RESEARCH REPORT

1. Name **(ID No.: SP04201)**

Jasmine BURGUET

2. Current affiliation

Ecole Nationale Supérieure des Télécommunications de Paris

3. Research fields and specialties

☐ Mathematical Sciences ☐ Engineering Sciences

4. Host institution

Okayama University

5. Host researcher

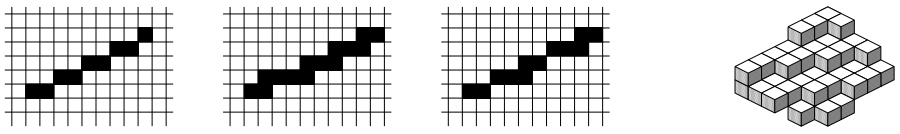
Dr Yukiko Kenmochi

6. Description of current research

My research takes place at the frontier of Mathematics and Computer Science, in a field called *Discrete Geometry*. The aim is to consider geometrical/topological properties of discrete sets, more particularly *digital sets*. Such sets are composed of digital elements such as *pixels* (for *pic*ture *el*ements) in 2D, i.e. unit squares centered on points of $\mathbb{Z}^2$, or *voxels* (for *vo*lume *el*ement) in 3D, i.e. unit cubes centered on points of $\mathbb{Z}^3$. Digital sets are widely present in computer science, since data are implicitly discrete in computers. For instance in 2D, images that one displays on computer screens are discretized, or in medical imagery, 3D Magnetic Resonance Images (MRI) are also discrete.

The purpose of discrete imagery is to compute or define in discrete sets relevant notions existing in continuous geometry (like paths, curvature, ...). In order to do it, contrary to classical approaches, we do not compute continuous approximations of the discrete sets, but we define tools directly on these sets. Indeed, continuous calculi sometimes generate numerical problems that do not appear if we use discrete values. Moreover, it could be more efficient to work directly on original data instead of computing approximations.

For example, a classical question existing in discrete geometry is the following one: given a set of pixels (resp. voxels) X, are the elements of X defining a straight line (resp. a plan)? In the following figures, we can see several examples of sets of discrete elements. Contribute to give an answer to this question is the purpose of my research at Okayama University.



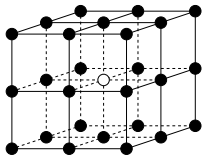
7. Research implementation and results under the program

Title: Local description of discrete combinatorial surfaces

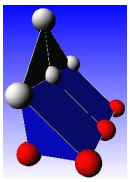
Description of the research activities:

During my research activities, I worked on 3D discrete sets. More precisely, the subject concerned *discrete surfaces*. Let us suppose that we consider a 3D discrete set O.

We work on the voxels of the border B of O, i.e. the voxels that have at least a neighbor in $\overline{O}$ (see in the following figure (a) the 26 neighbors - black points - of the central white point). For all points of B, the aim is to check *locally* if they are considered to be on a discrete surface, and if so if they are locally planar or not.
For instance, in figure (b), voxels are represented by dots, in order to highlight their relations with their neighbors. The four upper points are not considered to be on a discrete surface, since in their neighborhoods, they do not locally separate the interior of the volume defined by the whole points from the exterior (see the flat zone composed of two triangles between these points: the interior is locally empty). On the contrary, the other points are located on a discrete surface.

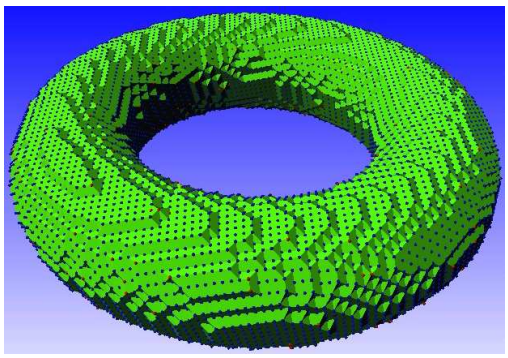


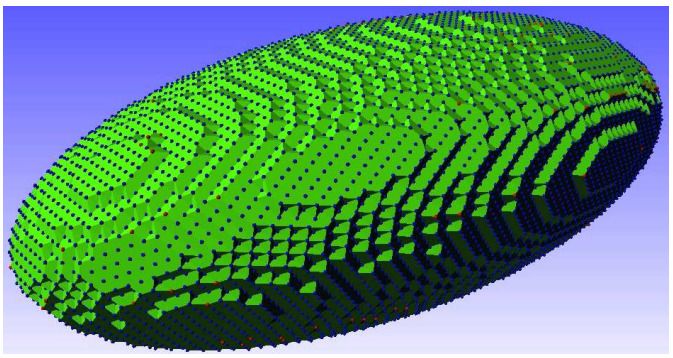
(a)



(b)

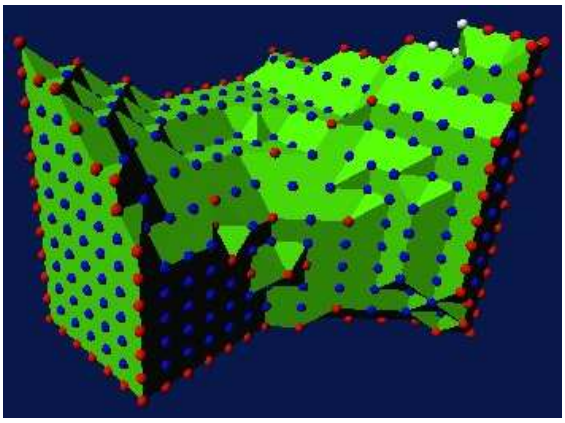
In previous works, it was established that among the 2^{26} possible configurations for the neighborhood of a point p, there exist 6,028 configurations such that p is on a discrete surface. Among these configurations, only 34 are planar (i.e. these configurations may appear in discrete planes).
My contribution was first to generate "regular" simple objects and to examine the proportions of planar, surface and non-surface configurations. I made tests on objects defined by surfaces like ellipsoids, paraboloids, thorus and so on. From the first results I obtained, it seems that most of the points of the border are planar points. In following figures, blue points correspond to planar points, red points to surface points that are not planar, and white points to non-surface points. Let us consider for instance the thorus. Its border is composed of 9752 points. Among these points, 9476 are planar and only 276 are non-planar surface points. There is no non-surface point. In the ellipsoid, there are 10666 points, 10448 planar points, 218 non-planar surface points and no non-surface points.

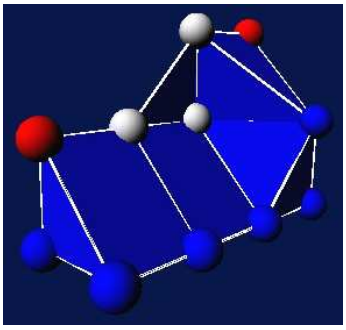




In the tests I made, only a few objects presented non-surface points in their borders. See for example the two following figures: the object on the left is obtained from an hyperbolic paraboloid intersected with a cubic bounding box.

Non-surface points appear on top right of the figure, at a place where the bounding box cut the object. We removed the flat zone created by the white points (see right figure where we display the white points and their neighborhoods). In all of our tests, white points appeared only at the intersection of objects and bounding boxes.





From these results, it seems that on regular objects, most of the border points are planar points, i.e. only 34 configurations among the 2^{26} possibilities. This is an interesting result. Indeed, we plan to use this previous observation in a problem of 3D images automatic classification, in order to know if a given object is regular or not, by examining the proportions of the different configurations appearing. Moreover, we need to improve our observations with a larger set of objects, and a larger range of parameters.
Another perspective is to propose a new classification among the 5,994 non-planar surface points. For example, we need to check if only a few configurations appear among the set of non-surface point belonging to the border of regular objects.

8. Comments

This program allows me to start a new research collaboration with Dr Kenmochi. We agree to say that there are several ways to explore, starting from the work we made together in her laboratory at Okayama University.
Moreover, during my stay in Japan, I went to the MIRU conference devoted to research in imagery, in Hakodate at Hokkaido. There, I met several Japanese researchers involved in research in imagery, and I had the possibility to discuss with them about many interesting topics. I also visited the Pr Imiya's laboratory at Chiba, and he presented me the different projects he leads, especially in robotics.
Finally, I learned many things about the Japanese universities, through my visits at Hakodate University, Tokyo and Chiba Universities and Okayama University.
All of these experiences were really enriching.

9. Advisor's remarks

During her stay in our laboratory, we could have very deep discussion on discrete geometry for 3D computer imagery, and this will be the very good start for the collaboration work in our future.

RESEARCH REPORT

1. Name: Vincent Chanron **(ID No.: SP04202)**

2. Current affiliation:

Design of Open Engineering Systems Laboratory – University at Buffalo – Buffalo, NY 14260 USA

3. Research fields and specialties:

Engineering Sciences – Mechanical Engineering – Multidisciplinary Design and Optimization

4. Host institution:

Knowledge Information System Laboratory – Kyoto University

5. Host researcher:

Professor Shinji Nishiwaki

6. Description of your current research

My research deals with the decomposition and coordination of decisions in the design of complex engineering systems, which has become a great challenge. Companies who design these systems routinely allocate design responsibility of the various subsystems and components to different people, teams or even suppliers. The mechanisms behind this network of decentralized design decisions create difficult management and coordination issues. However, developing efficient design processes is paramount, especially with market pressures and customer expectations. Standard techniques to modeling and solving decentralized design problems typically fail to understand the underlying dynamics of the decentralized processes and therefore result in suboptimal solutions. My research aims to model and understand the mechanisms and dynamics behind a decentralized set of decisions within a complex design process. By using concepts from the fields of mathematics, economics, and engineering science, including Game Theory and Nonlinear Control Theory, we model decentralized design problems and provide efficient solutions.

The first goal of my research is to establish the first steps towards understanding the mechanisms of decentralized decision processes. This includes two major steps: studying the convergence characteristics, and finding the final equilibrium solution of a decentralized problem.

The second goal of my research is to propose robust design processes that could be used in decentralized design environments in order to achieve optimal product development. To do so, they need to achieve different specific goals. The first one is to be convergent in most cases, meaning that the designers involved in the design process will have no problem achieving a final solution. This process should also be *quickly* convergent, and should avoid the too common expensive iterations between the designers. Finally, the final solution should yield an optimal final product, in terms of engineering technical requirements, since it is the most common way of evaluating the quality of an engineering product.

7. Research implementation and results under the program (As much as possible, describe the contents and results of your research in a manner that is easily understandable to a non-specialist in your field.):

My main tasks in the Knowledge Information Laboratory have been to get to know the research carried out in this laboratory and getting involved in one of their research projects, namely the development of an integrated design environment for space satellite structures. My own research was at a point where many results had been obtained, but they needed to be validated on a large engineering design case study, and that is exactly what this project had to offer. This design case study, in collaboration with the Japan Aerospace Exploration Agency, aims at solving a component arrangement subproblem, and a structural design subproblem in an optimal way to have the satellite meet the design requirements. My experience in decentralized design brought a new way at looking at this problem, in order to make comparison between collaborative and decentralized design possible. The main tasks were to get to know the rather large problem formulation (which uses NASTRAN, Matlab and iSIGHT as software to carry out calculations), and run simulations of the case study whose results still remain to be analyzed.

