Final Report Summary - MAO-ROBOTS (Methylaluminoxane (MAO) activators in the molecular polyolefin factory)

Executive Summary:
MAO-Robots has focused a combination of very different techniques on the MAO problem like never before: Only the application of converging chemical, spectroscopic, neutron scattering and computational lines of investigation afforded the following major achievements:

- Extensive work was undertaken to synthesize methylaluminoxane (MAO) in a continuous fashion: a continuous as opposed to a batch wise production process allows a better control of product parameters, especially considering the relatively slow equilibration of MAO solutions. A first set-up using controlled gas-phase reactions however was not successful. A second set-up using a flow-type reactor allows a more precise control of the MAO product. This continuous liquid phase reactor (CLPR) system was optimized and is operational under routine conditions on lab and semi-technical scale.

- A beyond-state-of-the-art modelling methodology for screening the reactions that lead to the formation of MAO has been developed. Application of the methodology by state-of-the-art computational techniques enables solving the structure of MAO as a function of size in silico.

- Significant advance in understanding the main structural principles of MAO: combined experimental and computational efforts clearly point to MAO being a mixture of species with average molecular weight about 1800-2000 g/mol. The species are cage-like structures that can take various shapes and sizes in the range of 8-10Å showing an aspect ratio of 6-10.

- Important role of trimethylaluminium (TMA) on MAO structure and activity quantitatively defined: MAO mixtures contain a variable number of associated TMA, and there is strong evidence that the associated TMA generates the sites of cocatalytic activity.
• Gained precise mechanistic understanding on the role of certain structural characteristics of MAO in the activation of single-site olefin polymerisation catalysts: Two possible modes of catalyst activation by MAO were detected. Either by Lewis-acid abstraction of an alkyl or halide ligand from the pre-catalyst or by reaction of the pre-catalyst with an MAO-derived AlMe₂⁺ cation.

• Kinetic methods established as rapid-screening methodology for catalysts and catalyst activators like MAO. From a single experiment this method provides quantitative rate data for structure-function relationships, as well as the concentration of active species.

• A quantitative relationship between polymer molecular weight and the trimethylaluminium (TMA) content of MAO was established.

• The influence of additives on structural elements of MAO were assessed.

• We achieved synthesizing beyond-state-of-the-art ethyl-isobutylaluminoxane (EBAO) able to polymerize ethene with same performance as state-of-the-art MAO. EBAO is a more economical alternative to MAO and in addition more environmental-friendly due to its solubility in aliphatic solvents.

To summarize, although it has been investigated intensively for 30 years in both industry and academia, more has been learnt about its nature and composition than ever before during the MAO-Robots project. This beyond-state-of the-art knowledge is giving a profound basis for controlling MAO and EBAO activated polymerisation processes.

Project Context and Objectives:
The project “MAO-ROBOTS - Methylaluminoxane (MAO) activators as industrial robots in the molecular polyolen factory” addresses the aspects of call NMP2009-1.2-2 “molecular factory - manufacturing objects with predictable and controllable properties”. The consortium aims to perform research on nano-to-micro-sized systems used for industrial polyolen (PO) production in order to “develop sustainable processes for nano-structuring for specific applications which should present high potential industrial and/or market relevance.” Molecular PO factories consist of methylaluminoxane based structures and a transition metal complex often but not always anchored on a heterogeneous, nano-structured silica support. On the basis of an in-depth understanding of the molecular and supra-molecular assembly and construction principles of MAO the consortium intends to:

• Create MAO building blocks with “predictable and controllable properties” and optimum activation efficiency.

• Identify the most productive nano-to-micro structural arrangement (molecular factory layout) of the components MAO, transition metal complex and silica support in order to create “structures with controlled properties over multiple scales, multi-component structures, and the connection of self-ordered systems with conventionally produced structures and functions.”

• Establish the basis for reproducible production of the above-identified and newly designed molecular PO factories.

• Develop methods for analysis and quality control of the performance of the molecular PO factories on a laboratory scale.

• Open the way for transfer of the newly developed molecular factories from the laboratory scale to industrial polyolen production “to develop sustainable processes for nano-structuring for specific applications which should present high potential industrial and/or market relevance “

• Stimulate the broader application of nano-structured MAO for an increased spectrum of molecular factories, thereby accessing a broader application range directed towards different specialty polyolen-based products “as one effective step in a greater production process which creates new, wellperforming cost-efficient final products.”

Project Results:
See above executive summary for project highlights or for further details the corresponding scientific publications listed below.

Potential Impact:
MAO is a key activator for a large section of the industrial production of polyolefins (POs). World polyolen production has risen from 25.6M tons in 1983 to 150M tons in 2010, with a total market value of several billion US-$. Of an annual world volume of 20 Mt Linear Low Density Polyethylene (LLDPE), approximately 10% is being produced via processes that are based on MAO. The so-called single-
site catalysts which require activation by MAO show the highest growth rates, about 10% per annum, with an estimated market of 220-
250M dollars worldwide. Therefore the potential impact of beyond state-of-the-art MAO is enormous, simply because of the huge
volume of the PO market. Assuming new tailor-made MAO will lead to an increase of the MAO based PO production by 10 %, this
already gives 200 000 t/a of additional polyolefins produced via beyond state-of-the-art MAO based molecular factories. The
contribution of MAO to the full PO production costs is roughly 20-50€/t. By boosting the activation efficiency by a factor of two this
translates into an annual saving in production costs of 20-50M€ per year.

