TECHNOLOGY FOR THE POLYCONDENSATION OF THIN FILMS OF POLYMER WITH HETEROATOMS IN THE BACKBONE

Converting solar energy into electric energy is the only fully ecological way to obtain electrical energy and therefore, in parallel to work on classic semiconductor solar cells, investigations on applications of π–conjugated polymers in photovoltaics are being pursued worldwide, especially in laboratories in the most developed countries.

The research presented here fits in with broader worldwide trends of seeking various combinations of polymer and molecular materials suitable for producing the most efficient, long-lifetime, and cheap-to-produce solar cells. This search for new polymer materials for use in photovoltaics stems from specific mechanical properties of polymers that are unmatched by inorganic semiconductors, particularly their elasticity, feasibility for use in manufacturing large surface devices, ease of processing, and low production costs.

Techniques for preparing thin films of π–conjugated polymers with heteroatoms in the backbone – mainly via the methods of thermal vacuum evaporation, chemical vapor phase transport, and spin-coating, on the basis of the process of aromatic diamine polycondensation with aromatic dialdehydes – are being studied and further developed in terms of their applications in producing polymer optoelectronic devices with layered architecture, such as electroluminescent diodes and photovoltaic cells.

The most important element of photovoltaic solar cell structure is the p-n junction, which can be made by the following two methods:

1. manufacturing p-n junctions on an interface between a thin film of π–conjugated polymer with heteroatoms in the backbone, which is an electron donor, and a thin film of π–conjugated polymer or molecular material playing the role of electron acceptor,
2. manufacturing p-n junctions in the volume of a film which is a composite of two π–conjugated polymers, or a composite of conjugated polymer and π–conjugated material.

The use of these technologies will allow for the controlled deposition, on various substrates, of polymer thin films with properties adequate for the role a layer will then play within a multilayered photovoltaic solar cell, i.e. a donor layer absorbing incident photons of solar radiation and an acceptor layer, where the two of them constitute p-n junction, layers transporting electrons or holes, and electrode.

An issue of great importance that needs to be taken into account in the production of polymer solar cells is fitting the width of its energy gap, corresponding to the fundamental absorption edge of a donor film, to the energy of a quantum of electromagnetic radiation of 700 nm wavelength, which corresponds to the photon density maximum in the solar light spectrum (about 1.8 eV).

These aims are being pursued via computer modeling of the electron structures of both donor and acceptor as well as through computer simulations of technological conditions of polymer thin film deposition.

All of these technological methods are based on a polycondensation process between aromatic diamines and aromatic dialdehydes of various structure and conformations.

The chemical vapor deposition (CVD) method can be carried out in vertical or horizontal setup. The essence of this method involves using a forked stream of neutral gas argon transport agent, whereby the dopant flows over boats containing diamine and dialdehyde and takes up their molecules. These partial streams transporting molecules merge into one stream, which is associated with mixing reagents, and then the stream flows into a reaction chamber impinging on the substrate. While flowing around the substrate, reagent molecules diffuse towards its surface where processes of polymer chain

Fig. 1. Technological setup for producing polymer layered structures (J. Weszka)

forming or elongation occur. The factors influencing the film structure and its electronic properties are: the temperatures of the reagents, their difference (controlling the proportions of polycondensation reagents), stream flow rate, and film thickness.

The technology of vacuum evaporation and CVD opens up the possibility of polycondensation-based manufacturing of polymer thin films. The polycondensation process runs within the adsorption layer formed upon the substrate surface, and then upon the polymer layer having so formed. This method is suitable for preparing thin films of polymers insoluble in organic solvents. An additional and rather significant feature of this technology appears to be the high purity of the deposited films, which is of great importance for optoelectronic applications. These methods render feasible the doping and protonation of polymer films with heteroatoms in the backbone.

The manufacturing costs of polymer thin film are comprised of: rotary pump exploitation costs, the costs of using the gaseous transport agent (argon), purchasing monomers (diamines and dialdehydes) and dopants, and the use of electrical energy for heating monomers.

