



# KIPS – ESPCI

## Workshop on Polymer Science

### 2013

November 28–29, 2013  
ESPCI ParisTech, Paris



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## Kyoto Institute of Polymer Science (KIPS)

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KIPS is a non-profit organization founded on January 1, 2000 without any particular building and funding. Its members, consisting of polymer researchers in Kyoto, collaborate with each other to innovate polymer science. Its main purpose is (1) to activate polymer science by providing various forums including scientific meetings, workshops, seminars, lecture courses, etc., (2) to foster young polymer scientists of the next generation through the activities above, and (3) to contribute to new developments of the society and to solution of problems. Over 50 professional polymer scientists and around 100 graduate students of Kyoto University belong to KIPS at present.

KIPS has been organizing domestic symposia for young polymer scientists every three years since 2006 inviting the most active young polymer scientists from Kyoto University and other universities as the oral speakers. The most recent one was held on December 7, 2012.

KIPS has been providing an annual comprehensive course of lectures on polymer science for industrial researchers and engineers since 2009. More than 100 people have accomplished the course so far.

KIPS also takes partnerships with foreign groups to organize international symposia and other events and to perform international exchanges. Thus far KIPS held joint symposia three times with NIST (1st in Kyoto in September 2000, 2nd in Gaithersburg in March 2003, and 3rd in Kyoto in May 2005) and once with ESPCI ParisTech (in Kyoto University Katsura Campus on November 28–29, 2011). The second joint symposium with ESPCI will be held in Paris on November 28–29, 2013. It is a great opportunity for the KIPS members to know the activity of the ESPCI ParisTech members and to develop the collaboration.

KIPS is cooperating with PII Foundation “Institute for Chemical Fibers, Japan”, which gives financial supports to the KIPS activities.

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## PII Foundation “Institute for Chemical Fibers, Japan”

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On the basis of the donation of 200,000 JPY from a fiber-trading company to the former Kyoto Imperial University, this Foundation was originated in 1936 in the University campus for promoting science and technology of chemical fibers. Since then, it had continued its service for 76 years until April 1, 2013, when it became formally independent of Kyoto University, reorganized as a public interest incorporated (PII) foundation prescribed by the new law enforced in 2008.

The Foundation today is involved in business to promote science and technology of polymer materials in general. Its business activities include the organization and/or sponsoring of public lecture meetings, international conferences, educational courses for young polymer researchers, and a research grant.

For the historical reason, the Foundation today is in close cooperation with Departments of Polymer Chemistry and Materials Chemistry, Graduate School of Engineering, Kyoto University, and their cooperating Laboratories, as well as with Kyoto Institute of Polymer Science (KIPS), which is a nonprofit society of the polymer scientists mainly from Kyoto University. The Foundation is also indebted to its supporting industries for their donations.



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# Programme

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## Thursday, November 28

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09:00 – 09:15 | LANGEVIN THEATER

Opening

09:15 – 09:45 | LANGEVIN THEATER

**Makoto Ouchi**

*Next-Generation Precision Polymerizations: Precise Control of Position, Sequence, and Topology for Polymer Chains*

09:45 – 10:15 | LANGEVIN THEATER

**Renaud Nicolaÿ**

*Functional materials and reversible*

10:15 – 10:45 | LANGEVIN THEATER

**Masaya Yamamoto**

*Design of hydrogel biomaterials for tissue regeneration*

10:45 – 11:15 | CHAMPETIER ROOM

Coffee Pause

11:15 – 11:45 | LANGEVIN THEATER

**Jean Baudry**

*Hydrogel capsules as granular materials*

11:45 – 12:15 | LANGEVIN THEATER

**Hirokazu Hasegawa**

*Network Microdomain Morphology via Guided Self-Assembly of ABC Triblock Terpolymer*

12:15 – 12:45 | LANGEVIN THEATER

**François Tournilhac**

*Control of cationic ring opening polymerization of epoxies by supramolecular chemistry*

12:45 – 15:00 | CHAMPETIER ROOM

Lunch and Poster Session

15:00 – 15:30 | LANGEVIN THEATER

**Yoshihiro Sasaki**

*Multifunctional nanogel hybrids for potential biomedical applications*

15:30 – 16:00 | LANGEVIN THEATER

**Tetsuharu Narita**

*Dynamics of tough hydrogels having permanent and transient crosslinks*

16:00 – 16:30

Pause

16:30 – 17:00 | LANGEVIN THEATER

**Tsuyoshi Koga**

*Structure Formation and Rheology of Associating Polymers and Gels*

17:00 – 17:30 | LANGEVIN THEATER

**Costantino Creton**

*Fracture of elastomers: new molecular insights*

18:15 – 19:30

**Les Vedettes du Pont-Neuf**

*Boat Trip on the Seine*

19:45 | "LE BOUILLON RACINE" RESTAURANT

Diner

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## Friday, November 29

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09:00 – 09:30 | LANGEVIN THEATER

**Hiroyuki Aoki**

*Conformation of single polymer chain in a thin film studied by super-resolution fluorescence microscopy*

09:30 – 10:00 | LANGEVIN THEATER

**Cécile Monteux**

*Dynamics of reactive amphiphiles*

10:00 – 10:30 | LANGEVIN THEATER

**Mikihito Takenaka**

*Directed-Self assembly of block copolymers*

10:30 – 11:00 | CHAMPETIER ROOM

Coffee Pause

11:00 – 11:30 | LANGEVIN THEATER

**Corinne Soulié**

*Supramolecular polymers and colloids*

11:30 – 12:00 | LANGEVIN THEATER

**Hironori Kaji**

*Solid-State NMR Analysis of Organic LEDs and Organic Solar Cells*

12:00 – 12:30 | LANGEVIN THEATER

**Michel Cloître**

*Emulsion droplets and capsules made from stimuli-responsive amphiphilic copolymers*

12:30 – 14:00 | CHAMPETIER ROOM

Lunch

14:00 – 14:30 | LANGEVIN THEATER

**Kazuo Tanaka**

*Development of POSS-based Functional Materials*

14:30 – 15:00 | LANGEVIN THEATER

**Alba Marcellan-Parisot**

*Hybrid Hydrogels: from covalent to hybrid networks*

15:00 – 15:30 | LANGEVIN THEATER

**Masatoshi Tosaka**

*Strain-induced Crystallization of Network Polymers*

15:30 – 16:00 | LANGEVIN THEATER

**Émilie Verneuil**

*Dynamic Wetting on a Thin Film of Soluble Polymer: Effects of Nonlinearities in the Sorption Isotherm and of Glass transition*

16:00 – 16:30 | LANGEVIN THEATER

Closure





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## List of poster presentations

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- P 1** "Topological interaction between semiflexible ring polymers"  
D. Ida
- P 2** "Statistical Thermodynamic Theory of Heat-induced Gelation and Crosslinked Structure of Methylated Polyrotaxanes in Water"  
Hiroyuki Kojima
- P 3** "Structural and mechanical properties of nanogel-crosslinked materials"  
Sada-atsu Mukai
- P 4** "Fabrication of Cellulose Nanofibers Grafted with "Concentrated" Polymer Brushes for Highly Lubricating Materials in Aqueous Medium and Resin Nanocomposites"  
K. Sakakibara
- P 5** "Preparation of nanogel-cross-linked particles in inverse micrometer-sized emulsion"  
Y. Tahara
- P 6** "Microgel-Core Star Polymers via Living Radical Polymerization: Smart Synthetic Strategy and Functional Compartments"  
T. Terashima
- P 7** "Molecular Weight between Entanglements for Polysaccharides"  
Junichi Horinaka
- P 8** "Polymer materials combining polycondensation and supramolecular chemistry"  
Reda Agnaou
- P 9** "Water-resistant UVB-shielding films from water-borne nanostructured latexes"  
Aggeliki Triftaridou
- P 10** "Design of nano-structuring agent: towards high-performance and annealing-free polymer solar cells"  
Sébastien-Jun Mougner
- P 11** "Innovative tough elastomers: Designed sacrificial bonds in multiple networks"  
Étienne Ducrot
- P 12** "Protected polythiol copolymers and their one-pot deprotection and functionalization"  
Morgane Le Neindre
- P 13** "Shear induced orientation of cocontinuous nanostructured polymer blends"  
Cinzia Rotella
- P 14** "One-pot synthesis of glycopolymers and gel formation in presence of borax"  
Evdokia K. Oikonomou
- P 15** "Stress strain relation of highly stretchable dual crosslink gels having permanent and transient crosslinks"  
Koichi Mayumi
- P 16** "Reversible adhesion of hydrogels in aqueous media"  
Jennifer Macron

## Control of Sequence and Chain Topology for Vinyl Polymers

M. Ouchi and M. Sawamoto

Department of Polymer Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Email: ouchi@living.polym.kyoto-u.ac.jp

Biopolymers such as DNA and proteins are expressing their functions based on sequence and shape (topology) as well as the functional groups. These structural factors should be essence for “macromolecules” effectively to coordinate variety of functional groups. On the other hand, for synthetic polymers, development of living polymerizations has allowed us control of molecular weight and precise syntheses of end-functionalized polymers and block copolymers; however, sequence regulation and universal control of topology still remains unexploited. In this work, our efforts have been directed to design of bond singularity for living polymerizations toward control of sequence and topology.

**Sequence Control** Radical polymerization, typical chain-growth polymerization, is useful to synthesize (co)polymers of high molecular weights carrying variety of functional groups. Here, control over selectivity of growing radical species for next monomer could lead to sequence regulation, but the

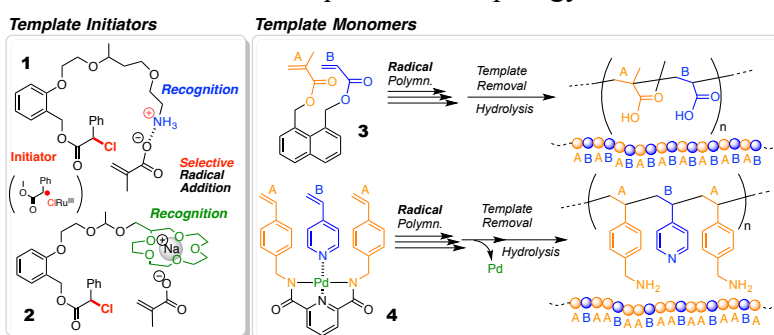


Figure 1. Template Molecules toward Sequence Control in Radical Polymerization

selectivity control depends on reactive ratio, which is generally hard to change. We have thus designed “template” with bond singularity (e.g., cleavable and recognizable) for initiators (1, 2, Figure. 1 [1], [2]) and monomers (3, 4 [3], [4]) in radical polymerizations to lead to selective radical addition and periodic sequence of copolymers over the inherent reactive ratios. Recently, our efforts were directed to molecular design for iterative radical addition reactions of single vinyl monomer like step-wise process, which is also presented.

**Topology Control** A cyclic initiator in which covalent bond between pre-active species and leaving group is incorporated would give cyclic polymer via ring-expansion polymerization. In this paper, we provide an effective system for “living cationic ring-expansion polymerization”, a precisely controlled ring-expansion via a carbocationic growing species (Figure 2) [5]. Crucial is the use of a cyclic hemiacetal ester, or a carboxylic acid vinyl ether adduct as an

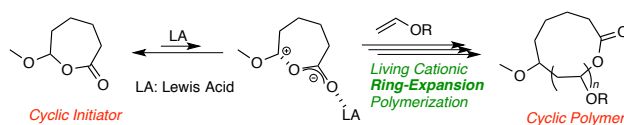


Figure 2. Living Cationic Ring-Expansion Polymerization

initiator where, upon coupled with a Lewis acid, the endocyclic activated carboxylate reversibly generates a growing carbocation associated with a nucleophilic ester anion within a single molecule. The ring-expansion polymerization was really “living” as demonstrated by the monomer-addition experiment. This approach was further applied for unique block copolymers such as “cyclic block” and “tadpole block” consisting cyclic and linear chains.

[1] Ida, S.; Terashina, T.; Ouchi, M.; Sawamoto, M., *J. Am. Chem. Soc.* **2009**, *131* (31), 10808-10809. [2] Ida, S.; Ouchi, M.; Sawamoto, M., *J. Am. Chem. Soc.* **2010**, *132* (42), 14748-14750. [3] Hibi, Y.; Tokuoka, S.; Terashina, T.; Ouchi, M.; Sawamoto, M., *Polym. Chem.* **2011**, *2* (2), 341-347. [4] Hibi, Y.; Ouchi, M.; Sawamoto, M., *Angew. Chem., Int. Ed.*, **2011**, *50* (32), 7434-7437. [5] Kammiyada, H.; Konishi, A.; Ouchi, M.; Sawamoto, M., *ACS Macro. Lett.*, **2013**, *2* (6), 531-534.

## Curriculum Vitae – Makoto Ouchi

**Title:**

Associate Professor

**Affiliation:**Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University  
Kyoto-Daigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan**Telephone, Fax, e-mail, Website:**

Tel/Fax: +81-75-383-7127

e-mail: [ouchi@living.polym.kyoto-u.ac.jp](mailto:ouchi@living.polym.kyoto-u.ac.jp)URL: <http://living.polym.kyoto-u.ac.jp/index.html>**Education:**

BS: Department of Polymer Chemistry, Faculty of Engineering, Kyoto University (1996)

MS: Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University (1998)

Ph.D.: Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University (2001)

**Professional Appointments:**

Researcher, Toyota Central R&amp;D Labs, Inc., 2001-2004

Assistant Professor, Kyoto University, 2004-2010

Associate Professor, Kyoto University, 2010-

JST-PRESTO Researcher, 2013-

**Awards:**

Young Scientist Prize of the Annual Kobe Polymer Research Symposium (2011)

Polymer Journal Zeon Award (2012)

**Research interest:**

Living Cationic/Radical Polymerization, Polymerization Catalyst, Sequence Control, Template

**Selected representative publications:**[1] Lutz, J. F.; Ouchi, M.; Liu, D. R.; Sawamoto, M., Sequence-Controlled Polymer. *Science* **2013**, *341*, 628.[2] Kammiyada, H.; Konishi, A.; Ouchi, M.; Sawamoto, M., *ACS Macro. Lett.*, **2013**, *2* (6), 531.[3] Lee, S. H.; Ouchi, M.; Sawamoto, M., Chain Center-Functionalized Amphiphilic Block Polymers: Complementary Hydrogen Bond Self-Assembly in Aqueous Solution. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 4498.[4] Lee, S. H.; Ouchi, M.; Sawamoto, M., Supramolecular X-Shaped Homopolymers and Block Polymers by Midsegment Complementary Hydrogen Bonds: Design of Bifunctional Initiators with Interactive Sites for Metal-Catalyzed Living Radical Polymerization. *Macromolecules* **2012**, *45* (9), 3702.[5] Fujimura, K.; Ouchi, M.; Sawamoto, M., Ferrocene Cocatysis in Metal-Catalyzed Living Radical Polymerization: Concerted Redox for Highly Active Catalysis. *Acs Macro Lett.* **2012**, *1* (2), 321.[6] Hibi, Y., Ouchi, M.; Sawamoto, M. Sequence-Regulated Radical Polymerization with a Metal-Templated Monomer: Repetitive ABA Sequence by Double Cyclopolymerization. *Angew. Chem. Int. Ed.* **2011**, *50*, 7434.[7] Ouchi, M., Badi, N., Lutz, J. F.; Sawamoto, M. Single-chain technology using discrete synthetic macromolecules. *Nat. Chem.* **2011**, *3*, 917.[8] Ida, S., Ouchi, M. & Sawamoto, M. Template-Assisted Selective Radical Addition toward Sequence-Regulated Polymerization: Lariat Capture of Target Monomer by Template Initiator. *J. Am. Chem. Soc.* **2010**, *132*, 14748.[9] Ida, S., Terashima, T., Ouchi, M. & Sawamoto, M. Selective Radical Addition with a Designed Heterobifunctional Halide: A Primary Study toward Sequence-Controlled Polymerization upon Template Effect. *J. Am. Chem. Soc.* **2001**, *131*, 10808.[10] Ouchi, M., Terashima, T. & Sawamoto, M. Transition Metal-Catalyzed Living Radical Polymerization: Toward Perfection in Catalysis and Precision Polymer Synthesis. *Chem. Rev.* **2009**, *109*, 4963.

