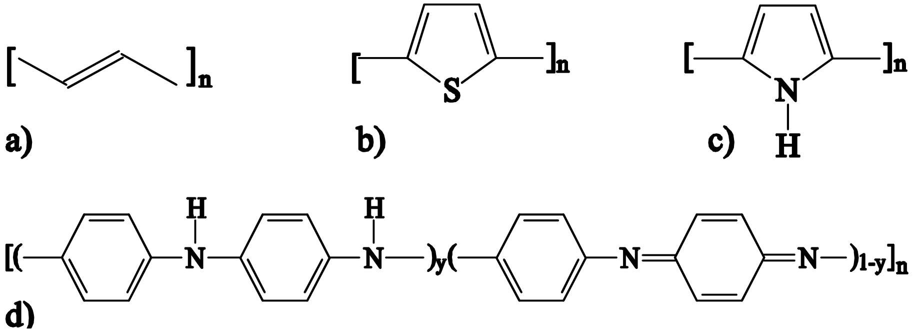

Figure 1. Molecular structure of a) $(CH)_x$, b) PT, c) polypyrrole and d) PANI [29].

Electrical conductivity can be increased by many orders of magnitude by doping chemically or electrochemically. The doping process is typically oxidation (p-type) but reduction (n-type) is also possible. As an example to illustrate the chemical doping process $(CH)_x$ is used. The following reaction can be used for p-type doping of $(CH)_x$:

$$2\left(NO^{+}PF_{6}^{-}\right)_{y/2}+\left(CH\right)_{x}\rightarrow\left(N_{2}O_{2}\right)\Big|_{gas}+\left[\left(CH\right)^{+y}\left(PF_{6}^{-}\right)_{y}\right]_{x} \tag{1}$$

In this or any other analogous reaction (NO^{+}) is the oxidizing agent. PF_6^- assures charge neutrality and determines the overall properties of the end product. N_2O_2 is a surplus, in this case a gas, which has to be considered and often eliminated. The reaction is carried out in a suitable solvent. Solubility or processability of the doped polymer is one of most important factors when ICPs are used in applications and the above-mentioned counter ions, such as PF_6^-, may facilitate suitable solvents [29, 30]. In the early states, ICPs were unstable in room atmosphere, solubility was poor and the processing materials were often toxic.

One of the most examined conjugated polymers is PANI, which has relatively high conductivity and stability in room atmosphere and at elevated temperatures [3, 4, 5, 31, 32, 33, 34, 35, 36]. The different oxidation states of PANI are shown in Figure 2.

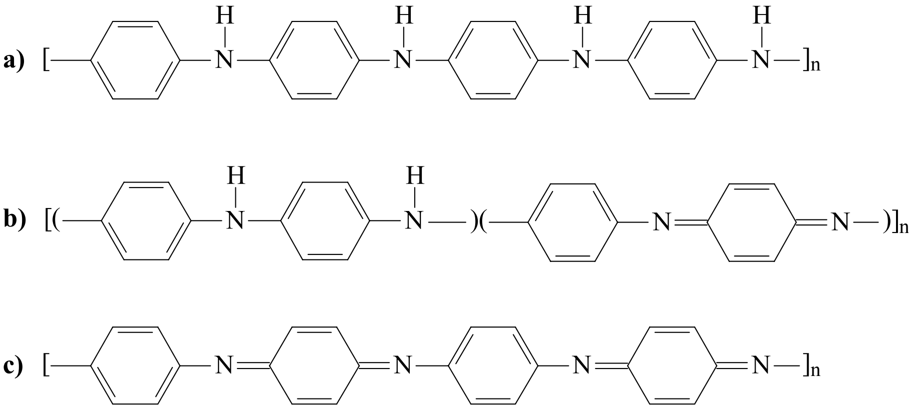

Figure 2. Different oxidation states of PANI: a) fully reduced LeucoEmeraldine Base (PANI-LEB), b) half-oxidized Emeraldine Base (PANI-EB), and c) completely oxidized PerNigraniline Base (PANI-PNB) [31, 39].

PANI-EB is stable in air and used in most of the cases as the starting material in the doping process. PANI-EB is different from most other ICPs since it has amine and imine nitrogens in its conjugated backbone. Doping of PANI can be done from PANI-EB by acid base complexation [2, 39, 29, 42] or from PANI-LEB by oxidative doping [37, 42]. In both doping processes the electrically conducting emeraldine salt is formed. Today, the most developed method to obtain conducting PANI is to protonate PANI-EB with a functionalized organic acid. For this purpose, camphorsulfonic acid (CSA) or dodecylbenzenesulfonic acid (DBSA) are usually used. The chemical structures of these acids are shown in Figure 3.

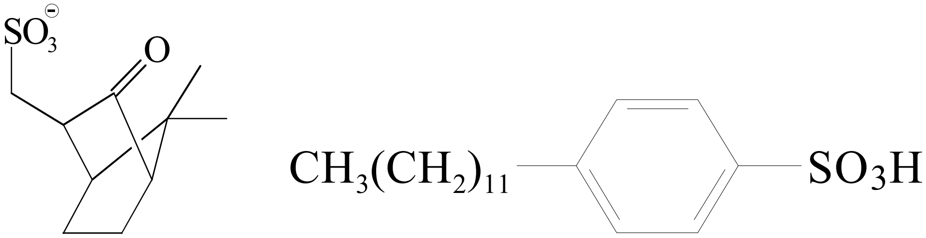

Figure 3. Chemical structures of functionalized organic acids: CSA (left) and DBSA (right) [38, 39].

These acids serve two purposes; protonating PANI and making the complex more soluble in different solvents due to the long polymer tail. Protonating of PANI-EB leads to the conducting emeraldine salt form as shown in Figure 4.

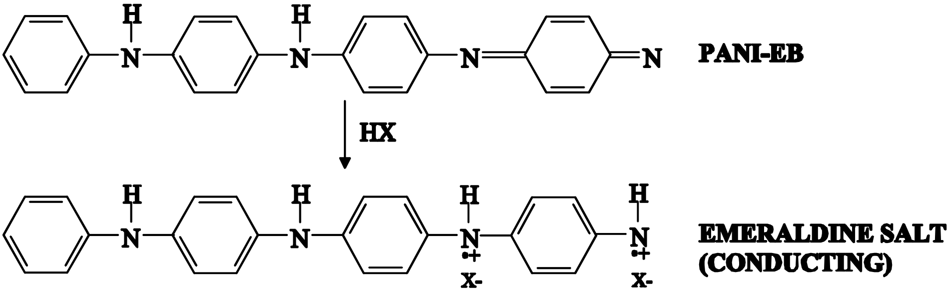

Figure 4. Doping by protonation of PANI-EB. Here $\boldsymbol{X}^-$ *denotes* CSA^- *or* $DBSA^-$ *corresponding to the functionalized organic acid [2, 39, 29].*

Doping can be done with PANI as a powder or in solution. In this work, PANI-EB powder is doped with CSA and further doped with DBSA in solution.

In Figure 5, the conductivity of trans-polyacetylene (Trans-$(CH)_x$), PANI and Poly(3,4-ethylenedioxythiophene) (PEDOT) are shown as a function of doping and compared to inorganic materials [29].

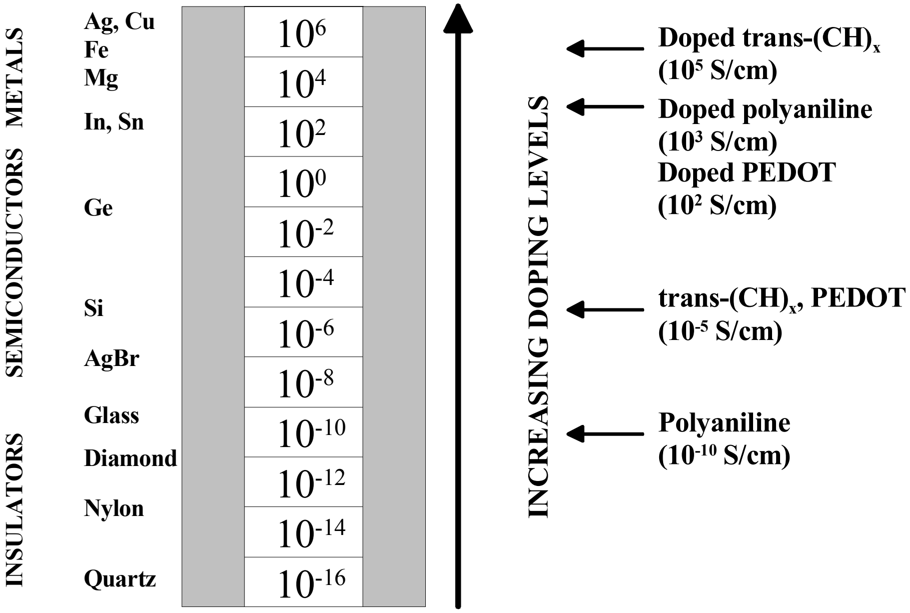

Figure 5. Typical conductivities of inorganic and electronic polymers [3, 29].

1.2 Solubility of PANI for printing inks

When ICPs are used as a printing ink, miscibility in different organic solvents or water is needed. The solubility of ICPs is relatively poor and suitable solvents are difficult to find, at least in cases where the polymer is in the highest conductive (doped) form. Depending on the choice of solvent, the conductivity of the solution can be higher or lower than that of the doped PANI powder. Different solvents for undoped PANI-EB are listed in Ref. [39] and some solvents for fully protonated PANI with CSA and DBSA are shown in Table 1 [40, 41]. PANI in aqueous solutions has not been studied in this thesis but studies can be found in Ref. [42].

Table 1. Solubility of PANI in different solvents and resulting conductivities [40].

Solvent	**Solubility (wt-%)**	**Conductivity in film (S/cm)**
CSA doped		
m-cresol	2–10	300
dichloroacetic acid	2–6	80
hexafluoropropanol	2–4	60
benzylalcohol	0.5–2	10^{-4}
chloroform ($CHCl_3$)	0.5–2	1
formic acid	2–4	10^{-2}
dimethylsulfoxide(DMSO)	1–2	10^{-2}
N-methylpyrrolidone (NMP)	2–4	10^{-4}
DBSA-doped		
toluene	1–7	87

The demands on PANI formulas concern viscosity, solid content (dry thickness), particle size, adhesion to substrate, wettability, evaporation rate, conductivity, process temperature, suitability for printing equipment, stability, pot life and cost. The demands on the substrates concerning flexibility, thickness, softening temperature, melting point, temperature coefficient, chemical resistance, recycling, etc., are not covered in this work. The substrates used in the experiments are chosen to be suitable for the respective PANI solutions.

