

The First Mitsui Chemicals International Symposium on Catalysis Science

(MICS2003)

Date March 17 (Mon.) - 18 (Tue.), 2003

Place Kazusa Akademia Hall

(Kisarazu, Chiba Prefecture, Japan)

Organized by: Mitsui Chemicals, Inc.

Surpported by:Chiba Prefecture/ Sodegaura City/ Ichihara City/ Kisarazu City/ Mobara City
The Chemical Society of Japan/ The Society of Polymer Science, Japan/ Catalysis Society of Japan/
The Japan Petroleum Institute/ The Society of Synthetic Organic Chemistry, Japan



Message

Catalysis science - key technology for the sustainable development of society

~ The symposium provides an excellent opportunity to boost research exchanges beyond organizational barriers ~



Dr. Hiroyuki NakanishiPresident
Mitsui Chemicals, Inc.

Mitsui Chemicals feels most honored to have hosted the First Mitsui Chemicals International Symposium on Catalysis Science.

The 20th century has been called the century of science and technology, and indeed remarkable progress in science and technology has brought greater material wealth to our lives. In the 21st century, however, in order for human beings to enjoy true happiness and in a better environment, it is becoming increasingly important to create knowledge that will allow us to achieve sustainable development in our daily lives and economic activities. Japan has therefore decided to concentrate on four priority areas: life science, information technology, nanotechnology and new materials, and the environment. The field of catalysis science underpins development in all these four priority areas, and provides the basis for creating high-performance materials and substances controlled at the nano level. In light of this, it is no exaggeration to say that progress in catalysis science will lead to sustainable development of the chemical industry in the 21st century.

At Mitsui Chemicals, Inc., our corporate vision is to become a general chemical company with a strong presence in the global market, and to make a broad contribution to society by providing high-quality products and services via innovation and creativity in materials and matter, with minimal impact on the global environment (keeping

in harmony with the global environment). In 1958 Mitsui Chemicals became the first company to commence commercial production of low-pressure polyethylene, and has since continued to play a leading role internationally in the development of catalysts for polyolefin production. In April 2002, we established the Catalysis Science Laboratory, a facility dedicated to comprehensive research in the field of catalysis science which is of growing importance as a next-generation technology. Next, to commemorate the founding of the Catalysis Science Laboratory, we decided to host international symposia on catalysis science, the first of these focusing on polymerization catalysis.

For this symposium we were fortunate to obtain the services of twelve leading experts in catalyst research and development from industry and academia, both here in Japan and overseas. The presentations by these researchers and scientists allowed us to share the findings of their work at the cutting edge of catalysis science, and offered some insight into their approach to everyday research activities. All in all, it was a most worthwhile symposium.

Finally, we hope this symposium will help increase recognition of the Mitsui Chemicals Catalysis Science Laboratory as a global center for catalysis research, and a place where researchers from around the world can share research knowledge and engage in productive dialogue across organizational barriers.

Program

${\sf March\,17}{\sf Mon.}$

	9:30 ~ 9:55	Opening Remarks
	10:00 ~ 10:45	Plenary Lecture Ryoji Noyori (Nagoya University, Japan) Molecular Catalysis : Today and Tomorrow
	10:50 ~ 11:30	Walter Kaminsky (University of Hamburg, Germany) Metallocene and Late Transition Metal Catalysts for Ethylene/Cycloolefins Copolymerization
	11:30 ~ 12:10	Hiroshi Shirai (Asahi Kasei Corporation, Japan) Ethylene Copolymerization by Half-Sandwich Metallocene Catalysts
	13:30 ~ 14:10	Krzysztof Matyjaszewski (Carnegie-Mellon University, U.S.A.) The Art of ATRP (Atom Transfer Radical Polymerization)
	14:10 ~ 14:50	Tobin J. Marks (Northwestern University, U.S.A.) New Catalysts and Catalytic Processes for Single and Multiple Site Olefin Polymerization
	15:10 ~ 15:50	Thomas M. Connelly (DuPont Company, U.S.A.) Recent Advances in DuPont's Versipol Polymerization Technologies
	15:50 ~ 16:30	Maurice S. Brookhart (University of North Carolina) Olefin Polymerizations Using Late Transition Metal Catalysts
	16:30 ~ 17:10	Tatsuya Miyatake (Sumitomo Chemical Co., Ltd., Japan) Phenoxytitanium-based Olefin Polymerization Catalysts
	18:30 ~ 20:30	Official Dinner Party

March 18 Tue.