## **Thiocarbonyl and thioester moieties as thiol protecting groups for controlled radical polymerization**

Morgane Le Neindre and Renaud Nicolay

*Matière Molle et Chimie, ESPCI-CNRS (UMR 7167) 10 rue Vauquelin, 75005 Paris, France. (0033-1-40795114 ; [renaud.nicolay@espci.fr](mailto:renaud.nicolay@espci.fr))*

Controlled radical polymerization is a robust and powerful technique that allows preparing well-defined functional architectures from a wide range of monomers. Among the numerous chemistries employed in macromolecular engineering, thiol chemistry currently stands as one of the most versatile tool for synthesis of functional polymers and materials. However, thiol groups are not compatible with controlled radical polymerization processes since they induce irreversible chain transfer. Therefore, a simple methodology to prepare well-defined polythiol copolymers by controlled radical polymerization was developed to address this limitation.

The use of xanthate, dithiocarbamate and thioacetate moieties as thiol protecting groups was investigated. Model reactions were conducted to study the effect of these protecting groups during controlled radical polymerization of acrylates, methacrylates and styrenics. The deprotection of these moieties by aminolysis was also investigated. Following this methodology, polythiols were obtained by copolymerizing (meth)acrylates with functional monomers carrying a xanthate moiety and subsequent aminolysis of the thiol protecting group. Both atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization were successfully employed to prepare well-defined polythiols.

However, polythiols proved to be difficult to handle since these polymers are prone to gel formation due to oxidative coupling between pending thiol groups. To prevent such side reactions, one-pot deprotection and functionalization procedures that avoid polythiol manipulation were studied. Functionalizations were exemplified with 6 different thiol-X reactions. Thiol-ene radical addition was not conclusive since it led to partial gelation of the sample. However, one-pot deprotection and functionalization via thiol-halogen nucleophilic substitution, thiol-epoxy ring opening, thiol-isocyanate reaction, thiol-acrylate Michael addition and thiol-disulfide exchange were quantitative and led to well-defined polymers, exemplifying the potential of polythiols for the preparation of functional materials.

## Curriculum Vitae - Renaud Nicolay

### Title:

Assistant Professor at École Supérieure de Physique et Chimie Industrielles (ESPCI-ParisTech)

### Affiliation:

Soft Matter and Chemistry Laboratory, École Supérieure de Physique et Chimie Industrielles  
ESPCI-ParisTech, 10 rue Vauquelin, 75005 Paris, France

### Telephone, Fax, e-mail, Website:

Tel: +33-1-4079-5114

Fax: +33-1-4079-5117

e-mail: [renaud.nicolay@espci.fr](mailto:renaud.nicolay@espci.fr)

URL: <http://www.mmc.espci.fr/spip.php?rubrique79>

### Education:

Master's degree in Chemistry, École Supérieure de Chimie Organique et Minérale, Cergy, 2003

Master's degree in Chemistry and Physico-Chemistry of Polymers, Pierre et Marie Curie University, Paris, 2004

Ph.D. in Polymer Chemistry, Pierre et Marie Curie University, Paris, 2008

Ph.D. in Polymer Chemistry, Carnegie Mellon University, Pittsburg, 2009

### Professional Appointments:

Postdoctoral Researcher at the Eindhoven University of Technology (TU/e), the Netherlands, 2010

Assistant Professor at ESPCI-ParisTech, Paris, France, 2010

### Awards:

Prix Jean Langlois de Diffusion de la Recherche, ESPCI-ParisTech, 2012

Astrid and Bruce McWilliams Fellowship, Carnegie Mellon University, 2009

Excellence in Graduate Polymer Research, American Chemical Society, 2009

### Research Interest:

Controlled radical polymerization, dynamic covalent polymer chemistry, macromolecular engineering

### Selected representative publications:

Nicolay, R., "Synthesis of Well-Defined Polythiol Copolymers by RAFT Polymerization." *Macromolecules* **2012**, *45*, 821-827.

Nicolay, R.; Kwak, Y., "ATRP with Alkyl Pseudohalides Acting as Initiators and Chain Transfer Agents: When ATRP and RAFT Polymerization Become One." *Isr. J. Chem.* **2012**, *52*, 288-305.

Nicolay, R.; Kamada, J.; Van Wassen, A.; Matyjaszewski, K., "Responsive Gels Based on a Dynamic Covalent Trithiocarbonate Cross-Linker." *Macromolecules* **2010**, *43*, 4355-4361.

Nicolay, R.; Kwak, Y.; Matyjaszewski, K., "A Green Route to Well-Defined High-Molecular-Weight (Co)polymers Using ARGET ATRP with Alkyl Pseudohalides and Copper Catalysis." *Angew. Chem., Int. Ed.* **2010**, *49*, 541-544.

## Design of hydrogel biomaterials for tissue regeneration

M. Yamamoto, H. Toda and Y. Tabata

Department of Biomaterials, Kyoto University, Sakyo-ku, Kyoto 606-8507, Japan

Email: masaya@frontier.kyoto-u.ac.jp

Lineage specification of stem cells is a major challenge for successful tissue regeneration and cell transplantation. Recently, the immobilization of cell signaling proteins [1] and the elasticity of culture substrates [2] have been extensively investigated as biological and physical signals to regulate the lineage specification of stem cells. On the contrary, it has been demonstrated that three-dimensional (3-D) culture could enhance biological activities of cells compared with two-dimensional (2-D) culture [3]. The objective of this study is to obtain the fundamental knowledge of mesenchymal stem cells (MSC) cultured in a sandwiched condition with bio-functional hydrogels as a 3-D culture model. The bio-functional hydrogels were prepared through the immobilization of a cell signaling protein on poly(acrylamide) hydrogels with different crosslinking densities. As the cell signaling protein, ephrin B2 of an Eph signal ligand was employed to stimulate the osteoblastic differentiation of MSC [4]. A direct binding between ephrinB2 and EphB4 via the cell-cell contact is required to activate the ephrinB2-EphB4 signaling [4]. In this study, based on the site-specific interaction between IgG Fc domain and protein A, the immobilization of ephrinB2 in an orientation-regulated manner was designed to achieve the efficient ligand-receptor binding.

Acrylamide and *N,N'*-methylenebisacrylamide were co-polymerized to prepare poly(acrylamide) hydrogels with varied elasticity. The elasticity was assessed in terms of hydrogels storage modulus. Then, both rat tail collagen type I and protein A were immobilized on the surface of the hydrogel by the sulfo-succinimidyl ester activation method. The resulting hydrogel was exposed to the solution of a recombinant chimeric protein of ephrinB2 and IgG Fc domain to immobilize ephrinB2 on the hydrogel in an orientation-regulated manner [1]. Human MSC were sandwiched between the resulting bio-functional hydrogels and cultured to evaluate their proliferation and osteoblastic differentiation comparing with those normally cultured. When sandwich-cultured between the bio-functional hydrogels, MSC showed enhanced osteoblastic differentiation in terms of the Runx-2 gene expression, which is similar to those on the corresponding bio-functional hydrogel in the 2-D culture condition. This result suggests that cell signaling pathways in MSC could be activated by the cell signaling proteins even in the sandwiched condition.

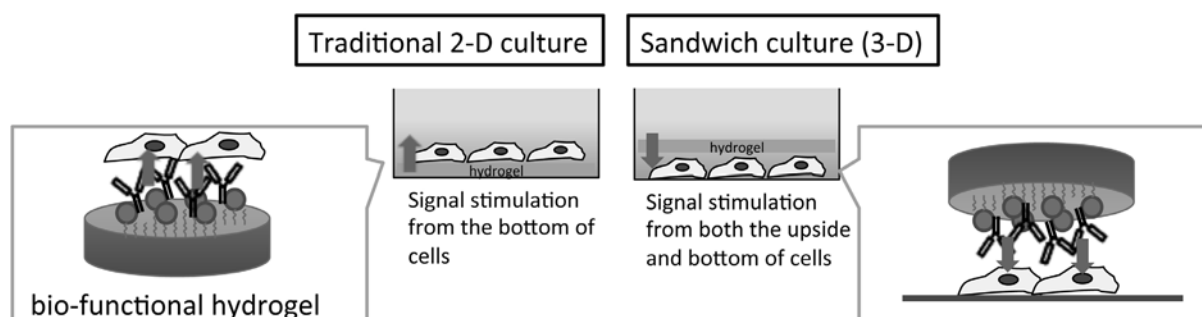


Fig. 1 Sandwich culture with bio-functional hydrogels as a three-dimensional culture model.

[1] H. Toda, M. Yamamoto, H. Kohara, and Y. Tabata, *Biomaterials*, **32**, 6920 (2011).

[2] A. Engler et al., *Cell*, **126**, 677 (2006).

[3] M. Yamamoto, S. Rafii, and S.Y. Rabbany, *Adv. Drug Deliv. Rev.* in press (2013).

[4] A. Pennisi et al, *Blood*, **114**, 1803 (2009).

## Curriculum Vitae - Masaya Yamamoto

**Year of birth:**

1971

**Title:**

Associate Professor

**Affiliation:**

Department of Biomaterials, Institute for Frontier Medical Sciences, Kyoto University  
53 Kawara-cho Shogoin, Sakyo-ku, Kyoto 606-8507, Japan

**Telephone, Fax, e-mail, Website:**

Tel: +81-75-751-4108

Fax: +81-75-751-4646

e-mail: masaya@frontier.kyoto-u.ac.jp

URL: [http://www.frontier.kyoto-u.ac.jp/te02/index\\_en.html](http://www.frontier.kyoto-u.ac.jp/te02/index_en.html)

**Education:**

BS: Department of Polymer Chemistry, Kyoto University (1994)

MS: Department of Polymer Chemistry, Kyoto University (1996)

Ph.D: Department of Polymer Chemistry, Kyoto University (1999)

**Professional Appointments:**

Visiting Scientist, Institute for Polymer Research, Dresden, Germany (1999)

Assistant Professor, Kyoto University (2000)

PRESTO Researcher, JST (2002)

Visiting Fellow, Weill Medical College of Cornell University, USA (2007)

Associate Professor, Kyoto University (2011)

**Awards:**

Global Education Seminar Presentation Award (The academy of Pharmaceutical Science and Technology, Japan 2012)

Award for Encouragement of Science (Japanese Society for Biomaterials 2010)

Young Investigator Award (Japanese Society for Regenerative Medicine 2010)

Nagaishi Award (Institute for Frontier medical Sciences, Kyoto University 2006)

Finalist Commendation (The Takeda Techno-Entrepreneurship Award 2001)

Young Scientist Award (The 5th Conference on Cardiovascular Disease Science 2001)

**Research interest:**

Polymeric biomaterials, Tissue engineering, Regenerative medicine, Drug delivery systems, Stem cell manipulation

**Selected representative publications:**

T. Ishimoto, T. Nakano, Y. Umakoshi, M. Yamamoto, Y. Tabata, "Degree of biological apatite c-axis orientation rather than bone mineral density controls mechanical function in bone regenerated using recombinant bone morphogenetic protein-2", *J Bone Miner Res.*, **157**, 398, 2012.

H. Toda, M. Yamamoto, H. Kohara, Y. Tabata, "Orientation-regulated immobilization of Jagged1 on glass substrates for ex vivo proliferation of a bone marrow cell population containing hematopoietic stem cells", *Biomaterials*, **32**, 6920, 2011.

M. Yamamoto, D. James, H. Li, J. Butler, S. Rafii, S. Rabbany, "Generation of Stable Co-cultures of Vascular Cells in a Honeycomb Alginate Scaffold", *Tissue Eng. Part A*, **16**, 299, 2010.

## **Hydrogel Capsules As Granular Materials**

**L Rolland, N Bremond, J. Baudry, J Bibette,  
LCMD-ESPCI**

We have developed millimetric oil droplets coated by hydrogel layer. These materials behave as a granular wet material from which we can vary the rest angle from  $35^\circ$  down to zéro. We have built an hour glass out of these liquid grains and did study their flow as a fonction of the friction coefficient. We present the first hour glass that allows a quantitative understanding of its different flow regimes.



## Jean BAUDRY

### Address :

Laboratoire Colloïdes et Matériaux Divisés  
UMR 7195, UPMC, ESPCI  
10 Rue Vauquelin,  
75231 Paris cedex 05

[jean.baudry@espci.fr](mailto:jean.baudry@espci.fr)

+33 (0)1 40 79 51 68

[www.lcmd.espci.fr](http://www.lcmd.espci.fr)

### Education :

- Ph.D. Physics, Ecole Normale Supérieure de Lyon 1999. (Advisor: P. Oswald)
- Agrégation de sciences physiques (1993)
- Ecole Normale Supérieure de Lyon (1990)

### Experience :

- Postdoc (2001-2005) then CNRS position since 2005  
*Laboratoire Colloïdes et Matériaux Divisés, ESPCI, Paris*
- Research Fellow (2000-2001)  
*Department of Physics & Astronomy, Edinburgh, UK*
- Postdoc (1998-2000)  
*Département de Physique des Matériaux, UCBL, Lyon, France*
- Doctorate (1994-1998)  
*Laboratoire de Physique, ENS Lyon, France*

### 5 most relevant publications :

- *Force-Velocity Measurements of a Few Growing Actin Filaments*, C. Brangbour, O. du Roure, E. Helfer, D. Démoulin, A. Mazurier, M. Fermigier, M.-F. Carlier, J. Bibette and J. Baudry, *PLoS Biology* 9 e1000613 (2011)
- *Chiral Colloidal Clusters*, D. Zerrouki, J. Baudry, D. Pine, P. Chaikin and J. Bibette, *Nature*, **455** 380 (2008)
- *Acceleration of the recognition rate between grafted ligands and receptors with magnetic forces*, J. Baudry, C. Rouzeau, C. Goubault, C. Robic, L. Cohen-Tannoudji, A. Koenig, E. Bertrand, and J. Bibette, *PNAS* **103**, 16076 (2006)
- *Microscopic artificial swimmers*, R. Dreyfus, J. Baudry, M. L. Roper, M. Fermigier, H. A. Stone & J. Bibette, *Nature* **437**, 862- (2005)
- *Experimental evidence of a large slip effect at a nonwetting fluid-solid interface*, J. Baudry, A. Tonck, D. Mazuyer and E. Charlaix, *Langmuir* **17** (2001) 5232

## Network Microdomain Morphology via Guided Self-Assembly of ABC Triblock Terpolymers

H. Hasegawa, M. Takenaka, K. Saijo, S. Akasaka, A. Mitani, T. Osaka,  
G. Sakaguchi, M. Wakabayashi, T. Ishii, A. Inoue and T. Chidiwa

Department of Polymer Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Email: hasegawa.hirokazu.3v@kyoto-u.ac.jp

ABC triblock terpolymers tend to undergo two-step microphase separation when they are cast from solution in selective solvent. The resulted microdomain morphology is not in equilibrium. However, the non-equilibrium process can lead to a variety of unexpected morphology including unusual network morphologies.

We investigated the microdomain morphologies of the as-cast films of polystyrene-*block*-polyisoprene-*block*-poly-1,4-dimethylsiloxane linear triblock terpolymer (PS-*b*-PI-*b*-PDMS) with various compositions synthesized via sequential living anionic polymerization. Since the films were cast from solution in toluene, which is selective to PS and PI and poor to PDMS component, two-step microphase separation (Fig. 1) took place during solvent evaporation, i.e., PDMS microphase separates first from the other two components. We call this process “guided self-assembly” because the PDMS microdomains regularly arranged in space should act as the guides and direct the subsequent microphase separation of PS and PI components. The PI-PDMS junction points are fixed on the microdomain interfaces and it restricts the second-step microphase separation between PS and PI components. The resulting microdomain structures are non-equilibrium structures, some of which exhibit unusual network morphologies of core-shell types. The structure of the as-cast films was analyzed by 3D electron tomography (3D-TEM) and small-angle X-ray scattering (SAXS) with synchrotron radiation source (Spring8). Unexpectedly from the non-equilibrium structures, some of the as-cast films exhibited very well-defined SAXS patterns with extremely regular structures. In addition to the well-known equilibrium cubic morphology of double Gyroid networks (or  $Ia\bar{3}d$ ), we found two different double network morphologies with non-cubic unit cells and PDMS-PI core-shell networks. One has an orthorhombic unit cell with the symmetry of space group  $Fddd$ , which is different from the  $Fddd$  single network structure found in the triblock terpolymers or in the weakly-segregated PS-*b*-PI diblock copolymer. The other one has a tetragonal unit cell and is considered as an elongated P-surface (or Plumber’s Nightmare) network structure. Both of them have the core-shell type networks with double-network structures as revealed by 3D TEM. In addition, we have observed double diamond (or D-surface) network structure of the core-shell type as well as the single-diamond network structure by 3D TEM. In the latter network structure, PS network and PDMS-PI core-shell network have almost the same volume and divide the space into two halves having the mirror images. Thus, we found five different network morphologies out of ten samples with different compositions in the limited composition range of  $f_{PS}$  between 0.33 and 0.41. This range resembles to the composition range of double Gyroid morphology ( $0.33 \leq f_{PI} \leq 0.37$ ) in PS-*b*-PI diblock copolymer [1].

