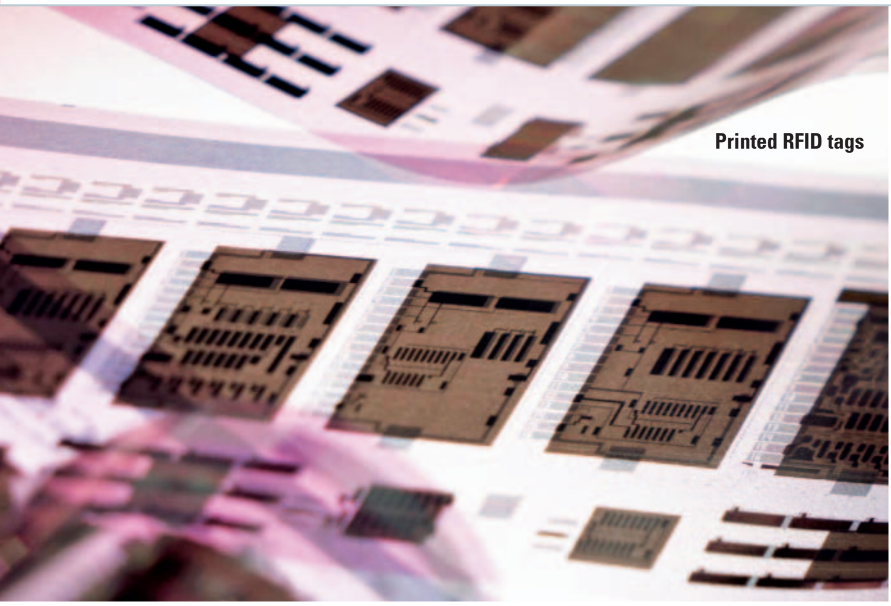

Printed Electronic Circuits. With organic electronics, an exciting new technology has emerged. For example, printed RFID tags represent a practically fraud-proof method for product identification. Application areas range from cost-effective theft prevention up to complex electronic product codes (EPC).

Off the Reel

HENNING ROST

Very soon, printed electronics will open up new markets and applications in the most varied ways. In the past, the implementation of first products frequently seemed hardly more than future dream. However, during the past three years, the company PolyIC in Fürth, Germany – a joint venture between Leonhard Kurz GmbH & Co. KG and Siemens AG – has made significant and continuous progress along the road to first products. Recently, a decisive milestone was reached: for the first time, PolyIC presented prototypes of 13-MHz RF tags whose manufacture is based entirely on reel-to-reel printing techniques. The resulting devices consist of printed polymer electronic components including film-based antennas. Similarly, logic circuits in the form of ring oscillators have been produced with modern printing techniques [1].

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What is RFID?

With Radio Frequency Identification systems, the radio signals emitted by a transmitter are received by a transponder (also known as a tag). The use of radio signals permits information to be transmitted without physical contact, whereby – unlike barcode readers – direct visible contact is not necessary. Future RFID systems will be able to read information at greater distances, and even through products, if required.

All the RFID tags discussed in this article are passive, which means that they do not have an own power supply, but are energised exclusively via the radio signal of the reading unit (transponder).

The transponder itself is a relatively simple system consisting of an antenna and a chip with transistors. Hereby, the number of transistors can vary from a few dozen up to several thousand, depending on the amount of memory and the number of other functions integrated in the transponder. The antenna is tuned precisely to the RFID tag's transmission frequency. As already mentioned, the chip is powered solely via the transmission signal. By means of the built-in antenna, the tag is thus able to transmit its stored information to the transponder.

The maximum reading distance between an RFID tag and a transponder is determined primarily by the operating frequency, but also by design aspects, whereby three worldwide frequency ranges for RFID transmission have been established. These frequency bands are defined by international regulations, have different technical properties, and therefore different application areas (Table 1).

Nowadays, RFID identification is already in widespread use, for example by wholesalers for bulk packages. However, the classical, silicon-based chip technology that has been around for a long time is rarely used below the pallet or container level. The main reason is that the unit costs for such RFID chips are simply too high to permit low-value goods like yoghurt pots to be "tagged" individually (Fig. 1).