8. Please add your comments (if any):

The JSPS summer program is a great way to discover the way research is carried out in Japan, and to witness the everyday life of Japanese researchers. I learnt technical skills, but also human skills as the work methods are relatively different from what I was used to. It also gave me a good insight of what it would be like to come to Japan as a post-doc and it is a great way to promote Japanese research worldwide.

Beyond that, my stay was a wonderful experience, both in the lab and outside the lab. I made good friends in Japan, I started a research collaboration that will hopefully lasts, and I discovered a beautiful country and can understand a little better now.

9. (If any) Advisor's remarks:

It was a great pleasure for us that we have invited Vincent Chanron in our lab for two months. We made a lot of fruitful discussions concerning his research topic with him. I hope that we will keep doing the collaborative research with him and his group.

Finally, I would like to offer my appreciation to JSPS for giving him a chance to stay in Kyoto.

RESEARCH REPORT

1. Name:COLONNA Anne (ID No.: SP04203)

2. Current affiliation: PhD student

Laboratoire d'Optique et Biosciences Ecole Polytechnique

INSERM U451 - CNRS UMR7645 91128 Palaiseau Cedex

3. Research fields and specialties

☐ Humanities ☐ Social sciences ☐ Mathematical and Physical Sciences

☐ Chemistry ☐ Engineering Sciences ☐ Biological Sciences

☐ Agricultural Sciences ☐ Medical, Dental and Pharmaceutical Sciences

☐ Interdisciplinary and Frontier Sciences

4. Host institution: Kobayashi Laboratory

Department of Physics, University of Tokyo, 113-0033

5. Host researcher: Professor Takayoshi Kobayashi

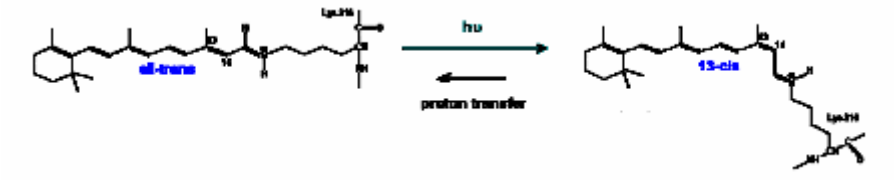
6. Description of your current research

The aim of my PhD is the study of a bacterial protein called Bacteriorhodopsin.

Study of this protein is of high interest to understand photoinduced biological processes as vision and energy transduction of organisms including humans. its high resistance to extreme conditions makes this protein interesting for commercial application as optical data storage or electronic ink for example.

Bacteriorhodopsin is a transmembrane protein found in the bacterium Halobacterium salinarum. Next is a schematic representation of this proein:

Its role is to convert light to a proton gradient which will be used to generate energy. Its simple photosynthetic system makes it a key model to understand other photoinduced biological processes. The photoreceptor molecule, located inside the protein, is called the retinal. Up to now, it is thought that photoreceptor retinal responds to light by undergoing a structural modification called isomerization described below:



This isomerisation takes place in few hundred femtoseconds (1 femtosecond = 10^{-15} second). Is this isomerization the first photoinduced event is still an open question. To be able to monitor faster event than isomerization, we need to use femtosecond laser spectroscopy. We managed to show that the first photoinduced event is actually a charge displacement in the retinal and in its environment called polarization, faster than 11fs (time resolution of our measuring system).[PNAS 101, 7971-7975 (2004)]. This ultrafast polarization is required for proper operation of the protein. We now need to futher understand the relative role of ultrafast polarization and ultrafast isomerization, and eventually their interplay.

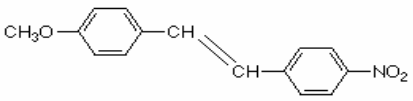
7. Research implementation and results under the program:

Title of your research plan:

Spectroscopic studies of an isomerizable molecule.

Description of the research activities:

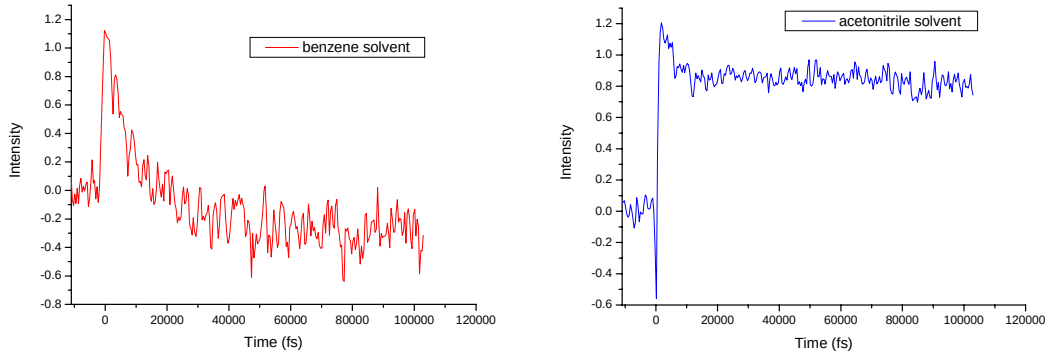
To get a better understanding of the photoisomerization process in bacteriorhodopsin (see part 6) we decided to study another isomerizable molecule: 4-methoxy-4'-nitrostilbene (MONS). The chemical structure of this protein is shown next



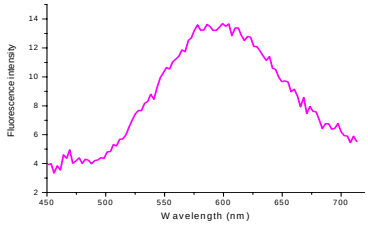
An important feature of MONS is its ability to follow the reaction through a range of environments and allow then to get to a deeper understanding of the important role that solvent plays in chemical reactions.

Two kinds of experiments have been carried out on the sample: pump-probe experiments and fluorescence spectra analyses. In pump probe experiments, the sample is first excited, at time t by an ultrashort laser pulse with a chosen wavelength (pump) and left to evolve. A second pulse (probe) goes through the sample. Intensity of this pulse is monitored and allows checking the evolution of the sample. Next picture

show typical pump probe results with two different solvents whose effect can clearly be seen:



Principles of the second experiment can be explained as follows: light can be absorbed and reemitted by matter very fast and this is called fluorescence. When the light is reemitted at different wavelength, energy of the absorbed light is channeled into other things in the absorbing substance. Controlling this emitted light gives information on the matter at the atomic level. Next is a characteristic fluorescence emission spectrum of the studied sample.



8. Please add your comments (if any):

This internship was of great interest, as much for my work as for cultural discovery. It included both theoretical and experimental part and allowed me to see many aspects of the experiment: not only the laser part but also samples preparation and data analysis. I thank Professor Kobayashi and his group to have allowed me to be involved in such a project.

RESEARCH REPORT

1. Name : Ana Colovic (ID No.: SP04204)

2. Current affiliation: University of Paris 9 – Dauphine, France

3. Research fields and specialties:

☐ Humanities ☑ Social Sciences ☐ Mathematical and Physical Sciences
☐ Chemistry ☐ Engineering Sciences ☐ Biological Sciences
☐ Agricultural Sciences ☐ Medical, Dental and Pharmaceutical Sciences
☐ Interdisciplinary and Frontier Sciences

4. Host institution: National Institute of Science and Technology Policy (NISTEP)

5. Host researcher: Naoki Saito, Director, The Third Policy-Oriented Research Group

6. Description of the current research:

I am preparing a PhD thesis on inter-firm networks in Japanese industrial districts. My doctoral research focuses on networks between small and medium-sized enterprises (SMEs). After an extensive analysis of the existing literature related to networks and industrial districts as well as theoretical literature in the organizational science field, I conducted a fieldwork in Japan from October 2002 to April 2003. During this period I interviewed 42 entrepreneurs and local government officials in eight industrial districts: Ota ward in Tokyo, Higashi Osaka, Hitachi, Kiryu, Suwa, Hamamatsu, Musashi Murayama and Taito ward in Tokyo. The data that I collected enabled me to distinguish different types of networks and develop a typology of SME networks in Japan. Moreover, I analysed in detail the functioning of each network type.

During the fieldwork I could also acquire information about cluster development and industry-academia-government cooperation in Japan. That is the reason why I am now studying these topics.

7. Research implementation and results under the program

Title of the research plan:

The university-industry cooperation and its implementation in different regions of Japan (Japanese Cluster Policy and its Implementation)

Description of the research activities:

During the last ten years or so, there has been increasing interest in developing clusters– agglomerations of innovative firms in high-tech industries. The triggers for such interest were the cluster success stories (such as the Silicon Valley) on one hand and the need to find new directions for industrial development in a globalizing world on the other. In many countries, we could witness a growing reflexion on how to generate and promote clusters. Japan is no exception. The implementation of the Industrial Cluster Plan, designed by METI and the Intellectual Cluster Plan, designed by MEXT has started since 2001.

During the summer program I studied cluster development in Japan. My research activities were various:

Study of written materials

My first important activity was to study the research reports, discussion papers, articles and books on clusters, university-industry cooperation, cluster policy and other relevant issues. My colleagues at NISTEP provided various materials, both in Japanese and in English.

My seminar

On July 26 I presented my doctoral research at a seminar organized by NISTEP. The seminar was open to the wider audience including persons outside NISTEP. I was happy to see many attendants from different fields. That was an exceptional opportunity to discuss my research results with Japanese specialists.

The information about my seminar can be found in the NISTEP Newsletter No. 190:
www.nistep.go.jp/NISTEP_News/news190/news190.html

Fieldwork

During my stay at NISTEP I conducted fieldwork in three areas that are targeted by the MEXT and METI cluster plans: Hamamatsu, Sapporo and TAMA (Technology Advanced Metropolitan Area).

My first research trip was to Hamamatsu. I attended a seminar on industry-university cooperation there. I also interviewed the key person in charge of implementation of the Intellectual Cluster Plan and one entrepreneur, whose company produces high-tech products through research collaboration with universities.

During my research trip in Sapporo I interviewed several officials, researchers, key persons for cluster development and entrepreneurs. The focus of my research was the bio-industry in Hokkaido. The fieldwork was particularly interesting since I was able to discuss the industry-university-government cooperation with the members of the academia, industry and government officials - all the parties involved.

In Hachioji, which is within the TAMA area I interviewed the president of the TAMA TLO (Technology Licensing Organization). This was the opportunity to learn more about the role, activities and problems of TLOs in Japan as well as the advancement of the TAMA Industrial cluster project. Before interviewing TAMA TLO's president, I discussed TAMA Cluster project with a senior research fellow in RIETI (Research Institute of Economy, Trade and Industry), who provided extensive information and research materials on this project.

Discussions with researchers and officials

I had several discussions about clusters and industry-university collaboration with my advisor Mr. Saito and researchers at NISTEP. I also had a chance to meet officials in charge of the cluster plan at MEXT.