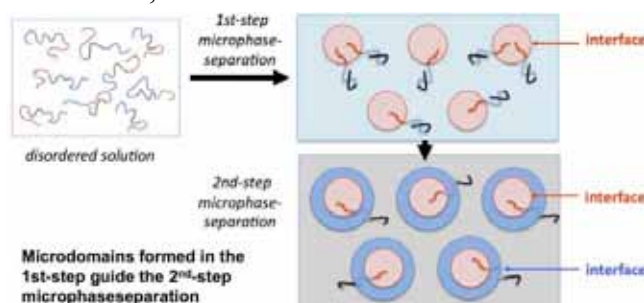


Fig.1 Control of two-step microphase separation using the third microdomains to guide the 2<sup>nd</sup>-step phase separation

[1] H. Hasegawa *et al.*, *Macromolecules*, **18**, 67 (1985).

## Curriculum Vitae – Hirokazu Hasegawa

Year of birth:

1948

**Title:**

Senior URA & Director

**Affiliation :**

Research Administration Center, Graduate School of Engineering, Kyoto University  
1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan

**Telephone, Fax, e-mail, Website :**

Tel: +81-75-383-2834

Fax: +81-75-383-2833

e-mail: [hasegawa.hirokazu.3v@kyoto-u.ac.jp](mailto:hasegawa.hirokazu.3v@kyoto-u.ac.jp)

URL: <https://www.rac.t.kyoto-u.ac.jp/ja>

**Education:**

BS : Department of Polymer Chemistry, Faculty of Engineering, Kyoto University (1972)

M.S. & Ph.D. : Department of Macromolecular Science, Graduate School of Engineering,  
Case Western Reserve University (1977, 1979)

**Professional Appointments:** (*title, place, year*)

Instructor, Kyoto University, 1978

Associate Professor, Kyoto University, 1995

Professor, Kyoto University, 2009

Senior URA & Director of Research Administration Center, 2013

**Awards:**

Society of Polymer Science Japan (SPSJ) Award, 2002

**Research interest:**

Polymer Morphology, Block Copolymers and Polymer Blends

**Selected representative publications:**

S. Akasaka, T. Okamoto, T. Osaka, T. Matsushita, H. Hasegawa, “3D Analysis of the Lattice Defects in the Gyroid Network Structure of a Block Copolymer / Homopolymer Blend – The Line-like Defects in the Gyroid Network Structure–“. *Euro. Polym. J.*, **47**, 651-661 (2011)

Vincent H. Mareau, Satoshi Akasaka, Taketsugu Osaka, Hirokazu Hasegawa, “Direct Visualization of the Perforated Layer/Gyroid Grain Boundary in a PS-*b*-PI/PS Blend by Electron Tomography”, *Macromolecules*, **40**, 9032-9039 (2007)

Keiko Takahashi, Hirokazu Hasegawa, Takeji Hashimoto, Vasilios Bellas, Hermis Iatrou, Nikos Hadjichristidis, “Four-Phase Triple Coaxial Cylindrical Microdomain Morphology in a Linear *Macromolecules*, **35**, 4859-4861 (2002)

## Control of cationic ring opening polymerization of epoxies by supramolecular chemistry.

François Tournilhac, Thomas Vidil, Ludwik Leibler

Controlling the potlife and structure of the network at gelation is a crucial point in thermoset processing. As for cationic polymerization of epoxy monomers, difficulties arise from the high exothermicity of oxirane rings' opening. Moreover, in many processes involving epoxy resins, it is not possible to play with temperature and solvent as the reactive mixture is supposed to work close to room temperature and in bulk.

In order to better control the kinetics of reaction and gelation of such systems, we recently suggested the use of supramolecular initiators instead of conventional Lewis acid initiators.<sup>1</sup> To this end, an anilinium tetrafluoroborate, already known as valid initiator, is stabilized into a pseudorotaxane architecture, using 18-crown-6 as host molecule (figure 1a). The obtained complex is quiescent at room temperature. Raising the temperature permits the release of the anilinium tetrafluoroborate ion pair which in turn efficiently triggers the ring opening polymerization.

Alternatively we also demonstrated that the rate of polymerization, induction of a retardation period and conversion at the gel point may be finely tuned without departing from room temperature, with the help of supramolecular chemistry.<sup>2</sup> In this case, the propensity of hydroxyl moieties to promote the activated monomer (AM) mechanism and the chelating ability of polyether groups and crown ethers towards the cationic species involved in this regime are combined to efficiently control the process at the propagation stage (figure 1b).

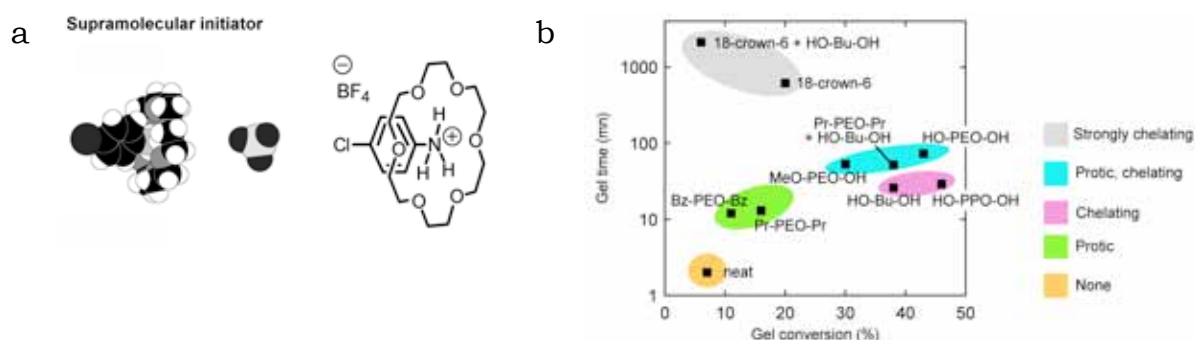


Figure 1 a: Structure of the supramolecular initiator, BF<sub>3</sub>-4-chloroaniline•18-crown-6 complex designed for the control of epoxy ring opening polymerization. b: Simultaneous control of the reaction rate (gel time) and structure of the network at gelation (gel conversion) by combination of protic and chelating additives.

<sup>1</sup> Vidil, T.; Tournilhac, F.; Leibler, L.; *Polymer Chemistry* **2013**, 4, 1323-1327

<sup>2</sup> Vidil, T.; Tournilhac, F.; *Macromolecules* (in press)

## Curriculum Vitae - François Tournilhac

### Title(s):

Research Director at CNRS

### Affiliation:

Soft Matter and Chemistry Laboratory, Ecole Supérieure de Physique et Chimie Industrielles  
ESPCI-ParisTech, 10 rue Vauquelin, 75005 Paris, France

### Telephone, Fax, e-mail, Website:

Tel: +33-1-4079-4630

Fax: +33-1-4079-5117

e-mail: [francois.tournilhac@espci.fr](mailto:francois.tournilhac@espci.fr)

URL: <http://www.mmc.espci.fr>

### Education:

Master's degree in engineering, Ecole Centrale des Arts et Manufactures, Paris (1984)

Ph.D. in Physical Chemistry : Université Pierre et Marie Curie, Paris (1989)

### Professional Appointments:

Researcher at CNRS (National Center for Scientific Research), Paris 1988

Habilitation, Université Pierre et Marie Curie, Paris 1998

Director of Research at CNRS, Paris 2002

### Awards:

CNRS Bronze medal, 1991

### Research interest:

Supramolecular and reversible chemistry, polymer chemistry and physics, composites, materials.

### Selected representative publications:

P. Cordier, F. Tournilhac, C. Soulié-Ziakovic, & L. Leibler "Self-mending and thermoreversible rubber from supramolecular assembly." *Nature* **451**, 977-980 (2008)

D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler "Silica-like malleable materials from permanent organic networks." *Science* **334**, 965-968 (2011)

T. Vidil, F. Tournilhac, L. Leibler "Control of cationic epoxy polymerization by supramolecular initiation" *Polymer Chemistry*, **4**, 1323-1327 (2013)

## Bioinspired lipid engineering: Control of membrane nanotube formation by external field

Y. Sasaki, S. Sawada, K. Akiyoshi

*Department of Polymer Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*

*Email: sasaki.yoshihiro.8s@kyoto-u.ac.jp*

Biological lipid nanotubes, known as tunneling nanotubes, that connect biological cells over a long distance were recently discovered as a new cell-to-cell communication system [1]. Lipid nanotubes are cylindrical nanoscale objects composed of a lipid bilayer membrane and have also been attracted attention due to their applications in bionanotechnology. For instance, lipid nanotube-based devices with micro- or nano-scale networks have been applied in single-molecule analysis [2]. Here, we introduce novel methods to prepare tailor-made lipid nanotubes, which can be used to transport biological molecules via internal water phase or hydrophobic bilayer membrane. By applying various external stimuli including shear stress to surface-immobilized liposomes on a solid substrate, we obtained long range membrane-bound lipid nanotubes arranged in a well-controlled direction [3]. The lipid nanotube engineering provides a novel and facile fabrication strategy for artificial cell membrane array inter-connected via the lipid nanotubes.

By applying shear flow (several hundred mL/min) to immobilized liposomes via avidin-biotin interactions onto inside wall of a channeled chamber, tubulation of the liposomes was clearly observed by fluorescence microscopy. The nanotubes were formed from at least 40% of the liposome (based on the number of liposomes) under current condition. Fluorescence intensity analysis of the microscopic images showed that the diameters were less than 500 nm, although it was difficult to determine the exact diameters of nanotubes from the microscopic image because of the optical limit of the fluorescence microscope. In most cases, extended (down-stream) ends of the nanotubes were connected with another liposomes. Under the same flow condition, the free liposomes were washed away from the flow channel. Strong bias was found in the direction of tubulation, indicating the nanotubes were formed parallel to the direction of fluid flow. The presence of an internal water phase provided by lipid bilayer membranes was also confirmed by using confocal laser scanning microscopy. The nanotubes have a confined space to accommodate at least high molecular weight dextran molecules. The inner spaces of the lipid nanotubes were maintained for at least 5 days.

Mechanical force of the formation of tubular membrane from giant liposome was reported to be several pN, which is comparable with the force generated by shear flow in this study (several pN for 10- $\mu$ m liposomes). Fluorescence microscopic observation confirmed that the lipid nanotubes have a confined space to accommodate biological molecules. Although the present work represents the initial phase of research in shear stress-induced membrane nanotube formation, the simplicity of this system is promising as an efficient and versatile technique to produce lipid nanotubes for use in biotechnology and nanotechnology.

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- [1] J. Hurtig, D. T. Chiu, B. Onfelt, *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology*, 2 (2010) 260.
- [2] S. M. Christensen and D.G. Stamou, *Sensors*, 10, (2010) 11352.
- [3] Y. Sekine, K. Abe, A. Shimizu, Y. Sasaki, S. Sawada and K. Akiyoshi: *RSC advances*, 2 (2012) 2682.

**Curriculum Vitae - Yoshihiro SASAKI****Year of Birth:**

1972

**Title:**

Associate Professor

**Affiliation:**

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku,  
Kyoto 615-8510, Japan

**Telephone, Fax, e-mail, Website:**

Tel: +81-75-383-2823

Fax: +81-75-383-2589

e-mail: sasaki.yoshihiro.8s@kyoto-u.ac.jp

URL: <http://www.labonet.info/akiyoshi/>**Education:**

BS: Department of Polymer Chemistry, Kyoto University (1995)

MS: Department of Synthetic and Biological Chemistry, Kyoto University (1992)

Ph. D: : Department of Synthetic and Biological Chemistry, Kyoto University (1999)

**Professional Appointments:**

Researcher, JSPS (1998-1999)

Assistant Professor, Nara Institute of Science and Technology (1999-2007)

Overseas Researcher, MEXT (2002-2003)

Research Associate, University of Notre Dame, USA (2003)

Associate Professor, Tokyo Medical and Dental University (2008-2012)

Researcher of PRESTO, Japan Science and Technology Agency (2008-2011)

Associate Professor, Tokyo Medical and Dental University (2012-present)

**Awards:**

CSJ Presentation Award for Industries (The Chemical Society of Japan, 1996)

NAIST Academic Prize (Foundation of Nara Institute of Science and Technology, 2004)

CSJ Presentation Award for Industries (The Chemical Society of Japan, 2005)

Takagi Award (The Society of Non-Traditional Technology, 2010)

**Research Interest:**

Biomimetic Chemistry: Bio-Nano Devices: Organic-Inorganic Hybrid Nanomaterial

**Selected representative publications:**

Sekine, Y., Moritani, Y., Ikeda-Fukazawa, T., Sasaki, Y., Akiyoshi, K. "A Hybrid Hydrogel Biomaterial by Nanogel Engineering: Bottom-Up Design with Nanogel and Liposome Building Blocks to Develop a Multidrug Delivery System" *Adv. Healthcare Mater.* 10.1002/adhm.201200175 (2012)

Sekine, Y., Abe, K., Shimizu, A., Sasaki, Y., Sawada, S., Akiyoshi, K. "Shear Flow-Induced Nanotubulation of Surface-Immobilized Liposomes" *Rsc Advances*, 2, 2682-2684 (2012).

Sasaki, Y., Tsuchido, Y., Sawada, S., Akiyoshi, K. "Construction of Protein-Crosslinked Nanogels with Vitamin B6 Bearing Polysaccharide", *Polym. Chem.*, 2, 1267-1270 (2011).

Sasaki, Y., Mukai, M., Kawasaki, A., Yasuhara, K., Kikuchi, J. "Switching of the Enzymatic Activity Synchronized with Signal Recognition by an Artificial DNA Receptor on a Liposomal Membrane", *Org. Biomol. Chem.*, 9, 2397-2402 (2011).

Sasaki, Y., Akiyoshi, K. "Nanogel Engineering for New Nanobiomaterials: From Chaperoning Engineering to Biomedical Applications", *Chem. Rec.*, 10, 366-376 (2010).

## Dynamics of tough hydrogels having permanent and transient crosslinks

Koichi Mayumi, Guylaine Ducouret, Alba Marcellan, Costantino Creton, Tetsuharu Narita

Laboratory of Soft Matter Science and Engineering (SIMM), UMR7615

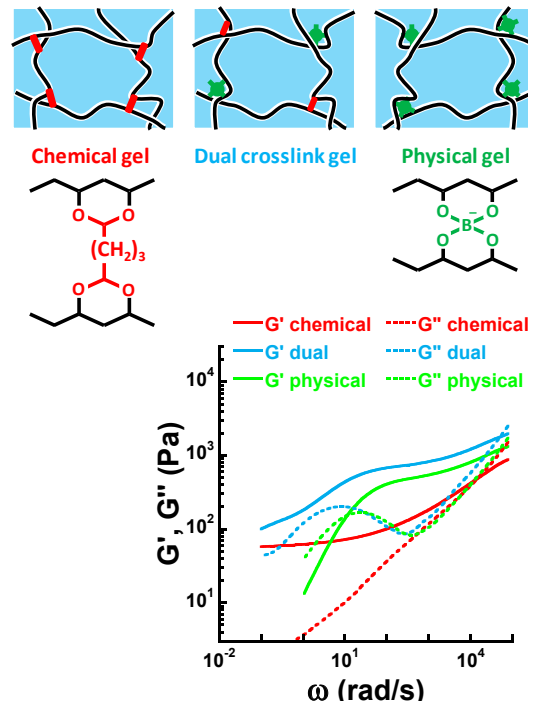
ESPCI ParisTech / CNRS / UPMC

Hydrogels, 3D polymer networks swollen in water, are considered as good candidates for biomedical applications such as artificial cartilage, vessels, prosthetic joints. In order to overcome their mechanical weakness (low deformability, brittleness), various improvements of crosslinking methods have been proposed in these last 10 years. One of the successful strategies is to introduce sacrificing bonds which break and reform during deformation of the network, which are able to dissipate strain energy and suppress local stress concentration in the gels.

We have developed a simple model hydrogel having permanent crosslinks and transient crosslinks simultaneously based on poly(vinyl alcohol). This PVA “dual crosslink” hydrogel, synthesized by the complexation of a chemical PVA gel with borate ions, have a single characteristic time (time of dissociation of PVA-borate interaction). Our PVA dual crosslink gels with optimized crosslinkers' concentrations show high mechanical toughness and deformability.