2 Processing methods for PANI

The potential applications in printable organic electronics, functional packages and other plastic or paper-based products have increased throughout the development of low-cost and fast manufacturing techniques. Numerous different methods have been proposed for ICPs, such as PANI, PEDOT and Poly(3-hexylthiophene) (PHT). Some of the proposed methods have already been realized on the industrial scale [43, 44, 45, 46, 47, 48, 49, 50, 51, 52].

It is improbable that one specific printing or manufacturing technique can cover all the needs in the industry. Small line width and thin layers are necessities for some applications. In other cases perhaps, high speed is needed but lower resolution can be used. For example, in UV lithography and NIL processes the line widths are in the micrometre or submicrometre range whereas in manufacturing techniques such as GRAVURE or FLEXO the achieved line widths are tens of micrometre [53, 54, 55, 57]. When choosing a suitable printing method, line width, thickness and speed are critical, but price, viscosity, aligning accuracy of printed layers, existing printing devices, suitability of solvent, new processing combinations, suitability of substrates, etc., must be considered as well.

Processes for both step-by-step and continuous processes are described in this chapter. The methods studied and used in Papers I–VI include FLEXO and GRAVURE methods, which are known as printing techniques, and UV lithography and NIL methods known as patterning or manufacturing techniques. The main difference between these is that in the first two cases ICPs are transferred directly from solution to the final design while in the second two the material is first coated as a homogenous layer on the substrate and then an extra step is needed to achieve the desired design. Table 2 shows the typical process resolution and the ink parameters for GRAVURE, FLEXO, NIL and rrNIL. These values have been used as a guide for our PANI ink preparation.

Table 2. Typical process parameters used in this work. Achieved resolution, film thickness, ink viscosity, typical solvent and estimated throughput are shown.

	Printing		**Patterning**		
	GRAVURE [54, 55, 57]	FLEXO [54, 55, 57]	UV [56]	NIL	rrNIL
Resolution (μm)	75	75	~ 2	0.006 [65]	< 0.1*
Film thickness (μm)	2–5	3–8	0.1–5	~ 0.01–0.5	~ 0.01–0.5
Ink viscosity (mPas)	50–200	50–500	N/A	N/A	N/A
Typical solvents	toluene, alcohols, esters, water	water, alcohols, esters	N/A	N/A	N/A
Throughput (m^2/s)	10	60	~ 0.1*	~ 0.0001*	~ 0.005*

* Author's estimate

These manufacturing or patterning methods for PANI are chosen because of their potential use in high-volume processes. It is difficult to evaluate the superiority of different methods since the best method for production depends on the chosen application. As the ultimate goal a novel continuous rrNIL method for PANI is developed. In this method, high-volume manufacturing with submicrometre line width was realized.

2.1 Step-by-step methods

Step-by-step methods are typically used in microelectronic manufacturing for processing Si-based electronics (Si-wafers) [56]. In a step-by-step process the substrate is moved to a position where it stops and processing occurs. This technique offers smaller line width and/or better alignment accuracy between the layers compared to continuous roll-to-roll methods such as FLEXO or GRAVURE. Using step-by-step methods, it is possible to process a huge number of Si-wafers or printed circuit boards in hours (> 1000 pcs/hour). However, continuous roll-to-roll GRAVURE manufacturing offers a thousand times faster process speed [57]. The flexibility and the size of the substrate determine the process in most of the cases. Both step-by-step and continuous techniques are needed in the case of PANI.

2.1.1 UV lithography

UV lithography is one of the most commonly used patterning methods in the electronics industry, and is readily available in many research laboratories. This method enables good reproducibility of the polymer structures, even on a micrometre scale. As shown in Chapter 1, electrically conducting PANI can appear in different oxidation states. The protonation and deprotonation of PANI can be controlled chemically or by irradiation. For example, PANI doped with CSA dissolved in m-cresol and mixed with a photoinitiator has been patterned directly with UV light through a mask, as reported by D.M. de Leeuw et al. from Philips [58, 59]. In this method the illuminated part of PANI reduced to the non-conducting form. This method has been used for demonstrating all-polymer circuits, where PANI works as electrodes or interconnects in devices.

UV-assisted lithography is one of the first proposed industrial-scale patterning methods for PANI. M. Angelopoulos et al. from IBM have shown an *in situ* doping process where undoped PANI becomes doped (conductive) upon UV or electron beam (Ebeam) radiation [60, 3]. Conducting polymers such as water-processable PANI (PanAquas) have also been used as a discharge layer or direct Ebeam patternable conducting resist, where the exposed part becomes insoluble in water. The reported line widths are down to 0.25 micrometre when using this technique [3].

Integrated circuit (IC) devices typically need a number of different processing steps. Materials are layered on top of silicon, plastic or other substrates and aligned on top of each other. The process is complex and consists of deposition, patterning and etching steps. A typical photolithography process in microelectronics has been shown in Refs. [3, 56]. In the UV lithography, one of the main targets has been integrating PANI into the same manufacturing process as inorganic materials.

In Paper I, PANI is used in a conventional photolithographic process on a polycarbonate (PC) substrate (see Figure 6 and *step a* therein). Similar processes to pattern conducting polymers have been proposed earlier [61] but normally additional dedoping or etching steps are used (Figure 6 and *step b* therein). In the first mentioned case, *a),* the final structure is planarised and adding extra layers is more easily done. However, the second case, *b),* is more compatible with other printing methods described in this work.

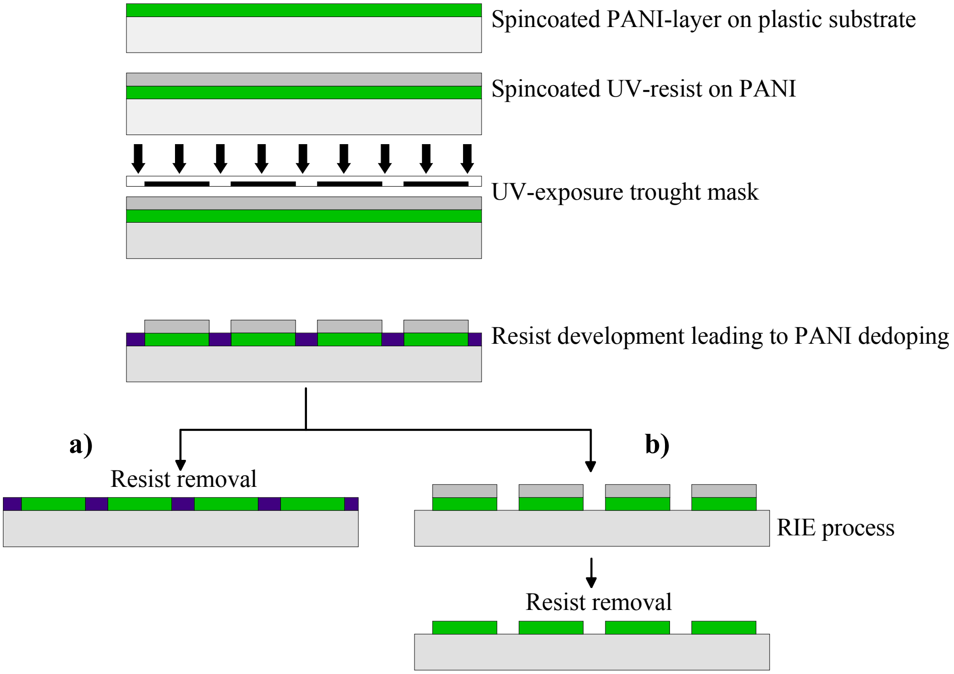

Figure 6. Schematic presentation of photolithographic process for PANI. After development of the UV resist, a planarized structure can be achieved by diluting the remaining resist with a suitable solvent (step a; also shown in Paper I). An extra step, such as reactive ion etching (RIE), can be used (step b) to remove the non-conductive PANI layer.

2.1.2 Nanoimprinting

Demands on decreasing the size in microelectronic components have driven the development of novel low-cost patterning methods to the submicrometre scale. The NIL [62, 63, 64, 65, 66] process was originally developed for the realization of inorganic nanostructures [67], nanodots [62], nanowires [68], field effect transistors [69, 70] and optical gratings [71]. Today, the smallest achieved feature with thermal NIL is 6 nm [72, 73]. Other nanofabrication techniques, such as immersion lithography, scanning beam lithography, replica moulding (RM), step-and-flash imprint lithography (SFIL), microtransfer moulding (μTM), micromoulding in capillaries (MIMIC), solvent assisted micromoulding (SAMIM) and microcontact printing (μCP), are described in Refs. [74, 75].

At the beginning of NIL, polymethylmethacrylate (PMMA) was used as an imprint resist in most of the cases. The schematic process of thermal NIL is shown in Figure 7 (left), where the thermoplastic PMMA resist is heated above its glass transition (T_g) temperature. The resist changes its viscosity above T_g and fills the empty areas in the mould. Pressure and time are other factors that influence the NIL process. Flow simulations for different thermoplastic materials are presented in Refs. [76, 77]. In NIL, residual layers always remain on the surface, as shown in Refs. [62–72] and it can be removed by using RIE or other etching methods [78, 79, 80, 81]. In the case of imprinted PMMA lines, a conventional lift-off process (metal evaporation and resist dissolving) is used for finishing an electrically conducting structure.

The imprint process for an electrically conductive PMMA/PANI-CSA blend is shown in Figure 7 (right). The main difference from the PMMA process is using a reverse stamp. Also, the electrically conducting structure is finished after the RIE process and no extra step is needed (Papers II–III).

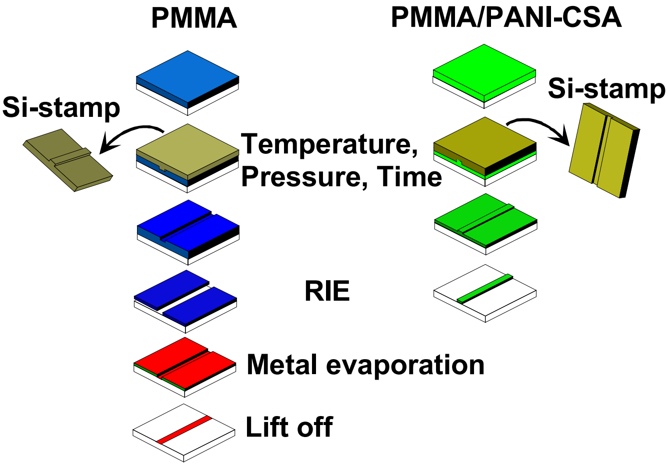

Figure 7. NIL process steps for insulating (left) and conducting (right scheme) materials when an electrically conducting line is prepared. PMMA or electrically conductive PMMA/PANI-CSA blend is spin-coated on a glass substrate. In both cases a silicon stamp is pressed against the film at 140°C and 15 MPa for 10 minutes, but for conducting blends a reverse stamp is used. As a result, a PMMA or PMMA/PANI-CSA structure is formed. RIE is used to remove the residual layers. In the case of PMMA, extra metal evaporation and a lift-off process step are needed to make an electrically conducting structure.