9:30 ~ 10:15	Plenary Lecture Jean-Marie Lehn (Louis Pasteur University,France) From Supramolecular Self-Organization to Dynamic Combinatorial Chemistry
10:20 ~ 11:00	Yoshio Okamoto (Nagoya Universtiy, Japan) Stereocontrol in Radical Polymerization Using Lewis Acids
11:00 ~ 11:40	Kurt W. Swogger (The Dow Chemical Company, U.S.A.) Molecular Architecture Using New Generation Catalysts
11:40 ~ 12:20	Norio Kashiwa (Mitsui Chemicals, Inc., Japan) Catalyst Innovations in Polyolefin Industry at Mitsui Chemicals
12:25 ~ 12:30	Closing Remarks
14:00 ~ 16:30	Site Tour Mitsui Chemicals Ichihara Works Mitsui Chemicals Sodegaura Research Center



Magical Power

Digest March 17 Mon.

Prof. Ryoji Noyori

Nagoya University, Japan

Molecular Catalysis: Today and Tomorrow

Chemistry is beautiful, exciting, and beneficial formankind.

To maximize the benefits of chemical processes, the establishment of sophisticated chemical conversion processes that conserve resources and energy and are environmentally-friendly is a priority. To continue serving human needs, the chemical industry requires ecochemical industrial technologies. All the types of molecular compounds can be synthesized by organic chemistry, and perfect chemical reactions with 100% yield and 100% selectivity is the target. A production method for formic acid derivatives that



uses nontoxic CO₂, which can be used as both solvents and reactants, as a supercritical fluid, and a synthesis method for adipic acid that uses hydrogen peroxide, which generates neither hazardous substances nor useless wastes, as an oxygen resource are examples of

vitally important production methods. Following the principle of producing only what is needed, "racemic switch" is required in medicine development for switching from racemic compound medicines to single enantiomeric medicines. Asymmetric hydrogenation technology with a BINAP catalyst has made a great contribution in this field.

Prof. Walter. Kaminsky

University of Hamburg, Germany

Metallocene and Late Transition Metal Catalysts for Ethylene/Cycloolefins Copolymerization

Ziegler-Natta catalyst and Phillips catalyst, which have conventionally been used as catalysts in industrial polyolefin productions are so-called multi-site catalysts, which contain multiple active-site structures. Single-site catalysts stemming from the "metallocene catalyst" developed by Prof. Kaminsky have attracted a great deal of attention as polymerization catalysts with high development potential for polymer production with targeted structures because of their uniform nature in active-site structures, and consequently have been investigated



worldwide. Controlling polymeric structures has become possible in terms of tacticity, molecular weight and its distribution, and so forth. Polyolefins with excellent properties including strength, rigidity, and transparency have been synthesized such as high tacticity polypropylenes, linear low-density polyethylenes, and polyolefin elastomers. Prof. Kaminsky developed the technolo-

gy for polymerizations of strained cyclic olefins such as norbornene and has been able to achieve non-ring opening copolymerization using metallocene catalyst technology, which has led to the creation of cyclic olefin copolymers (COC) with unprecedented structures. This polymer is expected to be applied for engineering plastics.



Dr. Hiroshi Shirai

Asahi Kasei Corporation, Japan

Ethylene Copolymerization by Half-Sandwich Metallocene Catalysts

Research on ethylene copolymerization has widely been undertaken using metallocene catalysts. Among polymers, cyclic olefin copolymers (COC) is one of the most important engineering plastics possessing high thermal stability and excellent optical properties. Dr. Shirai and his associates have conducted research on copolymerization of ethylene and some monomers using non-bridged half-sand-

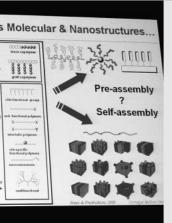
wich metallocene / MAO catalytic system, instead of using the conventional metallocene (with a structure where the metal is sandwiched by two cyclopentadienyl (Cp) type lig-

ands). They have found that non-bridged half-sandwich zirconium and titanium complexes having dithiocarbamate ligands with sulfur coordination or phenoxy ligands with oxygen coordination show an exceedingly high activity in



ethylene/norbornene copolymerization. Interesting results have been obtained on microstructures of those polymers.





