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Soft
Materials

Soft Materials

There are 114 different types of atoms.*
 As for molecules, which are specific combinations of atoms, their varieties are infinite.
 Immensely diverse materials are artificially divided into different groups based on their utility or purpose.

There is a category called metallic materials.
 Materials can be divided into organic and inorganic materials.
 Structural materials, used to construct large structures such as buildings and bridges, are yet another category.
 Materials that possess particular functions are called functional materials, and they include optical functional materials and electrically conductive materials.

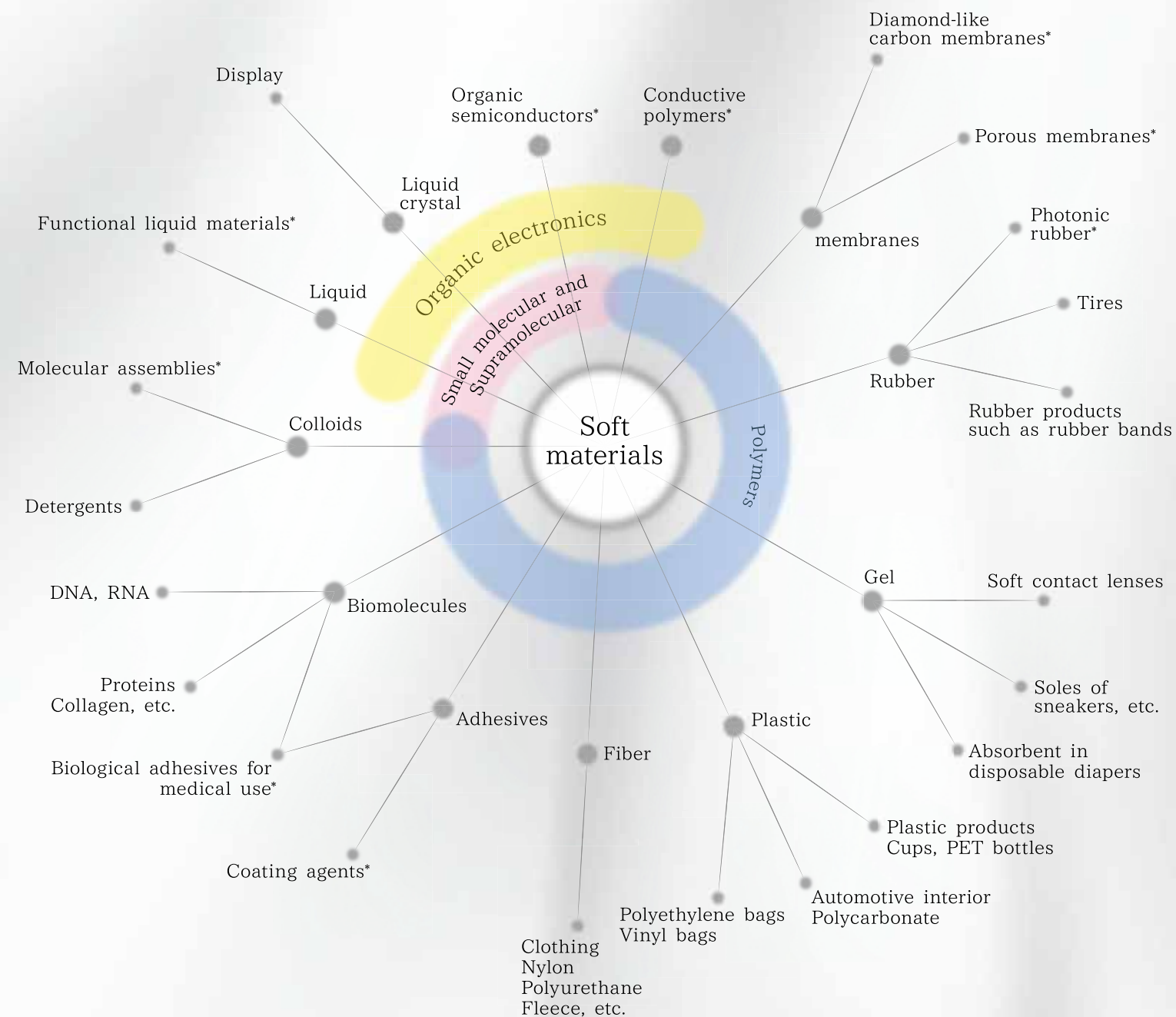
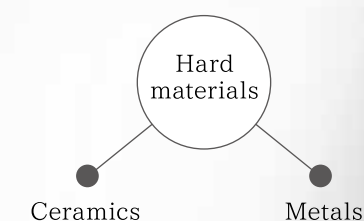
Amid the different existing classifications, materials can be divided into soft Materials and hard materials, focusing on the hardness of materials.
 In this issue, we will feature soft materials.