In order to understand mechanical properties of the PVA dual crosslink gel, we performed systematic uniaxial tensile tests on the stress strain relation of highly deformable dual crosslink gels over a wide range of extension ratio and strain rates. We propose a new analysis method and are able to separate the stress into strain and time dependent terms from stress-strain curves, calculating the reduced stress. The strain dependent term is derived directly from rubber elasticity while the time dependent term is due to the failure of physical cross-links and can be represented as a time dependent shear modulus.

In order to interpret the time dependent term, we performed linear microrheological measurements based on diffusing-wave spectroscopy (DWS) and comparison with the corresponding chemical and physical gels were made. For the dual crosslink gel a maximum of  $G''$  was observed. We show that this relaxation mode corresponds to the associative Rouse mode characterized by  $G' = G'' \sim \omega^{0.5}$ , different from that of the physical gels ( $G' \sim \omega^2$ ,  $G'' \sim \omega^1$ ). The viscoelastic relaxation in large strain is essentially identical to the relaxation observed in small strain and can be modeled as an associative Rouse mode. We propose a stress relaxation mechanism of the PVA chains in the presence of elastically inactive but associative transient cross-links which induces incomplete stress relaxation.



Reference

T. Narita, K. Mayumi, G. Ducouret, P. Hébraud; *Macromolecules*, 46, 4174 (2013)



**Tetsuharu Narita, Ph.D.**

Research associate of CNRS (CR1)

**Affiliation**Laboratory of Soft Matter Science and  
Engineering (**SIMM**)*10 rue Vauquelin**75005 Paris*Mixed research Unit (**UMR7615**) of:*France*Ecole Supérieure de Physique et Chimie Industrielle  
(**ESPCI ParisTech**), Centre National de la Recherche  
Scientifique (**CNRS**), Université Pierre et Marie  
Curie (**UPMC**, Paris 6 University)

Tel : +33 (0)1 40 79 46 78

Tetsuharu.narita@espci.fr

**Education**

1998 – 2000 Ph.D. in Polymer Science, Hokkaido University, Sapporo (Supervisor: Prof. Yoshihito Osada)

**Career**

2007 – Research associate (1st class) of CNRS (ESPCI, Paris)

2003 – 2007 Research associate (2nd class) of CNRS (ESPCI, Paris)

2002 – 2003 Postdoctoral fellow (ESPCI, Paris)

2000 – 2002 Postdoctoral fellow (Université Louis Pasteur, Strasbourg)

2000 – 2000 Postdoctoral fellow (Hokkaido University, Sapporo)

**Research Interest**

- Physical chemistry of polymer solutions and gels
- Light scattering for dynamics of soft matter
- Rheology of polymer solutions and gels including new techniques:
  - o Microrheology by dynamic light scattering and diffusing-wave spectroscopy
  - o High frequency non-invasive rheology by surface fluctuation specular reflection spectroscopy

**Selected Publications**T. Narita, K. Mayumi, G. Ducouret, P. Hébraud; *Macromolecules*, 46, 4174 (2013)

Viscoelastic Properties of Poly(vinyl alcohol) Hydrogels Having Permanent and Transient Cross-Links Studied by Microrheology, Classical Rheometry, and Dynamic Light Scattering

S. Rose, A. Marcellan, D. Hourdet, T. Narita; *Macromolecules*, 46, 5329, (2013)

Dynamics of Hybrid Poly(acrylamide-co-N,N-dimethylacrylamide) Hydrogels Containing Silica Nanoparticles Studied by Dynamic Light Scattering

X. Di, K. Z. Win, G. B. McKenna, T. Narita, F. Lequeux, S. R. Pallela, Z. Cheng; *Phys. Rev. Lett.*, 106, 095701 (2011)

Signatures of Structural Recovery in Colloidal Glasses

T. Kajiyama, C. Monteux, T. Narita, F. Lequeux, M. Doi; *Langmuir*, 25, 6934 (2009)

Contact-Line Recession Leaving a Macroscopic Polymer Film in the Drying Droplets of Water-Poly(N,N-dimethylacrylamide) (PDMA) Solution

## Structure Formation and Rheology of Associating Polymers and Gels

Tsuyoshi Koga

Department of Polymer Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Email: tkoga@phys.polym.kyoto-u.ac.jp

Associating polymers, which are water-soluble polymers partially modified by hydrophobic groups, form various kinds of associated structures, such as intramolecular micelles, flower-type micelles, and physical gels. Due to such associated structure formation, aqueous solutions of associating polymers show characteristic rheological properties such as shear thickening, i.e., the steady shear viscosity increases with the shear rate. We have been studying the molecular mechanism of the associative structure formation and rheological properties of associating polymers by using statistical mechanical theories and molecular simulations [1-4]. In the presentation, we will discuss several topics on the associating polymers as shown below.

In the case of telechelic associating polymers which carry short hydrophobic groups at their chain ends, we study the molecular origin of characteristic rheological properties by using a transient network theory [1-2] and a non-equilibrium molecular dynamics (NEMD) simulation [3]. By NEMD simulations, we succeeded, for the first time, to show shear thickening of transient networks of telechelic polymers (Fig.1(a)). It is shown that shear thickening is mainly caused by the stress from the bridge chains highly stretched by the shear flow. We also find that fracture and shear banding of the transient network occur in the shear-thinning regime at high shear rates (Fig.1(b)).

In the case of associating polymers with many hydrophobic groups along a chain, the network formation (gelation) is suppressed by the intramolecular association. It is, however, expected that the transition from intramolecular to intermolecular associations by shear flow induces drastic change in rheological properties. By NEMD simulations, we found that drastic shear thickening occurs by gelation induced by shear flow (Fig.2).

It is well-known that clay/polymer mixtures show drastic changes in rheological properties by shear flow. In the presentation, we will discuss the formation of associated structures including gelation under shear flow studied by using molecular simulation methods (Fig.3).

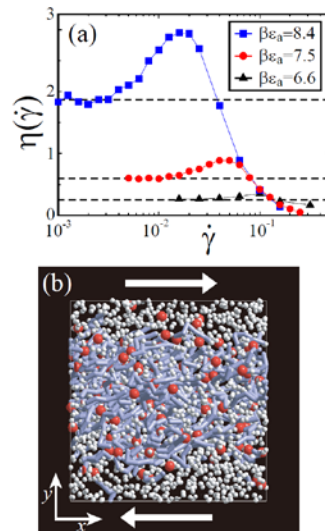


Fig.1: NEMD simulation results of telechelic associating polymers showing (a) shear thickening and (b) shear banding [3].

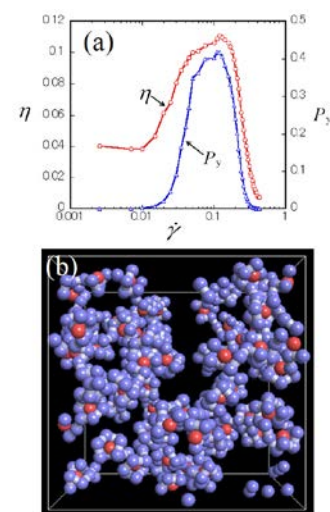


Fig.2: NEMD simulation results of colloid/polymer mixtures showing (a) shear thickening induced by gelation and (b) intra- and intermolecular micelles.

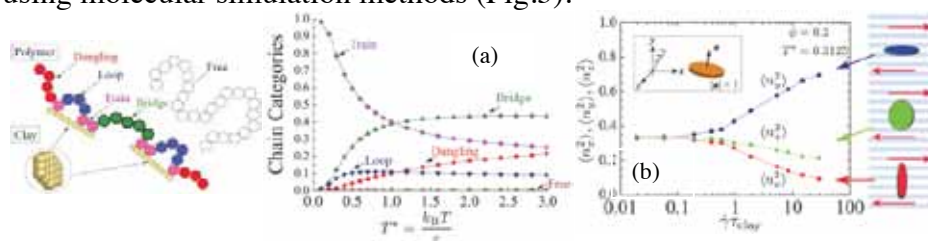


Fig.3: Molecular simulation results of clay/polymer mixtures showing (a) associative structures and (b) the orientation of clay particles under shear.

- [1] T. Koga and F. Tanaka, *Macromolecules*, **43**, 3052 (2010). [2] T. Koga, *et. al.*, *Langmuir*, **25**, 8626 (2009). [3] T. Koga and F. Tanaka, *Eur. Phys. J. E*, **17**, 115 (2005). [4] T. Koga, *et. al.*, *Macromolecules*, **41**, 9413 (2008).

## Curriculum Vitae – Tsuyoshi Koga

**Title:**

Professor

**Affiliation :**

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University  
Kyoto-Daigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

**Telephone, Fax, e-mail, Website :**

Tel: +81-75-383-2705

Fax: +81-75-383-2705

e-mail: [tkoga@phys.polym.kyoto-u.ac.jp](mailto:tkoga@phys.polym.kyoto-u.ac.jp)

URL: <http://www.phys.polym.kyoto-u.ac.jp>

**Education:**

BS : Department of Physics, Faculty of Science, Kyushu University (1988)

Ph.D. : Department of Physics, Graduate School of Science, Kyushu University (1993)

**Professional Appointments:** (*title, place, year*)

Postdoctoral Research Fellow, JSPS (Japan Society for the Promotion of Science), 1993

Researcher, Hashimoto Polymer Phasing Project, JST (Japan Science and Technology Agency),  
1994

Assistant Professor, Kyoto University, 1998

Visiting Scholar, University of Cambridge, 2001

Associate Professor, Kyoto University, 2009

Professor, Kyoto University, 2012

**Research interest:**

Polymer Physics, Polymer Statistical Mechanics, Computational Polymer Science

**Selected representative publications:**

T. Koga and F. Tanaka, “Theoretical Predictions on Normal Stresses under Shear Flow in Transient Networks of Telechelic Associating Polymers”, *Macromolecules*, **43**, 3052-3060 (2010)

T. Koga, F. Tanaka, I. Kaneda, F.M. Winnik, “Stress Buildup under Start-Up Shear Flows in Self-Assembled Transient Networks of Telechelic Associating Polymers”, *Langmuir*, **25**, 8626-8636 (2009)

T. Koga and F. Tanaka, “Molecular origin of shear thickening in transient polymer networks: A molecular dynamics study”, *Eur. Phys. J. E*, **17**, 115-118 (2005)

## High-strength elastomers inspired from double networks hydrogels

*Etienne Ducrot<sup>a</sup>, Markus Bulters<sup>b</sup>, Costantino Creton<sup>a</sup>*

<sup>a</sup> Laboratory of Soft Matter Science and Engineering, ESPCI ParisTech-UPMC-CNRS, 10 Rue Vauquelin 75231 Paris Cédex 05

<sup>b</sup>DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands

*etienne.ducrot@espci.fr*

We propose here a generic method to reinforce weak elastomers without using fillers. This method could be particularly interesting in the biomedical or high tech applications where pure polymers with specific physical properties (transparency, resistance to UV or temperature) are used but have poor mechanical properties.

In recent studies on the reinforcement of hydrogels. Gong et al have shown that hydrogels synthesized with two interpenetrating networks with very different levels of crosslinking and conformations of chains have a fracture toughness significantly enhanced relative to a single homogeneous network<sup>[1][2][3]</sup>. Their mechanical properties are enhanced through breaking the bonds of the more crosslinked and highly stretched minority network while avoiding crack propagation through the less crosslinked and unstretched majority network<sup>[4]</sup>.

We applied this method to acrylic elastomers and successfully prepared poly(alkyl acrylate) elastomers containing isotropically prestretched chains at different volume fractions, using sequential swelling/polymerization steps. Samples containing prestretched chains show an impressive enhancement of properties compared to networks polymerized in one step. Both initial modulus and fracture toughness are enhanced while retaining a negligible hysteresis and residual deformation upon unloading, which is impossible in simple networks. Our best samples show a 50 times increase in true stress at break and in fracture toughness, making those materials as tough as some filled elastomers. Our methodology holds great promise to improve the extensibility, toughness and tune the non-linear elasticity of elastomers previously thought to be mechanically too weak to be used in mechanically demanding applications.

[1] Gong, J. P.; et al, *Y. Adv. Mater.* **2003**, *15*, 1155-1158.

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[3] Gong, J. P. *Soft Matter* **2010**, *6*, 2583.

[4] Brown, H. R. *Macromolecules* **2007**, *40*, 3815-3818.

## Curriculum Vitae - CRETON Costantino

### Title(s)

Directeur de Recherche at the CNRS  
Head of International relations ESPCI ParisTech

### Affiliation

Laboratory of Soft Matter Science and Engineering, ESPCI ParisTech, 10 Rue Vauquelin, 75231 ParisCédex 05, France

### Telephone, Fax, e-mail, website:

Tel: +33 1 40 79 46 83  
Fax: +33 1 40 79 46 86  
e-mail: [Costantino.Creton@espci.fr](mailto:Costantino.Creton@espci.fr)  
url : <http://ccreton.ppm.d.espci.fr/>  
<http://www.ppm.d.espci.fr/spip.php?rubrique10&lang=en>

### Education :

1985 : Materials Science & Engineering degree, Ecole Polytechnique Fédérale de Lausanne, Switzerland  
1988: Master of Science, Cornell University, USA  
1991 : Ph. D. Cornell University, USA

### Professional Appointments:

1992-1993 : Research Fellow, IBM Almaden, USA  
1994-2001: CNRS Researcher (Assistant Professor) at the ESPCI, Laboratory of Physical Chemistry of Polymers, Paris, France  
2001- : CNRS Research Director (Professor) at the ESPCI, Laboratory of Physical Chemistry of Polymers, Paris, France

### Awards:

2000 Adhesion Society meeting (USA), best paper award  
2002 Polymer Prize of the French Polymer Society (France)  
2007 Prix Dédale of the French Adhesion Society  
2008 Polymer Physics Prize of the Journal of Polymer Science: Polymer Physics  
2011 Wake Medal of the UK Society of Adhesion and Adhesives  
2013 Prize for Excellence in Adhesion Science, The Adhesion Society (USA)

### Research Interests:

Adhesion and Fracture of Soft Materials, Mechanics of Hydrogels, Nonlinear Elasticity of Elastomers, Soft Adhesives

### Selected Publications:

1. Nase, J., A. Lindner, and C. Creton, *Pattern formation during deformation of a confined viscoelastic layer: From a viscous liquid to a soft elastic solid*. Physical Review Letters, 2008. **101**(7): p. 074503.
2. Creton, C., et al., *Large-Strain Mechanical Behavior of Model Block Copolymer Adhesives*. Macromolecules, 2009. **42**: p. 7605-7615.
3. Courtois, J., et al., *Supramolecular Soft Adhesive Materials*. Advanced Functional Materials, 2010. **20**(11): p. 1803-1811.
4. Mzabi, S., et al., *A critical local energy release rate criterion for fatigue fracture of elastomers*. Journal of Polymer Science: Polymer Physics, 2011. **49**: p. 1518-1524.
5. Sudre, G., et al., *Reversible adhesion between a hydrogel and a polymer brush*. Soft Matter, 2012. **8**(31): p. 8184 - 8193.
6. Zhang, H., et al., *Nanocavitation in Carbon Black Filled Styrene-Butadiene Rubber under Tension Detected by Real Time Small Angle X-ray Scattering*. Macromolecules, 2012. **45**(3): p. 1529-1543.

## Conformation of single polymer chain in a thin film studied by super-resolution fluorescence microscopy

Hiroyuki Aoki

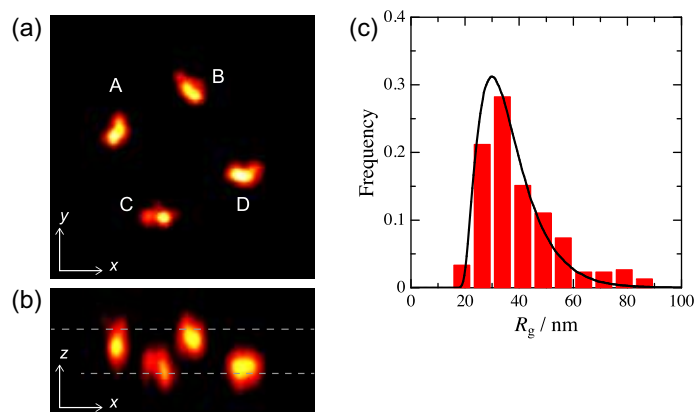
*Department of Polymer Chemistry, Kyoto University, Nishikyo, Kyoto 615-8510, Japan*

*E-mail: aoki@photo.polym.kyoto-u.ac.jp*

The unique physical properties of polymer materials result from the complexity of the conformation and dynamics of a polymer chain due to large degrees of freedom. In order to understand the fundamental properties, the direct observation of individual molecules would provide valuable information. Fluorescence imaging is the most effective method to detect a single molecule embedded in a bulk medium; however, the spatial resolution is limited to  $\sim 200$  nm due to the diffraction limit of light. We have developed fluorescence imaging techniques beyond the diffraction barrier for the real-space observation of the conformation of a single polymer chain [1-3]. Here we introduce a super-resolution microscopy method, photo-activated localization microscopy (PALM), which allows the fluorescence imaging with the spatial resolution of 20 nm.