Attending seminars

I attended several seminars on clusters and university-industry cooperation.

My short article

I wrote a short article, which will be published in the NISTEP Newsletter No.192 in October 2004. This article deals with cluster development and the role of networks. It is partly based on the data from the fieldwork I conducted during the JSPS Summer Program.

8. Comments

I would like to express my gratitude to JSPS, CNRS and NISTEP for enabling me to take part in this program. My special thanks go to Mr. Naoki Saito, my advisor for accepting me at the Third Policy-Oriented Research Group. I warmly thank Ms. Noriko Uesugi, Senior Research Fellow, who arranged everything for me and took care of me throughout the program. I also thank all the members of the Third Policy-Oriented Research Group for their time and help.

The program was perfectly organized, dense and meaningful. This research experience was extremely enriching for me.

9. Advisor's remarks

Thanks to the kind supports given by JSPS and other relevant organizations, we were very happy to accept Ms. Colovic as a visiting researcher, who has spent truly fruitful days at NISTEP. During her relatively short stay, she conducted as many site visits as possible to various types of Japanese regional clusters, including Hamamatsu and Sapporo, which should be essential for this area of policy research. She has also attended many relevant seminars on clusters policy and university-industry cooperation, and presented her own lecture on her doctoral research at a NISTEP seminar on 26 July, which attracted wider range of audience. Through these processes, we believe she has effectively improved her knowledge and insight on recent development of Japan's regional clusters and their potential interface with the industrial agglomeration, and has further enriched her previous analyses on the effectiveness of public policy in this field. (Another significant factor for her efficient field-study was her good Japanese language skills, which has greatly helped the smooth communication on the occasion of the interviews and exchange of opinions with local people concerned.)

Her areas of research are actually our common matters of interest and one of the hottest issues in Japan's S&T policy. We very much expect her study report to be concluded and published incorporating main results of this visiting research, which could give significant policy implications and lessons not only for the French public sector but also for the Japanese government in deliberating and formulating their advanced regional clusters policy. We also hope that her experience of this stay should further expand the opportunities of research exchange and cooperation between Japan and France in this field, particularly between CNRS and Japanese public research institutes including NISTEP.

RESEARCH REPORT

1. Name: GILLOT Frederic (ID No.: SP04205)

2. Current affiliation:

IRCCyN MO2P Team, Centrales Nantes

3. Research fields and specialties: Mechanical Engineering, Rapid Prototyping

☐ Humanities ☐ Social sciences ☐ Mathematical and Physical Sciences
☐ Chemistry X Engineering Sciences ☐ Biological Sciences
☐ Agricultural Sciences ☐ Medical, Dental and Pharmaceutical Sciences
☐ Interdisciplinary and Frontier Sciences

4. Host institution: Masuzawa Laboratory, IIS, University of Tokyo.

5. Host researcher: Pr. Masuzawa T.

6. Description of your current research

Our work is mainly focused on new Rapid Tooling (RT) processes, and how they can be used for lead time enhancement and cost saving when fabricating industrial dies. Hence, innovating way of planning die fabrication are investigated, using an Hybrid Mold approach, i.e. by building the die like a puzzle made from parts fabricated with different kinds of processes (RT and conventional processes). Moreover, new fields of utilisation for RT parts are explored, in order to improve the RT process integration in our approach.

7. Research implementation and results under the program (As much as possible, describe the contents and results of your research in a manner that is easily understandable to a non-specialist in your field.):

Title of your research plan:

Study on the viability of Direct Metal Laser Sintered electrodes for micro-EDM.

Description of the research activities:

Rapid tooling (R.T.) is now commonly used to reduce lead time and cost to create prototype moulds for plastic parts. However, certain shapes and geometries can not be created using conventional processes.

Electro-Discharge Machining (EDM) is a non conventional removal process option for

manufacturing geometrically complex or hard material parts. Nevertheless, electrodes need to be created first. They are commonly machined in a block of copper or graphite.

Researches have been undertaken to build electrodes using an RP process. Many direct or indirect manufacturing methods have been investigated to create such electrodes. The most suitable R.T. process is to directly sinter a metallic powder with a laser beam (Selective Laser Sintering, SLS).

The major intrinsic drawback of EDM is the tool wear. It affects the accuracy of the machined components. This tool wear becomes critical when small electrodes are used in micro-EDM. This process enable to drill small diameter holes with a diameter less than 500 micro-meter and with a high ratio Length / diameter.

Our research program covers a range of major topics in micro-EDM, ranging from 3D electrodes manufacture, to the tool wear rate involved

Hence, using Direct Metal Laser Sintering (DMLS) process from EOS, we have realized Micro Electrical Discharge Machining (micro-EDM) Electrodes with complex design. Material sintered is Direct Metal Powder with an average grain size of 20 μm.

Then micro-EDM has been achieved successfully. It has revealed that the electrode wear is high during rough machining, and the global shape of the electrode is modified during finishing machining, due to thermal instability of the electrode material.

Nevertheless, these drawbacks can be avoided by machining the die using several electrodes, one electrode after the other. Moreover Rapid Tooling processes offer such possibility to create at the same time similar thin parts on the same support.

Indeed, dimensional accuracy of Rapid Prototyped electrodes is not yet good enough to realize functional dies, and the material used is not suitable for industrial micro-EDM purposes. Nevertheless, such approach is very interesting regarding the lead time it takes (half a day vs. more than one week) to build micro-electrodes, and the possibility Rapid Tooling processes offers to build complex features without increasing this lead time. Furthermore, using the same support, a high number of electrode can be produced at the same time.

The basic feasibility of rapid-prototyped electrode for 3D micro-EDM was confirmed through experiment during my work at IIS

9. (If any) Advisor's remarks:

Mr. Gillot's work was one of the more satisfactory ones when I think about my past experience of accepting foreign researchers/students. He deepened his knowledge about micro-EDM and die & mold fabrication during his stay in our laboratory. Moreover, he could carry out real experiment for confirming the feasibility of very new application of SLS. I felt the effective period of stay was a little too short, because some considerable part of the staying period was spent for introduction and other formal activities. But, I felt we should accept it, because such activities are also necessary. After all, my impression is that this program offers a very good opportunity for foreign young researchers to experience Japan and Japanese way of research works.

RESEARCH REPORT

1. Name: **GIRAUD Marion** (ID No.: **SP0 4206**)

2. Current affiliation: **Laboratoire de Chimie Inorganique, University Paris-Sud, Orsay, France.**

3. Research fields and specialties:

☐ Humanities ☐ Social sciences ☐ Mathematical and Physical Sciences

☒ **Chemistry** ☐ Engineering Sciences ☐ Biological Sciences

☐ Agricultural Sciences ☐ Medical, Dental and Pharmaceutical Sciences

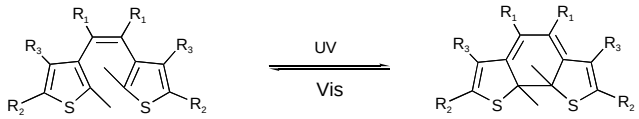
☐ Interdisciplinary and Frontier Sciences

4. Host institution: **Dept. of Chemistry and Biochemistry, Graduate school of engineering, Kyushu University, Fukuoka**

5. Host researcher: **Pr. M. Irie**

6. Description of your current research

Photochromic systems have been attracting much attention for their potential applications in optical memory and optical switching devices. Among many families of organic photochromes, dithienylethenes derivatives are considered to be the most promising photochromic candidates for that achievement because they usually undergo thermally irreversible and fatigue resistant photocyclizations between their colorless open-ring and colored closed-ring forms, as shown below



Besides the color change, photo-switching of the structure can also be exploited to reversibly control a wide range of properties (luminescence, redox and magnetic properties). The purpose of my PhD thesis work is to synthesize and study complexes with diarylethene based ligands, and to investigate if the metal-centered properties can be influenced by the photochromism (changes in metal interaction, in ligand field for instance) and vice-versa, if the photochromic properties are improved or lowered by the presence of the metal ion. For that purpose I synthesized thiazole-based diarylethenes capable of binding a metal ion, the resulting complexes and studied them.

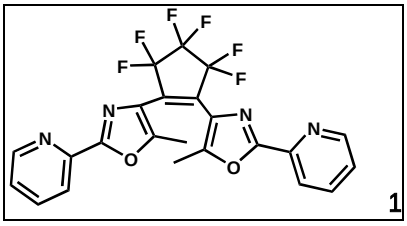
7. Research plan

Title of your research plan: **Synthesis and studies of diarylethenes**

Description of the research activities:

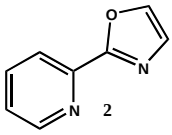
The aim of the work was to synthesize the target compound **1**, which as been

chosen for 2 reasons: (1) ability of coordinating metal ions through bidentate cavities, (2) introduction of the oxazole ring as the aryl group, which is not very common in diarylethene chemistry

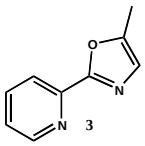


1

The first step of the synthetic scheme consists in obtaining either compound **2** or **3** .

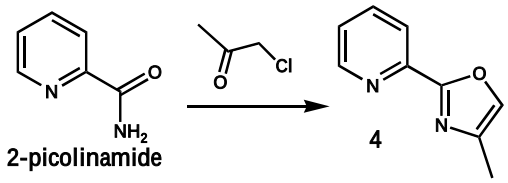


2



3

For compound 2, the synthesis worked but the purification failed, I wasn't able to separate the desired compound from the crude product so I couldn't go on the synthesis. I tried to investigate another synthesis that could be used to obtain compound 3 and investigated different synthetic conditions to get compound **4** as reported below.

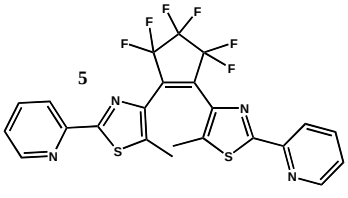


2-picolinamide

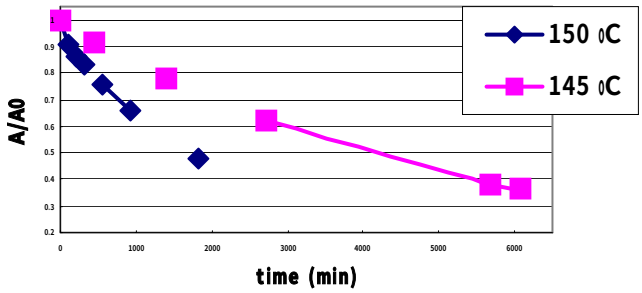
4

Interest has been particulary focused on the solvent, the temperature and the number of equivalents of carbonyl halide.

In parallel, I tried to study the thermal stability of compound **5** synthesized in France in a mesitylene solution. The figure below shows the fading curves at different temperatures. I have now to pursue this work by processing all the collected data.