Assuming film thickness of about 50 nm and surface dimension 1 cm x 1 cm, material density < 1 g/cm^3, film mass $< 5 \times 10^{-6}$ g. As this is a polycondensation process one can estimate the use of individual monomers at $< 2 \times 10^{-6}$ g. The gas flow rates applied and low temperatures of monomers $< 200^0$C indicate that the costs of film deposition are rather low.

The method may be applicable for producing layered photovoltaic structures of not just small but also of larger surface area.

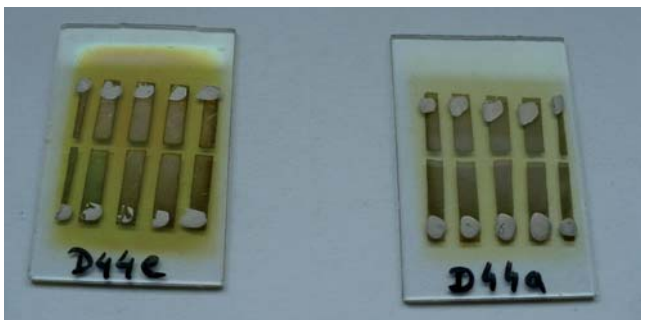


Fig. 2. Photovoltaic polymer structures (J. Weszka)

CONTACT DETAILS
Centre of Polymer and Carbon Materials,
Polish Academy of Sciences
ul. M. Curie-Skłodowskiej 34, 41-819 Zabrze
phone: 48 (032) 271-60-77
Authors
Jan Weszka, e-mail: jan.weszka@cmpw-pan.edu.pl
Marian Domański, Barbara Hajduk

LOW MOLECULAR WEIGHT BASIC DENDRIMERIC PEPTIDES AS A NEW GENERATION OF ANTIMICROBIAL AGENTS

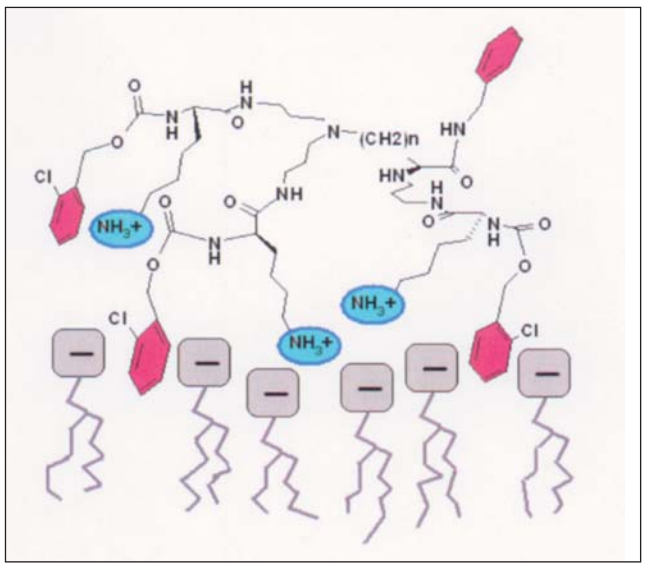
The introduction of β-lactam antibiotics into clinics was one of the milestones in the treatment of bacterial infections over many decades. However, their improper use has resulted in the development of multi-drug resistant strains, generating a global public health problem worldwide. Therefore, many laboratories are engaged in searching for compounds that are structurally new and/or act according to alternative mechanisms.

Low molecular weight peptide dendrimers (molecules with tree-like structure) developed in our laboratory express a wide spectrum of activity against Gram(+), Gram(-) and fungi. Among them several groups are characterized by high activity, particularly against Gram(+) including MRSA 43300 strain, Gram(-) including penem resistant *E. coli* ATCC® BAA-198 (ESBL) and the *C. albicans* family. Their mechanism of action imitates the mechanism of defensins – natural linear antimicrobial peptides that are an important element of the self-defense system of many organisms. It involves the adhesion of positively charged branched molecules to negatively charged biomembranes followed by cell lysis. Recently discovered branched derivatives are characterized by activity in the range of already used peptide antibiotics (vankomycin, polymyxin), low toxicity, and enzymatic resistance.