The definition of soft materials is somewhat vague.
 Can a material be called a soft material solely on the basis of its softness?
 What are the chemical bonding states of soft materials?
 How soft are soft materials?
 How do you create them?

A wide variety of materials are categorized as soft materials simply because they are “soft.”
 There must be more depth to the meaning of being soft.

Some materials are valuable because of their softness.
 Soft materials are now attracting the attention of many people.

* Based on the nomenclature determined by the International Union of Pure and Applied Chemistry (IUPAC) in 2012



*major research of soft materials at NIMS

What are soft materials?

“What is the history of the development of soft materials? What are the latest developments with soft materials, and what is the current status of soft material research at NIMS? We asked Izumi Ichinose, director of the Polymer Materials Unit at NIMS, about these issues.

Soft materials are multifarious

For materials for manufacturing, a certain level of hardness makes the shaping process easier and helps retain the shape. However, hard materials are not suitable for every need. For example, it is vital for clothing materials to be soft in texture. Also, if automobile tires were made of hard materials, riding would be uncomfortable.

Most of soft materials, which are fibers and rubbers for instance, used to be harvested in nature (i.e., from plants and animals), processed and used for various purposes.

On the other hand, with progress in the modernization of society and industrialization, making materials lighter has become important. Generally, hard materials such as soil, metal and wood are heavy. With respect to structural materials that are used to build large constructions such as bridges, their characteristic of being heavy is in fact crucial. However, with respect to automobiles, aircraft, certain building materials, electronics products and precision machines, the use of light materials is becoming increasingly more important.

The rapid advancement in and spread of science after 1900 led to the prevalence of organic synthesis, including the development of artificial soft materials. As the molecular structure and bonding state associated with soft materials of natural origin had been identified, research and development of artificial soft materials also advanced. Today, artificial soft materials are considered to be major materials and are used in combination with hard materials such as metals and ceramics. Representative soft materials include plastics, synthetic rubbers, synthetic fibers, liquid crystals, gels and biomolecules, and their demand is continuing to increase.

Development of soft materials at NIMS

Since its foundation in 2001, NIMS has been making great efforts in research on soft materials, particularly on polymer materials. Since there was no such research function in the two predecessors of NIMS (the National Research Institute for Metals and the National Institute for Research in Inorganic Materials), NIMS set up a new research unit referring to research establishments overseas, especially the Max Planck Institute in Germany. It has been over 10 years since soft materials research began at NIMS. Today, such efforts are beginning to pay off in diverse ways.

NIMS has developed new soft materials such as filtration membranes made of porous carbons, electrically conductive organic materials, adhesive agents with new functions, and smart polymers. What is important next is to consider environments where these materials will be used, says Izumi Ichinose of NIMS.

“When developing a new material, you need to think about what it is for. For example, if a material is intended for display purposes, we use a material with optical and electronic functions. Also, the environment in which such material is used changes. I expect that materials that can be used in close vicinity to the human body including wearable circumstances or in one’s living environment might have demand. If you were to try to make something that is comparable to a display device with 4K or higher resolution, which is becoming mainstream nowadays, you would have almost no chance of winning the market competition in terms of many aspects such as production cost. However,

if a new material enabled furnishings and clothing to have unprecedented richness and depth of colors, the material would be valuable. From such viewpoint, I am attempting to develop organic materials such as those that are wearable or that can be used in everyday life to meet individuals’ preferences. I keep human interface materials in mind.”

Looking ahead to the future of soft materials

At NIMS, we are developing new functional materials using various polymer processing technologies, and seeking new ways of using them. At the same time, we are also engaging in basic research on a macromolecular assembly having a new molecular structure or unique physical properties.

The right way to design new physical properties is to go back to the viewpoint of molecular structures. But that approach is insufficient when dealing with macromolecules. That is because in gigantic molecules such as macromolecules, the physi-

cal properties of the material are greatly influenced by factors such as the length of the molecule, the degree of bending in the molecule, and the arrangement of the molecule relative to the adjacent ones. We aim to identify the behavior of macromolecules from various viewpoints in order to apply the research findings to the electronics or biological fields.