5



8. Comments

My stay in Pr. Irie's laboratory will remain as a great and memorable experience for me. Even if the syntheses have not been successful, I learned a lot in diarylethene chemistry and photochemistry and enjoyed benefiting from an excellent scientific environment:: for 6 weeks, I had the opportunity to attempt syntheses I've never tried before, to attend very interesting lab meetings and to join all this group made of very high quality researchers and students. I was very glad to exchange points of views about research and life in general with them. I was very impressed by their knowledge and their independence at work. Besides, I met very nice and open-minded persons (both Japanese and Western people) and I hope we can keep in touch in the future.

It was my first time in Japan and in Asia in general and the discover was worth the journey. It was both cultural and fun and I've really enjoyed living abroad : I've been to very beautiful and peaceful places and also to very frenzy ones. Riding a bike almost every day was of course just a treat !!!! Only one regret: not to know as much Japanese language as I would have wanted to !!!! Well now learning Japanese would be another challenge for me after finishing my PhD so I can come back soon again !!!

9. (If any) Advisor's remarks:

Miss Marion Giraud spent really active two months in our laboratory as a JSPS Summer Program fellow. She designed a new photochoomic molecule with a chelating ability and synthesized it. At the same time she examined the physico-chemical properties of a photochromic compound, which she prepared in her laboratory in Paris. In such short time, she quickly mastered several new methods and techniques developed in our laboratory. In addition to the scientific activity, she enjoyed Japanese style student life and her stay also activated Japanese students in my laboratory. Her stay in our laboratory was really fruitful to both of us.

Pr. Masahiro Irie

RESEARCH REPORT

1. Name: Ladmiral Vincent (ID No.: SP04207)

2. Current affiliation:

Doctoral course, Chemistry department, University of Warwick (UK), Prof. D.M. Haddleton

3. Research fields and specialties:

☐ Humanities ☐ Social sciences ☐ Mathematical and Physical Sciences

☒ Chemistry ☐ Engineering Sciences ☐ Biological Sciences

☐ Agricultural Sciences ☐ Medical, Dental and Pharmaceutical Sciences

☐ Interdisciplinary and Frontier Sciences

4. Host institution: Institute for Chemical Research, Kyoto University

5. Host researcher: Professor Fukuda Takeshi

6. Description of your current research

Glycopolymers, synthetic sugar-containing macromolecules are attracting ever increasing interest from the chemistry community due to their role as biomimetic analogues (carbohydrates are known to be involved in cell recognition processes which play a key role in numerous phenomena based on cell-cell interaction such as fertilization, embryogenesis, immune defense, microbial and viral infection, etc…) and their potential

commercial applications. Over the past ten years, decisive progress has been made in polymer science. One of the most important development is the discovery of living radical polymerization techniques such as Atom Transfer Radical Polymerisation (ATRP), Nitroxide Mediated Radical Polymerisation and Reversible Addition-Fragmentation chain Transfer (RAFT) Polymerisation. These new techniques enable synthetic chemists to finely control the architecture of the macromolecules and combine the advantage of radical polymerization (versatility, ease of use, robustness…) and of ionic polymerization (control of the length of the polymeric chain, reactive chain extremities,…). The term living refers to the fact that polymeric chains obtained by these techniques are still reactive that is to say polymerization can be carried on by adding some monomers. Thanks to these techniques it is now possible to accurately design and synthesize macromolecules featuring numerous structures (star-shaped polymers, block copolymers, gradient copolymers…) and various functionalities.

My current research is two-fold.

1) Synthesis of new carbohydrates monomers and studying their polymerization under ATRP

conditions. Amphiphile block copolymers-polymers that possess one hydrophilic end and one hydrophobic end- are made and their self assembly (micelles or monolayers formation) behaviour is studied. Such polymers can spontaneously form, in water, ball like structure called micelles (the non-polar parts of the molecules clump into the center of the micelles whereas the polar parts of the molecules presents themselves for interaction with the water molecules on the outside of the micelle.

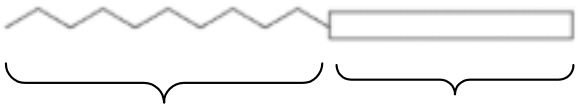


Fig.1 Amphiphile block copolymer

These micelles could be used as powerful drug delivery prototype systems by solubilizing and protecting from the organism non water soluble drugs. Moreover, carbohydrates on the outside of the micelles could play the role of the targeting system thanks to their biological activity.

2) Synthesis of new functionalized initiating reagents for ATRP. The initiator moiety remains on the extremity of the macromolecules after the polymerization and can be used to add properties to the polymers. A new succinimidyl ester initiator has been synthesized and used successfully to polymerise by ATRP Polyethylene glycol methacrylate and two sugar-carrying methacrylates. This succinimidyl ester reacts easily with the free primary amine present in proteins and enables us to attach covalently a polymer chain to a protein. This technique is known as Pegylation. The polymers bound to the protein-based drug can enhance the solubility of the protein in the blood stream and protect the protein from the immune defence. Slow degradation of the polymer would lead to a slow and control release of the drug in the organism, consequently reducing the frequency of drug intake and allowing the drugs to be taken orally rather than intravenously.

Biotin also known as vitamin H is responsible for growth and metabolism in humans. The glycoprotein Avidin interacts very strongly with biotin. This system actually features the highest affinity known so far, and is in consequences used extensively for tissues detection and proteomics. I recently synthesized new Biotin-tagged initiators, and tested them in Atom Transfer Radical Polymerisation of several monomers.

7. Research implementation and results under the program (As much as possible, describe the contents and results of your research in a manner that is easily understandable to a non-specialist in your field.):

Title of your research plan:

Study of the grafting of biotin-tagged polymers to an avidin monolayer by quartz Microbalance.

Description of the research activities:

Quartz crystals can produce electricity when pressure is applied in certain crystallographic direction, or produce strain when submitted to electricity. These phenomena are called piezoelectric effects. When electricity is applied to a quartz crystal, it starts oscillating at its resonance frequency. Sauerbrey discovered that this resonance frequency decreases if matter is deposited on the quartz surface. This discovery soon led to the design of a new quantitative device to measure very small masses i.e. the Quartz Crystal Microbalance (QCM). This new tool is now extensively used in biotechnology to study protein-substrate interaction, surface and membrane technology, thin film formation, Drug research (molecular interaction)…

My collaboration with Prof. Fukuda's research group consisted in investigating by QCM the avidin-biotin system as a potential polymer film anchor to study polymer-protein interaction, and the QCM as an in situ tool for monitoring polymerization kinetics. Here are the results of this work.

a) Study of the ATRP of a sugar-carrying methacrylate in water and water/methanol mixtures : In order to study the interaction of Concanavalin A (a lectin which interacts specifically with α-glucose) with a polymer deposited on a QCM through an avidin-biotin linkage, we wanted to investigate the Copper Mediated Polymerisation (ATRP) of a glucose-based monomer. This monomer is commercially available and, to our knowledge, no study of its polymerisation under ATRP conditions had been done so far. In water or water/methanol mixtures copper mediated polymerisation is known to proceed very quickly even at room temperature. Moreover, transfer of the radical of the growing chain to the solvent can also occur in such system. This transfer phenomenon actually "kills" a growing polymeric chain. Indeed, living radical polymerisation relies on the existence of an equilibrium between a reactive polymeric chain bearing a radical and a "dormant" species. When the rate of polymerisation is too fast, too many radicals coexist, propagating chains grow at different rate and might react with one another (these termination reactions stop any further growth or reactivation of the polymeric chains). When transfer occurs, the polymeric chains stop growing and cannot be reactivated anymore, they are "dead". In spite of all our attempts to tune the reaction conditions (increasing the monomer concentration, varying the water/methanol ratio, adding different quantities of deactivator to slow down the reaction, adding ammonium chloride or bromide to prevent the catalyst deactivation…) we couldn't prevent totally transfer or termination from happening and only average control over the polymerisation was achieved as the polydispersities (PDi) measured by Size Exclusion Chromatography reveal ($PDi_{(obtained)}$=1.6, $PDI_{(controlled)}$=1-1.3). Nevertheless, Biotin initiators were successfully used to synthesise in a living manner PPEGMA (Poly(PolyEthyleneGlycol MethAcrylate)) (average molecular weight=30000g.mol^{-1}, PDi=1.25) and block copolymers of PPEGMA and PGEMA (polyGlucoseEthylMethAcrylate) (Biotin-PPEGMA-*b*-PGEMA, average molecular weight = 75000g.mol^{-1}, PDi=2.5, PPEGMA/PGEMA weight ratio=40/60).

b) Avidin is a glycoprotein existing as a tetramer (Mw=104000g.mol^{-1}) and features 4 binding sites for biotin. In order to study the potential use of the Avidin-biotin system as an anchor for polymeric brushes, two approaches were considered. The “grafting from” technique consists in growing the polymer from an avidin-biotin coated surface and should lead to dense polymer brushes. The “grafting to“ technique requires to synthesize the biotin-tagged polymeric chains in solution and graft them to an avidin-coated surface, this usually leads to less dense brushes. As avidin interacts strongly and irreversibly with hydrophobic surfaces, we treated a silicon wafer with triethylchlorosilane and successfully coated it with avidin. Ellipsometry measurement confirmed the formation of a thin protein monolayer on the silicon surface. In Anisole, at 70°C, under ATRP conditions, using the sacrificial initiator technique developed by Prof. Fukuda, a PolyMethyl Methacrylate (PMMA) brush was synthesized on the silicon wafer surface using “grafting from” method. The brush average thickness (75Å) was measured by ellipsometry. This previous result though needing further confirmation shows for the first time, to our knowledge, that the avidin-biotin system can be used to grow polymer brushes from a silicon surface in organic solvent. The “grafting to” method was then monitored by QCM. To do so, a monolayer of avidin must first be deposited on the gold film constituting the electrode of the QCM. First attempts only gave multilayers. By decreasing the concentration of the avidin phosphate buffer solution to 0.01mg.mL^{-1} monolayer formation was monitored by QCM. Using the same concentration of biotin-tagged PPEGMA (Mn=30000g.mL^{-1}) a polymer brush was grafted on the avidin monolayer. Due to the steric hindrance of the comb-like PPEGMA and the usual lower density of brushes obtainable with the “grafting to” technique, an expected low occupation (30%) of the avidin sites was achieved. Subsequent additions of the same solution of polymer did not result in any increase of the mass deposited on the QCM, suggesting that the bound polymer prevent accessibility to the unoccupied sites of avidin. When a Phosphate Buffer Solution of biotin-free PPEGMA was injected into the avidin-coated QCM cell, no mass increase was detected. This shows that the biotin-avidin interaction is specific and that PPEGMA does not bind to avidin through physical adsorption. The block copolymer Biotin-PPEGMA-*b*-PGEMA was also deposited on an avidin-coated QCM plate. Only 20% of sites occupation was achieved with this polymer. This can be ascribed to the stronger steric hindrance of this polymer and the error made when estimating its molecular weight by NMR. QCM monitoring of Concanavalin A interaction with the carbohydrate block copolymer bound to avidin was planned, but unfortunately we ran out of time. This study will be carried on in the next few months in Warwick University in collaboration with Prof. Fukuda’s laboratory.