The innovation here is the application dendrimeric of peptides for designing a new generation of antimicrobial agents characterized by a wide spectrum of activity, high effectiveness, low toxicity, and resistance to enzymatic hydrolysis. Their branched structure makes them particularly effective against multiresistant strains from both the Gram(+) and Gram(-) family (MRSA and ESBL). The distinctive philosophy of their synthesis has yielded economically attractive low molecular weight compounds that are easy to produce and purify.

The design of these dendrimeric peptides and their application as antimicrobial agents are unique, their invention being covered by one Polish patent and two patent applications.

Postulated mechanism of biomembrane – dendrimer interactions



CONTACT DETAILS

1) Institute of Organic Chemistry,
Polish Academy of Sciences
ul. Kasprzaka 44/52, PO Box 58, 01-224 Warszawa
phone: 48 (022) 343-22-07
Authors
Zofia Urbańczyk-Lipkowska, e-mail: ocryst@icho.edu.pl
Piotr Polcyn

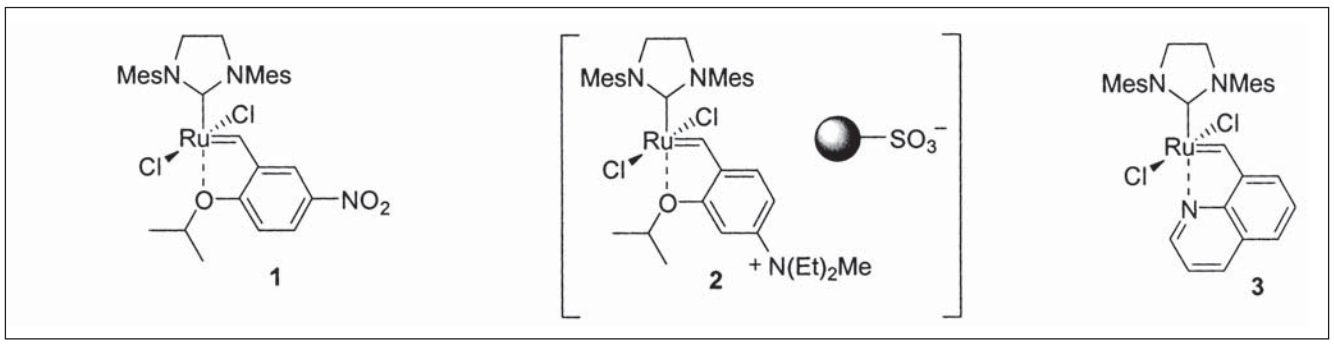
2) Industrial Chemistry Research Institute
ul. Rydygiera 6, 01-063 Warszawa
phone: 48 (022) 633-85-65
Author
Jolanta Janiszewska

NEW RUTHENIUM COMPLEXES AS OLEFIN METATHESIS CATALYSTS

Recent decades have seen a burgeoning of interest in olefin metathesis, as witnessed by a rapidly growing number of elegant applications. In particular, the development of efficient and selective ruthenium catalysts has been the key to the widespread application of olefin metathesis in organic synthesis. Since 2002 we have been developing new catalysts for this transformation [1]. Catalyst 1, developed by us (USA 6867303), has already found several applications in both academic and industrial laboratories, including Boehringer-Ingelheim GmbH. Polymer 2 is a highly active catalyst, particularly in cross-metathesis reactions, as used, for example, in the screening of some steroidal inhibitors of 17β-hydroxysteroid dehydrogenase type 1, useful in the treatment of estradiol dependent diseases like breast cancer or endometriosis [2, 3]. Analogues of Catalyst 3 will be commercialized soon [4]. Further catalysts are currently being developed by us in close cooperation with Degussa AG and other commercial and academic partners. Some of our catalysts and their applications have been reviewed in journals [5, 6].