Prof. Krzysztof. Matyjaszewski

Carnegie - Mellon University, U.S.A.

The Art of ATRP (Atom Transfer Radical Polymerization)

Controlled radical polymerization is among the most rapidly developing areas of polymer science. Atom transfer radical polymerization (ATRP) in the field has actively been studied worldwide since the first paper was published in 1995, and has undergone explosive development. The main reason for such development is its simple process capable of preparing tailor-made functional macromolecules. Applications of ATRP technology are expected to have ripple effects in industry amounting to \$20 billion a year. Prof. Matyjaszewski and his associates have been conducting research in three directions: (1) understanding of reaction

mechanisms, and of the relation between molecular structure and reactivity of the involved reagents, (2) optimization of the process, and (3) designing, synthesis, and characterization of macromolecules with controlled topologies, compositions, and functionality. They have successfully synthesized nano-order controlled materials using



ATRP technology such as carbon nanocylinders with a 20 nm diameter, 200 nm long molecular brushes with 400 side chains, and ~ 20 nm diameter silica colloids grafted with ~ 1000 side chains. ATRP can easily be combined with other types of polymerizations, hence, block copolymerization with polyolefin, for example, can be performed, which can be used as blend compatibilizers for commodity polymers and improve their properties and performances.

for Quality Life

On March 17 the symposium opened with a speech by Mitsui Chemicals President Hiroyuki Nakanishi, chairman of the MICS2003 organizing committee.

The plenary lecture was delivered by Professor Ryoji Noyori, Nobel Prize laureate in Chemistry 2001. This was followed by lectures from seven quest speakers. The question-andanswer time at each session attracted numerous questions from the floor, resulting in very lively discussions.

Prof. Tobin J. Marks

Northwestern University, U.S.A.

New Catalysts and Catalytic Processes for Single and Multiple Site Olefin **Polymerization**



Single-site olefin polymerization catalysts have enabled unprecedented control over polymerization activity and selectivity as well as tailoring of macromolecular architectures. Nevertheless, understanding of catalyst-cocatalyst interactions and ability to exploit them to synthesize new polymeric materials is at a very early stage. Prof. Marks and his associates have focused on three interconnected aspects of single-site polymerization catalysts. (1) Structures and thermodynamic stability of metal cationcocatalyst anion pairs, (2) Molecular dynamics and stereoselectivity in polymerization of these ion pairs, and (3) Design of multiple site catalyst systems where cooperativity between single-site catalytic centers is significantly enhanced by using polynuclear catalysts and cocatalysts. The results of these cooperative effects can include significantly enhanced polymerization catalytic activity, selectivity, chain branching, and unusual comonomer incorporation characteristics.

Dr. Thomas M. Connelly

DuPont Company, U.S.A.

Recent Advances in DuPont's Versipol, **Polymerization Technologies**

Growing out of discoveries of palladium and nickel--diimine ligands by Prof. Brookhart catalysts with at the University of North Carolina, DuPont has collaboratively with him developed technologies for the homo- and co-polymerizations of ethylene with a variety of polar monomers. These catalysts can produce various polymers from ethylene through a mechanism named "chain walking." Examples include HDPE, LLDPE, and VLDPE oil. Ethylene / acrylate copolymer can also be synthesized. Iron-based catalysts with pyridylbisimine ligands bearing three

nitrogen as coordination atoms are highly active, and form high-density polyethylene and higher olefins. The obtained higher -olefins have features such as linearity, and high quality due to a low inter-

nal olefin content, which make them attractive commercially. As a result of a comprehensive screening test, nickel complexes with oxygen, nitrogen, or phosphorus as coordination atoms have been identified as effeccatalysts for polar monomer copolymerization.



These new ligands allow a great deal of flexibility in the design of processes for specific polymerization, particularly for highly value-added polymer produc-



Prof. Maurice. S. Brookhart

University of North Carolina, U.S.A.