Another disadvantage of silicon chips is their mechanical susceptibility. By contrast, printed RFID tags offer several advantages, which are highly welcome at the individual product level. The RFIDs being discussed here are printed on thin, flexible plastic films. Supplied as low-cost, mass produced "off the reel" items, they are easily handled and can also be integrated into existing manufacturing and packaging lines.

Nonetheless, it must be pointed out that in terms of electric complexity and memory capacity, today's printed RFID tags are nowhere near the possibilities offered by highly integrated silicon chips. But for typical applications such as product identification or proof of authenticity, printed RFID tags are perfectly adequate. Both methods – the classical silicon-based RFID technology and the new printed RFID tags – offer specific advantages, and in combination they complement each other perfectly.

Frequency band	Frequency	Application area
LF (Low Frequency)	125–135 kHz	Animal identification
HF (High Frequency)	13.56 MHz	Smart cards, automation
UHF (Ultra High Frequency)	860–950 MHz	Pallet identification

Table 1. Frequency ranges for RFID transmission

Translated from Kunststoffe 5/2007, pp. 97–101

The Materials Used

RFID tags contain a large number of organic field-effect transistors (OFETs), but a functional circuit is only obtained by connecting them intelligently. Fig. 2 shows the typical 'top gate' construction of an OFET. An OFET consists of only a few layers, and thus has a reasonably simple structure. And that is precisely the reason why it is possible to make electronic components by means of additive printing processes.

Fig. 1. Still a vision: yoghurt pots "tagged" with PolyID

Polyethylene terephthalate (PET) has proved to be a suitable substrate material for printed RFID transponders, as it has the necessary properties: thin, flexible, smooth surface, printable, commercially available in large quantities, and relatively cheap.

For the electrodes, both intrinsically conductive plastics (e.g. PEDOT/PSS) as well as nanoparticles or metals are suitable [2, 3].

Probably the scientifically most interesting and currently most intensively investigated part of an OFET is the organic semiconductor, which – in the case of printed electronics – mostly consists of a plastic with conjugated polymer backbone [4]. Here, alkyl-substituted polythiophenes represent a frequently used material class.

Polyalkylthiophenes, in particular poly(3-hexylthiophene) PHT, exhibit good charge carrier mobility and are described as efficient semiconductors in polymer RFID tags [5]. Solubility in organic solvents and special rheological properties – and thereby printability – are ensured by substituting the thiophene rings with alkyl chains. The structural formula for PHT, which is frequently specified in very general terms, only represents a part of reality. If PHT is synthesised from asymmetric monomers, many different "triads" are formed in the polymer backbone (Fig. 3).

Hereby, a PHT that mainly contains HT-HT (head-to-tail) triads, exhibits better effective conjugation and creates densely packed, quasi-crystalline structures in the solid body, in which the polymer chains as well as the aromatic π-electron systems are arranged lamellarly. These so-called regioregular polyalkylthiophenes are featured by lower intermolecular separation between the individual polymer chains. All of this results in higher charge carrier mobility, which is precisely the material property necessary for the manufacture of highly efficient RFID tags, for example.

Three patented basic synthesis routes plus several derived processes exist, which produce regioregular, i.e. mainly HT-HT-linked polyalkylthiophenes. In the first step, the aim of these routes is to create an asymmetric monomer with high yield and purity by means of regioselective "insertion" of metallic species in α-position to the sulphur atom of the thiophene ring. Polymerisation then occurs through a transition metal catalysed reaction of the metallised side of this monomer with a carbon-halogen link of another structurally identical thiophene monomer by means of XY cleavage (Fig. 3). The actual reason for the occurrence of these triads lies in the fact that in a few of the monomer modules the X and Y leaving groups are exchanged, as opposed to the ideal chemical structure.

Nonetheless, under tightly controlled reaction, all three routes result in highly regioregular polythiophenes with a structural purity in excess of 95 % (determined with ^{1}H-NMR spectroscopy), which are very well suited for use in polymer electronic components.

With the original McCullough route [6], the monomer 2-bromine-3-alkylthiophene is metallised first with lithium and then magnesium, followed by polymerisation (Fig. 4), whereby polymerisation effectiveness depends greatly on the quality of the chemicals used. Another important factor is precise temperature control during reaction.