A major drawback to the method is the high catalyst loading needed to perform most metathesis reactions and its toxicity. Our catalysts can be used in smaller quantities and more easily removed/recycled. We anticipate that with our research we will make a significant scientific and commercial impact. To do so, we are constantly seeking *industrial partners* interested in further developing and commercializing our catalysts, and *application groups* who plan to expand the scope of the technology to polymer, fine chemicals and pharmaceutical areas.

[1] Grela K., Michrowska A., Bieniek M. (2006). *Chem. Rec.* 6, 144.
[2] *J. Am. Chem. Soc.* (2006). 128, 13261.
[3] Solvay Pharmaceuticals. *Tetrahedron Lett*. (2008). 49, 3019.
[4] *Organometallics. (*2006). 25, 3599.
[5] Thayer A.M. (2007). *Chemical & Engineering News*. 85(07), 37.
[6] Schrodi Y., Pederson R.L. (2007). *Aldrichimica Acta*. 40(02), 45.



CONTACT DETAILS
Institute of Organic Chemistry,
Polish Academy of Sciences
ul. Kasprzaka 44/52, PO Box 58, 01-224 Warszawa
phone: 48 (022) 343-21-17
48 (022) 632-66-81
Authors
Research team directed by Karol Grela, e-mail: grela@icho.edu.pl

NEW FLUORESCENT SUBSTRATE FOR ASSAYING *LOVASTATINE ESTERASE* AND ITS IMMOBILIZATION FOR BIOTECHNOLOGICAL SYNTHESIS OF SIMVASTATINE

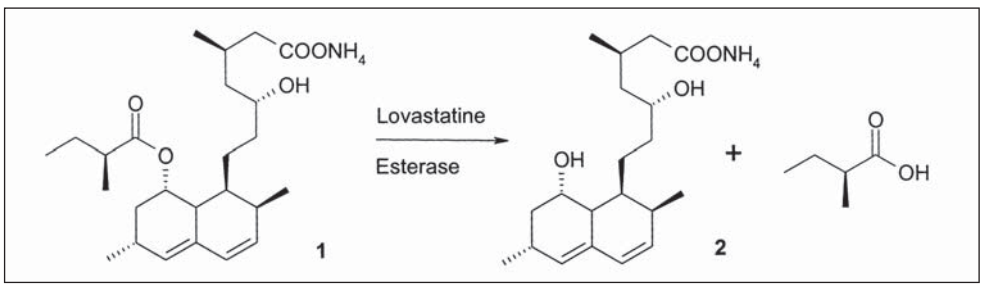
Lovastatine and Simvastatine are structurally related compounds that are used in medicine as potent antihypercholesterolemic agents. Simvastatine is less toxic than Lovastatine and its therapeutic doses used clinically are smaller. Therefore, Simvastatine is commonly used in medicine to control hypercholesterolemia.

In the biotechnological production of Simvastatine, Lovastatine is used as a substrate and the mixture of ammonium salts of Simvastatine and Lovastatine (1) is obtained (EP 84111759.1; EP 84111760.0; USP 5,223,415). The best and efficient way to separate both compounds is selective enzymatic hydrolysis of Lovastatine ammonium salts (1) which leads to diol 2 and 2-methyl butyric acid. For this reaction, the immobilized enzyme *Lovastatine esterase* can be used, greatly simplifying the whole process [1].

Our laboratory has designed a method for immobilizing the target enzyme, showing that such a biocatalyst can be used for hydrolysis of compounds 1 for 6 months without significant loss of selectivity and activity. In addition, new fluorescent substrates derived from coumarine for enzymatic assay of *Lovastatine esterase* were obtained. These compounds are very useful in enzyme purification and immobilization processes.