When macromolecule is formed through the self-organization of small molecules, it is called a supramolecular polymer. In February 2014, NIMS succeeded in controlling the length of supramolecular polymers for the first time in the world. The control of the self-organization process is the most fundamental and basic step in material designing. We don’t expect to be able to produce a new material using supramolecular polymers in the immediate future, but we believe that our knowledge and experience will be useful in establishing guidelines for designing new materials.

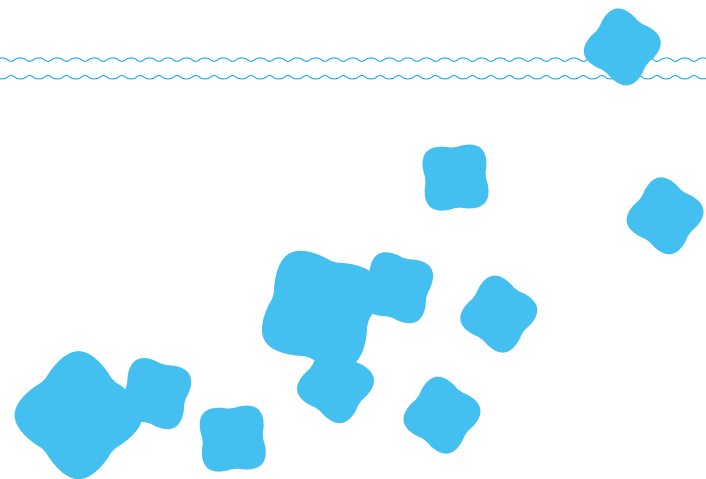
“Since NIMS is a national research institute, ensuring public credibility is essential. In addition, it is critical for us to maintain a broad vision to gain new knowledge. And this vision must be our original, not based on somebody else’s idea. We aim to apply our vision all the way to the material. To achieve this, I believe that in-depth basic research is the key.” (Ichinose)

More than 20 years have passed since the winner of the 1991 Nobel Prize for physics Pierre-Gilles de Gennes made his acceptance speech titled “Soft matter.” Soft materials with new functions may change our lives.



Izumi Ichinose
Unit Director, Polymer Materials Unit,
Advanced Key Technologies Division, NIMS

How to Create Soft Materials



Controlling the lengths of polymers

Polymers are used commonly in soft materials. A polymer is defined as a long string-like molecule consisting of numerous covalently bonded small molecules (i.e. monomers). The process of linking monomers is called polymerization, and the kinds of monomers and the polymerization method used determine the characteristics of the resulting soft materials.

For example, polyisoprene ((C₅H₈)_n), which is a chain of n molecules of isoprene (C₅H₈), is a synthetic rubber that is stretchable just like natural rubber.

During the polymerization, the end of this string structure holds a so-called “growing species,” which is capable of reacting with monomers. Depending on the kinds of growing species, polymerization is classified into different types such as ionic polymerization (anionic and cationic polymerization), in which ionic species are used, and radical polymerization, in which radicals¹ are used.

Currently, radical polymerization is most commonly used in industrial applications due to the availability of diverse monomers.

In general, the lengths of these “strings” (or polymers) differ greatly. This is due to inconsistent “initiation” and “propagation” of polymerization among different polymers, and by side reactions related to the chain transfer and termination reaction of radicals. These inconsistencies make quality control challenging.

So-called living polymerization was developed to achieve more precise polymerization (i.e., making the lengths of polymers consistent) by controlling the initiation and the propagation of polymerization and preventing side reactions.

Living polymerization was first reported in 1956 for anionic polymerization (living anionic polymerization), and thereafter, its application was extended to polymerization using other growing species. However, it had been more difficult to control the highly

reactive free radicals used in radical polymerization than to control the stable anions and cations used in ionic polymerization. In 1995, living polymerization was finally achieved also for radical polymerization; since then, living radical polymerization has been established as a new polymerization technique and used widely as a method to create high-quality and high-performance polymers.

In recognition of their accomplishments in research and development of living radical polymerization, Professor Mitsuo Sawamoto at Kyoto University and Professor Krzysztof Matyjaszewski at Carnegie Mellon University received numerous awards including the NIMS Award in July 2014.