In conclusion, PGEMA was synthesized with moderate control under aqueous ATRP conditions. Biotin-Avidin system was proven reliable in the grafting of water-soluble polymers to an hydrophobic

surface. First results in surface-initiated ATRP of PMMA using a biotinylated avidin monolayer were very encouraging. QCM proved to be a very powerful technique to study surface modification.

8. Please add your comments (if any):

Collaboration with Prof. Fukuda's laboratory will carry on next academic year, by the way of exchange of chemicals and scientific advice.

RESEARCH REPORT

1. **Name**:LE GAC Séverine (ID No.: SP04208)

2. **Current affiliation**: Université des Sciences et Technologies de Lille, Laboratoire de Chimie Organique et Macromoléculaire, France.

3. **Research fields and specialties**: Chemistry, Biological Sciences

4. **Host institution**: Department of Medicinal Chemistry, Faculty of Pharmaceutical Sciences, The University of Tokushima, Shomachi, Tokushima, Japan.

5. **Host researcher**: Pr. Yoshinobu Baba

6. **Description of your current research:**

My Ph.D work was in the field of microfluidics and μTAS (micro-Total Analysis Systems). This consists in the development of devices having characteristic dimensions in the range of some microns (1-100) towards high-throughput and automated analysis and mostly dedicated to biological and chemical applications. The current development of such microsystems is accounted for by (i) their small size, which results in (ii) a possibility of placing a series of independent devices on a single chip and also in (iii) analysis rapidity, and (iv) by the possible automation of the analysis. Microfluidics applications cover a wide range such as on-site analysis (medical and environmental analysis), biological analysis (genomic, proteomic, cell...), forensics...

My former work precisely dealt with the development of a microfluidic device for protein sample analysis using electrospray ionization-mass spectrometry techniques (ESI-MS). For that purpose, we came to the development of different modules to be further integrated on a single system, such as (i) a chromatographic module based on a polymer monolithic phase for sample treatment and cleaning, (ii) a digestion microreactor based on the same kind of stationary phase and dedicated to protein lysis into a peptide mixture, (iii) a fully integrated interface to mass spectrometry for sample ionization. The subsequent and current work is to develop the same kind of microsystem for protein analysis but using another type of mass spectrometry technique, MALDI-MS (Matrix Assisted Laser Desorption Ionization), which provide complementary information on protein samples. In addition to this, the research group, I'm working with, has recently got interests in using microfluidics for organic chemistry applications.

7. **Research implementation and results under the program:**

Title of your research plan: Electrophoretic separations of biological species (mostly DNA, but also proteins, RNA) using commercial microfluidic devices.

Description of the research activities:

My work in Japan focused on electrophoretic separations of biological species at the microchip-level using commercial chips and apparatus. Thus, I used the microfluidic systems developed by Agilent and Hitachi. The former one exists for DNA, RNA but also protein samples whereas the latter one is rather dedicated to DNA samples. Chips are made of plastic material, PMMA (polymethylmethacrylate) for the Hitachi chip (Fig 1B) and glass for the Agilent one (Fig 1A). Both systems rely on the same principle and are operated using a similar approach.

Fig 1A: *Agilent glass chips (protein, RNA, DNA, cell).*

Fig 1B: *Hitachi PMMA-based chip*

The separation is driven by the application of a voltage in the channels as depicted in Figure 2. Under the created electrical field, species acquire a mobility which depends on their size and charge as well as on the analysis conditions (voltage value, ionic concentration…). In addition to this, channels are filled with a sieving media (MC or methyl cellulose-based gel) which acts as a matrix for the separation. Thus, species do not migrate in the same way in the channels and can thus be separated. Detection is achieved at the channel outlet using fluorescence techniques; compounds being coupled to a fluorophore moiety.

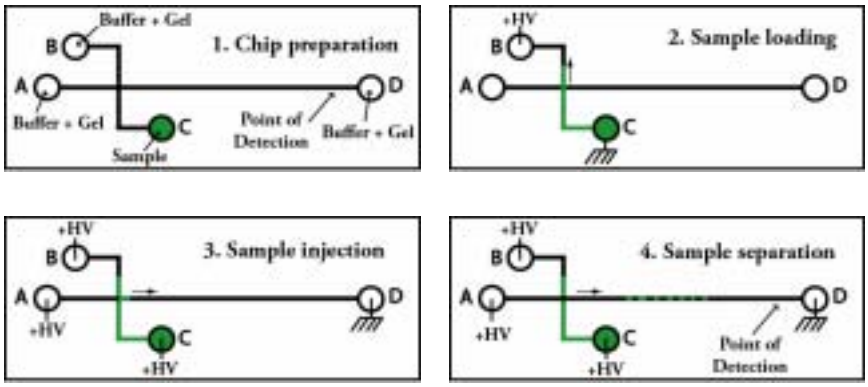
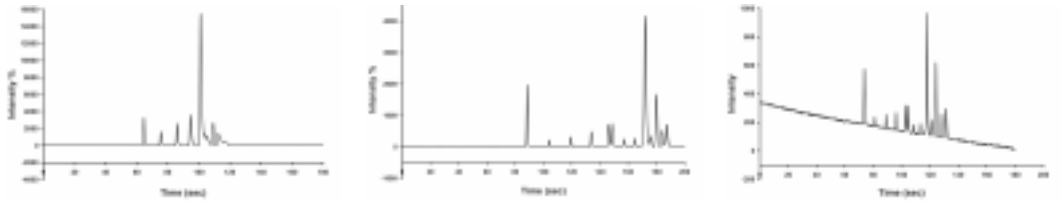


Fig 2: *How analysis proceeds: from chip preparation to sample separation*

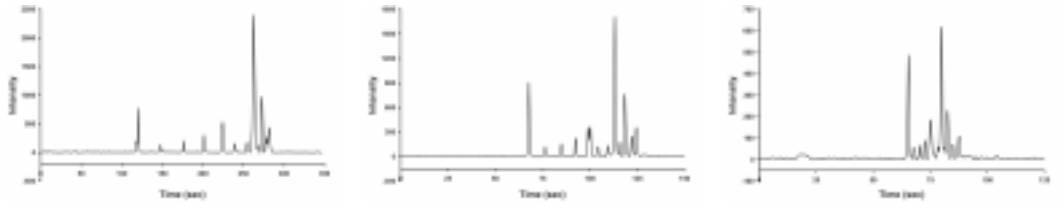
I first tried both systems for a DNA ladder sample according to the conditions and solutions provided by the constructor. Then, I more deeply worked with the Hitachi

system and changed several analysis parameters (gel quality and concentration, injection time and voltage, sample concentration, voltage value) so as to see their influence on the separation quality (Fig. 3).



9 µL sample, $Volt_{sep}$ = 750V, native gel. 1 µL sample, $Volt_{sep}$ = 600V, native gel. 1 µL sample, $Volt_{sep}$ = 600V, gel 2/3 dil.

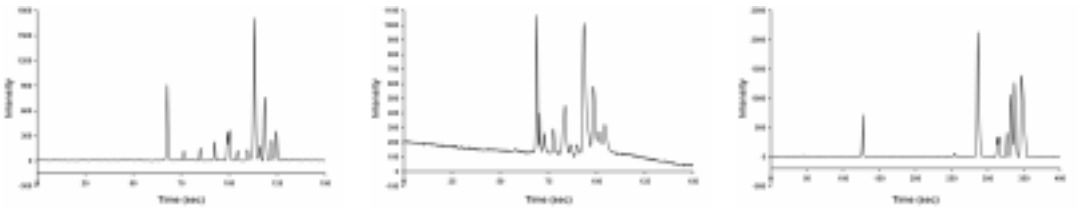
Fig 3: *Influence of the analysis conditions: separation of a 100 bp DNA ladder.*



1 µL sample, $Volt_{sep}$ = 500V, 0.7 % MC gel. 1 µL sample, $Volt_{sep}$ = 600V, 0.4% MC gel. 1 µL sample, $Volt_{sep}$ = 600V, 0.1% MC gel.

Fig 4: *Influence of the gel concentration on the separation time and quality (sample: 100 bp DNA ladder).*

Finally, still working with the Hitachi system, I prepared MC gels in a 0.1 to 0.7 % concentration range and used them on a series of DNA samples (100 bp ladder, 1 kbp ladder, HindIII λ DNA). This allowed me to see how to change the analysis conditions depending on the studied sample.



100bp ladder, $Volt_{sep}$ = 600V, 0.4% gel 1 kbp ladder, $Volt_{sep}$ = 600V, gel dil 1/3. HindIII λ DNA, $Volt_{sep}$ = 500V, 0.7% gel

Fig 5: *Analysis of different DNA samples(1 µL)*

8. Please add your comments (if any):

During my stay in Japan in my host institution, I had the opportunity to use techniques and approaches which are complementary to my research work in France. Till now I had only worked with pressure-driven techniques to move liquids in the channels and MS-based techniques for the detection of the biological species. Here, I was using electro-driven pumping and optical detection means, which are both prevalent in the field of microfluidics. In addition to this, I'm familiar with protein and peptide samples whereas, here, my research focused on DNA samples. Hence, this stay in Japan allowed me to discover other complementary aspects in the field of microfluidics for analytical applications I'm working in.

9. (If any) Advisor's remarks:

Dr. LE GAC Séverine did excellent experiments systematically on the analysis of DNA using microchip electrophoresis during her short stay. These experiences will be valuable for her future carrier. I believe she will become an active scientist in this field in the near future.

RESEARCH REPORT

1. Name
MALOD, Guillaume (ID No.: SP04209)

2. Current affiliation
Laboratoire PRiSM, Université de Versailles

3. Research fields
Mathematical Sciences

4. Host institution
Japan Advanced Institute For Science and Technology

5. Host researcher
Prof. ONO, Hiroakira

6. Description of current research

For my PhD I studied algebraic complexity classes defined by Valiant. These classes are algebraic equivalents of the classical P and NP classes, i.e. the fundamental study of how some problems are "easy" to solve and have fast algorithms, while others are "hard". I studied different models of computation with a computing power between expressions (where one cannot use an intermediate result more than once) and circuits (the more intuitive notion where partial results, once computed, can be used at will). The fact that circuits are more powerful than expressions, i.e. that computations where one can re-use previously computed results are more efficient, seems intuitively true but is still not proved and is a major open question, both in this setting and in the classical boolean setting.
I'm also interested in non-classical logics such as modal and temporal logic, i.e. logics which are often more suited than classical logic for real-world problems in artificial intelligence, linguistics, automated reasoning,. . . In a collaboration with Prof. Gabbay, we showed how to add locality predicates to modal and temporal logics and to give a sound and complete set of axioms and inference rules. This idea is closely linked to so-called "hybrid logics", which are modal logic with additional symbols to name states. This and several associated operators and binders can add a great level of expressivity to these logics, which, given appropriate proof systems and technical tools, could then be applied to a wide range of fields, from knowledge representation to software verification. On a theoretical level, they can be seen as an interesting blend of ideas from propositional and classical logic.