Recently, efforts have centered on developing new single-site catalysts in research on olefin polymeriza-tion catalysts. While most work has used early transi-tion metals, Prof. Brookhart and his associates have focused on using late transition metals, particularly Ni (II) and Pd (II). They first reported in 1995 that Ni and Pd complex catalysts -diimine ligands were capable of polymerizing ethylene and -olefins to high molecular weight polymers while only low molecular weight



polymers had been obtained with conventional late transimetal complexes. Incorporation of bulky substituents in aromatic rings in diimine ligands was the key to this historical discovery. Polymers produced by copolymerizing ethylene,

and 1, 2-disubstituted olefins have branched structures, which could never be obtained with conventional early transition metal catalysts. They identified that the branched structure is a result of unique reaction mechanisms in which catalysts move on polymer chains during the course of the polymerization, differing from those of convention-



Dr. Tatsuya Miyatake

Sumitomo Chemical Co. Ltd

Phenoxytitanium-based Olefin Polymerization Catalysts

Since Prof. Kaminsky and his associates discovered the metallocene catalyst system, development of new metallocene catalyst systems has been undertaken worldwide aiming at improvement of catalytic activity, copolymerizability, and tacticity. Meanwhile, Sumitomo Chemical has been conducting research focused on non-metallocene catalysts, which include no Cp ligands such as metal alkoxides. In 1989, Dr. Miyatake and his associates developed a novel titanium complex catalyst system with thiobisphenoxy ligand bearing oxygen and sulfur as coordination atoms. This catalyst system is thought to be promising because it not only replaces metallocene catalysts in olefin polymerizations but also is possibly capable of creating



new polymeric materials. However, although the thiobisphenoxy-titanium catalyst shows good polymerization performance with various monomers, it shows poorer catalytic activity in ethylene and propylene polymerizations than advanced metallocene catalysts. Subsequently, they developed a novel high performance catalyst (PHENICS catalyst) in 1998 by combin-

ing the Cp ligand with a bulky phenoxy ligand in order to improve catalytic activity. The PHENICS catalyst not only shows a high ethylene polymerization activity equivalent to the activity of other metallocene catalysts but also can promote copolymerizations of ethylene and conjugated dienes such as butadiene and isoprene, of ethylene and styrene or norbornene, furthermore of propylene and 1-butene, hence being expected to be a next generation catalyst for olefin polymerization.





Magical Power

Digest March 18 Tue.

Prof. Jean-Marie Lehn

Louis Pasteur University, France

From Supramolecular Self-Organization to Dynamic Combinatorial Chemistry

Supramolecular chemistry is based on "self-organization", the generation of supramolecular architecture by molecules while they recognize each other. Supramolecular chemistry is intrinsically a dynamic chemistry in view of lability of bondings (interactions) connecting molecular components of a supramolecule. Because of its ability to exchange its constituents, a supramolecule can incorporate diversity and a combinatorial concept. By analyzing inorganic self-assembling processes through self-recognition, templating, and interconversion features, a concept of dynamic combinatorial chemistry (DCC) was formulated. Whereas the conventional combinatorial

chemistry is based on simple assembly of library molecules, DCC is capable of realizing a virtual combinatorial library (VCL) by letting library molecules search for all pos-

sible combinations by themselves while they are reversibly assembling, and consequently by letting them construct a target substance with the best compatibility in molecule recognition. The DCC / VCL concept can be applied to organic chemistry as well as biological recognition, catalysts, and materials. A new material "Dynamer" was



proposed by applying the concept to polymers. (Supramolecular chemistry: A field proposed by Prof. Lehn in 1978. An assembly system chemistry generating chemical and physical functions not available with individual molecules by assembling numerous basic units represented by molecules.)

Prof. Yoshio Okamoto

Nagoya University

Stereocontrol in Radical Polymerization Using Lewis Acids

Stereocontrol in polymerization reactions is of vital importance in polymer science and the polymer industry because polymer properties greatly vary depending on stereostructures. While the radical polymerization method is widely used in industry, radical polymerization capable of stereocontrolling is a new area. Prof. Okamoto and his associates have recently found that radical polymerizations in the presence of fluoroalcohols or Lewis acids such as rare-earth metal trifluo-romethanesulfonates have significant stereo-controlling

capability in the syntheses of polymers such as poly (vinvl esters)

poly(methacrylic esters), and poly(acrylic esters) They have materialized

radical poly-merizations with high stereocontrolling of acrylamide and methacrylamide by optimizing reaction conditions with this catalyst system, and also found the possibility of living poly-merization capable of high degree control of molecular weight.