2.2 Continuous methods

The fundamental understanding of the continuous roll-to-roll manufacturing processes was already documented a hundred years ago when GRAVURE and FLEXO methods were developed [57]. In these methods the active materials have typically been in solution form. A number of other methods have been developed and used when printing newspapers, magazines, paper and plastic packages, envelopes and antistatic coatings. The most commonly used continuous processing techniques in the graphic industry are offset, GRAVURE, FLEXO and inkjet. To demonstrate the possibilities for PANI, GRAVURE (Paper IV) and FLEXO (Paper V) techniques are chosen.

Continuous rrNIL of polymers has also been used in industrial scale manufacturing of optical elements such as holograms. In that case the materials used in the process are normally plastic films or polymer layers coated on the web. In the latter case the coating of a uniform layer can be done by the printing method mentioned above. To pattern PANI at room temperature a rrNIL technique was used. A combinatorial method where GRAVURE is used together with rrNIL in the same process cycle has also been developed.

2.2.1 Rotogravure printing

GRAVURE is one of the oldest printing techniques used in industry. GRAVURE has typically been used for printing magazines with high volumes (more than 500,000 copies) since metallic printing rolls are resistant to different solvents and durability is high. However, printing rolls are expensive. The principle of the continuous GRAVURE process is shown in Figure 8. The printing method is quite simple: the printing ink is transferred from the ink container direct to the engraved metallic cylinder and transferred to the web. In GRAVURE the image elements are engraved into the printing cylinder, whereas the non-image areas are at the original level. The resolution is 40–140 lines/cm. Typically, the minimum achieved lateral resolution is 75 micrometre when industrial equipment is used.

In the printing process the printing cylinder is inked and the ink is removed from the non-image area by blading (doctor blade) before the ink is transferred to the substrate. Due to the engraved pits on the roll, the method enables the transfer of different amounts of material in different locations. An optical microscope image of an engraved gravure roll is shown in Figure 9. Here, cell depths of 14, 26 and 33 micrometre are shown (70 lines/cm). Typical GRAVURE creates "dot type" images and is not suitable for printing lines (wires). The term *intaglio* is used in cases where the engraved roll contains lines. Then, much higher viscosity inks are needed.

The basic principle of GRAVURE is shown in more detail in Refs. [54, 55, 57, 82, 83, 84]. Since the transfer roll is metallic (normally Cr-plated), most organic solvents can be used with this technique. The ink transfer from the printing cylinder to the web can also be controlled by adjusting the pressure between the rolls, in contrast to FLEXO where only the physical and chemical properties of the image plate, substrate and ink define the amount of transferred ink.

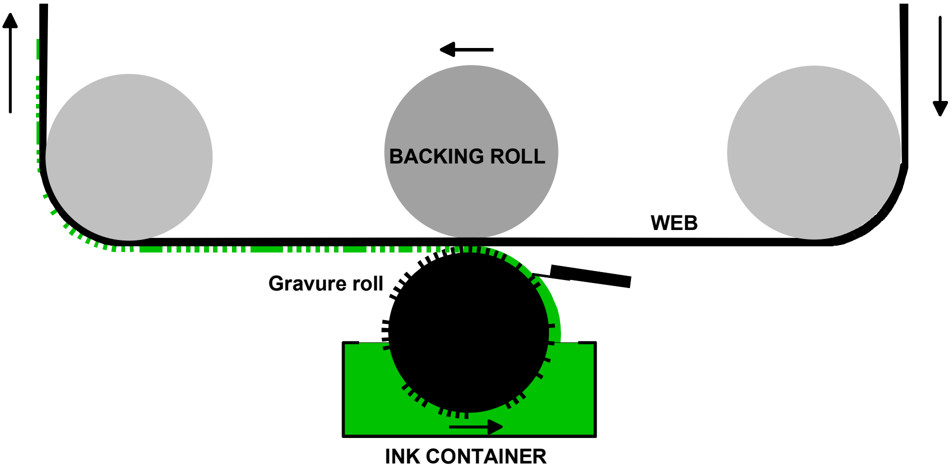

Figure 8. Schematic principle of the continuous (roll-to-roll) GRAVURE process. The printing ink is transferred from the ink container to the engraved metallic cylinder. The printing cylinder is inked and the ink is removed from the non-image area by blading (doctor blade) before the ink is transferred to the substrate. The transfer from the cylinder can be improved by increasing the pressure between the gravure and backing rolls.

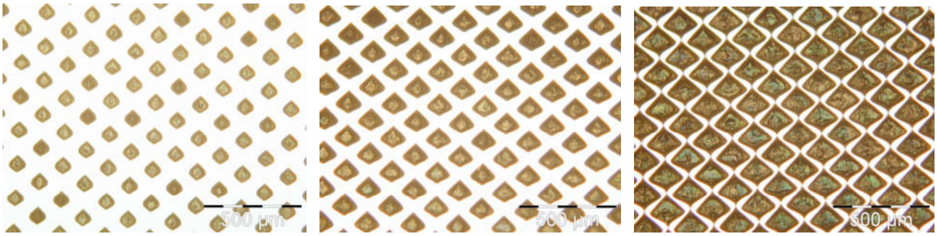

Figure 9. Examples of engraved cylinder surfaces. In this case the cell depths are 14, 26 and 33 micrometre (from left to right) when the resolution 70 l/cm was kept constant.

2.2.2 Flexographic printing

FLEXO is commonly used for printing food packages, bags and envelopes. In the flexible image plate the image element is raised above the non-image area. In the FLEXO process the printing ink is first transferred to the so-called anilox roll and the surplus is removed by blading (doctor blade). The ink is transferred from the anilox to the flexoplate, which contains the desired pattern. The flexoplate transfers the image to the web. A schematic picture of FLEXO is shown in Figure 10.

The anilox roll is ceramic or chromium coated containing cells with widths corresponding to 200–600 lines/cm. The flexible printing plate is made of photocurable rubber, as described in Refs. [31, 32]. The typical resolution in the photopolymer plate is approximately 60 lines/cm (50–100 micrometre). The printing ink transfers from the flexoplate to the web using only light pressure. In GRAVURE the pressure may be 100 times higher. In the FLEXO method the chemical and physical properties of the ink and the substrate are more important than in GRAVURE. Methods to treat web surfaces are presented in Ref. [85] and FLEXO more thoroughly in Refs. [53, 54, 55, 57, 86]. FLEXO has recently been used for realizing silver-ink printed antennas for radiofrequency identification (RFID) [87].

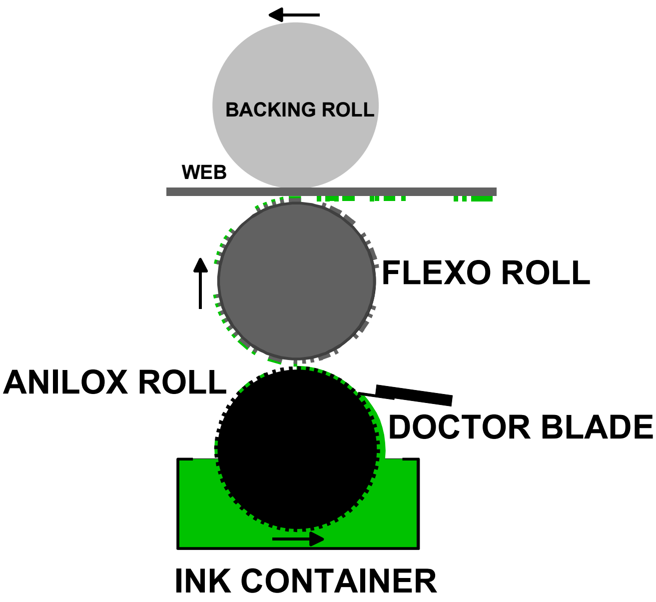

Figure 10. Principle of the continuous (roll-to-roll) FLEXO process. The printing ink is transferred from the ink container to the anilox cylinder, where surplus ink is removed by blading (doctor blade) before the ink is transferred to the flexoplate. From the flexoplate ink is transferred to the web using only light pressure.

2.2.3 Roll-to-roll nanoimprinting lithography

The NIL (or hot embossing) process, where a roll is used to fabricate patterns with nanometre resolution, has been proposed in Refs. [88, 89], where a thin electroplated nickel or plastic master is wrapped onto the cylinder and used for making microlens arrays in a UV-curable resin layer. rrNIL processes are used for thermoplastic polymers or films in industry [90, 91, 92] and for structuring textile fibres [93] but scientific publications on the process are difficult to find.

Continuous rrNIL of PANI was shown for the first time in Paper IV. In this paper a method where a gravure printing unit is used to form a film in the same process cycle right before an rrNIL unit is shown. This combination enables continuous processing. A schematic picture of rrNIL and the printing roll is shown in Figure 11. In the process, a Ni-shim or other flexible master is wrapped onto the cylinder to create the printing pattern. In this work, Ni-stamps were fabricated using an electroplating technique, but many different ways of fabricating nanoscale dimensions in stamps are shown in Refs. [94, 95, 96]. An antiadhesion layer on the Ni-stamps is normally used to avoid material sticking to the Ni-master [97].

When the rrNIL roll and the backing roll are pressed against each other the printing pattern can be transferred to the coated web or to the plastic film. When thermoplastic materials are used the printing roll is normally heated above the T_g of the material. Unlike the thermal NIL process, the temperature in the material increases locally above T_g only in the place where the printing roll makes contact with the material, the so-called NIP. In rrNIL for PANI, room temperature is used.

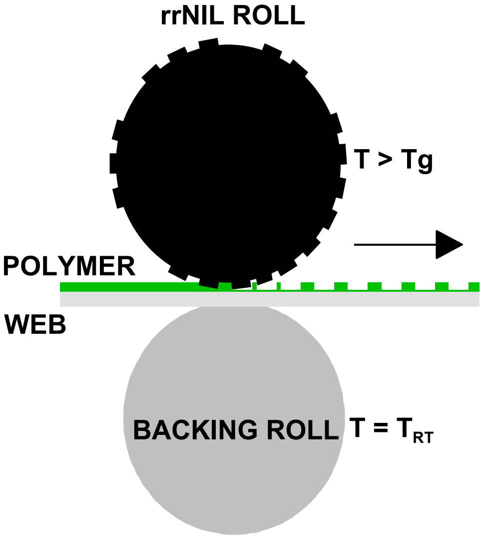

Figure 11. Schematic picture of rrNIL where a Ni-shim is wrapped on the printing roll. The printing cylinder is a tube and an electrical heater can be added inside the cylinder.