7. Description of the research activities:

I had the opportunity to give two talks at the beginning of my visit. The first one focused on work I did for my PhD regarding algebraic complexity, not directly related to the work done in the lab here, but I believe it gave an introduction to some aspects of this fundamental field from theoretical computer science. The second one concerned hybrid logics.
This led us to the problem I studied during my stay, namely an extension of the sorting idea from hybrid logics to include other possible "sorts of information". The result of this research is twofold. On one hand it is easy to introduce such a general framework and add the basic satisfaction operator of hybrid logic and devise a complete proof system. Proof theoretic

techniques are a major focus of Prof. Ono's lab at JAIST and we therefore focused on this issue, but also because a complete proof system is the first essential step toward automating deduction for possible applications. The defined logic is elegant and general in the sense that basic hybrid logic can be seen as a special case. On the other hand it seems very difficult to add more powerful properties, such as binders, even though this would yield a very nice and expressive logic. Indeed, with binders we would be able to talk about paths and express properties of fairness in the execution of computer programs for instance. In other words, we obtained a good basis for future work.

RESEARCH REPORT

1. Name: Mattioni Laetitia (ID No.: SP04210)

2. Current affiliation: Laboratoire de Physique de la Matiere Condensee et des Nanostructures. Universite Lyon I, Lyon. France

3. Research fields and specialties:

☐ Humanities ☐ Social sciences ☐x Mathematical and Physical Sciences

☐ Chemistry ☐ Engineering Sciences ☐ Biological Sciences

☐ Agricultural Sciences ☐ Medical, Dental and Pharmaceutical Sciences

☐ Interdisciplinary and Frontier Sciences

4. Host institution: Department of Material Science and Engineering. Faculty of Engineering. University of Fukui, FUKUI.

5. Host researcher: Prof. Shuichi TANOUE

6. Description of your current research

To enhance mechanical and rheological properties of polymer melts, fillers are added to the polymer matrix. This reinforcement may be controlled by many factors such as filler shape, size, surface treatment, compatibility with the matrix, and the filler's tendancy to aggregate. Polymer properties such as its chemical nature and chain length are also important. Numerous studies -experimental as well as numerical- have been carried out to point out some of the interlinked phenoma involved in the reinforcement process. One way to simplify and clarify the problem is to work with a model system. In this framework, we studied the dynamical and rheological properties of polymer melt systems containing various concentrations of spherical Lennard-Jones nanoparticles through Monte-Carlo simulations.

We used the well established Bond Fluctuation Model. We first studied the static and dynamical properties of pure polymer system varying chain length and monomer density. The results show that this lattice model reproduce correctly the Rouse dynamics of short chains and the reptation dynamics of long entangled chains. Using the blob size as the scaling variable, all datas (for instance coefficient of diffusion D) for various length and densities collapse into a single mastercurve. As no force is involved in this lattice model, we develop a new method to compute viscoelastic properties.The viscosity obtained are in good agreement with the Rouse and reptation models.

We then introduce spherical fillers into the polymer melt (highest density). They live off lattice and interact with the monomers through a Lennard-Jones potential. We looked at the influence of filler content, surface treatment (through Lennard-Jones parameters) and polymer chain length on the dynamical and viscoelastic properties of the system. This numerical results shed new light on the reinforcement effect.

7. Research implementation and results under the program (As much as possible, describe the contents and results of your research in a manner that is easily understandable to a non-specialist in your field.):

Title of your research plan: Rheological properties of polymer/clay nanocomposites

Description of the research activities:

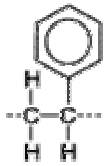
In order to modify polymeric materials properties fillers are added to the polymer matrix to form composites materials. When the particle size comes down to nanometer scale, the nanocomposite exhibit much more favorable properties than its microscale equivalent. polymer/clay nanocomposites are formed through the union of two very different materials with organic and mineral pedigrees. The hybrid compositions, however, exhibit large increases in tensile strength, modulus, and heat distortion temperature as compared with the pristine polymer. The composites also have lower water sensitivity, reduced permeability to gases, and a smaller thermal coefficient of expansion. Additionally, nanocomposites impart a level of flame retardance and UV resistance all without any loss of clarity.

To understand the processibility and also the structure relationship of these materials, one must understand the detailed rheological behavior of these nanocomposites in the molten state. That is the reason why we will focus in this study on the study of the rheological properties of polystyrene/organoclay melts. To match the clay surface polarity with the polarity of the polymer (and thus obtain better mixing conditions), the inorganic exchange cations on the gallery surfaces of smectite clay have been replaced by di-methylbenzyl stearyl ammonium ion. Nanocomposites were prepared using the melt intercalation technique. The clay is first intercalated into the matrix by an organic modifier and then exfoliated in a co-rotating, intermeshing twin-screw extruder. Mechanical exfoliation -contrary to reactive exfoliation- present the advantages of being a fast process (less than 10 min as compared to hours) and of being a thermodynamically driven process (no danger of clay re-aggregation). But this technique requires a thermally stable clay.

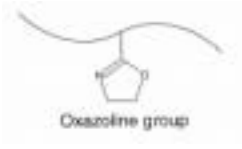
Dynamic oscillatory shear measurements were performed using a ARES rotational rheometer. In this kind of rheological experiment, time dependant strain ($\gamma(t)=\gamma_o \sin(wt)$) is applied and the resultant shear stress, $\sigma(t)= \gamma_o(G'\sin(wt)+G''\cos(wt))$, is measured. G' is called storage modulus and G", loss modulus. Both of them are recorded as a function of frequency at constant strain amplitude γ_o.

In this study, measurement temperature (which is always set above glass transition temperature) is varied as well as clay content and screw speed used during extrusion process. The role of a compatibilizer group, oxazoline, was also investigated by replacing half of the polystyrene content by its oxazoline modified counterpart :

Polystyrene



OPS: Polystyrene modified with oxazoline group



Rheological datas (cf fig 1) show that adding a small amount of organoclay (5% weight) into the polystyrene matrix significantly enhances both storage and loss modulus. Moreover, if half of the polystyrene chains bears oxazoline group, modulus values is further enhanced.

Young modulus, obtained from tensile tests, show the same kind of results. Pure polystyrene's modulus has indeed a value around 3400 Mpa, this value increase up to around 3600 when 5 %w of organoclay is added and reaches 3800 Mpa when polystyrene chains are modified with oxazoline groups.

Concerning the miscrostructure of these materials, TEM photographs show great differences between samples depending on screwspeed and OPS content. There is in fact a deep relationship between structure and properties for this kind of material.

And to put it in a nutshell, the best mechanical and rheological properties for this PS/organoclay nanocomposite are achieved when the clay is fully exfoliated and has kept its lamellar structure. To modify polystyrene by adding oxazoline group appears here to be of crucial importance to optimize the material properties.

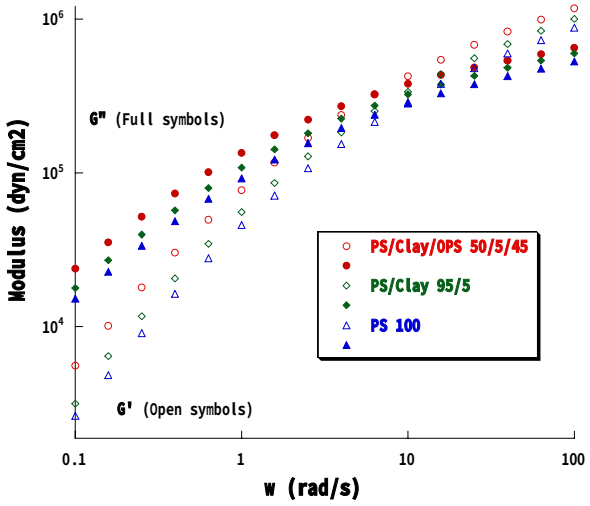


Fig1: Storage (G', open symbols) and loss (G", full symbols) modulus as a function of frequency (w) for pure polystyrene (PS 100), PS and 5% of clay (PS/Clay 95/5) and PS with 45% of OPS and 5% of clay (PS/Clay/OPS 50/5/45). Experiments were performed at 5% strain and at T=180 C using 25 mm parallel plate geometry

RESEARCH REPORT

1. Name: **NACHAT Rachida** （ID No.**: SP04211** ）

2. Current affiliation:

3. Research fields and specialties:

□ Humanities □ Social sciences □ Mathematical and Physical Sciences

□ Chemistry □ Engineering Sciences **□ Biological Sciences**

□ Agricultural Sciences □ Medical, Dental and Pharmaceutical Sciences

□ Interdisciplinary and Frontier Sciences

4. Host institution: **Department of Dermatology, Asahikawa Medical College, Japan**

5. Host researcher: **Akemi ISHIDA-YAMAMOTO, M.D., Ph.D**

6. Description of your current research

Expression of peptidylarginine deiminases in the epidermis, and their role in the production of the Natural Moisturising Factor.

Among the various post-translational modifications of proteins, one of the less well-known is undoubtedly **deimination** (conversion of protein arginine residues to citrulline residues). However, deimination defects have been associated with several human diseases. For example, the abnormally high degree of myelin basic protein deimination observed in multiple sclerosis patients was proposed to be involved in myelin degeneration characteristic of this debilitating disease. Moreover, rheumatoid arthritis-specific auto-antibodies detect deiminated forms of fibrin. Some histones were recently shown to be also deiminated, suggesting that deimination play a role in the regulation of gene expression. Deimination is catalysed by a family of calcium-dependent enzymes, the peptidylarginine deiminases (**PADs**). The existence of 5 isoforms encoded by 5 different genes has been demonstrated in rodent and man. The tissue-specific and differentiation-dependent expression of PADs is poorly known. In epidermis, the first tissue where a PAD was identified, cytokeratins K1 and K10, and two Intermediate Filament Associated Proteins, filaggrin and trichohyalin, were shown to contain citrullines . Deimination of these proteins in the lower *Stratum Corneum* may result in their unfolding due to loss of ionic bonds. Subsequently, filaggrin is degraded into amino acids that are the main components of the **Natural Moisturising Factor** (NMF). The NMF plays a key role in absorption of UV light and in maintaining **hydration** of the upper layer of epidermis. Therefore it is essential for optimum

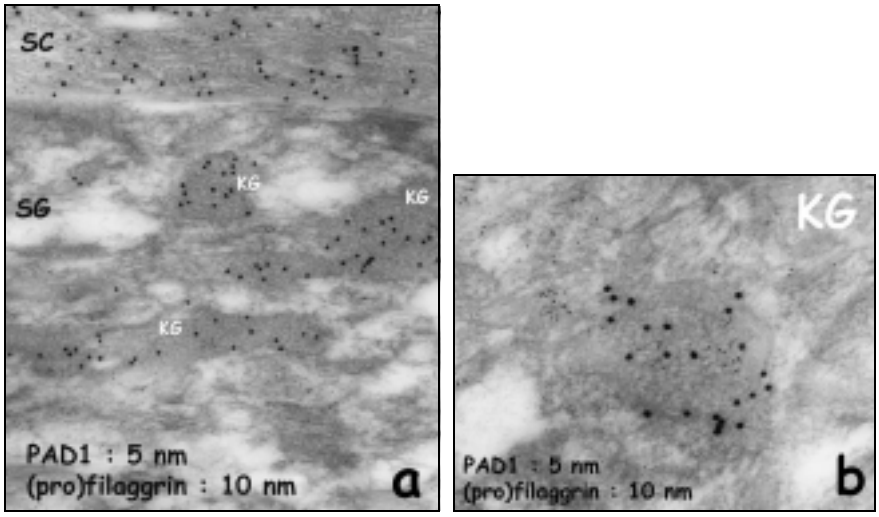
barrier function of the epidermis and for desquamation.