In the Rieke route [7], zinc is used as the metallising agent. Handling of the necessary highly reactive Rieke zinc (Zn*) and thereby control of the reaction itself (Fig. 5) requires great experimental skill, and is considered by experts to be relatively difficult.

The initial compound for the McCullough-Grignard metathesis procedure [8] is 2.5-dibromine-3-alkylthiophene, i.e. analogous to the Rieke route. Here, no strict temperature control is required for the polymerisation process (Fig. 6). The reaction can even take place under reflux, so that this route also appears to be principally suited for up-scaling.

Ionic and/or metallic species in the form of reactive by-products and adhering source material are identifiable in the end products of all three procedures, which can lead to an undesirable intrinsic conductivity of the polymer. High ion concentrations can result in an increased 'off' current in the transistor, which in turn has a negative effect on the transistor's switching behaviour.

Therefore, cleaning of the polythiophene is of utmost importance with all three routes. The preferred methods are solid-liquid and liquid-liquid extraction, cleaning by means of multiple precipitation, as well as treatment with ion-absorbing agents, whereby every manufacturer makes a secret of his cleaning process. Nonetheless, it can be safely assumed that cleaning of the raw synthesis products requires a considerable effort, if the materials are to be used for polymer electronic components.

The Manufacturing Process

The main advantage of printed electronics as opposed to conventional silicon-based electronics is that polymer electronic components can be produced far more easily and quickly. Whilst conventional electronics require ultra-clean surroundings (cleanrooms) as well as complex vacuum and high-temperature processes, the manufacture of polymer electronics is considerably simpler. Although there are different approaches for the production of polymer electronics, some of which also involve vacuum processes, the economically most promising and advantageous process is printing.

Apart from the substrate, the polymers required for the different transistor levels are soluble in commercially available organic solvents, enabling them to be ap- ▶

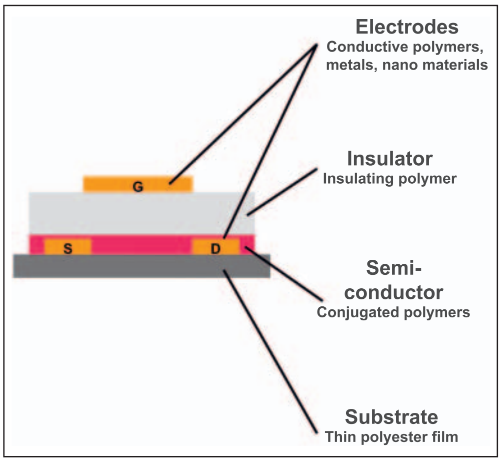

Fig. 2. Structure of an organic field-effect transistor (OFET)

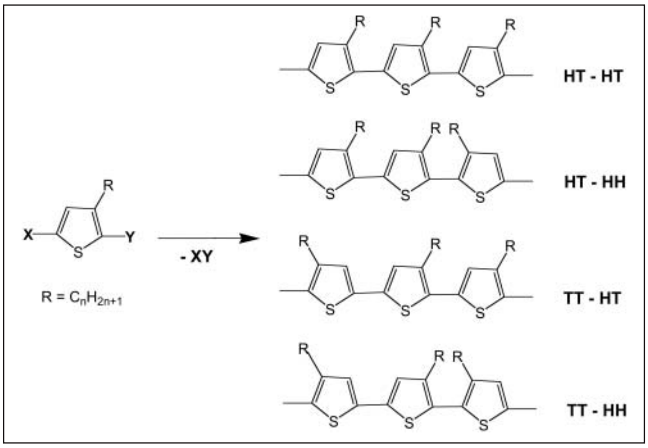

Fig. 3. PHT reaction: triads in polyalkylthiophenes (PHT)