3 Experimental

3.1 UV lithography

The PANI-EB (from Panipol OY) used in Paper I was converted from an insulator to a conductor with a doping process presented in Ref. [98] using CSA. The PANI-CSA powder was diluted with m-cresol to a 4 wt-% solution. The PANI-CSA solution was spin or spray coated to form an electrically conducting film (110 μm, 100 S/cm) on a PC substrate.

Photoresist AZ5214E from Clariant (positive) was spin coated on top of the PANI layer and baked for 15 minutes at 90^{o}C. The photoresist was then exposed using a normal lithographic exposure tool through a glass mask. The irradiated part was dissolved with a strongly alkaline developer solution (AZ351, 1:3 with water) for 1 minute and flushed with pure water. The PANI layer makes direct contact with the developer in the parts where the photoresist has been removed. Here, PANI deprotonates and changes its conductivity from conductor to insulator. Finally, the rest of the photoresist was flushed away using isopropanol, as shown in the schematic process in Figure 6 a).

If one wants to remove the residual PANI layer, RIE can be used as shown in the alternative process line in Figure 6 b). The etching rate for PANI was determined in Paper III. Unlike inorganic conductors in microelectronics, the etching step and planarisation step later on are not needed. This decreases the number of steps in the process.

3.2 Nanoimprinting lithography (NIL)

In Papers II and III a nanoimprinting process where PANI was mixed with PMMA and used as an electrically conducting resist is demonstrated. PANI doped with CSA was mixed with PMMA to form a (PMMA/PANI-CSA) blend in m-cresol [99, 100]. The amount of PANI-CSA was 10–40 wt-% in the blend, corresponding to a conductivity of 0.07–10 S/cm. The m-cresol blend was spin coated on the glass substrate at a speed of 2000 rmp and baked for 1 hour at 80^{o}C. The T_g of PMMA/PANI-CSA blend equals the T_g of pure PMMA 105^{o}C (950 000 M_w from Cipec Ltd.)

The electrically conductive film was spin coated on the glass substrate followed by imprinting with a silicon stamp. The imprinting experiments were performed using a commercial pressure cylinder. The sample was heated to 140°C and cooled back to room temperature under pressure. The silicon stamp was attached to a Teflon plate, allowing the stamp to adjust itself with the substrate. The controllable parameters of the imprint process window were temperature, pressure and time. The used temperature 140°C was well above PMMA's T_g, to ensure low enough viscosity when a pressure of 15 MPa was used.

The Si-stamp was processed using UV lithography and RIE. The stamp manufacturing process is presented in Ref. [95]. A stamp patterned with grating structures is used. The gratings were 500 nm deep with 5 µm lines and spaces. A 5 x 5 mm^2 stamp size was used for the imprint process. One stamp was used for several experiments and cleaned between experiments by flushing with acetone and isopropanol to remove polymer residuals. Other possible PANI blends in NIL are reported in Refs. [101, 102, 103].

3.3 Rotogravure printing (GRAVURE)

In Paper IV, PANI-DBSA in toluene solution is used as the ink when printing conductive patterns on a paper substrate. The ink preparation for GRAVURE was the following: PANI-EB powder was dried in a vacuum oven for 24 hours and added to formic acid. PANI was protonated using DBSA [104] leading to $PANI(DBSA)_{1.0}$. The formic acid was then evaporated and the PANI(DBSA) slowly mixed with toluene. In the experiments, 5 wt-% and 8 wt-% solutions were used, corresponding to viscosities of 0.02 Pa s and 0.05 Pa s respectively.

In the experiments a sheet-type laboratory-scale gravure instrument (IGT Reprotest) and an industrial scale roll-to-roll gravure (Metso Corp.) instrument (Figure 13) were used. The viscosity of the PANI-DBSA solutions changes as a function of shear rate, as shown in Figure 12. As seen in the figure, the viscosity at typical shear rate values in the process (> 800 1/s) is still slightly lower than for typical gravure inks (0.1 Pa s, see Table 2). An industrial pilot machine was used to demonstrate the high-volume production capability. In the experiments, conducting lines were printed on a paper substrate at a speed of 100 metre/minute and line width down to 60 micrometre.

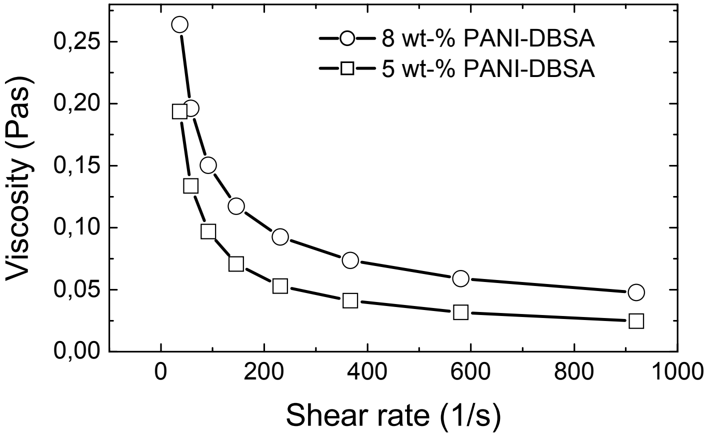

Figure 12. Viscosity as a function of shear rate in PANI 5 wt-% (□) and PANI 8 wt-% (○) in toluene solution. As seen in the picture, the obtained viscosities of 0.02 Pa s and 0.05 Pa s are slightly lower than those typically used in GRAVURE (Paper IV).

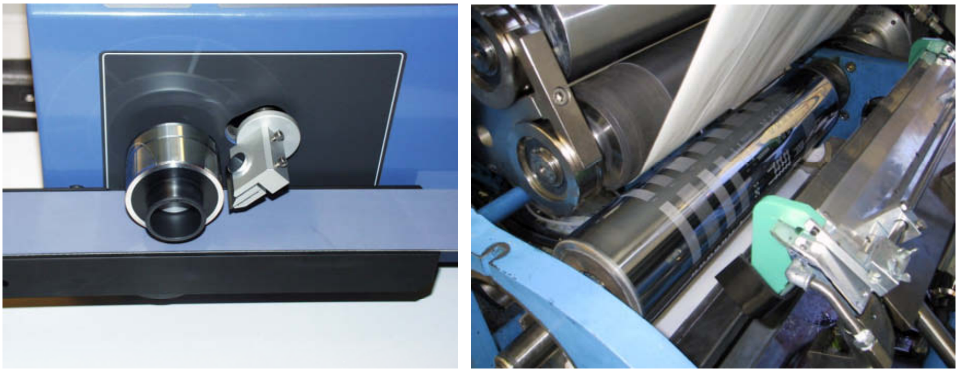

Figure 13. The laboratory-scale gravure (IGT Reprotest, left) and industrial gravure device (Metso corp., right) used in the PANI-DBSA experiments. The widths of the printing cylinders are 50 mm, and 60 cm respectively (Paper IV).

3.4 Flexographic printing (FLEXO)

In Paper V the laboratory-scale flexotester Flexiproof 100 (R K Print Coat Instruments Ltd.) was used to evaluate the continuous flexo-process for PANI.

As an example, OFETs were manufactured, where the source-drain electrodes were printed using this method. The flexoprinter, mask design and manufactured flexoplate are shown in Figure 14. In the plate, the line widths and spacings of the interdigitated electrodes vary from 100 to 400 micrometre, as the numbers in the design show. 100 micrometre-thick Polyethylene terephthalate (PET) or Poly(ethylene-2,6-naphthalate) PEN films were used as substrates.

PANI-DBSA in toluene solution from Panipol OY was used in the experiments. The viscosity and the solid content of the PANI ink were modified (by adding or evaporating solvent) to be more suitable for FLEXO. The viscosity was varied from 0.06 Pa s up to 0.120 Pa s, corresponding to solid contents of 6 wt-% and 9 wt-%. In addition, a gelated (close to 95 wt-%) PANI was used for comparison.

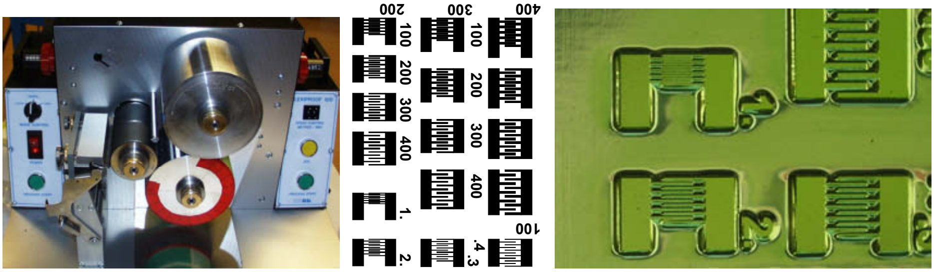

Figure 14. The laboratory-scale flexotester (Flexiproof 100 from R K Print Coat Instruments Ltd.) (left) where the web size is 10 cm, and an example of the design (middle) and flexoplate (right) that will be wrapped onto the roll. This plate consists of interdigitated finger structures used as source and drain electrodes in OFETs.

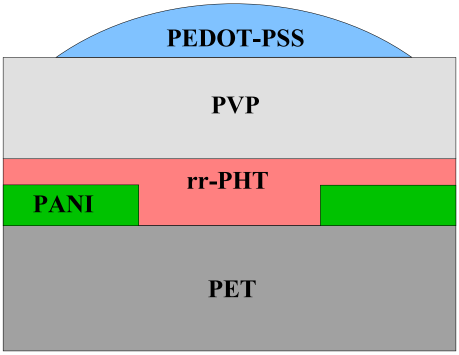

Figure 15. Schematic picture of OFET where the printed PANI is used as electrodes.

Figure 15 shows a schematic picture of the OFET structure. The source and drain electrodes were produced as described above. A semiconductor Regio-regular poly(3-hexylthiophene) (rrPHT) in chloroform solution (4 mg/ml) and an insulator Poly(vinylphenol) (PVP) in isopropanol solution (100 mg/ml) were spin coated in room atmosphere at 1000 rpm. Finally, gate electrodes were prepared by casting PEDOT:Polystyrenesulfonate (PEDOT:PSS) onto the transistor channel region so that the droplet only covers the interdigitated source drain finger structure area.

3.5 Roll-to-roll nanoimprinting lithography (rrNIL)

In the rrNIL study, Paper VI, the gravure printing unit and the nanoimprinting unit are used consecutively to act on the web in a single cycle. In the rrNIL experiments the PANI-DBSA 6 wt-% toluene solution was diluted with cellosolve (7:3) to obtain a lower evaporation rate in the ink (conductivity was 3 S/cm). In the process the polypropylene (PP) web is coated with PANI solution using the gravure technique, dried and patterned with the rrNIL unit. A gravure roll having a cell structure that transfers 8 cm^3/m^2 of liquid to the substrate was used, indicating a 480 nm dry thickness of the polymer film. PP (12 micrometre thick) was used as a flexible substrate. Web speeds of 0.2–1.0 metre/minute and pressures of 5–14 MPa were used in the experiments. During rrNIL the temperature was kept constant at 25°C. Other low-temperature imprint (or room temperature hot embossing) processes are reported in Refs. [105, 106].