The chemical synthesis of Simvastatine is complicated and uneconomical. Direct chemo-enzymatic synthesis from Lovastatine is simple and efficient although it requires larger amounts of *Lovastatine esterase* enzyme. Effective immobilization of this enzyme yields a biocatalyst which can be used several times without any loss of activity. This biocatalyst can be also used in a continuous processes of Simvastatine production, fulfilling all the requirements of green chemistry principles. The new fluorescent substrates obtained are widely applicable for assaying *Lovastatine esterase* activity, which is of great importance for Simvastatine production.

[1] Schimmel T.G., Borneman W.S., Conder M.J. (1997). *Appl. Env. Microb*. 1307-1311.



CONTACT DETAILS
Institute of Organic Chemistry,
Polish Academy of Sciences
ul. Kasprzaka 44/52, PO Box 58, 01-224 Warszawa
phone: 48 (022) 343-21-20
Authors
Ryszard Ostaszewski, e-mail: rysza@icho.edu.pl
Waldemar Kurek, Dominik Koszelewski, Dorota Patralska, Olga Piotrowska

ULTRAPURE ELEMENTS

We offer ultrapure manganese (Mn) and magnesium (Mg) for use in Molecular Beam Epitaxy (MBE) and other semiconductor technologies, obtained via a new method of purification – particularly effective for the removal of oxygen, carbon and sulfur contaminants.

Ultrapure manganese $_{25}Mn^{54,936}$ (m5N8; t5N7)*

Results of analysis using atomic absorption spectroscopy and spark source mass spectrometry (in ppm):

Li < 0.05	Na < 0.03	P < 0.1	Ca < 0.08	Cu < 0.2
B < 0.01	Mg < 0.06	S < 0.07	Cr < 0.08	Zn < 0.2
C < 0.1	Al ≈ 0.5	Cl < 0.1	Fe < 0.5	
F < 0.1	Si ≈ 0.8	K < 0.08	Ni < 0.1	

Available ultrapure manganese (Mn) products:
- Pieces 10 mm and smaller (see photograph).
- Ingots: $\Phi = 6$, $\Phi = 10$, $\Phi = 12.5$, $\Phi = 15$, $\Phi = 17$ and $\Phi = 20$ mm and $20 \div 30 \pm 3$ mm length (see photograph).

Note that the density of Mn is ≈ 7.4 g /cm^3.

All products are vacuum packed in glass ampoules to prevent oxidation. Delivery time for all products: 2-3 weeks, although a number of pieces (≈50÷100 g) are always in store, ready for immediate dispatch.

Ultrapure magnesium $_{12}Mg^{24.312}$ (m6N; t5N8)*

Results of analysis using spark source mass spectrometry (in ppm):

Li < 0.02	Na ≈ 0.1 ± 0.05	P < 0.03	K ≈ 0.1 ± 0.05	Fe ≈ 0.1 ± 0.05
B < 0.02	Al ≈ 0.25 ± 0.05	S ≈ 0.07 ± 0.03	Ca ≈ 0.1 ± 0.05	Cu < 0.05
F < 0.03	Si ≈ 0.2 ± 0.1	Cl < 0.05	Mn < 0.05	Zn ≈ 0.2 ÷ 0.8

Available ultrapure magnesium (Mg) products:
- Pieces ≈ (10 x 20, 10 x 10, 10 x 5) mm^2 plates, about 1-2 mm thick cut into pieces from bigger plates (see photograph).
- Ingots ϕ 10 10÷25 mm length (see photograph); ϕ 15, ϕ 20 mm, and ϕ 25 mm 20÷30 mm length (see photograph).

* The prefix "m" indicates purity with respect to the metallic content only; the prefix "t" indicates purity with respect to all contaminants. "N" signifies a number of "9's".