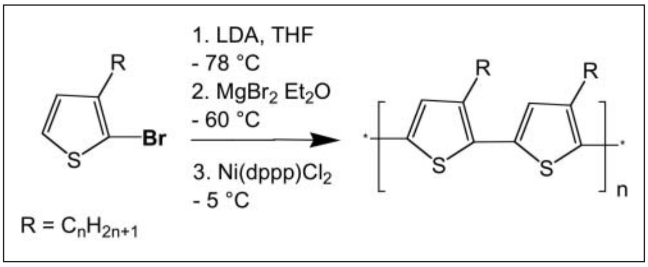

Fig. 4. PHT reaction: original McCullough route

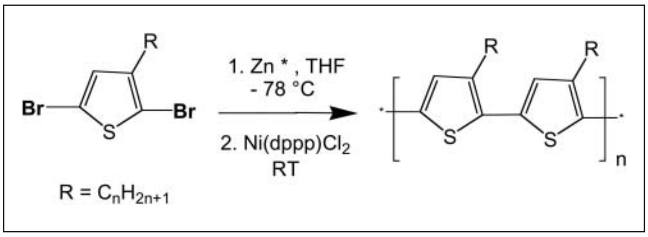

Fig. 5. PHT reaction: Rieke route

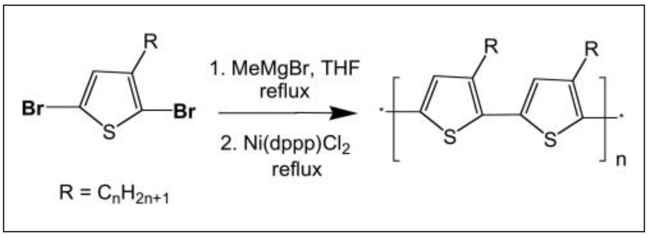

Fig. 6. PHT reaction: McCullough route 2 (Grignard metathesis)

plied in the form of electronic ink, e.g. through additive printing [4]. Of course, a prerequisite is that solvents employed do not attack the underlying layers. If this is ensured, electronics can be manufactured very cost effectively in continuous printing processes, very similar to newspaper printing. Hereby, various printing processes are used, which can be classified in letterpress, gravure, and flat printing. The classification is based on how the imaging element, e.g. a pressure roller, is designed. Flexographic printing belongs to the letterpress methods, whereby the image to be printed is placed on the pressure roller as a raised, flexible plastic layer. Conversely, offset printing belongs to the flat printing methods, whereby the image to be printed is defined by means of water-repellent and water-absorbing areas on a smooth roller. In all cases, the required image is transferred to a substrate by means of a structured plate (or roller).

Today's standard printing methods have typical resolutions above 100 µm. For organic circuits however, resolutions of less than 20 µm are desirable for circuit design reasons (see [4]). Apart from optical aspects, printed electronics place additional demands on printing technology. On the one hand, fine connecting lines are required as circuit tracks to permit current flows, whilst on the other hand, clearly separated areas without direct contact are needed to prevent short circuits.

Each of the layers shown in Fig. 2 has a specific electric function. Consequently, the printing parameters cannot be adapted simply by means of additives, as is normally done in the printing business, as this would mostly have a severe negative influence on the electrical properties. And finally, a very high register accuracy (determines the respective positioning accuracy of individual colours and is therefore a criterion for printing quality) must be ensured in order to obtain the required superposed, electrically functional structures. Here, it must be pointed out that in addition to the usual optical check during printing, the printing process must also include a corresponding electrical check that works reliably also at high printing speeds.

Because the modified printing techniques permit printed RFID tags to be produced in extremely large quantities, the unit costs are correspondingly low, as already mentioned above. At present, forgeries – which must always be expected in the application fields for RFID technology – are impossible even with extremely high and therefore uneconomical costs, simply because the necessary manufacturing know-how is novel and very demanding. It is only the close interrelation between materials science, electronics, and printing technology that permits the manufacture of printed organic electronics.

i **User**

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From Product Codes up to Flexible Solar Cells

RFID transponders represent an outstanding first application area for printed electronics. Apart from very simple RFID applications such as anti-theft protection in supermarkets, today's producers also have a great interest in methods to protect their branded quality goods (brand protection, Fig. 7) as well as fending off copycats (anti-counterfeit).

Future developments of this fascinating technology will lead to "item-level tagging" by means of "electronic product codes" (EPC), i.e. individual numbering of practically every single product. This is achieved by storing a serial number in every RFID tag. After readout, this number can be compared with a database, and supplies the required information.