Figure 1a shows a PALM image of single poly(butyl methacrylate) (PBMA) chains in a film with thickness of 210 nm. The conformation of each chain is clearly observed in the PALM image. PALM achieves also in the depth resolution of  $\sim 50$  nm; therefore, the three-dimensional information is available. Figure 1b shows the reconstruction image of the cross-section orthogonal to the film

plane. The chain dimension for each chain is directly evaluated from the PALM image. Figure 1c shows the histogram of the radius of gyration. The experimental data was in good agreement with the theoretical curve for a Gaussian chain. Thus, the PALM is a powerful tool to study the chain conformation. The application of PALM for the conformational analysis of a polymer chain in ultra-thin films will be presented.



**Figure 1:** Three-dimensional PALM images of single PBMA chains (a, b) and the histogram of the radius of gyration (c).

[1] H. Aoki, M. Anryu, S. Ito, *Polymer*, 46, 5896 (2005).

[2] H. Aoki, K. Mori, S. Ito, *Soft Matter*, 8, 4390 (2012).

[3] H. Aoki, K. Mori, T. Takahashi, S. Ito, *Chem. Phys.*, 419, 54 (2013).

## Curriculum Vitae – Hiroyuki Aoki

**Year of birth:**

1973

**Title:**

Associate Professor

**Affiliation:**

Advanced Biomedical Engineering Research Unit, Kyoto University,  
Nishikyo, Kyoto 615-8510, Japan

**Telephone, fax, e-mail, website:**

Tel: +81-75-383-2613

Fax: +81-75-383-2617

e-mail: aoki@photo.polym.kyoto-u.ac.jp

URL: <http://www.nano-imaging.org/>

**Education:**

BS: Department of Polymer Chemistry, Kyoto University (1996)

MS: Department of Polymer Chemistry, Kyoto University (1998)

Ph.D.: Department of Polymer Chemistry, Kyoto University (2001)

**Professional appointments:**

Assistant Professor, Kyoto University, 2001

Associate Professor, Kyoto University, 2006

**Awards:**

Inoue Research Award for Young Scientists (Inoue Research Foundation, 2002)

Konica Imaging Science Award (Konica Imaging Science Foundation, 2002)

Award for Encouragement of Research in Polymer Science (Society of Polymer Science, Japan, 2008)

Young Scientist Lectureship Award (Society of Polymer Science, Japan, 2008)

SPSJ Award for the Outstanding Paper in Polymer Journal (Society of Polymer Science, Japan, 2009)

**Research interests:**

Polymer thin film, single molecule spectroscopy, super-resolution optical techniques

**Selected representative publications:**

H. Aoki, K. Mori, S. Ito, "Conformational Analysis of Single Polymer Chains in Three Dimensions by Super-resolution Fluorescence Microscopy", *Soft Matter*, 8, 4390-4395 (2012).

T. Ube, H. Aoki, S. Ito, J. Horinaka, T. Takigawa, T. Masuda, "Relaxation of Single Polymer Chain in Poly(methyl methacrylate) Films under Uniaxial Extension Observed by Scanning Near-field Optical Microscopy", *Macromolecules*, 44, 4445-4451 (2011).

R. Sekine, H. Aoki, S. Ito, "Conformation of Single Block Copolymer Chain in Two-Dimensional Microphase-Separated Structure Studied by Scanning Near-Field Optical Microscopy", *J. Phys. Chem. B*, 113, 7095-7100 (2009).

## **Dynamics of reactive amphiphiles at liquid interfaces**

C. Monteux, F. Lequeux, P. Perrin, N. Pantoustier, L. Talini, C. Tribet, E. Chevallier

I will present a first example where we use a photoswitchable azobenzene surfactant which can change shape and hydrophobicity under UV or blue light. We have studied experimentally and theoretically the influence of light on the adsorption and desorption fluxes of these surfactants at the scale of a single air-water interface [1]. We found that light stimulation induces a flux of desorption of the surfactants from the interface and studied how this phenomenon can influence the stability of foams made with these surfactants.

In a second example I will present results concerning soft colloidal particles, PNIPAM microgel particles, which can be used to stabilize emulsions. We track their adsorption dynamics at the air-water interface using microscopy measurements [2]. We will show that unlike hard colloidal particles, their adsorption is spontaneous due to the surface activity of NiPAM monomers and moreover the particles self-assemble at the interface.

1. Chevallier et al, *Soft Matter*, 2011
2. Cohin et al. *rheologica acta*, 2013



## Curriculum Vitae – Cécile Monteux

### Titles :

Chargé de recherche CNRS

### Affiliation :

Soft Matter Science and engineering, ESPCI, 10 rue Vauquelin

### Telephone, Fax, email, website

Tel : +33 1 4079 4745

Email : [cecile.monteux@espci.fr](mailto:cecile.monteux@espci.fr)

<http://www.ppm.d.espci.fr/?article185>

### Education

Master's degree, Ecole Européenne de Chimie, Polymères et Matériaux, Strasbourg (2000)

PhD in Physical Chemistry, Ecole Normale Supérieure, Lyon (2004)

Postdoctoral fellow at Stanford University (2005)

Postdoctoral fellow at ESPCI (2006)

### Professional appointments

Chargé de recherche (Centre National or Scientific research) 2<sup>nd</sup> class (2007), First class (2011)

### Research interests

Dynamics of polymers and colloids at liquid interfaces, interfacial rheology, foams, emulsions, capsules, wetting of complex liquids

### Selected publications

"Wetting properties of charged and uncharged polymeric coatings- Effect of the osmotic pressure at the contact line", A. Tay, F. Lequeux, D. Bendejacq and C. Monteux, *Soft Matter*, 7, 4715-4722 (2011)

"Photofoams : remote control of foam stability by exposure to light using an azobenzen surfactant", E. Chevallier, C. Monteux, F. Lequeux and C. Tribet, *Langmuir*, 28, 2308-2312, (2012)

" Tracking the interfacial dynamics of PNIPAM soft microgels particles adsorbed at the air-water interface and in thin-liquid films", Y Y. Cohin, M. Fisson, K. Jourde, G. Fuller, N. Sanson, L. Talini and C. Monteux\*, *Rheologica Acta*, 52 , 445-454 (2013)

## Directed self-assembly of block copolymers

M. Takenaka and H. Hasegawa

Department of Polymer Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Email: takenaka@alloy.polym.kyoto-u.ac.jp

Extremely regular and fine nanopatterns that block copolymers (bcp) exhibit in ultrathin films are a promising candidate as the etching masks for the new and facile approach for downsizing in nanolithography. The major problem is to solve the problem how to align the bcp microdomains in a single-crystal-like array with the minimum defects. The solution is the directed self-assembly (DSA) in which the microdomain formation of the bcp is guided by the patterns prefabricated on the substrates by the top-down techniques[1]. Here we demonstrate the two techniques of DSA, one is graphoepitaxy and the other is chemical registration. To attain defect-free stripe nanopattern, we applied graphoepitaxy to self-assembly of poly(styrene-*b*-dimethylsiloxiane) (PS-*b*-PDMS)[2]. A Si-grating substrate was employed to direct the self-assembling process of PS-*b*-PDMS. The pitches of the Si grating substrates coated with PDMS. The stripe patterns in grooves are well orientated in parallel to groove walls and have long-range order.

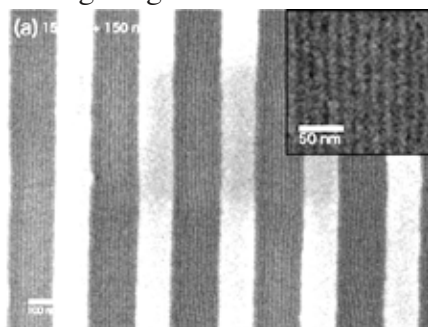


Fig. 1 SEM image of PS-*b*-PDMS on grating Si substrates with PDMS coat for 150 nm/150 nm.

As for chemical registration, we demonstrated that polystyrene-block-poly(methyl methacrylate) (PS-*b*-PMMA) can self-assemble in a well-aligned, long-range ordered nanopattern over arbitrarily large areas with chemically pre-patterned templates prepared by electron-beam (EB) lithography[3]. The epitaxial grown cylindrical microdomain formed a defect-free hexagonal lattice although the chemically patterned substrate had some defects in its pattern and errors in pattern position. Furthermore, it was demonstrated that the self-assembly process can interpolate points between the pattern generated by EB lithography, thus multiplying the pattern density as shown in Figure 2.

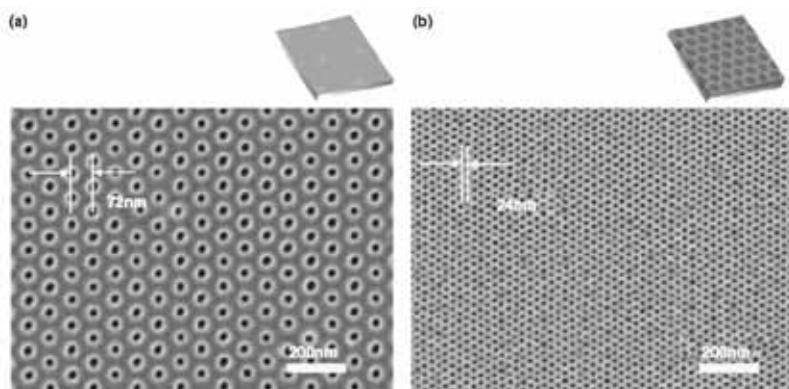


Fig. 2 (a) SEM image of EB resist on Si wafer surface for a chemically pre-patterned template with  $d_s = 72$  nm. (b) SEM image of cylinder structures of PS-*b*-PMMA with  $d_o = 24$  nm self-assembled on the chemically pre-patterned template.

[1] M. Takenaka and H. Hasegawa, *Current Opinion in Chemical Engineering*, **2**, 88-94 (2013).

[2] M. Takenaka et al, *J Polym Sci Part B Polym Phys*, **48**, 2297-2301 (2010).

[3] Y. Tada et al, *Macromolecules*, **41**, 9267-9276 (2008).

## Curriculum Vitae - Mikihito Takenaka

### Title(s):

Associate Professor

### Affiliation :

Department of Polymer, Graduate School of Engineering, Kyoto University  
Kyoto-Daigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

### Telephone, Fax, e-mail, Website :

Tel: +81-75-383-2622

Fax: +81-75-383-2623

e-mail: takenaka@alloy.polym.kyoto-u.ac.jp

URL: <http://alloy.polym.kyoto-u.ac.jp/~takenaka>

### Education:

BS : Department of Polymer Chemistry, Faculty of Engineering, Kyoto University (1986)

Ph.D. : Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University (1993)

### Professional Appointments: (title, place, year)

Instructor, Kyoto University, 1997

Lecturer, Kyoto University, 2006

Associate Professor, Kyoto University, 2011

### Awards:

CERI Best Paper Award, 2008

Award

### Research interest:

Block Copolymer Physics, Phase Transition of Polymeric Materials, Polymer Composite

### Selected representative publications:

Mikihito Takenaka and Hirokazu Hasegawa, "Directed self-assembly of block copolymers", *Current Opinion in Chemical Engineering*, **2**, 88-94 (2013)

Mikihito Takenaka, " Analyses of Structures of Rubber-Filler Systems with Combined Scattering Methods ", *Polymer Journal*, **45**, 10-19 (2013)

Yasuhiko Tada, Satoshi Akasaka, Hiroshi Yoshida, Hirokazu Hasegawa, Elizabeth Dobisz, Dan Kercher, Mikihito Takenaka, "Directed self-assembly of diblock copolymer thin films on chemically-patterned substrates for defect-free nano-patterning", *Macromolecules*, **41**, 9267-9276 (2008)

Mikihito Takenaka, Tsutomu Wakada, Satoshi Akasaka, Shotaro Nishitsuji, Kenji Saijo, Hirofumi Shimizu, Myung Im Kim, and Hirokazu Hasegawa, "Orthorhombic *Fddd* Network in Diblock Copolymer Melts", *Macromolecules*, **40**, 4399-4402 (2007)

## **Supramolecular Polymers and Colloids**

C. Soulié-Ziakovic, L. Leibler

ESPCI, Soft Matter and Chemistry Laboratory

Supramolecular polymers are classically regarded as assemblies of oligomers linked to each others by terminal H-bonding groups. Indeed, in solution, they show typical polymer-like properties and long relaxation times that can be attributed to the existence of temporary chains through directional interactions. Yet, the same oligomers, constituted of a soft and weakly polar central chain and two stiff and polar end-groups can also be regarded as ABA triblocks. In this consideration, two types of supramolecular interactions can compete: the supramolecular association through H-bonds and the microphase separation of chains on one hand and H-bonding groups on the other hand, along with the possible crystallization of the latter. We studied model systems constituted of a polyether spacer terminated at both ends by identical or different H-bonding groups selected among thymine (Thy) and diaminotriazine (DAT). Hetero-association Thy/DAT is much stronger than the self-associations Thy/Thy and DAT/DAT. However, Thy/Thy compounds are semi-crystalline whereas other combinations are amorphous. We demonstrate that phase separation and crystallisation play the major part in self-association of these compounds. We also show that microphase separation is driven by crystallization of the H-bonding units.

In a second step, we used supramolecular chemistry to prepare stable dispersions of carbon nanotubes (CNTs). Classically, dispersions of CNTs can be achieved through steric stabilisation induced by adsorbed or grafted polymer chains. Yet, in both cases, the surface modification of CNTs surfaces is irreversible and the chemical nature of the polymer chains imposes the range of solvents in which CNTs can be dispersed. To avoid this limitation, we attached DAT-end-functionalized polystyrene chains onto the surface of CNTs modified with complementary Thy units and obtained stable dispersions in apolar and aprotic solvents. By using polyether chains (PPO/PEO-DAT), stable dispersions could be obtained in polar and protic solvents. Further on, the chains were detached by using DMSO, a competitor of the Thy/DAT association, and CNTs were recovered. Thus, the reversible nature of the supramolecular interactions offers an easy way to recycle CNTs as well as the possibility to disperse the same functional CNTs in a broad solvent range, by simply adapting the chemical nature of the stabilizing chains to the dispersing medium.

## Curriculum Vitae – Corinne Soulié-Ziakovic

### Title(s):

Associate Professor

### Affiliation:

Soft Matter and Chemistry Laboratory, Ecole Supérieure de Physique et Chimie Industrielles  
ESPCI-ParisTech, 10 rue Vauquelin, 75005 Paris, France

### Telephone, Fax, e-mail, Website:

Tel: +33-1-4079-4630

Fax: +33-1-4079-5117

e-mail: [corinne.soulie@espci.fr](mailto:corinne.soulie@espci.fr)

URL: <http://www.mmc.espci.fr>

### Education:

Master's degree in engineering, Ecole Supérieure de Chimie Organique et Minérale, Paris (1989)

Ph.D. in Inorganic Chemistry : Université Pierre et Marie Curie, Paris (1993)

### Professional Appointments:

Assistant professor at ESPCI, Paris 1989

Associate professor at ESPCI, Paris 1994

Associate professor Classe Exceptionnelle at ESPCI, Paris 2009

### Research interest:

Supramolecular and reversible chemistry, nanoparticles, composites, materials.