Our main interest is the following: **Which PAD(s) is involved in filaggrin deimination?**

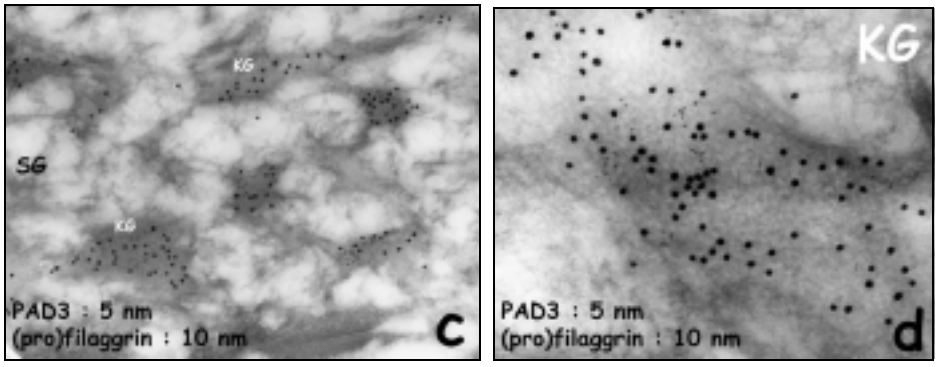
7. Research implementation and results under the program (As much as possible, describe the contents and results of your research in a manner that is easily understandable to a non-specialist in your field.):

In order to more precisely define the localization of PADs in human epidermis, immunoelectron microscopy was performed using anti-PADs and anti-(pro)filaggrin antibodies.

Immunoelectron microscopy shows co-localization of PAD1 and PAD3 with (pro)filaggrin in keratohyalin granules.



Co-localization of PAD1 and (pro)filaggrin in keratohyalin granules (KG), a) X 25 000, b) X 50 000 SG : stratum granulosum, SC : Stratum corneum



Co-localization of PAD3 and (pro)filaggrin in keratohyalin granules (KG), c) X 25 000, d) X 50 000 SG : stratum granulosum

It is still unclear which PADs contribute to the deimination of filaggrin, but the co-localization of PAD1, PAD3 and (pro)filaggrin in the keratohyalin granules suggests that a single enzyme or the combination of the two enzymes might be involved in the process.

Title of your research plan:

Ultrastructural Localization of Peptidylarginine Deiminases in normal human epidermis

Description of the research activities:

Human skin, as well as other tissues, is known to contain protein bound citrullines. The conversion of arginine residues to citrulline residues is catalyzed by a peptidylarginine deiminase (PAD) in a calcium-dependent manner. Although the existence of five isoforms of PAD (type 1, 2, 3, 4/5 and 6) was reported in rodents and human, their tissue distribution and function have yet to be explored. In order to analyze the different isoforms of PAD expressed in human epidermis, we produced and characterized anti-peptide antibodies highly specific for each one. Western blotting analysis of epidermal extracts revealed PADs type 1, 2 and 3 presence, and confirmes RT-PCR results. Immunohistochemical and confocal microscopy analyses allowed us to localize their expression. PAD type 1 and 2 were expressed in all the living layers of human epidermis, whereas PAD3 immunoreactivity was confined to the stratum granulosum where the enzyme seems to be co-localized with (pro)filaggrin. The aim of this study will be i) to elucidate the ultrastructural localization of peptidylarginine deiminases in normal human epidermis by immunoelectron microscopy analyses using our anti-PAD antibodies, and ii) to know whether one particular PAD is colocalized with (pro)filaggrin.

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8. Please add your comments (if any): I learnt a lot during this training with the Professor Akemi Ishida-Yamamoto. I really like working with her. I would like to thank the Professor Akemi Ishida-Yamamoto for her reception and for her teaching. I would like also to thank the Dr Mari Kishibe and the Dr Kyoko Kanno to have taken care of me. Thanks to all the department of dermatology of Medial college of Asahikawa and particularly the Professeur Hajime Lizuka. I would like to thank JSPS for supporting my research.

9. (If any) Advisor's remarks: Ms. Nachat has studied ultrastructural localization of PADs in the epidermis using immunoelectron microscopy methods. Although the methods were very difficult ones and needed highly advanced skills and patience, she mastered all the techniques needed and obtained very interesting results. She is one of the brightest and ablest PhD students I have worked with. I appreciate her great enthusiasm for research and her positive influence on young Japanese students and doctors in my department. I would like to thank JSPS for supporting her research.

RESEARCH REPORT

1. Name: Julien RUELLE (ID No.: SP04212)

2. Current affiliation:

Montpellier II University, Montpellier, FRANCE

Laboratory of Mechanics and Civil Engineering, CNRS UMR 5508,

Wood and Tree Mechanics Team

"Antilles-Guyane" University

UMR ECOFOG

Laboratory of "CIRAD-forêt" wood program

3. Research fields and specialties:

Interdisciplinary and Frontier Sciences (Wood science)

4. Host institution:

NAGOYA UNIVERSITY

Graduate School of Bio-agricultural Science

5. Host researcher:

Professor Takashi OKUYAMA

6. Description of your current research

Angiosperms are able to maintain their verticality (or define angle for branches) generating strong tension stresses on the upper side of the stem. This particular mechanical state is generally associated with important changes in the anatomical structure of the wood called tension wood by opposition to normal wood. Gravitropic reorientation related to the tension wood formation and corresponding high growth stress is an important mechanism. This fact is insufficiently taken into account by ecologists studying the competition for the light access in relation to specific mechanical constraints of certain ecosystems (dominant or occasional winds, difficulty or anchoring on hydromorphic grounds).

The reorientation of stems associated with generation of high growth stress level, measured in trees by some techniques giving values called growth stress indicators (GSI), opposed to less stresses wood are directly prejudicial to wood quality, by causing unexpected splits and deformations throughout the transformation process. Our work aims at understanding the origin of these defects and their variability between species and within the same species.

7. Research implementation and results under the program (As much as possible, describe the contents and results of your research in a manner that is easily understandable to a non-specialist in your field.):

Title of your research plan:

Analysis of the diversity of tension wood of tropical rainforest tree species

Description of the research activities:

During my first year of doctor curse in French Guyana I measured some properties, like growth stress indicators, drying shrinkage, on the wood of several tropical rainforest species. One of the aims of my work in Japan is to find some relation between ultra-structure and properties of these woods.

In the case of conifers reorientation of axis is due to the formation of a peculiar wood, called compression wood. A lot of techniques permit us to show relations between ultra-structure of conifers cell wall, especially orientation of the cellulose microfibrils in the cell wall (MFA), and growth stress indicators, drying shrinkage or longitudinal modulus of elasticity of macroscopic wood (fig. 1).

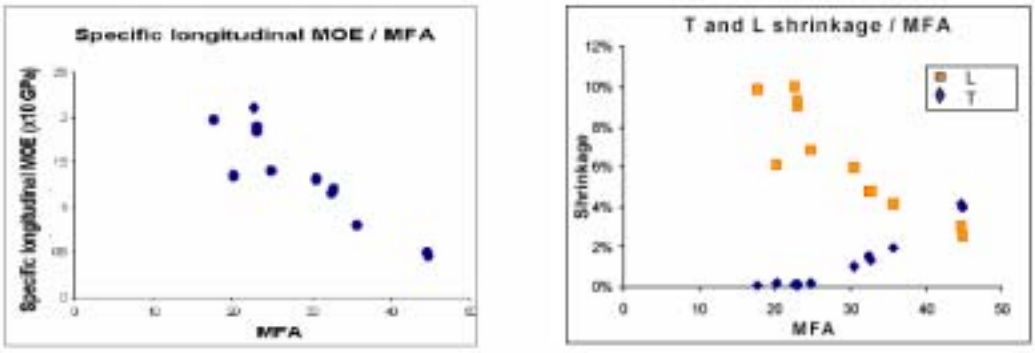


Figure 1: relation between microfibrilar angle (MFA) and properties of wood

Some of these techniques are not applicable to hardwoods. We try here to apply X-ray diffraction method on a tree from a tropical rainforest species: *Laetia procera.* This species presents a specific anatomical structure of tension wood (fig. 2). The X-ray diffraction method is only calibrated for softwoods; the aim of the study is to see if a value obtained with this technique applied to hardwoods can be linked with some physical or mechanical properties of the wood.

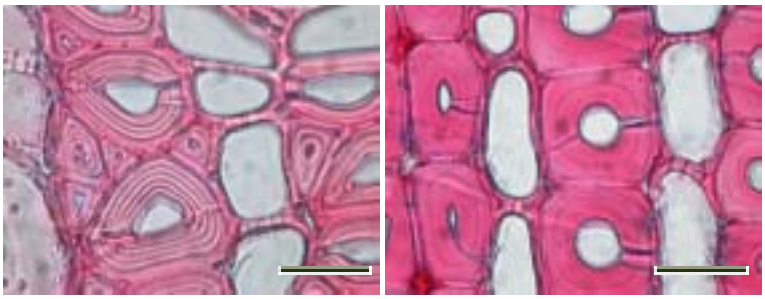


Figure 2: transversal thin sections details of tension wood (on the left) and of normal wood (on the right) of *Laetia procera* stained with safranin and alcian blue. Scale bars: 25 µm

The value taken from the X-ray diffraction profile of the specimen is the width of the curve at the intersection with curve tangents and baseline (in centimeters). We can see a relation between the value obtained with X-ray diffraction and all these properties except with the longitudinal drying shrinkage (fig. 3).