3.5.1 Roll-to-roll imprint device

The principle of the continuous process for PANI is shown in Figure 16. In the rrNIL unit, two rolls are pressed against each other, where the upper roll can be heated whereas the bottom roll (backing roll) is kept at room temperature. The Nickel-imprinting master is wrapped around the upper roll.

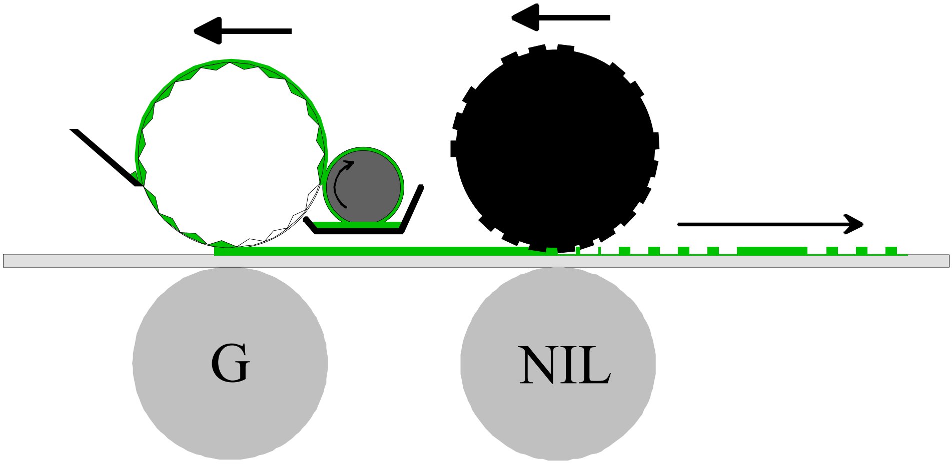

Figure 16. Principle of a continuous imprinting process. A gravure printing unit is used for coating the plastic or paper web and an NIL unit imprints the desired structure on the polymer in the same cycle. The rotation speeds of the units are synchronized (Paper VI).

The roll-to-roll process is always fast compared to the NIL processes, where tens of seconds or minutes are used. Printing speeds in the range of 0.2–20 metre/minute only give less than a millisecond to modify the surface if the NIP is short. A softer backing roll is used to increase the NIP length to give more time for the polymer to flow and form a replica from the master. In our experiments with a roll diameter of 66 mm and printing speed of 0.2 metre/minute at 5 MPa pressure, an imprinting time of 1,5 s was achieved.

In these experiments a novel printing tool was designed and manufactured. The design of the machine is shown in Figure 17 and a picture of the real device in Figure 18. The device includes three main parts: unwinder, printing units and rewinder. The four synchronized printing units are (from left to right): flexo, gravure and two nanoimprinting units. In the nanoimprinting unit the metallic roll is heated using an electrical heater located inside the roll.

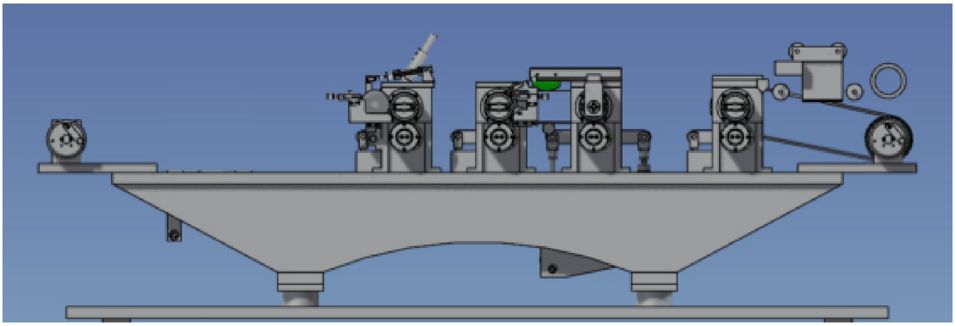

Figure 17. Schematic presentation of a custom-made roll-to-roll device for continuous nanoimprinting (Paper VI). From left to right: unwinder, flexo, gravure two nanoimprinting units and rewinder.

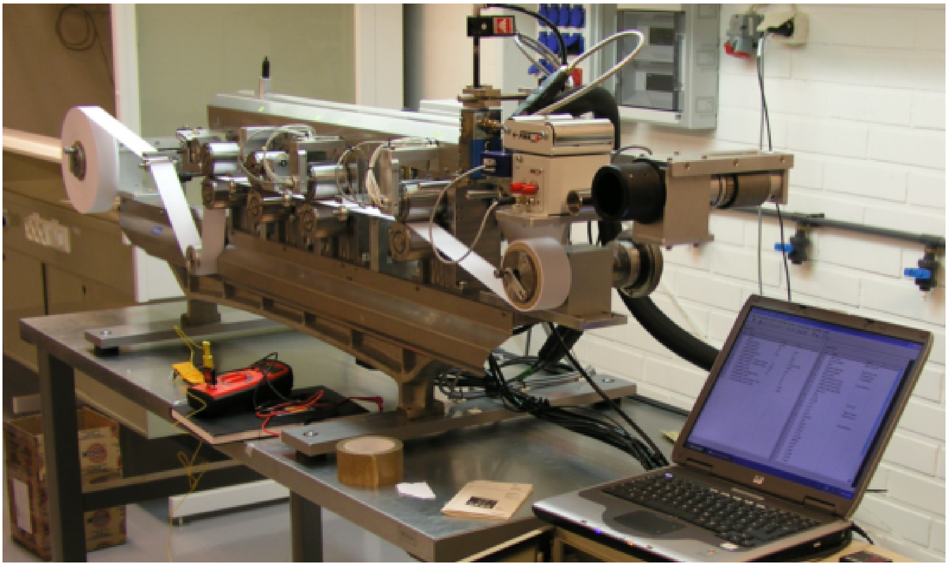

Figure 18. Roll-to-roll imprinter machine. The roll diameters are 66 mm and the total device length is ca. 2 m. The rotation speeds of the different rolls can be synchronized by computer and continuous processing is possible (Paper VI).

4 Results and discussion

This chapter is divided into five sections, and the main results of the papers are presented in each section. Section one shows the materials and parameters used in the UV lithography as well as the resolution achieved. Section two contains the main results of the NIL of PANI. Roll-to-roll methods such as GRAVURE and FLEXO, especially applied to PANI, are discussed in sections three and four respectively. Finally, the results of the novel rrNIL patterning of PANI as well as a combination of GRAVURE and rrNIL methods are shown and discussed in section five.

4.1 UV lithography of PANI (Paper I)

In this work a UV lithography was used for demonstrating passive components such as capacitors and resistors on flexible substrates or glass. Here a positive photoresist was used (see Figure 6a), which means that the irradiated part of the resist becomes more soluble in the developing but the same process can be done with negative resist as well. ICPs make possible novel concepts and processes in electronics. The solution-processable conductors offer a new way to design passive and active components.

In the case of a capacitor, PANI was coated and patterned on both sides of a substrate, which works as the dielectric layer in the component. In the case of a resistor, PANI was patterned as a resistive wire on top of a substrate. In resistors, the value needed can be tuned not only by the width and length of the UV patterned line but sometimes more practically by the thickness of the conductive layer. ICPs offer easily tuneable resistors from ca. 100 ohms up to 100 Gohms (nine orders of magnitude). In metallic thin film, tuning is done practically only using line width variation.

The UV lithography process was demonstrated by using PANI-CSA 4 wt-% in m-cresol or PANI-DBSA 4 wt-% in toluene. The dry thickness of the film after the solvent evaporation was 1–10 micrometre. The conductivity ratio between the conducting and non-conducting forms was 10^{10} in the case of PANI-CSA. The square resistance of the undoped PANI layer was 10–100 Ohm/sq when the film thickness was ca. 1 micrometre. Most forms of PANI can be used in the process. This is due to the deprotonation of PANI in alkaline solutions. The pH of typical developers is above 7.

One example of the UV lithography patterned PANI film is shown in Figure 19, where circuit boards were manufactured. This structure is presented in Paper I. The blue colour corresponds to PANI in insulating form and green in conducting form. The material conductivity limits the achieved values (in wires) to typically more than 100 ohms when the resolution is limited to 10 micrometre and the film thickness to 1 micrometre. In Figure 19 the width of the UV patterned wire was 250 micrometre. As a substrate, 100 micrometre-thick PC-film was used, but the only limitation in this process is chemical resistance to the solvent used in the PANI ink.

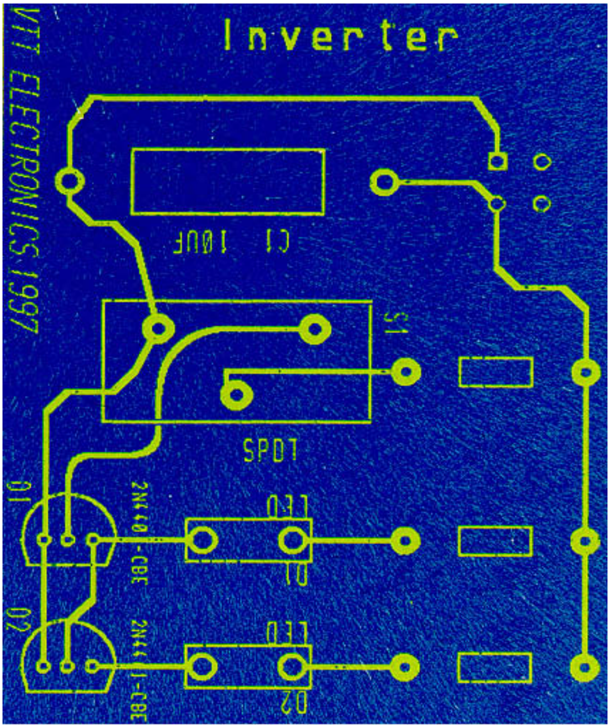

Figure 19. UV lithography patterned PANI-DBSA film on PC substrate. The blue colour corresponds to PANI in insulating form and green in conducting form (Paper I).

UV lithography processes for ICPs such as PANI make it possible to use the material as part of the traditional lithography process. One of the key problems in organic electronics is the alignment of the different layers in the device. Using a UV lithography method, an aligning accuracy of 2 micrometre can easily be achieved. Inorganic structures (metal-polymer) can be prepared with the same process. A limitation may be chemical treatments that are not suitable for PANI.