### Selected representative publications:

P. Cordier, F. Tournilhac, C. Soulié-Ziakovic, L. Leibler, **Self-mending and thermoreversible rubber from supramolecular assembly**, *Nature* **451**, 977-980 (2008)

Cortese J., Soulié-Ziakovic C., Cloitre M., Tencé-Girault S., Leibler L., **Order\_Disorder Transition in Supramolecular Polymers**, *J. Am. Chem. Soc.*, **133**, 19672–19675 (2011)

Cortese J., Soulié-Ziakovic C., Tencé-Girault S., Leibler L., **Suppression of Mesoscopic Order by Complementary Interactions in Supramolecular Polymers**, *J. Am. Chem. Soc.*, **134**, 3671–3674 (2012)

Prevoteau A., Soulié-Ziakovic C., Leibler L., **Universally dispersible Carbon Nanotubes**, *J. Am. Chem. Soc.*, **134**, 19961–19964 (2012)

## Solid-State NMR Analysis of Donor-Acceptor Structures in Organic Solar Cells

Hironori Kaji, Tatsuya Fukushima, and Subaru Fujimura

*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

*Email: kaji@scl.kyoto-u.ac.jp*

We are now facing serious and urgent problems relating to energy resources. To surmount the problems, organic solar cells (OSCs) are expected to be an inexpensive renewable energy source. Among various approaches, fabrication of bulk heterojunction OSCs, consisting of donor polymers and acceptor fullerene-derivatives, is one of the most successful approaches to achieving excellent photovoltaic properties. Typically,  $\pi$ -conjugated polymers are used for donor polymers. However, the solubility of purely  $\pi$ -conjugated polymers to organic solvents is relatively poor, which makes the synthesis and the device fabrication difficult. To solve this problem, alkyl side-chains have been attached to the  $\pi$ -conjugated polymers, which provide better solubility. The alkyl side-chains are found to influence the device performance; therefore, the understanding of the effect of alkyl side-chains is one of the crucial issues to design better OSCs.

In this study, we investigate the effect of alkyl side-chain lengths on the donor-acceptor structures and the device performances for OSC systems consisting of regioregular poly(3-alkylthiophene-2,5-diyl) (rrP3AT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM). Three types of rrP3ATs with different alkyl chain lengths were studied; regioregular poly(3-butylthiophene-2,5-diyl) (rrP3BT), regioregular poly(3-hexylthiophene-2,5-diyl) (rrP3HT), and regioregular poly(3-dodecylthiophene-2,5-diyl) (rrP3DDT), as shown in Figure 1. The power conversion efficiency (PCE) significantly depends on the alkyl chain lengths and the thermal annealing of the devices. It was found that <sup>1</sup>H spin-lattice relaxation experiments of solid-state NMR, which reveal the donor-acceptor heterojunction structure on the order of several tens of nanometers, clearly explain the difference in the PCE for these systems.

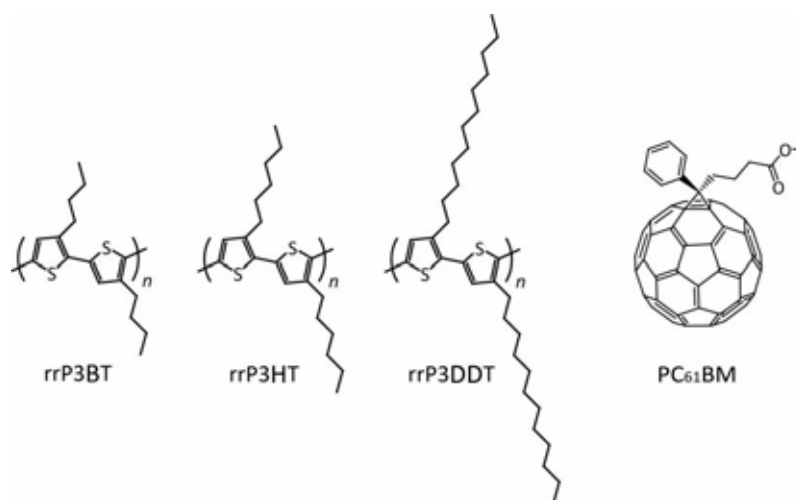


Fig. 1 Materials used in this study.

This research is granted by the Japan Society for the Promotion of Science (JSPS) through the “Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program),” initiated by the Council for Science and Technology Policy (CSTP) and by the New Energy and Industrial Technology Development Organization (NEDO) of the Ministry of Economy, Trade, and Industry (METI). This study was carried out with the NMR spectrometer in the Joint Usage/Research Center (JURC) at Institute for Chemical Research, Kyoto University.

**Hironori KAJI**

**Professor, Institute for Chemical Research, Kyoto University**

**JAPAN**

**CV**

**EDUCATION**

1985 - 1989      Kyoto University, Faculty of Engineering, B. Eng.

1989 - 1991      Kyoto University, Faculty of Engineering, M. Eng.

1991 - 1994      Kyoto University, Faculty of Engineering, Ph. D.; “Studies on Phase Separation in Silica Sol-Gel Systems Containing Formamide,” Ph. D. advisor : Professor Naohiro Soga

**EMPLOYMENT**

1994 - 2003    Assistant Professor, Kyoto University

1998 - 1999 Visiting Scientist, University of Massachusetts (as an International Fellowship by the Ministry of Education in Japan)

2002 - 2006    Japan Science and Technology Agency, PRESTO Researcher

2003 - 2009    Associate Professor, Kyoto University

2009 - Pres.    Professor, Kyoto University

**RESEARCH INTERESTS**

Organic LEDs / Organic Solar Cells / Solid-State NMR / Quantum Chemical Calculation / Synthesis

Hironori KAJI received his Ph. D in inorganic chemistry from Kyoto University in 1994 under the supervision of Professor Naohiro Soga. In 1994, he joined Institute for Chemical Research, Kyoto University, as Assistant Professor, where in 2003 he was promoted to Associate Professor and in 2009 to Full Professor. He was a visiting scientist in Prof. Klaus Schmidt-Rohr's group at University of Massachusetts from 1998 to 1999 (as an International Fellowship by the Ministry of Education in Japan). He was a research fellow of the Precursory Research for Embryonic Science and Technology (PRESTO) program in Japan Science and Technology (JST) Agency from 2002 to 2006. His research interests center on the fabrications of novel organic light-emitting diodes (OLEDs) and organic solar cells (OSCs), synthesis for the device fabrications, development of advanced solid-state NMR methodologies for the analysis of amorphous structures in the devices, and quantum chemical calculations to understand the structure-dynamics-property relationship for the devices.

## **Emulsion droplets and capsules made from stimuli-responsive amphiphilic copolymers**

**Michel Cloitre<sup>1</sup>, Clémentine Locatelli-Champagne<sup>1,2</sup>, Jean-Marc Suau<sup>2</sup>,**

<sup>1</sup> Matière Molle et Chimie, ESPCI ParisTech, 10 rue Vauquelin, 75005 Paris, France

<sup>2</sup> Coatex SAS, 35 Rue Ampère, 69727 Genay, France

The dispersion of hydrophobic substances in the form of controlled nanometer or micrometer-sized particles in aqueous solvents is central to the elaboration of many advanced materials. Important examples of applications include controlled and targeted delivery of drugs in medicine, dispersion of active substances in agriculture, elaboration of functional foods, and production of zero VOC coatings and paints. For a given application, the key to success resides in the choice of the encapsulating agent that encloses the hydrophobic substance and stabilizes the dispersion against coalescence. A great variety of solutions have been developed over the years but many of them remain limited in terms of final properties, complexity, versatility, and commercial availability for industrial-scale applications.

We will describe a flexible, scalable, and multipurpose emulsification technology that produces highly concentrated aqueous dispersions of hydrophobic particles with tunable size and interactions. The hydrophobic substance is emulsified in viscoelastic aqueous solutions of pH-responsive associative polymers consisting of associative groups sticking out a hydrophobic polyelectrolyte backbone. A variety of organic substances covering a broad range of viscosity and polarity can be encapsulated with a high degree of morphological and rheological control. To illustrate the potentiality of the technique, we will describe a general framework that connects the architecture and the composition of the amphiphilic copolymers used as surfactants to the surface and rheological properties of the continuous phase and ultimately to the characteristics of the final dispersion.



## Curriculum Vitae – Michel Cloitre

### Title:

Research Director at CNRS

### Affiliation:

Matière Molle et Chimie

ESPCI ParisTech, 10 rue Vauquelin, 75005 Paris, FRANCE

### Telephone, fax, e-mail, website:

Tel: +33-(0)1-40-79-51-15

Fax: +33-(0)1-40-79-51-17

e-mail: [michel.cloitre@espci.fr](mailto:michel.cloitre@espci.fr)

### Education:

PhD – Pierre et Marie Curie University (Paris, 1989)

### Professional Appointments:

CNRS Research Director, “Matière Molle et Chimie”, ESPCI (2001)

Teaches ‘Soft Matter and Development’ course at ESPCI

CNRS Research Scientist, the joint laboratory CNRS/Elf-Atochem (1996)

CNRS Research Scientist, Paris-Sud Orsay University (1991)

### Awards:

Groupe Français de Rhéologie (France), Maurice Couette Award, 2010

Society of Rheology (USA), Best paper Award, 2005

### Research interest:

- Structure and dynamics of soft matter: associative polymers, block copolymers, polymer-colloids, and colloidal suspensions.
- Rheology and tribology of concentrated suspensions and emulsions.
- Glasses and gels.

### Selected representative publications:

- J. Seth, C. Locatelli, F. Monti, R. T. Bonnecaze & M. Cloitre, “How do soft glassy materials yield and flow near solid surfaces?”, *Soft Matter* 8, 140-148 (2012).
- J. R. Seth, L. Mohan, C. Locatelli-Champagne, M. Cloitre & R. T. Bonnecaze, “A micromechanical model to predict the flow of soft particle glasses”, *Nature Materials* 10, 838-843 (2011).
- B. M. Erwin, M. Cloitre, M. Gauthier & D. Vlassopoulos, “Dynamics and rheology of colloidal star polymers”, *Soft Matter* 6, 2825 (2010).
- S.P. Meeker, R.T. Bonnecaze & M. Cloitre, “Slip and flow of soft particle pastes”, *Phys. Rev. Lett.*, 92, 198302 (2004).
- M. Cloitre, R. Borrega, & L. Leibler. “Rheological aging and rejuvenation in microgel pastes”, *Phys. Rev. Lett.* **85**, 4819 (2000).

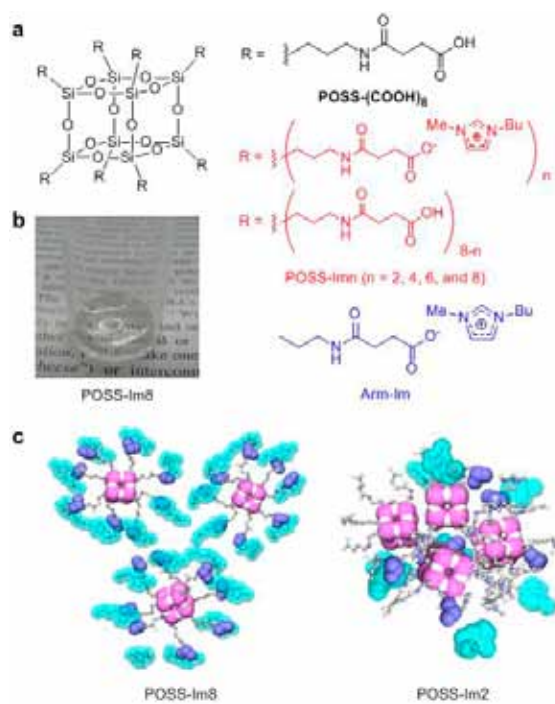
## Development of POSS-based Functional Materials

K. Tanaka and Y. Chujo

Department of Polymer Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Email: kazuol23@chujo.synthem.kyoto-u.ac.jp

A typical polyhedral oligomeric silsesquioxane (POSS) molecule possesses a cubic rigid ( $T_8$ ) structure represented by the formula  $R_8Si_8O_{12}$ , where the central inorganic core ( $Si_8O_{12}$ ) is functionalized with organic moieties (R) at each of the eight vertices. The rigid silica cube shows significant high thermal and chemical stability. Moreover, POSS can form a highly-symmetrical and star-shaped structure. Thereby, unique characteristics distinctly different from planar molecules can be expected due to such structural features. Thus, the rigid polyhedral structures have received considerable attentions as a building block for constructing functional molecules and nanometric materials. In this presentation, our recent works on advanced materials based on the functionalized POSS are reviewed. Initially, the effects on the thermal properties of ion pairs by connecting to POSS are demonstrated (Fig. 1).[1,2] A decrease of the melting temperature and an increase of the decomposition temperature of the ion pairs were simultaneously performed by connecting to POSS.[3] The roles of the structural features of POSS in the thermal properties of ionic pairs are explained.[4] Next, the POSS fillers for lowering refractive indices of polymer films will be introduced.[5] We rationally designed the series of modified POSS to produce the large exclusive volumes around POSS fillers without loss of thermal stability and mechanical property of the polymer matrices. The concept for system design and the results are explained in the presentation.



**Fig. 1** (a) Chemical structures of the ionic pairs. (b) The appearance of  $[POSS-(COO^-)_8][Bmim^+]_8$  at 25 °C. (c) The proposed conformations of the POSS-based ionic compounds.

**Table 1.** Chemical structures of octa-substituted POSS fillers and their filler effects in PMMA films

R	Refractive index <sup>a</sup>
Me	1.4916
Et	1.4901
Vinyl	1.4910
isoBu	1.4922
Octyl	1.4926
Octa	1.4917
Cp	1.4917
Ph	1.4956

<sup>a</sup>Measured by Abbe refractometer.

[1] Tanaka, K.; Chujo, Y. *Polym. J.* **2013**, *45*, 247–254.

[2] Tanaka, K.; Chujo, Y. *J. Mater. Chem.* **2012**, *22*, 1733–1746.

[3] Tanaka, K.; Ishiguro, F.; Chujo, Y. *J. Am. Chem. Soc.* **2010**, *132*, 17649–17651.

[4] Tanaka, K.; Ishiguro, F.; Chujo, Y. *Polym. J.* **2011**, *43*, 708–713.

[5] Tanaka, K.; Adachi, S.; Chujo, Y. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 5712–5717.

## Curriculum Vitae – Kazuo Tanaka

**Year of birth:**

1977

**Title:**

Assistant Professor

**Affiliation:**

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University  
Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

**Telephone, Fax, e-mail, website:**

Tel: +81-75-383-2608, Fax: +81-75-383-2607

E-mail: kazuo123@chujo.synchem.kyoto-u.ac.jp

HP: <http://chujo.synchem.kyoto-u.ac.jp/en/>

**Education:**

B.S.: Faculty of Engineering, Kyoto University (2000)

M.S.: Department of Synthetic Chemistry and Biological Chemistry, Kyoto University (2002)

Ph.D.: Department of Synthetic Chemistry and Biological Chemistry, Kyoto University (2004)

**Selected appointments:**

Postdoctoral fellow, Stanford University in USA (2004), Kyoto University (2005), and RIKEN (2006)

Assistant Professor, Kyoto University (2007)

**Awards:**

Young scientist lecture award; The Society of Polymer Science, Kansai (2009)

Encouragement of Research in Polymer Science; The Society of Polymer Science, Japan (2010).

Polymer Journal-Zeon prize (2011)

The Chemical Society of Japan Award for Young Chemists (2012)

**Research interest:**

Organic-inorganic hybrid materials, heteroatom-containing polymers, molecular imaging probes

**Selected representative publications:**

Unique Properties of Amphiphilic POSS and Their Applications, Tanaka, K.; Chujo, Y., *Polym. J.* 2013, 45, 247–254.

Advanced Luminescent Materials Based on Organoboron Polymers, Tanaka, K.; Chujo, Y., *Macromol. Rapid Commun.* 2012, 33, 1235–1255.

Advanced Functional Materials Based on Polyhedral Oligomeric Silsesquioxane (POSS), Tanaka, K.; Chujo, Y., *J. Mater. Chem.* 2012, 22, 1733–1746.

**Hybrid hydrogels: from covalent to hybrid networks.**

Alba Marcellan, Séverine Rose, Paul Elzière, Dominique Hourdet

Based on pioneering studies on self-assemblies of grafted copolymers in semi-dilute solutions<sup>1-2</sup>, we developed a new type of hybrid hydrogels. The concept relies on combining a covalent network with physical cross-links by adsorption of polymer at inorganic particle surface. Such gels imply a rather simple and versatile chemistry by copolymerization of monomer with chemical cross-linker in the presence of inorganic nanoparticle suspension (water). The first results of these so-called nano-hybrid hydrogels highlighted a very unusual combination of properties<sup>3</sup>: elasticity, strength, dissipation and strain at failure were seen to be simultaneously enhanced by silica nanoparticle addition.