March 18, the second day of the symposium, opened with plenary lecture from Professor Jean-Marie Lehn of Louis Pasteur University, the 1987 recipient of the Nobel Prize in Chemistry, followed by three guest speakers. The two days of MICS2003 were finally brought to a close with a speech by Mitsui Chemicals Managing Director Akihiro Yamaguchi.



Dr. Kurt W. Swogger

The Dow Chemical Company, U.S.A.



Molecular Architecture Using **New Generation Catalysts**

Dow Chemical has been developing and producing new polyolefins based on a concept called molecular architecture using original CGC catalysts (INSITE™ tech-

nology). These catalysts have a single catalytically active species, which allow catalyst functions to be modeled, and can control product properties for designs. This technology has created an unprece-

dented business model, which integrates catalyst science, production process designing, material sciences, and needs of customers and markets into a single integral approach. This new approach, called "SixDaySM" model by Dow Chemical, meets customer needs through polymer designing and economical production processes. The INSITE™ technology has been utilized to convert low cost materials to highly value-added products following this model, and R & D activities have been geared up in connection with customer needs. Subsequently, Dow Chemical has launched eight new product and achieved a great performance, a total 450,000 ton of polyolefin production in 2000. Moreover, they have been undertaking system development for efficient utilization of human resources to speed up R & D activities.

Dr. Norio Kashiwa

Mitsui Chemicals, Japan

Catalyst Innovations in Polyolefin Industry at Mitsui Chemicals

Polyolefins such as polyethylene (PE) and polypropylene (PP) are indispensable materials in the modern world, and their worldwide production has exceeded 80 million tons per year. 51% of PE and 95% of PP are produced using magnesium chloride-supported titanium catalysts (Ti/Mg catalysts). Mitsui Chemicals made the world's first patent application for these Ti/Mg. These catalysts enable production of PE with a narrow distribution at an activity level over 100 times greater than the conventional Ziegler catalyst.Introduction of electron donors in catalysts dramatically improved activity and tacticity of PP, innovated production processes and product qualities, and has brought about the current prosperity of the polyolefin industry. Metallocene catalysts are now in practical application at Mitsui

Chemicals. New "practical applications of singlesite catalysts" include the creation of long-chain branching polymers, and building and operation of a PE plant dedicated to metallocene usage, which products 200,000 ton per year. As for the future research efforts, Mitsui Chemical is working to create unique polymers based on advanced research achievements such as living polymeriza-

tions using post-metallocene catalysts at elevated temperatures, and incorporating functional groups in poly-olefins using metallocene catalysts. The focus is on nano-order control of topologies by chemical combinations of totally immiscible polymers in



terms of crystalline / amorphous or polar / nonpolar features. Radical polymerizations and ringopening polymerizations on polyolefin molecular chains have successfully been performed, which lead to materialization of nano-structure control of hybrids composed of polyolefins and polar

for Quality Life





Official dinner party

A dinner reception was organized for the first night of the symposium, and was attended by a total of 240 people : around 180 guests including the speakers, members of supporting / sponsoring organizations and researchers from industry, government and academia, plus a contingent of 60 from the host company, Mitsui Chemicals. The evening began with a speech by President Nakanishi of Mitsui Chemicals on behalf of the organizers, in which he thanked everyone who helped to make the symposium a success. President Nakanishi was followed by Akiko Domoto, Governor of Chiba, and Shinji Murai, chairman of the Society of Synthetic Organic Chemistry, Japan on behalf of the quests. Both gave humorous speeches that contributed to the relaxed atmosphere at the dinner. The informal part of the evening was then kicked off with a toast by Chairman Hattori of the Catalysis Society of Japan. Participants spent around two hours getting to know each other better, and enjoying a performance of Kisarazu Jinku drumming. The "Wajima-nuri" lacquered mouse pads given away to those at the dinner to take home were greatly appreciated by participants from



Site tour

Upon completion of all sessions at the symposium, a site tour took participants to the Sodegaura Center and the Ichihara works, Mitsui Chemicals main facilities for research, development, and manufacture of petrochemical products. At the Sodegaura Center participants watched a video introduction to the Center, then

sodegaura Center participants watched a toured the facility, including display rooms featuring Mitsui Chemicals products. They then moved on to the Ichihara works, where staff gave a detailed explanation on the polyethylene plant (MX plant), the first in Japan to employ metallocene catalysts. Participants asked a variety of questions throughout the tour, and we feel they went away with a much better understanding of Mitsui Chemicals' operations.