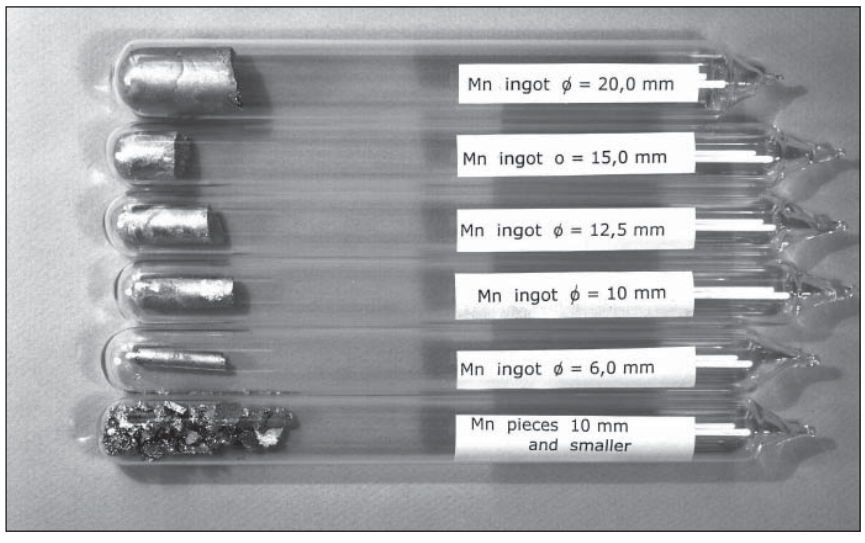


Fig. 1. Ultrapure manganese (A. Mycielski)

- Targets ϕ = 25.4 mm (1 inch) 3÷10 mm thickness (see photograph); ϕ = 50.8 mm (2 inches) 1.0÷1.6 mm thickness (see photograph).

Note that the density of Mg is 1.7 g/ cm^3.
All products are vacuum packed in glass ampoules to prevent oxidation. Delivery time for all products: 2-3 weeks, although a number of pieces (≈10 ÷20 g) are always in store, ready for immediate dispatch.

Ultrapure elements, Mn and Mg, are sold to about 80 laboratories in 17 countries.

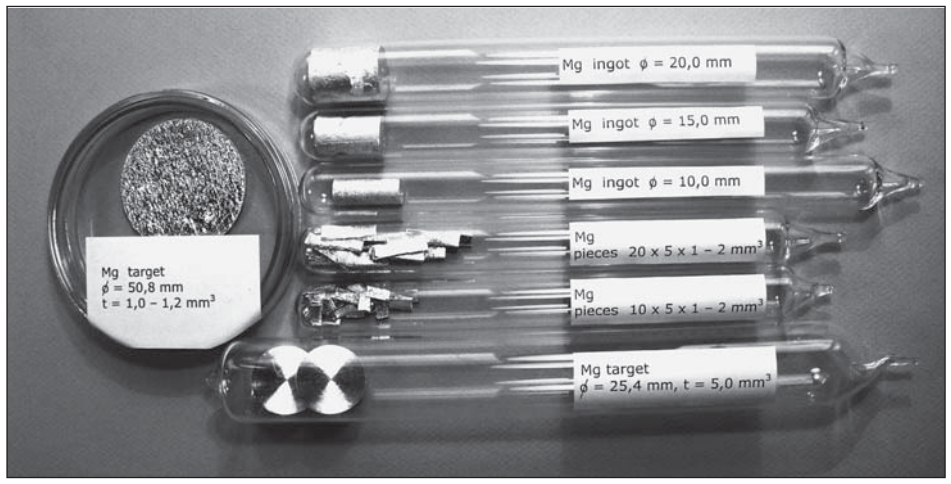


Fig. 2. Ultrapure magnesium (A. Mycielski)

CONTACT DETAILS
Institute of Physics,
Polish Academy of Sciences
al. Lotników 32/46, 02-668 Warszawa
phone: 48 (022) 843-70-01
Author
Andrzej Mycielski, e-mail: mycie@ifpan.edu.pl