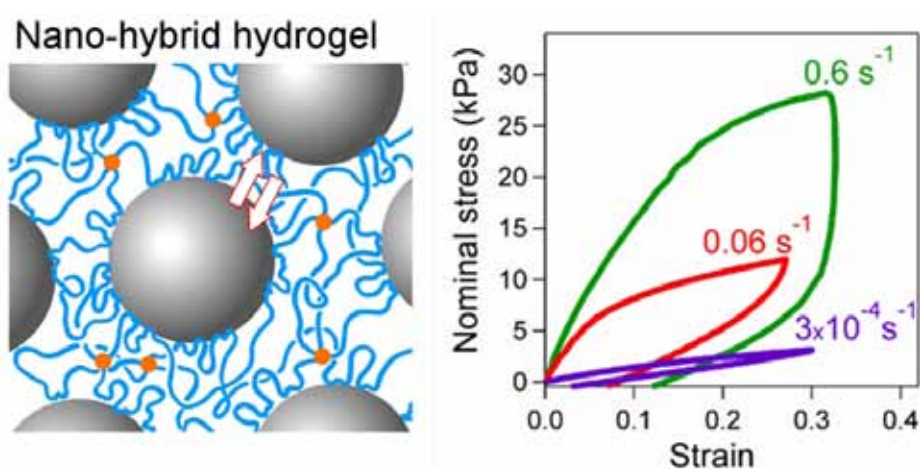


Fig.1: (a) Schematic representation of hybrid hydrogels combining covalent crosslinks (•) and physical interactions sketched by polymer chains adsorbed at the surface of nanoparticles. Arrows symbolize the exchange processes between adsorbed and unadsorbed polymer segments at particle surface. Note that structure is analogous to a double network: the chemical network controls the strain recovery thanks to the entropic restoring forces and nanoparticles promote transient and recoverable connectivity. (b) Illustration of strain rate effect on hybrid hydrogel<sup>4</sup>: loading-unloading cycles for varied strain rates (from  $3 \cdot 10^{-4} \text{ s}^{-1}$  to  $0.6 \text{ s}^{-1}$ ).

First insights on the structure (SANS) demonstrated that nanoparticles were well-dispersed in the gel, including after cyclic mechanical loading. The characteristic times involved in the nanoparticle/polymer association were investigated by large strain mechanical cycling varying the strain rate.<sup>4</sup> The mechanical behaviour of the hybrid hydrogel was observed to vary tremendously over a relatively small range of strain rates, ranging from almost non dissipative (at slow strain rates) to highly dissipative at high strain rates. However, upon cycling over time-scales of tens of seconds, the physical associations taking place between nanoparticles and the polymer network chains enabled the hydrogel to recover its initial mechanical properties. The main feature of this work is the remarkable role played by nanoparticles in the network to promote transient and recoverable connectivity by reversible adsorption/desorption processes. The strong strain rate dependence suggests that toughening mechanisms operating at standard strain rates, as often reported, maybe quite different at slower or larger strain rates.

1. Petit, Bouteiller, Brûlet, Lafuma, Hourdet, *Langmuir* 2007
2. Hourdet, Petit, *Macromolecular Symposia* 2010.
3. Carlsson, Rose, Hourdet, Marcellan, *Soft Matter* 2010
4. Rose, Dizeux, Narita, Hourdet, Marcellan, *Macromolecules* 2013

## Curriculum vitae – Alba Marcellan

### Title(s) :

Maître de conférences (assistant professor) at Université Pierre et Marie Curie (UPMC)

### Affiliation :

Soft Matter Sciences and Engineering Laboratory UMR 7615, Université Pierre et Marie Curie, École Supérieure de Physique et Chimie Industrielles.

UPMC-ESPCI-CNRS, 10 rue Vauquelin, 75005 Paris, France

Telephone, e-mail, website:

Tél: +33-1-4079-4682

e-mail: [alba.marcellan@espci.fr](mailto:alba.marcellan@espci.fr)

URL: <http://www.ppmd.espci.fr/>

### Education:

Master's degree in Materials Science and Engineering, École des Mines de Paris (2000)

Ph.D. in Materials Science, Mechanics and Modeling, École des Mines de Paris (2003)

### Professional Appointments: (title, place, year)

Maître de Conférences, UPMC (Université Pierre et Marie Curie), 2005

### Research interest:

Mechanical behaviour and fracture properties of hydrogels, elastomers and polymer fibres.

### Selected representative publications:

S. Rose, A. Dizeux, T. Narita, D. Hourdet, A. Marcellan, « Time dependence of dissipative and recovery processes in nanohybrid hydrogels », *Macromolecules*, DOI: 10.1021/ma400447j (2013).

A. Cristiano, A. Marcellan, R. Long, C.Y. Hui, J. Stolk, C. Creton, "An Experimental Investigation of Fracture by Cavitation of Model Elastomeric Networks", *Journal of Polymer Science Part-B Polymer Physics*, 48, p. 1409-1422 (2010).

A. Marcellan, A.R. Bunsell, L. Laiarinandrasana, R. Piques, "A multi-scale analysis of the microstructure and the tensile mechanical behaviour of polyamide 66 fibre", *Polymer*, 47, p. 367–378, (2005).

## Kinetics of Crystallization and Stress Relaxation in Strained Rubber Network

M. Tosaka

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan

Email: [tosaka@scl.kyoto-u.ac.jp](mailto:tosaka@scl.kyoto-u.ac.jp)

Quantitatively understanding of crystallization kinetics in strained polymer melt is still a challenging problem. This is due to experimental difficulties on quantification of extremely fast nucleation and growth in strained and supercooled polymer melt. Because the properties of most polymer products which are manufactured by injection molding or fiber spinning are largely affected by their internal fine structures, quantitative analysis of crystallization in strained polymer melt is significant.

In order to study the effect of constantly applied strain on crystallization kinetics, cross-linked natural rubber (NR) and synthetic *cis*-1,4-polyisoprene (IR) were adopted as the samples. The specimens were instantaneously expanded to a predetermined strain ratio,  $\alpha_s$ , using a specially-designed high-speed tensile tester [1]. Crystallization behavior after the cessation of deformation was investigated by the high-cycle wide angle X-ray diffraction (WAXD) measurements using the synchrotron source. Drastic progress of crystallization within a few hundred milliseconds was successfully revealed (Fig. 1).

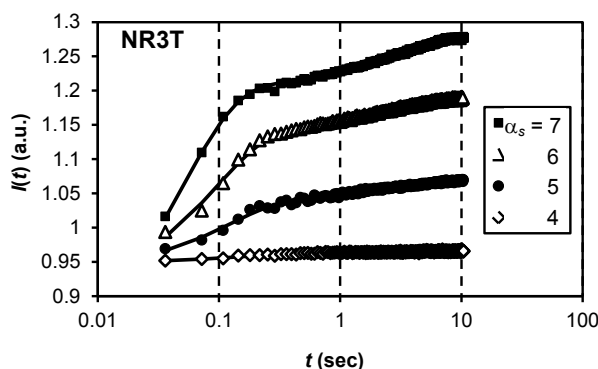


Fig. 1 Dependence of WAXD intensity  $I(t)$  with elapsed time.  $\alpha_s$  denotes the predetermined strain ratio.

The time-dependent change of diffraction intensity clarified coexistence of fast and slow crystallization processes. By fitting the data (e.g., in Fig. 1) with a double-exponential function,

$$I(t) = I_0 + I_f [1 - \exp(-t / \tau_f)] + I_s [1 - \exp(-t / \tau_s)]$$

time constants  $\tau_f$  and  $\tau_s$ , and amplitude  $I_f$  and  $I_s$ , respectively, were estimated for the fast and slow crystallization processes. The values of  $\tau_f$  were in the range of 50 to 200 ms, while  $\tau_s$  ranged between 2.5 and 4.5 s. Almost linear dependence of  $I_f$  and  $I_s$  on  $\alpha_s$  was clarified. The crystal lattice deformed almost linearly with the average nominal stress. For the fast process, correlation between crystallization and stress relaxation was not recognized, while linear relationship between them was found for the slow process [2]. Strain-induced crystallization was the major factor of stress relaxation. Some of the features found in the current study may be applicable to understand crystallization of other polymer species from oriented melt.

[1] M. Tosaka, K. Senoo, K. Sato, M. Noda, N. Ohta, *Polymer*, **53**, 864 (2012).

[2] M. Tosaka, D. Kawakami, K. Senoo, S. Kohjiya, Y. Ikeda, S. Toki, and B. S. Hsiao, *Macromolecules*, **39**, 5100 (2006).

## Curriculum Vitae – Masatoshi Tosaka

### Title:

Associate Professor

### Affiliation :

Institute for Chemical Research, Kyoto University  
Gokasho, Uji, Kyoto-fu 611-0011, Japan

### Telephone, Fax, e-mail, Website :

Tel: +81-774-38-3062

Fax: +81-774-38-3067

e-mail: [tosaka@scl.kyoto-u.ac.jp](mailto:tosaka@scl.kyoto-u.ac.jp)

URL: <http://rdb.kuicr.kyoto-u.ac.jp/researchers/view/13/en>

### Education:

BS : Department of Polymer Chemistry, Faculty of Engineering, Kyoto University (1987)

MS: Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University (1989)

Ph. D.: Doctor of Engineering, Kyoto University (2000)

### Professional Appointments: (title, place, year)

Employee, Asahi Chemical Industry Co., Ltd., 1989

Assistant Professor, Kyoto University, 1995

Associate Professor, Kyoto University, 2012

### Awards:

Young Scientist Award, The Society of Fiber Science and Technology, Japan, 1998

### Research interest:

Structure Analysis of Polymer Crystal, Crystallization of Linear Polymer, Strain-induced Crystallization of Polymer Network

### Selected representative publications:

Masatoshi Tosaka, Kazunobu Senoo, Kenta Sato, Miki Noda, and Noboru Ohta, "Detection of Fast and Slow Crystallization Processes in Instantaneously-Strained Samples of Cis-1,4-polyisoprene", *Polymer*, **53**, 864-872 (2012).

Masatoshi Tosaka, "A Route for the Thermodynamic Description of Strain-Induced Crystallization in Sulfur-Cured Natural Rubber", *Macromolecules*, **42**, 6166-6174 (2009).

Masatoshi Tosaka, Radostin Danev, and Kuniaki Nagayama, "Application of Phase Contrast Transmission Microscopic Methods to Polymer Materials", *Macromolecules*, **38**, 7884-7886 (2005).

Masatoshi Tosaka, Syozo Murakami, Sirilux Poompradub, Shinzo Kohjiya, Yuko Ikeda, Shigeyuki Toki, Igors Sics, and Benjamin S. Hsiao, "Orientation and Crystallization of Natural Rubber Network as Revealed by WAXD Using Synchrotron Radiation", *Macromolecules*, **37**, 3299-3309 (2004).

**Dynamic Wetting on a Thin Film of Soluble Polymer: Effects of Nonlinearities in the Sorption Isotherm and of Glass transition**

*Julien Dupas, Emilie Verneuil, Laurence Talini, Francois Lequeux<sup>a</sup>, Marco Ramaioli, Laurent Forny<sup>b</sup>*

<sup>a</sup> Laboratoire SIMM, ESPCI ParisTech-UPMC-CNRS, 10 Rue Vauquelin 75231 Paris Cédex 05

<sup>b</sup>Nestlé Research Center

*emilie.verneuil@espci.fr*

The wetting of a soluble polymer by its solvent is relevant to many different practical situations: dissolution of food powders, water in contact with a tablet of detergent, spreading on coatings,... Owing to the various coupled transfers between the solvent and the soluble substrate, the wetting dynamics of a solvent droplet onto a soluble polymer is complex. Here, we focus on the spontaneous spreading of a sessile water droplet on a hydrosoluble polymer film. We study two aspects: the effect of non-linearities in the sorption isotherm of the polymer absorbing water. <sup>[1]</sup> The polymer is then hygroscopic. And second, we investigate the effect of the glass transition in water content that the polymer undergoes when water is absorbed, on the wetting dynamics.

First, we demonstrate that the advancing of the droplet is controlled by the amount of liquid absorbed by the polymer. We show that the more hydrated, the more hydrophilic the substrate is, and the less the contact angle is. More importantly, we show that the hydration is controlled by the water transferring through the vapor phase by evaporation from the droplet itself, and by condensation onto the polymer. The condensed water will later diffuse through the polymer layer. We are able to derive a model to account for this hydration mechanism and its effects on the spreading dynamics. In particular, we show that the non-linearities in the sorption isotherms, a common feature shared by many hydrophilic polymers, result in a strongly distorted hydration profile of the substrate ahead of the contact line, and a dependence of the contact angle with the contact line speed that differs from the classical Cox-Voinov laws.

Second, we show how glass transition accelerates the spreading dynamics: starting from an initially glassy polymer layer, the polymer undergoes a glass transition from glassy to melt when the polymer is hydrated by the transfers of water ahead of the contact line of a spreading droplet. We demonstrate that wetting dynamics is accelerated when the polymer melts, and this wetting transition is sharp when plotted into a contact angle/contact line speed graph. We are able to quantitatively predict the transition by relating the water content of the polymer at the contact line to the contact line velocity. We show that the transition is due to drastic changes in the polymer properties upon melting, namely, the diffusion coefficient of water is much larger in melts, and the visco-elastic dissipation is maximized at the glass transition, yielding dissipation in the substrate.

[1] J. Dupas, et al., *Langmuir* **29** (40), pp 12572–12578 (2013)



**Curriculum Vitae – Emilie VERNEUIL**

**Title(s)**

Chargé de recherche at the CNRS

**Affiliation**

Laboratory of Soft Matter Science and Engineering, ESPCI ParisTech, 10 Rue Vauquelin, 75231 Paris Cédex 05, France

**Telephone, Fax, e-mail, website:**

Tel.: +33 1 40 79 47 42

Fax: +33 1 40 79 46 86

e-mail: [emilie.verneuil@espci.fr](mailto:emilie.verneuil@espci.fr)

url : <http://www.ppm.d.espci.fr/spip.php?article326>

**Education :**

2002 : Ecole Supérieure de physique et Chimie de Paris, France

2002: Master of Science, UPMC, Paris, France

2005 : Ph. D. UPMC, Paris, France

**Professional Appointments:**

2009: CNRS Researcher at the ESPCI, Laboratory of Physical Chemistry of Polymers (SIMM) Paris, France

**Research Interests:**

Wetting of soluble polymers by a solvent, Dissolution of polymer powders, Mechanical properties of polymer foams

**Selected Publications:**

1. J. Dupas, E. Verneuil, M. Ramaoli, L. Forny, L. Talini, F. Lequeux, " Dynamic Wetting on a Thin Film of Soluble Polymer: Effects of Nonlinearities in the Sorption Isotherm" *Langmuir* **29** (40), pp 12572–12578 (2013)
2. K.N. Nordstrom, E. Verneuil, PE Arratia, A. Basu, Z Zhang, AG Yodh, JP Gollub, DJ Durian "Microfluidic Rheology of soft colloids above jamming" *Physical Review Letters* **105** (17) 175701 (2010)
3. K.N. Nordstrom, E. Verneuil, WG Ellenbroek, TC Lubensky, JP Gollub, DJ Durian "Centrifugal compression of soft particle packings: Theory and experiment" *Physical Review E* **82** 041403 (2010)
4. E Verneuil, ML Cordero, CN Baroud, F. Gallaire "Laser-induced force on a microfluidic drop: origin and magnitude" *Langmuir* **25** (9) 512734 (2009)
5. E. Verneuil, R.J. Phillips, L. Talini, "Axisymmetric two-sphere sedimentation in a shear thinning viscoelastic fluid: Particle interactions and induced fluid velocity fields" *Journal of Rheology* **51** (6) 1343-1359 (2007)
6. M. Lamblet, E. Verneuil, P. Silberzan, T. Vilmin, L. Léger, "Adhesion enhancement through micropatterning at polydimethylsiloxane-acrylic interfaces", *Langmuir* **23** pp 6966-6074 (2007)
7. E. Verneuil, B. Ladoux, A. Buguin, P. Silberzan "Adhesion on microstructured surfaces" *The Journal of Adhesion*, **83** pp 1-24 (2007)
8. D. Bartolo, F. Bouamrirène, E. Verneuil, A. Buguin, P. Silberzan, S. Moulinet, "Bouncing or sticky droplets: impalement transitions on micropatterned surfaces", *Europhys. Lett.* **74** pp 299-305 (2006)



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## Posters

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## Topological interaction between semiflexible ring polymers

D. Ida and T. Yoshizaki

Department of Polymer Chemistry, Kyoto University, Katsura, Kyoto 615-8510, Japan

Email: ida@molsci.polym.kyoto-u.ac.jp

A Monte Carlo (MC) study is made of the second virial coefficient  $A_2$  of semiflexible ring polymers in the unperturbed ( $\Theta$ ) state by the use of the ideal discrete Kratky–Porod (KP) wormlike ring. The behavior of the effective volume  $V_E$  excluded to one ring by the presence of another, resulting only from the topological interaction, is examined as a function of the reduced contour length  $\lambda L$ , where  $\lambda^{-1}$  is the stiffness parameter and  $L$  is the total contour length. Figure 1 shows double-logarithmic plots of the dimensionless quantity  $\lambda V_E/L^2$  proportional to  $A_2$  against  $\lambda L$ . The MC data ( $\circ$ ) first increases along the theoretical values of the rigid ring (dotted straight line) in the range of  $\lambda L \lesssim 0.1$ , then deviates downward progressively from the line with increasing  $\lambda L$ , and finally decreases after passing through a maximum at  $\lambda L \simeq 5$ . An interpolation formula (solid curve) useful for practical purposes is constructed on the basis of the MC results so obtained. A comparison with available literature data for ring atactic polystyrene in cyclohexane at  $\Theta$  shows that the present MC results may qualitatively explain the behavior of the data.