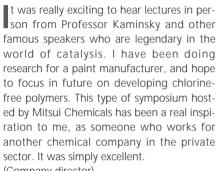


To commemorate the symposium

At the MICS2003 we heard plenary lectures by two recipients of the Nobel Prize in Chemistry: Professor Lehn (1987) and Professor Noyori (2001), and so to commemorate this great honor in perpetuity, we have named the main thoroughfare at our Sodegaura Center research facility Lehn-Noyori Promenade.







(Company director)

Professor Kaminsky's talk on metallocene catalysts expands the possibilities of polymerization. It was very interesting. (University student)

symposium with this many well-known Aspeakers is rare indeed. My area of study is polymers, so Professor Noyori's talk on "super-critical" was very helpful. I very much hope there will be more of these gatherings in future. (Company researcher)

had always found radical polymerization a very difficult technology to handle, so was very interested in what Professor get a lot out of the event.

Matyjaszewski had to say. At this symposium, enough time was allotted for each lecture, and all the speakers made their talks easy to understand, allowing participants to

(Member of industry association)

ats off to Mitsui for organizing a symposium of this magnitude! My field is chemistry, however I received an invitation and so decided to attend. In terms of broadening my knowledge, I heard a lot is certain to be of great use in the future. (Company researcher)

his must surely be the first time that a company has hosted an event attracting this many researchers at the cutting edge of their respective fields. Much of the content was very practical, and I was reminded anew of the growing importance of polymerization catalysis as a key technology over the last ten years. (Company researcher)

ertainly one doesn't often get the ✓ opportunity to attend a gathering with not one but two Nobel Prize winners, and I eagerly looked forward to attending this symposium. I work in polyolefin industry, so Professor Kaminsky's lecture was of particular value. (Company researcher)

y specialty is olefin polymerization, so I was particularly impressed by Professor Marks' lecture on the same field. Overall, the event was well run, and really there was nothing more I could have asked for. (Company researcher)

onsidering the prolonged slump in the impressed by the fact that a single company would host a symposium of this scale. The content was of course outstanding, and the staff doing their best to make sure everyone enjoyed the two days left me with a good impression as well. There was a real sense of hospitality. (Member of industry association)

Comment from the only high school student to attend the symposium

I am in my first year in high school, and in the future I hope to go to a science university. One day, my father told me about this symposium, so I decided to attend. All the lectures were in English, so some of them were difficult to understand. However, Professor Noyori's plenary lecture was easy to understand, and very worthwhile. I came from Shizuoka to attend, and just experiencing the atmosphere of a symposium was a real thrill for me. I hope to take part in the second and third symposia and absorb more on different subjects. I also felt that if there were a chemistry symposium for high school students like myself, this would enable us to learn more about chemistry.

Hironori Hara Science / mathematics course Shizuoka Prefectural Shimizu-Higashi High School



Quality information makes for quality people

Allow me, first of all, to thank you all for helping to make this sympo-

When we asked some of the world's top authorities in catalysis science to give lectures at MICS2003, without exception they were very enthusias-tic about the idea behind the symposium, and gladly agreed to take part. Those who assisted by presiding over the sessions were themselves very knowledgeable individuals, any one of whom I would have no hesitation in asking to speak at an event like this. The symposium was attended by a large number of individuals from industry, government and academic groups, including a high school student from Shizuoka who learned of the event on our website and decided to attend. I believe this symposium has also proved extremely useful in helping to nurture the next generation of scientists, and to give them the opportunity to experience the wonder of the discipline that is science. For example, having

lanaging Director Group Executive, R&D litsui Chemicals, Inc

Akihiro Yamaguchi

heard Professor Kaminsky's lecture, something suddenly occurred to Professor Noyori, who then asked one of our young researchers about it. That young researcher obtained some very valuable advice from Professor Noyori on approaches to research, and by



all accounts came away quite inspired. I think everyone who attended this gathering was able to absorb a great deal, by interacting with a variety of different cultures. In my view, this kind of "top-quality information" that leaves an indelible impression is enriching, and helps us to grow as individuals. I hope we can use the great success of this symposium as a springboard to a second and a third symposium, providing a forum for researchers from all over the world to interact and share ideas. Last but not least, I would like to express once again our gratitude for your kind cooperation and participation.