Conducting (doped) PANI is soluble in organic solvents to typically less than 10 wt-%. Therefore, dry thicknesses above one micrometre means at least 10 micrometre wet thickness. UV lithography offers a method for patterning PANI up to film thicknesses of 10–1000 micrometre (0.1mm–10 mm wet thickness) when spin coating or other coating methods are used to make such a film.

UV methods allow the use of PANI in its highest conducting (doped) form and it is a good candidate for applications where high conductivity is needed. However, developer penetration under the photoresist may cause deprotonation and affect the conductivity or the achieved resolution. In experiments, a 10 micrometre resolution for PANI is reported in Paper I. The resolution with pure AZ5214E resist in this process is 2–5 micrometre, but, due to the high surface roughness and solvent penetration under the UV resist, the achieved resolution in width is lower than in the patterned resist itself.

UV lithography offers a way to integrate ICPs as part of conventional processes in electronics. The microelectronics industry, which has made huge investments in UV lithography equipment, can take ICPs into the process as novel functional materials. The resolution is also reasonable when used in ICs. However, in sample size, UV lithography is typically limited to the wafer scale (< 200 mm) if compared to other methods such as GRAVURE or FLEXO where extending is more straightforward. Also, throughput is lower when compared to GRAVURE or FLEXO, as estimated in Table 2. Due to the toxicity of m-cresol, the process is not easily transferable to the industry, but nowadays toluene or water-based PANI-DBSA solutions can be used.

4.2 Nanoimprinting of PANI (Papers II–III)

NIL is used for patterning PANI structures down to 100 nm feature sizes. An atomic force microscopy (AFM) image (Figure 20) shows the three-dimensional grating structure consisting of 500 nm-deep grooves with 5 micrometre wide lines printed on a 1 micrometre-thick PMMA/PANI-CSA blend. In imprinting, 5 x 5 mm^2 silicon stamps were used. The pattern on the stamps consisted of at least 8 mm-long, 5 µm-wide lines and spaces. The grating pattern was defined by UV lithography and RIE [95]. The samples were heated to a temperature well above the Tg (105^{o}C) of PMMA, and cooled down to room temperature under pressure.

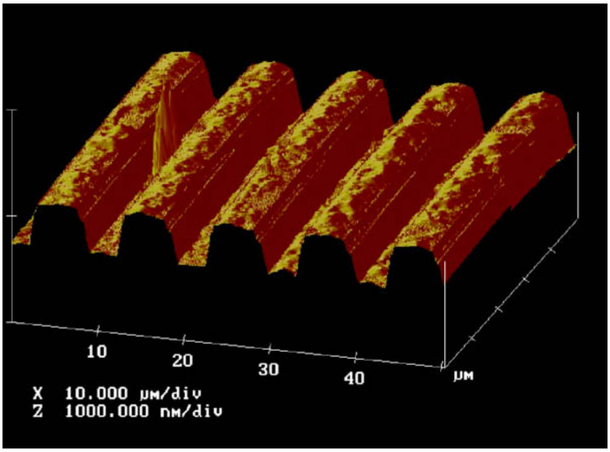

Figure 20. An AFM image of a nanoimprinted grating structure in a PANI/PMMA blend on microscope glass. The grooves are 500 nm deep with a 5 micrometre line width (Paper II).

The surface roughness is different on the top of ridges and on the bottom of the grooves. This is due to the Si-stamp used in the experiments. Typically, the surface roughness of the imprinted blend is smaller than in the unimprinted film. The same stamp can be used in several imprints. The blend showed some sticking to the silicon stamp and the stamp was cleaned with acetone and isopropanol between the experiments.

As known, in a thermal NIL process some residual film always remains in the imprinted material due to the viscous properties of the polymer. The typical thickness of the residue is 10–50 nm. The residue is removed using RIE. In PANI/PMMA blends the residual layer can also be seen by conductivity measurements since the residue is electrically conductive. In Figure 21, the resistance measurements for the parallel and perpendicular directions show that the residual layer is fully removed by RIE. The imprinted lines are completely separated from each other. The resistance is measured over 10 mm-long and ca. 5 micrometre-wide gratings. Anisotropy is larger than 10^4 for directions perpendicular and parallel to the imprinted polymer ridges. The conductivity in the perpendicular direction corresponds to the conductivity of the glass substrate used in this experiment; thereby, the anisotropy becomes larger than 10^4.

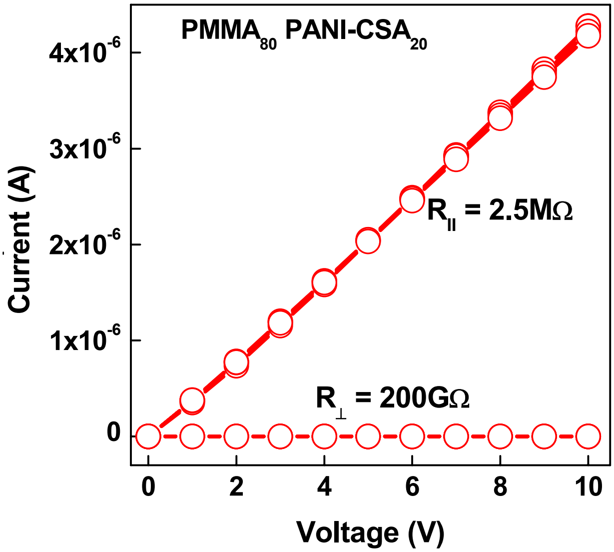

Figure 21. Resistance parallel and perpendicular to the ridges in the imprinted grating after RIE (Paper II).

The resistance of the PANI/PMMA film before and after NIL as a function of temperature are shown in Figure 22. In this experiment imprinting is done by using a flat Si-stamp. As shown in the figure, the resistance of the blend increases by a factor of 2 in the process due to the aging of PANI. The aging of PANI depends on humidity and temperature [36]. However, this change is relatively low and can be estimated when temperature and time are known. To avoid aging, a host polymer with lower T_g can be used but in that case the operating temperature of the final elements may also be lower. A better way to avoid aging is to use a shorter imprint time. The imprint in thermal NIL mainly depends on the viscosity of the polymer and the pressure used in process. In the rrNIL process (Chapter 4.5), PANI is imprinted at room temperature.

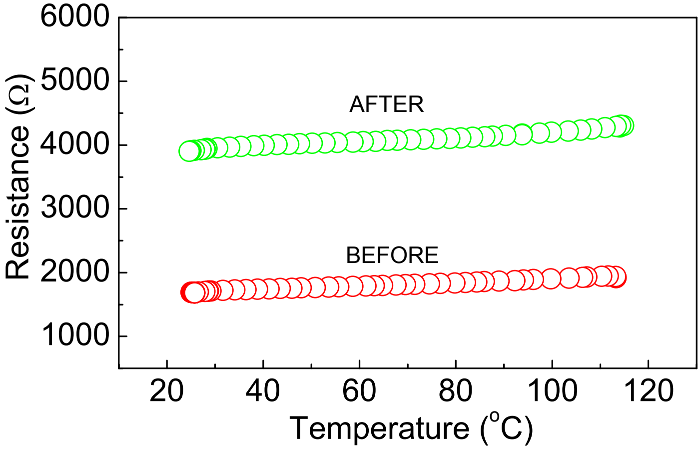

Figure 22. The resistance of the PANI/PMMA film before and after NIL as a function of temperature shows an increase by a factor of 2. This is due to the aging of the PANI (Paper II).

4.2.1 Etching rates for PANI and PMMA

The etching rates for PANI, PMMA and a PANI/PMMA blend using a CF_4/O_2 gas mixture are shown in Figure 23. RIE experiments were done using an ELECTROTECH 320 PC etcher. The etching was done in a CF_4/O_2 gas mixture containing 80% CF_4 and 20% O_2 at a pressure of 30 mTorr with 150 W RF-power. The reactive etching rate is 260 nanometre/minute for PMMA and increases by a factor of 3 for PANI-CSA. The conductivity does not change essentially due to RIE. However, the faster etching rate for PANI than for PMMA indicates that the conductive PANI in the blend will be etched first, which may affect the achieved conductivity results.

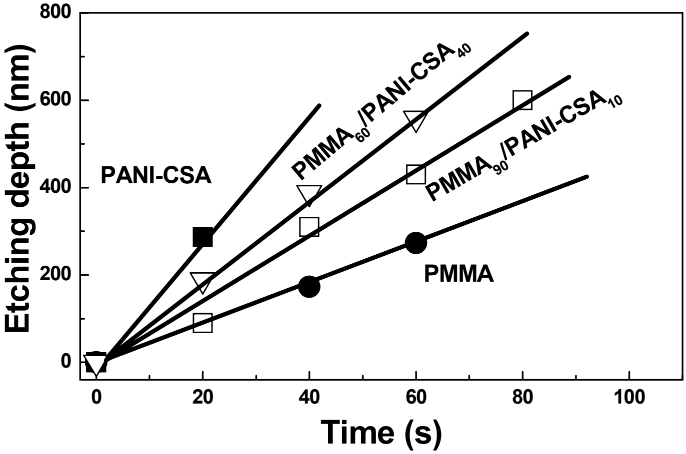

Figure 23. Etching rates for the PANI, PMMA and PANI/PMMA blends used in the experiments. The etching rate is linear for all studied polymers (Paper III).

4.3 Rotogravure printing of PANI (Paper IV)

In our work, PANI-DBSA in toluene solution printed with a printability tester (IGT) was used for optimizing the printing parameters. Figure 24 shows the resistance of lines printed with 24 micrometre-deep cells (70 lines/cm) as a function of the printing speed. As a substrate, 5 x 29 cm^2 sheets of the copy paper (amicus, 80 gsm, MetsäSerla) were used. The wet thickness of the ink was 15 micrometre when the viscosity was 0.02 Pa s. The conductivity of the ink was 10 S/cm.

Even though the printing cylinder consists of cells, line printing is possible due to the spreading of the PANI ink. The engraved conductive cell dot is spread ca. 30% when normal copy paper is used. Using spreading as part of the process allows the production of homogeneous coatings as well. In the case of porous paper, the ink also penetrates into the paper. Minimum line widths of 60 micrometre have been achieved on copy paper using this method. The same printing cylinder gives a nice diamond-type structure on PET, as seen in Figure 25.

When the pressure between the printing cylinder and the backing roll is higher, the electrical resistance of the printed lines decreases. This is due to the better transfer of the PANI ink, as seen in Figure 24 where pressure forces of 500 N and 1000 N are used on the rolls. The behaviour of PANI inks in GRAVURE also needs more research in the future. The porosity and the surface properties of the substrate are important when PANI-DBSA ink is printed on paper.