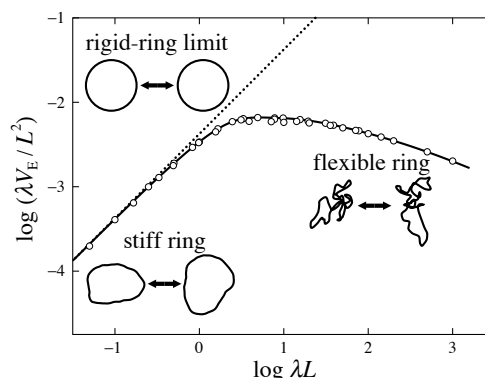


Fig. 1. Double-logarithmic plots of  $\lambda V_E/L^2$  against  $\lambda L$ .

## Statistical Thermodynamic Theory of Heat-induced Gelation and Crosslinked Structure of Methylated Polyrotaxanes in Water

Hiroyuki Kojima and Tsuyoshi Koga

Department of Polymer Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Email: kojima@phys.polym.kyoto-u.ac.jp

Heat-induced gelation of aqueous solutions of methylated polyrotaxanes was reported experimentally[1]. By means of several experimental techniques, such as X-ray diffractometry, small-angle neutron scattering, and dynamic light scattering, it has been suggested that aggregates of methylated  $\alpha$ -cyclodextrins (Me- $\alpha$ -CDs) are formed along each chain, and crosslinking occurs by forming crystal-like structures of Me- $\alpha$ -CDs with increasing temperature. It is thought that dehydration and aggregations of Me- $\alpha$ -CDs play an important role in this gelation. But, there seems to be a lack of theoretical understanding in this phenomena. In this study, to understand the relation between the sol-gel transition and the structure of Me- $\alpha$ -CD aggregates, we constructed a statistical-thermodynamic model considering (i) dehydration of Me- $\alpha$ -CDs, (ii) intramolecular and (iii) intermolecular aggregations of Me- $\alpha$ -CDs (Fig.1). We calculated the sol-gel transition line, and also examined the average length of the one-dimensional aggregates, and the multiplicity of the junctions.

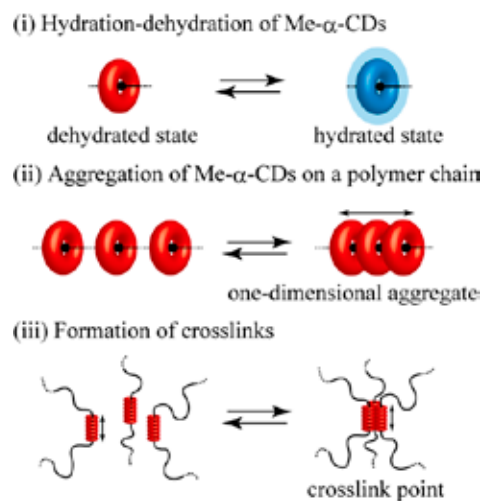


Fig. 1 Schematic pictures of (i) dehydration, (ii) intramolecular and (iii) intermolecular aggregations of Me- $\alpha$ -CDs.

[1] M. Kidowaki, C. Zhao, T. Kataoka, and K. Ito, *Chem. Commun.* **39**, 4102-4103, (2006).

### Structural and mechanical properties of nanogel-crosslinked materials

Sada-atsu Mukai,<sup>1,2</sup> Yoshihide Hahsimoto,<sup>1,2</sup> Yoshiro Tahara,<sup>1,2</sup> Shin-ichi Sawada,<sup>1,2</sup> Kazunari Akiyoshi<sup>1,2</sup>  
<sup>1</sup>Graduate School of Engineering, Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8510 Japan,  
<sup>2</sup>JST-ERATO  
 Email: mukai.sadaatsu.8e@kyoto-u.ac.jp

In aqueous solutions, cholesterol-bearing pullulan (CHP) molecules form gel-like spherical structure which is called nanogels. Nanogels have excellent properties as carriers for drug delivery system: for example, drug encapsulation ability and protein chaperon-like activity. Recently, we developed nanogel cross-linked materials such as nano- and micro-size gel particles, and macrogels. For the purpose of developing new nanogel-based functional materials, it is important to evaluate and control their mechanical properties. Mechanical properties depend on not only compositions but also gel structures. In this study, we prepared CHP nanogel-crosslinked materials which had internal structures, and measured viscoelastic properties. We observed macrogels by laser scanning confocal microscope and obtained 3-dimensional structures. We performed dynamic viscoelastic measurements by oscillating rheometer. We will compare their structures and viscoelastic properties, and discuss the relation between them.

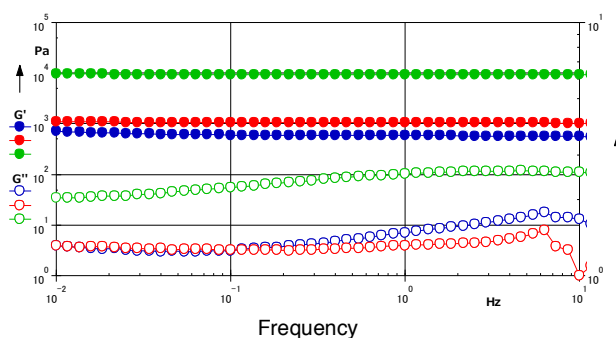


Figure 1. Frequency dependence of storage (closed circle) and loss (open circle) modulus. Red, blue and green symbols mean low PEG content nanogel-crosslinked gel, high PEG content gel and freeze-thaw porous gel, respectively.

### Fabrication of Cellulose Nanofibers Grafted with “Concentrated” Polymer Brushes for Highly Lubricating Materials in Aqueous Medium and Resin Nanocomposites

K. Sakakibara,<sup>1</sup> K. Maeda,<sup>1</sup> K. Ohno,<sup>1</sup> and Y. Tsujii<sup>1,2</sup>  
<sup>1</sup>Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan  
<sup>2</sup>CREST, Japan Science Technology Agency (JST)  
 Email: sakaki@scl.kyoto-u.ac.jp

Cellulose nanofibers (CNFs) possess good physical properties such as strength and elasticity. Their hybrid materials with well-defined polymeric grafts can be designed for a particular function with good mechanical properties, leading promising applications such as nanocomposites, ionics materials, biointerfaces, tribomaterials, and liquid crystals. As polymeric grafts, recent studies have revealed that the high-density polymer brushes, called “concentrated” polymer brushes (CPBs), have structures and properties quite different and unpredictable from those of traditional polymer brushes (Fig. 1A) [1]. Herein, we report on fabrication of CNF/CPB composite materials for high lubrication in aqueous medium (Fig. 1B). Another approach will be described for fabrication of plastic (HDPE) reinforced with CNFs using novel diblock-copolymer-type polymer dispersants as a versatile method toward resins nanocomposites (Fig. 1C).

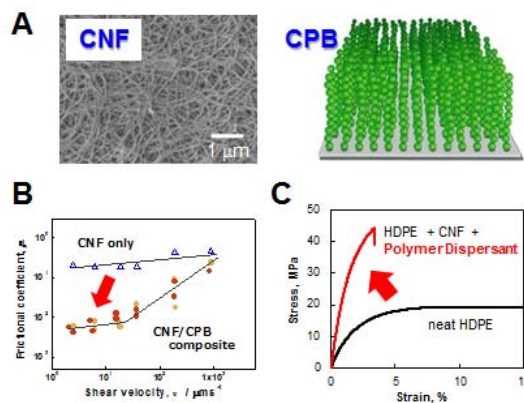


Fig. 1 (A) SEM image of CNF and a schematic illustration of CPB, (B) Plot of frictional coefficient ( $\mu$ ) of CNF-CPB composites, against shear velocity ( $v$ ), (C) S-S curves of HDPE-CNF composite with a polymer dispersant.

[1] Tsujii, Y.; Ohno, K.; Yamamoto, S.; Goto, A.; Fukuda, T. *Adv. Polym. Sci.* **197**, 1-45 (2006).

## Microgel-Core Star Polymers via Living Radical Polymerization: Smart Synthetic Strategy and Functional Compartments

T. Terashima and M. Sawamoto

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University  
Katsura, Nishikyo-ku, Kyoto 615-8510, Japan; Email: terashima@living.polym.kyoto-u.ac.jp

Microgel-core star polymers intriguingly have crosslinked cores that are covered and thereby solubilized by linear arms, to serve unique functional compartments for catalysis and molecular recognition [1]. We herein report the recent advances in the synthesis, characterization, and functions of microgel-core star polymers via metal-catalyzed living radical polymerization, focusing on the following topics (Figure 1).

**a) Fluorous microgel star polymers:** Capture of polyfluorinated compounds (PFCs) in water and stimuli-responsive release of the core-bound PFCs; water purification from PFCs.

**b) Arm-cleavable star polymers:** Direct analysis of microgel cores (molecular weight, size, density, viscosity); a novel synthetic strategy of well-controlled and functionalized microgels.

**c) Single-chain patched polymers:** New star polymers comprising a single main chain, obtained from the selective intramolecular crosslinking of self-folded amphiphilic copolymers in water.

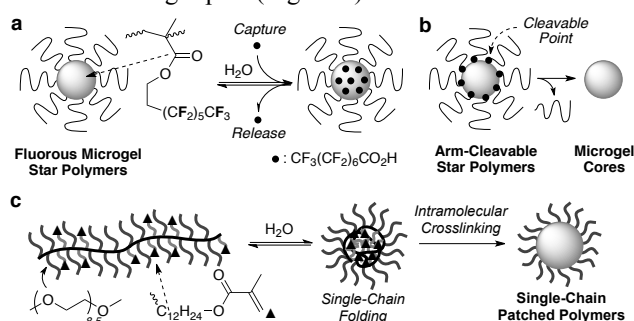


Fig. 1. Microgel-core star polymers: design and function.

[1] Terashima, T.; Sawamoto, M. in Matyjaszewski, K., Sumerlin, B. S. & Tsarevski, N. V. eds. *Progress in Controlled Radical Polymerization: Materials and Applications*, ACS Symposium Series **1101**, 65-80 (2012).

## Molecular Weight between Entanglements for Polysaccharides

J. Horinaka, Y. Urabayashi, R. Yasuda and T. Takigawa

Department of Material Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan  
Email: horinaka.junichi.5c@kyoto-u.ac.jp

The molecular weight between entanglements ( $M_e$ ) is the average spacing of entanglement network of polymers and  $M_e$  in the molten state ( $M_{e,melt}$ ) is a material constant reflecting the inherent nature of polymer chains. However, the relation between  $M_{e,melt}$  and the chemical structure of polymer chain has not been fully understood. In this study, we determined  $M_{e,melt}$  values for various polysaccharides from the rheology of concentrated solutions of polysaccharides, as shown in Table 1, and discussed their relation with the chemical structure in terms of the number of polysaccharide units between entanglements along the backbone ( $N_{unit}$ ). It should be noted that the linkage of monosaccharide units affects  $N_{unit}$  values; for example,  $N_{unit}$  for amylose is much larger than cellulose in spite of the same monosaccharide unit.

Table 1 Entanglement network of polysaccharides

polysaccharide	$M_{e,melt} / 10^3$	$N_{unit}$
cellulose	3.2-3.5	20-22
pullulan	11	68
curdlan	12	71
amylose	24-25	148-154
guar gum	4.6	19
tara gum	3.2	15
locust bean gum	2.7	13
gellan	2.3	14

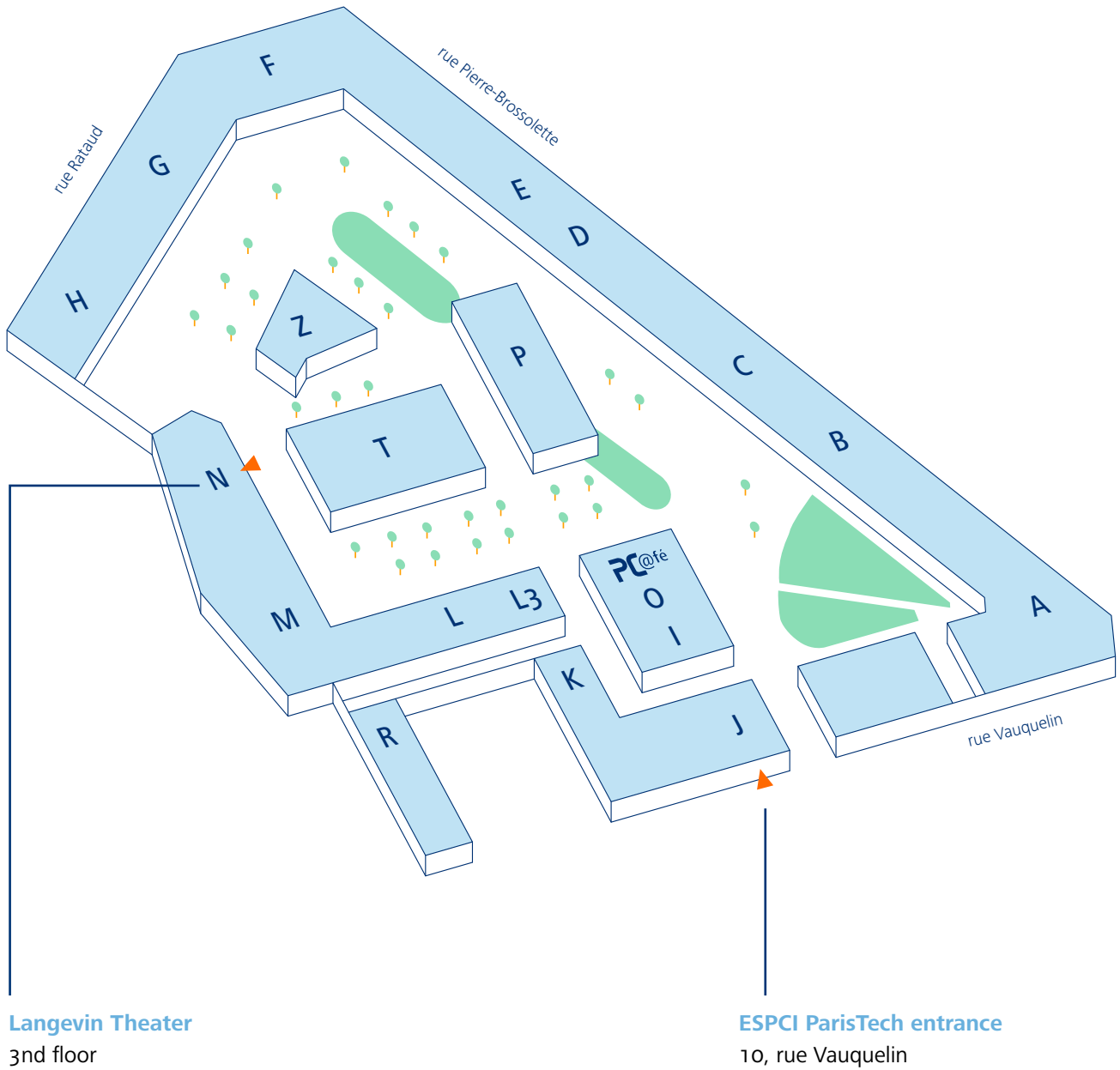
### References:

- Horinaka, J.; Yasuda, R.; Takigawa, T. *Carbohydr. Polym.*, **2012**, 89, 1018.
- Horinaka, J.; Yasuda, R.; Takigawa, T. *J. Polym. Sci. Part B: Polym. Phys.* **2011**, 49, 961.





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