Apart from pure RFID use, the new platform technology of printed organic electronics permits far more applications to be implemented: Based on organic polymers and the corresponding printing processes, numerous active as well as passive electric components can be manufactured for a wide range of applications,

Fig. 7. Brand protection with printed electronics

such as
- transistors,
- diodes,
- capacitors,
- circuit tracks,
- resistors,
- solar cells,
- sensors,
- memories, and
- batteries.

Singly or in combination, these components can be connected to provide the most varied functions, for example:
- sensors with RFID for reading radio signals,
- sensors for medical applications (e.g. blood testers),
- flexible displays,
- information labels,
- flexible solar cells,
- games,
- printed batteries, and finally also
- "smart objects" (applications with combined functions).

These few examples illustrate the enormous potential of the new printed electronics technology.

Polymer Electronics Still in Development Stage

In spite of the great advances made during recent years, polymer electronics are still in the development stage. Admittedly, first products are already commercially available, for example batteries, displays with organic LEDs, as well as prototypes of integrated circuits, solar cells and sensors. However, in order to open up the real mass markets, further efforts are necessary in the areas of materials, technology, and manufacturing processes.

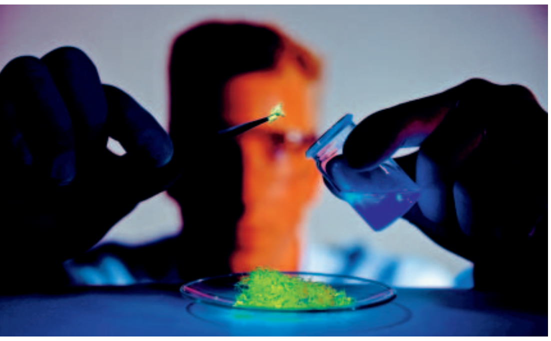

Fig. 8. Innovative products using new semiconductor materials: first laboratory tests

Compared with conventional inorganic materials such as silicon or gallium arsenide, the electric and electronic parameters of the functional polymers described here still offer considerable room for improvement. For example, this concerns intrinsic conductivity and charge carrier mobility, but also useful service life. In all of these areas a lot of research still remains to be done. One good case in point is the increasing demand for "n-type" organic semiconductors, in which conductance is provided by free electrons. However, most of these n-type materials are not stable when exposed to air, so that they require complex encapsulation in the component. In terms of stable semiconductors, and disregarding laboratory samples, only p-type conducting plastics are currently available (here, conductance is provided by defect electrons or 'holes'). For high-performance electronics however, the combination of both p- and n-type materials into a kind of CMOS technology is required – similar to that found in today's silicon electronics. Due to the mentioned lack of efficient organic n-type semiconductors, parallel efforts in the development of circuits with pure p-type semiconductors must be promoted (Fig. 8).

First Products Expected this Year

Polymer electronics represent a new platform technology for revolutionary electronic components based on electrically semi-conducting and insulation organic materials. This technology is not only considered as a competitive alternative to existing silicon-based electronics, but also opens up great opportunities for completely new applications, in which flexibility, low cost, high production quantities, and integratability in packaging are required.

Furthermore, modern printing techniques offer exciting possibilities for the use of polymer electronics in the most varied fields. It is here where the true advantages of polymer electronics come to play: thin, flexible electronic components on flexible substrates, in large quantities, cost-effective, and suitable for new mass markets. Admittedly, much development work must still be invested in suitable processes, as electrical functionality in printing techniques involves breaking completely new ground. But the first steps have already been made: The first printed electronic products 'off the reel' are expected from PolyIC in the course of 2007 (Fig. 9). ■

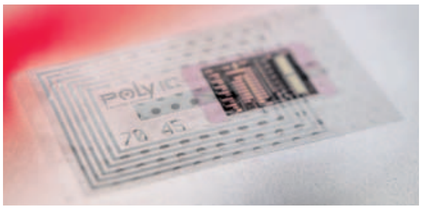

Fig. 9. First printed electronic products 'off the reel' (PolyID RFID tag)

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