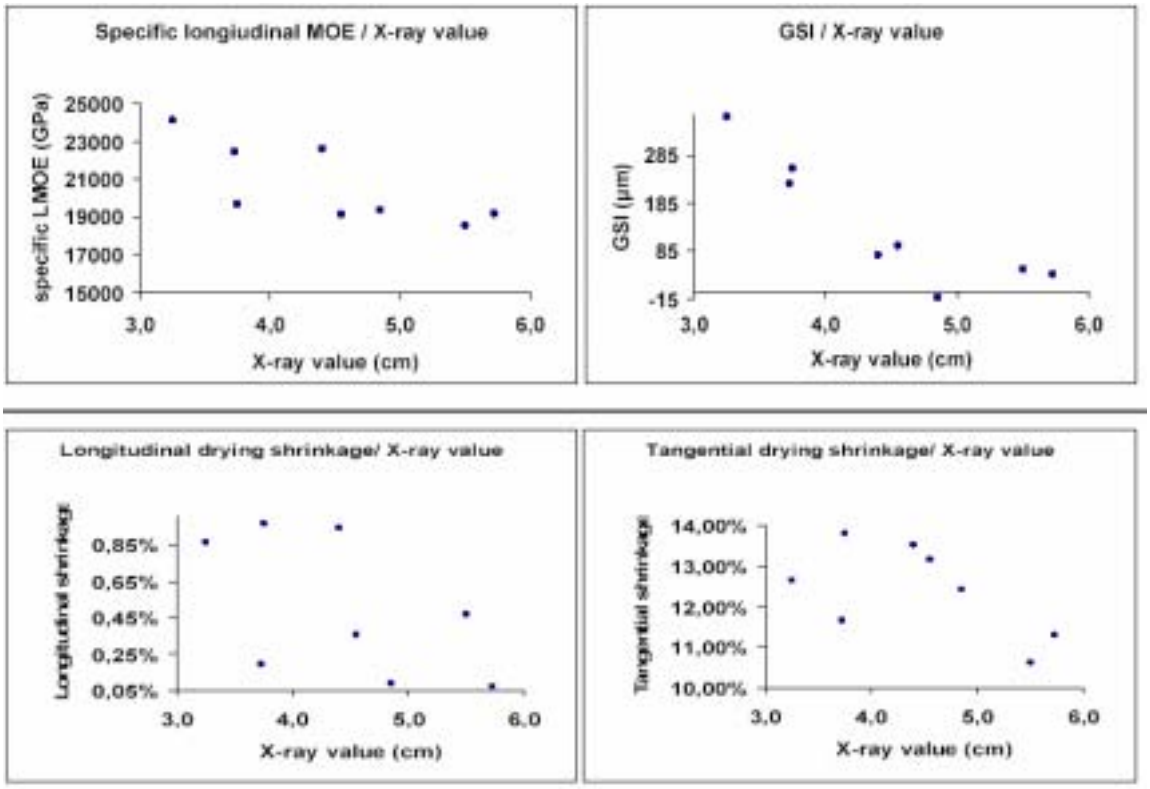


Figure 3: various relations between properties of wood and the value obtained from X-ray diffraction method on samples of *Laetia procera*

The results of this study lead us to explore the relation between MFA and wood properties for tropical rainforest species. Some techniques permit to measure directly MFA in wood, like method based on the orientation of the cross-field pit apertures, the orientation of iodine crystals that form in induced checks. Much of the current literature has been developed using these techniques that are very slow and tedious. It would be an important thing to reduce dramatically the time required to determine microfibril angles in hardwoods finding the correlation between MFA measured with these techniques and the values obtained by the X-ray diffraction method.

9. (If any) Advisor's remarks:

It is important to detect the mean MFA in relation to the wood properties, because the most wood properties came from the cell wall ultra-structure especially mechanical property of cellulose microfibril. Then MFA is the post important factor to understand the wood properties. In the case of hardwoods, the well known technique such as iodine method gives an unstable value because of the difficulty of removing the lignin between microfibrils partially. On the other hand, the X-ray method gives mean value even in the gelatinous fibers with shorter working time.

He is working hard to learn every measuring technique and is expected to classify the tension wood properties of tropical species through physical and anatomical properties that had not been worked so far.

RESEARCH REPORT

1. Name: SCIAMMA Ella (ID No.: SP04213)

2. Current affiliation:

The University of Texas at Austin. Electrical and Computer Science Department and Physics Department, Fusion Research Center.

3. Research fields and specialties:

☐ Humanities ☐ Social sciences ☐ Mathematical and Physical Sciences
☐ Chemistry ■ Engineering Sciences ☐ Biological Sciences
☐ Agricultural Sciences ☐ Medical, Dental and Pharmaceutical Sciences
☐ Interdisciplinary and Frontier Sciences

4. Host institution: Department of Engineering Physics and Mechanics, graduate School of Engineering, Kyoto University

5. Host researcher: Dr. Takashi Fujimoto

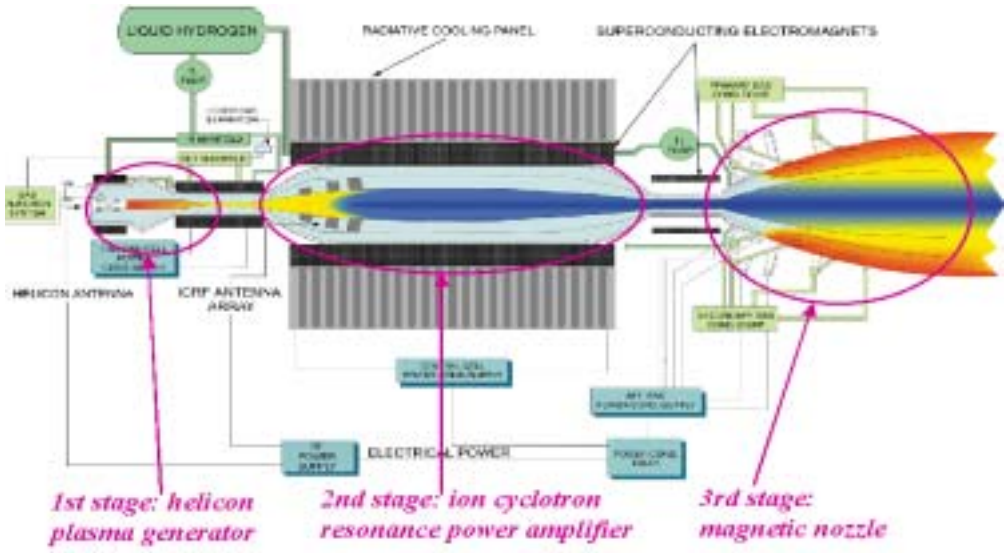
6. Description of your current research:

I am currently working under the supervision of Dr Roger Bengtson at the Fusion Research Center in the Physics department at the University of Texas at Austin (UTA), and the co-supervision of Dr Gary Hallock in the Plasma Quantum Electronics study area of the Electrical and Computer Science Engineering department.

My PhD project is to work with the Fusion Research Center (FRC) at UTA and the Advanced Space Propulsion Laboratory (ASPL) at NASA on the Variable Specific Impulse Magnetoplasma Rocket (VASIMR).

VASIMR is a high power, frequency-driven, plasma-based propulsion system consisting of three major magnetic cells:

- The forward cell where a neutral gas, the propellant, is injected and ionized by helicon discharge.
- The central cell which acts as an amplifier and heats the plasma to desired temperature and density by accelerating the ions with radiofrequency power at the ion cyclotron resonance.
- The aft cell is a magnetic nozzle which converts the cyclotron motion of the particles into axial velocity to provide thrust.



My work is to develop spectroscopy tools to make measurements in the Helium flowing plasma created in the prototype of the first stage of the VASIMR experiment and understand the operation of the helicon discharge in order to make it more efficient. My first objective is to estimate the electron temperature at different locations.

From different Helium neutral spectral line intensity ratios at different wavelengths, one can estimate the electron temperature using a collisional-radiative model.

To obtain these results on the electron temperature of the plasma in the VX-10 experiment, before going to Japan, I tried to use the results from a Collisional Radiative model developed by Dr. Goto at the National Institute for Fusion Science in Japan. But these results were for another experiment and were not applicable to the experimental conditions on the VX10. If I wanted to be able to apply it to our experiment, I needed to work directly with the model and not only with its results.

My supervisor and I had been in contact with Dr Fujimoto, who was the first creator of this CR model, and we had come to a point where the best thing for me, to make progress in my research, was to go to Japan and work with Dr Fujimoto for him to transmit his knowledge on plasma spectroscopy to me, and for me to use and understand the colliosional-radiative model.

7. Research implementation and results under the program (As much as possible, describe the contents and results of your research in a manner that is easily understandable to a non-specialist in your field.):

Title of your research plan:

Understanding of the Collisional Radiative model and introduction to polarization plasma spectroscopy.

Description of the research activities:

In Dr Fujimoto's lab, I worked on an experiment that produces a plasma very similar to the one produced in the VX10 experiment. I did spectroscopy measurements with Atsushi Iwamae, a Research Assistant of Dr Fujimoto's lab, on this CUSP experiment and learnt a different way to take data and do the calibration prior to the analysis.

I was also involved in their activities in plasma polarization spectroscopy, which is a new technique being developed now for the purpose of investigating anisotropy of a plasma, including an anisotropic velocity distribution of electrons in the plasma.

In parallel, I learnt how to use the Collisional Radiative model and implemented the parameters of the VX10 experiment in the code to obtain the theoretical results of the electron temperature for my experiment. I could then compare the theoretical results to my experimental results and have a good estimation of the electron temperature in the VX10.

We also went to visit Dr. Goto at the National Institute for Fusion Science in Toki and I could see the Large Helical Device, a fusion experiment using a helical discharge (like VX10) to create the plasma. It was a very interesting trip and a very good occasion for me to interact with Dr. Goto. Working in the same field, we'll have occasions to collaborate on projects and exchange ideas, and he already communicated data and knowledge to me during my stay in Japan.

Perspective of Research after this Program:

As soon as I'm back in the US, I will change my calibration method to use the one I learnt during my stay at Kyoto University and will redo my electron temperature analysis. I will then be able to compare my new experimental results (more accurate ones) to the results from the Collisional Radiative model I calculated this summer.

There are a lot of other theoretical calculations that can be achieved with the Collisional Radiative model and I will spend more time learning how to use it, with the help of Atsushi Iwamae via email.

It could also be interesting to try to do polarization spectroscopy on the VX10 now that I now how to do polarization spectroscopy measurements.

I'm hoping to come back to Kyoto soon to learn more from Dr. Fujimoto's lab and reinforce the collaboration that we begun this summer.

8. Please add your comments (if any):

This summer in Japan was a wonderful experience and my collaboration with Dr. Fujimoto's lab was very interesting and productive. The knowledge of Dr. Fujimoto and his student s on plasma spectroscopy is amazing and I was lucky to be able to learn from them.

This summer was also a very good experience for the discovery of Japanese culture and food… And of course, I was one of the luckiest people that were in Kyoto, city of beauty.

9. (If any) Advisor's remarks:

Dr. Bengtson is my long-time colleague, and from time to time, we discussed about plasma spectroscopy problems. This time, one of his students, Ella, got a chance to visit us. This was a good occasion to have a direct personal interaction between the two groups. When she came, we were just extending our plasma polarization spectroscopy experiment on our cusp plasma to a more comprehensive observation. She joined our experiment. She learned various experimental techniques which we developed for many years. She also learned the theoretical tool, the collisional-radiative model, which enables us to understand what is going on in this particular plasma. Before coming to Kyoto, she simply used the results by this model, and fitted her experimental data to curves. But, she understood how to proceed with this model and how to treat her experimental data and combine them. She also got some experiences in plasma polarization spectroscopy. I assume her plasma is quite interesting in this respect. Especially, plasma anisotropy is important for her objective: ion acceleration and conversion of the ion energy from the rotational to directional motions are anisotropic phenomena. I am certain that her experiences here are useful for her future endeavor and her stay here is a step forward to a fruitful collaboration between the two groups.