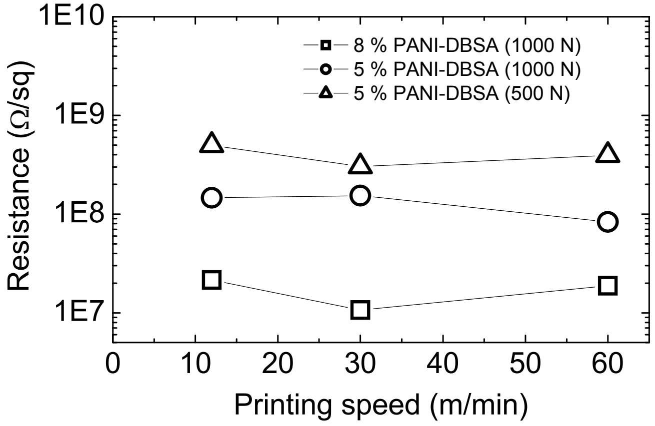

Figure 24. Sheet resistance of 5 wt-% (O) and 8 wt-% (□) PANI-DBSA ink and the effect of 500 N (Δ) and 1000 N (O) printing pressures on resistance (Paper IV).

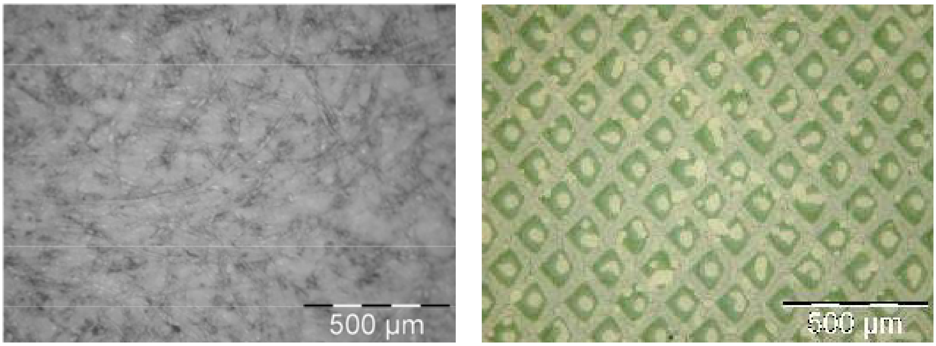

Figure 25. Gravure-printed PANI-DBSA on paper (left) and on PET substrate (right) using the same printing parameters. On the right the engraved cell pattern is easily seen.

Continuous roll-to-roll GRAVURE was demonstrated using an industrial-scale pilot gravure printer (Metso Corp.). In these experiments the substrate width was 60 cm and PANI structures printed with a speed of up to 100 metre/minute were demonstrated. The smallest line width was 60 micrometre, spreading ca. 30%

when the penetration into the paper was 1–5 micrometre measured with an optical microscope.

4.4 Flexographic printing of PANI (Paper V)

In the experiment, PANI-DBSA in toluene solution was optimized and used in the FLEXO machine. Optimizing was done by changing the viscosity and solid content, but no additives were used in the solution to achieve as high conductivity as possible. 100 micrometre-thick, 10 x 29 cm^2 PET or PEN samples were used as substrates. In the experiments, the viscosities used for PANI were relatively low when compared to commercially available flexo inks (see Table 2). However, even though the optical quality was barely tolerable, the electrical behaviour was good using the low viscosity ink. The viscosity of PANI-DBSA in toluene, achieved line widths, conductivity, and optical estimation of the surface uniformity are presented in Table 3. The printing speed in the experiments was 40 metre/minute.

Table 3. Viscosity and conductivity of the flexoprinted lines as well as estimation of the surface uniformity. The printing speed was 40 metre/minute (Paper V).

Solid Content	**Viscosity (25^oC)**	**Film thickness**	**Conductivity**	**Uniformity**
6.2 wt-%	0.006 mPa s	450 nm	8.5 S/cm	good
7.1 wt-%	48 mPa s	500 nm	1.0 S/cm	fair
9.0 wt-%	120 mPa s	630 nm	1.2 S/cm	fair
~95 wt-%	>1000 mPa s	7 µm	1.1 S/cm	poor

Figure 26 shows the flexoprinted source-drain electrode pairs using a ink viscosity of 0.12 Pa s. Even though the printed lines are typically spread by 25%, which is related to the relatively low viscosity of the ink, these structures were successfully used in OFETs. A roughness is readily seen on the PANI surface. The edges of the printed structures correspond to a non-ideal ink transfer from the flexoplate.

In the experiments, the PANI ink stuck to the flexo-printing plate, which had to be cleaned between the runs. Surface uniformity was best in the case of very low viscosity ink, which is due to the spreading of the ink. However, low viscosity ink may be difficult to control in a real process and PANI flexo inks need further modification before they will be suitable for commercial use.

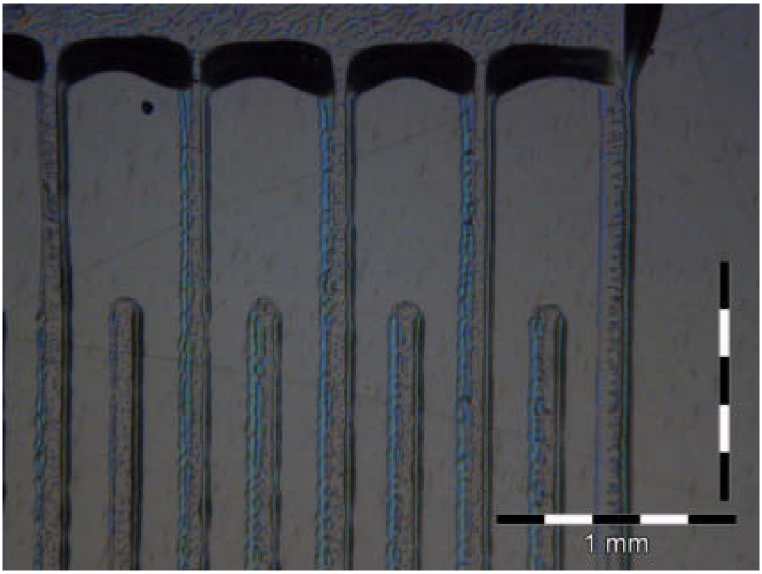

Figure 26. Flexo-printed source and drain interdigitated finger structure (0.12 Pa s, 6 wt-% PANI-DBSA in toluene). The printed line width is 125 micrometre, which corresponds to 25% spreading of the material during the printing process.

OFET characteristics curves are shown in Figure 27. The I–V characteristics of corresponding transistors show a clear gate voltage modulation of the drain current and a turn-on voltage close to 0 V. The current is also relatively large in the OFF region of the characteristics, resulting in a low switching ratio.

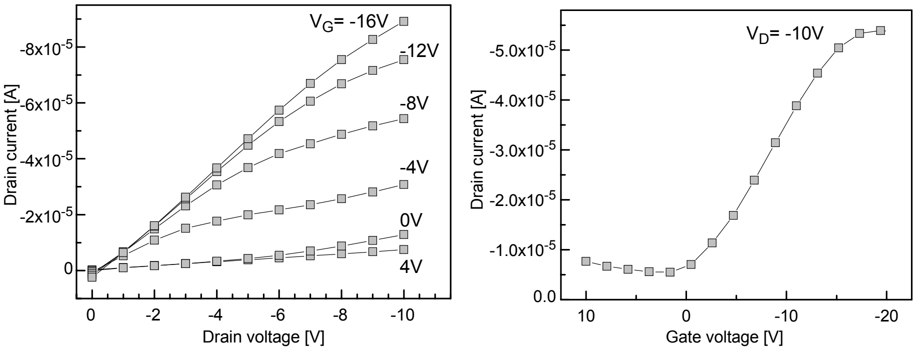

Figure 27. Output characteristics of a transistor utilizing source and drain interdigitated electrodes prepared by FLEXO. As the semiconductor rrPHT is used. The deviation from typical FET behaviour is related to the large dimension of the channel region (left). Transfer characteristics for the saturated region (V_D = -10V) (right) (Paper V).

4.5 Roll-to-roll nanoimprinting of PANI (Paper VI)

Gratings with 500 nm-wide lines were patterned into PANI film at a speed of 0.2–1.0 metre/minute and pressure of 5–14 MPa (Figure 28). The smaller demonstrated structure with rrNIL on PANI is 50 nm. During imprinting the temperature was kept constant at 25^{o}C. The PANI-DBSA conductivity of 3 S/cm does not change in the processes.

In this continuous rrNIL process a GRAVURE method was used for coating a homogenous layer on the PP film followed by curing the film and rrNIL. The flexible nickel stamps used in the experiments were fabricated by T. Haatainen et al. using electron beam lithography and electroplating [95]. In comparison to the PMMA/PANI-CSA blend used in thermal NIL, the PANI-DBSA film is softer and mechanical pressure may affect the final structure. This can be avoided by using an encapsulation layer on the top of printed structure. AFM image (Figure 28, left) shows that the height of the printed structures is ca 500 nm but the top of the printed ridges are not straight. This is due to the fluid properties of the material and a better result is achieved with a lower speed (longer imprint time).

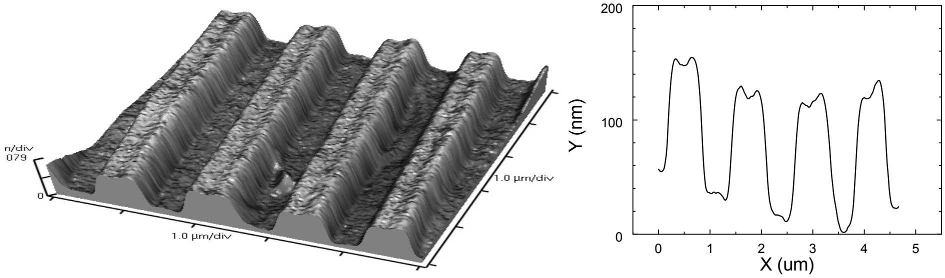

Figure 28. An AFM image of gratings patterned by rrNIL at a speed of 1 metre/minute at 14 MPa pressure. The patterned structures are well replicated from the Ni-master (Paper VI).

In Figure 29, resistivity measurements in directions parallel and perpendicular to the gratings show a four order of magnitude difference without RIE. This relatively small difference indicates that a residual layer exists. The residue thickness is 30–50 nm, verified using AFM. This thickness is the same as in the NIL process.