But the main impact of beyond state-of-the-art MAO-ROBOTS with controlled and improved nano-structure will be in the extension of
the application range to novel, specialty polymers. The research performed in MAO-ROBOTS is fully in line with the problems
formulated in many sections of the Strategic Research Agenda of the European Technology Platform SusChem,
(http://www.suschem.org/) e.g. section “Fundamental understanding of structure property relationship: The control and understanding
of the structure property relationships (SPR) of molecular systems is crucial for the intelligent processing of advanced materials.”

By this MAO-ROBOTS will contribute strongly to achieving the goals formulated in the Nanotechnology Action Plan of the EC by a
substantial reduction of

• Production costs: up to 20 to 60% of the molecular factory costs during polyolefin production costs are related to MAO. In
particular, the production of the MAO will become substantially more economical, creating by this way also an intermediate product
with strongly increased added value, since its efficiency in the process will be substantially increased.

• Environmental risks: MAO is dispersed in aromatic organic solvents like toluene which are strong pollutants. The solubility of MAO
in non-aromatic solvents is still poor. Attempts to improve this solubility have led to limited success so far, often with a concurring
decrease in activation efficiency. There will be substantial environmental savings due to the extremely reduced volume of substances to
be handled during the MAO-production and the corresponding reduction in the waste streams. The impact in saving aromatic solvents
is estimated to be of the order of 30% to 40% resulting in a total reduction of up to 430 tons of aromatic solvents.

• Work health and safety: MAO and its precursor TMA are highly pyrophoric components, which have to be handled with extreme
care during transport, storage and use, in particular when used in large quantities at industrial production plants. Beyond state-of-the-art
MAO-ROBOTS with boosted activation efficiency will be used in less excess ratios as in present production lines and will in that sense
reduce work health and safety risks during polyolen production via molecular factories.

The industrial partners involved in the project are among the leaders on the market. CHEMTURA is, besides US-based competitor
Albemarle, world-wide leader in MAO production and interested in increasing its market share. SABIC, DSM and LANXESS are leading
European PO producers and will guarantee the take up of the newly developed nano-technological-based molecular factories within
their existing production lines.

Dissemination is an integral part of the project MAO-ROBOTS.

• The dissemination activities include the presentation of results at conferences and at appropriate public events, information of the
media, and publication in international journals.

• The project homepage (http://www.uef.fi/mao-robots) provides general information of the project in a public area to stimulate the
dissemination and the use of knowledge. In an internal partner area data exchange via file uploading and downloading is supported so
that a high quality of technical documentation (via website) is assured.

• A long term dissemination effect of the project is education and training of students and young researchers in this field.

Workshops
The consortium organized an international workshop entitled “Methylaluminoxane (MAO) activators in the molecular polyolefin
factory” in Tutzing, near Munich, Germany, 19.-21. May 2014. The aim was to bring together experts in MAO synthesis, characterization
and theory, as well as polymerization catalysis and its industrial application, in order to discuss the current status of the field and
identify future trends and challenges for the application of MAO.

Publications:
Laine, Anniina; Linnolahti, Mikko; Pakkanen, Tapani A. “Alkylation and activation of metallocene polymerization catalysts by reactions

Ghiotto, Fabio; Pateraki, Chrysoula; Severn, John R.; Friederichs, Nic; Bochmann, Manfred “Rapid Evaluation of Catalysts and MAO
Activators by Kinetics: What controls polymer molecular weight and activity in metallocene / MAO catalysts?” Dalton Trans., 2013, 42,

Ghiotto, Fabio; Pateraki, Chrysoula; Tanskanen, Jukka; Severn, John R; Luehmann, Nicole; Kusmin, André; Stellbrink, Jörg; Linnolahti, Mikko; Bochmann, Manfred "Probing the Structure of Methylaluminoxane (MAO) by a Combined Chemical, Spectroscopic, Neutron Scattering, and Computational Approach" Organometalics, 2013, 32, 3354.


Training of students and young researchers:
In total two PhD students and 10 postdocs were employed during the MAO-Robots project.

Plan for the use and dissemination of foreground:

The consortium is currently preparing further publications in scientific journals. In addition, participation in international conferences is planned to disseminate project results. The project web page will be regularly updated until 2016.

The exploitation of project results will take place on two levels. The first level comprises beyond-state-of-the-art MAO and EBAO products. Synthesis and investigation of new MAO and EBAO products are tested on lab- and semi-technical scale. Scale-up production is planned if promising results will be the obtained in application tests by the PO producers. (Exploitation Phase 1). The commercialisation of new products will take place after the project end (Exploitation Phase 2). At this level the commercialisation will comprise not only the PO producers being involved in the project but the whole PO producing industry.

The second exploitation level is related to the use of new MAO and EBAO products in PO production. The use of the new technology in production will start after the project; here not only improved production processes are envisaged but also new added-value innovative PO materials.

List of Websites:
http://www.uef.fi/mao-robots

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