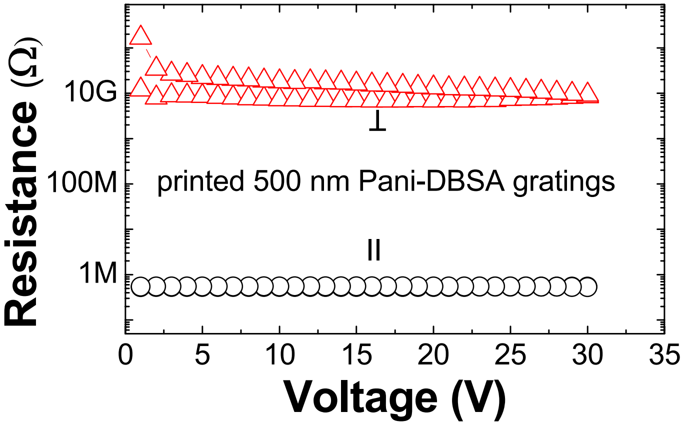

Figure 29. Resistance measurements on PANI-DBSA gratings made by rrNIL show a four order of magnitude difference, indicating that a residual layer still exists (Paper VI).

When comparing the thermal NIL process to rrNIL, many differences can be observed. In rrNIL for PANI-DBSA the temperature is normally kept at room temperature. Deformation of PANI is done below its T_g. The process time where the imprinted material is under pressure is short for rrNIL, from milliseconds to seconds, whereas for NIL minutes (or at least tens of seconds) are normally used. The pressure in rrNIL is typically more than ten times higher for the same imprint material. In rrNIL, a soft backing roll can be used, which increases the NIP size to 5 mm; therefore, for the minimum speed of 0.2 metre/minute, the effective imprinting time was estimated to be 1,5 s. rrNIL can be used to produce organic electronic or optoelectronic structures on flexible substrates, whereas NIL is suitable for other substrates as well.

4.6 Future outlook and problems

All of the printing and patterning methods presented in this work have potential for industrial-scale patterning of PANI. However, some optimization of the printing inks as well as process parameters is still needed. The main observations concerning the methods are listed and discussed.

UV lithography offers a way to integrate ICPs as a part of conventional processes in electronics. The potential of UV lithography is based on the possibility of combined metal-polymer (hybrid) structures, which can be made in the same process. In this method a planarisation step is not necessarily needed. The thickness of the film does not limit the use of the process. The resolution in this process can be down to 2–5 micrometre. A limitation would be a chemical treatment that is not suitable for PANI. Also, due to the high surface roughness of PANI, the solvent can penetrate under the UV resist and the achieved resolution in width is lower than in the patterned resist itself. Sample size in conventional microelectronics is typically limited to the wafer scale (< 200 mm), and will continue to be so in the future.

Thermal NIL is used for easily patterning PANI structures down to 100 nm feature sizes. This method offers an interesting possibility to manufacture nanoscale applications based on PANI. New material development is needed to achieve materials with well known T_g, which is one limiting factor today. Also etching parameters must be optimized for ICPs. This method is still a low-speed manufacturing method.

Roll-to-roll GRAVURE methods offer an excellent way to manufacture PANI structures with dimensions down to 50 micrometre. This is the only method that is not limited by solvents. When printing on paper-based substrates, the porosity of the paper affects the penetration of PANI and the surface roughness the uniformity of the film. PANI ink modification and ink-substrate interactions need more studies in the future.

Roll-to-roll FLEXO is often used in cases where the substrate is not perfectly flat. The printing plate is relatively low-cost and it is possible to use many designs. The method is easily scalable. In these experiments toluene was used as a solvent, but, due to the effect on rubber, the high evaporation rate and low viscosity, it is hard to control on the industrial scale. The method is more suitable for water or oil-based inks. Inks need further modification before they will be suitable for commercial use. Adhesion to the substrate and flexoplate must be optimized.

In the future, the high-speed rrNIL manufacturing method will offer a way to integrate nanoscale electronics and optoelectronics based on PANI. This is a high-speed method to produce submicrometre features. rrNIL is particularly interesting when it can be attached together with other roll-to-roll techniques. The viscoelastic properties of PANI need further studies as well as the basic understanding of the process.

5 Summary

In this thesis five different patterning or printing methods for inherently conducting PANI has been demonstrated. These methods cover scales from the submicrometre to the millimetre range. Different methods and materials were developed to the stage where they can be used to demonstrate different applications in electronics.

Two step-by-step methods are shown – UV lithography and thermal NIL – which are both useful when high-resolution and aligning is needed. It is possible to integrate these methods as part of the conventional microelectronic process. Processing speed and sample size are typically limited to the wafer scale in both methods.

In this thesis, three continuous processing methods were developed and used for PANI. GRAVURE, FLEXO and rrNIL are high-volume manufacturing methods and especially interesting when ICPs are used in everyday products. These methods can be part of a conventional printing process when magazines, packages or different labels are manufactured. These three methods also cover line widths from the submicrometre to millimetre scale. One of the most important tasks in the future will be to develop more suitable ICP inks for these techniques.

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Mäkelä, Tapio

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Towards printed electronic devices
Large-scale processing methods for conducting polyaniline

Abstract

In this work, five different patterning methods were developed to demonstrate the processing possibilities of polyaniline (PANI). Two different dopants, camphorsulfonic acid (CSA) and dodecylbenzenesulfonic acid (DBSA), were used to achieve PANI with high electrical conductivity that was soluble in various solvents. These solutions were used as printing inks in the processing.

PANI was used in step-by-step methods such as UV lithography and nanoimprinting lithography (NIL). The continuous methods used were rotogravure printing (GRAVURE), flexographic printing (FLEXO) and roll-to-roll nanoimprinting lithography (rrNIL). Dimensions from the submicrometre to the millimetre scale were demonstrated in both processing routes. The functionality of PANI within the studied methods is compared and problems in scaling up to high-volume manufacturing are discussed.

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Nimeke

Sähköäjohtavan polyaniliinin prosessointi painettavassa elektroniikassa

Tiivistelmä

Tässä väitöskirjatyössä tutkittiin sähköäjohtavan polymeerin, polyaniliinin (PANI), soveltuvuutta painettavan elektroniikan valmistuksessa. Työn tavoitteena oli kehittää liuosmaisille polymeereille soveltuvia valmistusmenetelmiä. PANI-pohjaisia rakenteita tuotettiin muovi- ja paperisubstraateille viittä erilaista kuviointimenetelmää hyödyntäen. Substraatit valittiin kemiallisten ominaisuuksien, hinnan ja saatavuuden perusteella. Erityistä huomiota on kiinnitetty massatuotantoon soveltuviin menetelmiin, joissa PANIa voidaan hyödyntää painomusteen tavoin. Painetut rakenteet analysoitiin optisella mikroskoopilla, atomivoimamikroskoopilla (AFM) sekä sähköisten mittausten avulla. Menetelmien hyödynnettävyyttä elektroniikan valmistuksessa on vertailtu ja arvioitu.

Kokeissa käytettävät sähköäjohtavat PANI-liuokset aikaansaatiin protonoimalla polyaniliini-emäs substituoidulla hapolla, tässä työssä joko kamfersulfonihapolla (CSA) tai dodekyylibentseenisulfonihapolla (DBSA). Protonointi nostaa polymeerin sähkönjohtokykyä useita kertaluokkia sekä aikaansaa liukenevuuden, joka on perusedellytys vietäessä materiaali tutkittuihin prosessointimenetelmiin. Protonoinnin poistaminen palauttaa polymeerin sähkönjohtavuuden eristeen tasolle. Tätä erityisominaisuutta on hyödynnetty yhdessä prosessointimenetelmässä (UV-litografia). Muut UV-avusteisen litografian lisäksi hyödynnetyt menetelmät ovat nanoimprinttaus (NIL), syväpaino (GRAVURE), flexopaino (FLEXO), sekä rullalta-rullalle-nanoimprinttaus (rrNIL). UV- ja NIL-menetelmissä kuviointi tapahtuu substraatin ollessa paikallaan, kun taas GRAVURE-, FLEXO- ja rrNIL-menetelmät ovat jatkuvia rullalta-rullallemenetelmiä. Edellä mainituilla menetelmillä katetaan viivanleveydet nanometreistä millimetritasolle.

Työssä on osoitettu PANIn hyödynnettävyys em. valmistusmenetelmissä sekä mahdollisuus johdepolymeerien prosessointiin; paitsi osana perinteistä elektroniikan valmistusta esim. UV-tekniikalla, myös uusia menetelmiä hyödyntäen. Painetut sähköiset rakenteet aikaansaavat funktionaalisille polymeereille uusia käyttökohteita tulevaisuudessa. Rullalta-rullallemenetelmät mahdollistavat materiaalien käytön elektroniikan massatuotteissa.

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Författarna
Mäkelä, Tapio

Namn

Prosessering av elektriskt ledande polyanilin för tryckbar elektronik

Referat

Doktorsavhandlingen behandlar möjligheterna att använda elektriskt ledande polymerer, speciellt polyanilin (PANI) för att tillverka tryckbar elektronik. Målsättningen var att utveckla tillverkningsmetoder för polymerer i lösning. PANI-baserade strukturer producerades på plast- och papperssubstrat med fem olika mönstringsmetoder. Substraten valdes utifrån kemiska egenskaper, pris och tillgänglighet. Speciellt betonades metoder lämpade för massproduktion, där PANI kan användas som en trycksvärta. De tryckta strukturerna analyserades med optisk mikroskopi, atomkraftmikroskopi (AFM) samt elektriska mätningar. Tillverkningsmetodernas lämplighet för framställning av tryckbar elektronik har utvärderats.

De elektriskt ledande PANI-lösningarna som användes vid försöken framställdes genom att protonera en PANI-bas med en substituerad syra, här antingen kamfersulfonsyra (CSA) eller dodecylbenzensulfonsyra (DBSA). Protoneringen höjer polymerens elektriska ledningsförmåga med flera tiopotenser och gör också att polymeren blir löslig, det senare en förutsättning för de undersökta framställningsmetoderna. En deprotonering återför polymeren till en elektrisk isolator. Denna specialegenskap utnyttjades i en processeringsmetod, ultraviolett litografi (UV). Metoderna som användes utöver UV-litografi var nanoimprintning (NIL), djuptryck (GRAVURE), flexotryck (FLEXO), och kontinuerlig (roll-to-roll) nanoimprintning (rrNIL). Vid mönstring med UV- och NIL-metoderna är subtratet stationärt medan GRAVURE-, FLEXO- och rrNIL-metoderna är kontinuerliga metoder. Dessa metoder täcker ett linjebreddsintervall från några nanometer till flere millimeter.

Arbetet påvisade PANIs användbarhet i ovan nämda tillverkningsmetoder. Dessa representerade dels processer som är konventionella vid elektronikproduktion såsom UV-litografi men även helt nya metoder. Tryckta strukturer ger funktionella polymerer helt nya användningsområden i framtiden. Roll-to-roll metoderna möjliggör tillämpningar inom massproducerad elektronik.

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