Creating desirable shapes using polymers with uniform lengths

Junko Aimi at NIMS has been conducting research primarily on block copolymers. A block copolymer consists of two or more

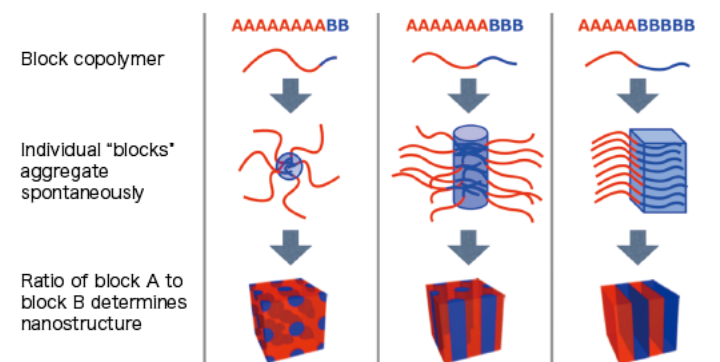


Fig. 1. Various block copolymers
Both block A and block B have a tendency to aggregate with their own block types. When these blocks are connected, various kinds of nanostructures are created based on the lengths of the resulting block copolymers.

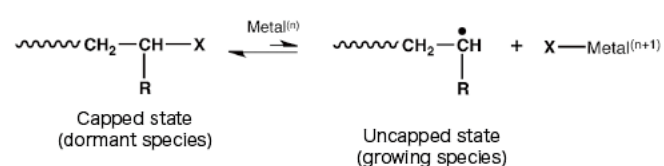


Fig. 2. Living radical polymerization
Professor Mitsuo Sawamoto and Professor Krzysztof Matyjaszewski publicized their studies around the same time. The major difference between their studies was the fact that Sawamoto used ruthenium and iron as transition metal catalysts whereas Matyjaszewski used copper. X is acting as a cap.

kinds of monomers as illustrated in Figure 1, and each kind of monomer forms clusters (blocks) in a polymer. Well-defined block copolymers are synthesized by living polymerization. The distinctive 3-dimensional nanostructure of a block copolymer is determined by how the two kinds of monomers, molecule A and molecule B, are linked together, in terms of length, ratio, and sequence.

“Precise control of the size and arrangement of the molecule A blocks and molecule B blocks allows the block copolymer to express its unique function. We are currently developing a new material for optoelectronic applications by creating a charge transporting pathway in a polymer film” (Aimi).

Now, let’s take a close look at living polymerization. Aimi says, “Ordinarily, the growing species at the end of a polymer is capped, but it is uncapped occasionally, which then allows the polymer to propagate” (Figure 2).

In normal chain-growth polymerization, the terminal of a polymer bears a growing species, and the growth of the polymer is essentially uncontrollable. In living radical polymerization, the terminal of a polymer holds a “dormant species.” A dormant species by itself does not induce propagation (capped state), but it can be converted into a growing species by a catalyst (uncapped state), allow-

ing polymerization of monomer molecules to proceed. During the propagation, most polymer terminals hold a dormant species (capped state), and thus, only a small amount of terminals holds a growing species, so hardly any side reaction takes place. Accordingly, this method enabled creating polymers of uniform length even in radical polymerization.

Furthermore, since a dormant species is capable of undergoing repeated reactions, it can be used to link m individuals of molecule A and then continue to link n individuals of molecule B in living radical polymerization. As such, this method allows creating various kinds of well-defined block copolymers. There are many different kinds of living radical polymerization, and this method is continuing to evolve.

Applying living polymerization to supramolecular polymers

In conventional polymers, monomers are linked in chain-like fashion by covalent bonds. On the other hand, so-called “supramolecular polymers” are a chain-like assembly formed by the phenomenon of “self-organization” where monomers spontaneously aggregate by relatively weak non-covalent bonds such as hydrogen bonds and coordinate

bonds. They are used in the fabrication of well-defined nanostructures. As demonstrated by the fact that important biological functional systems such as photosynthesis and nervous systems are the products of self-organization, supramolecular polymers are expected to revolutionize the fields of materials science and nanotechnology.

“What is intriguing about supramolecules is their reversible nature of being able to both assemble and dissociate due to the weak non-covalent bonds between molecules,” says Kazunori Sugiyasu. At the same time, this very characteristic of supramolecules makes them difficult to handle.

Self-organization of supramolecules basically occurs spontaneously. As well, due to their nature of readily assembling and dissociating, control over the growth of supramolecular polymers was once considered a very difficult task.

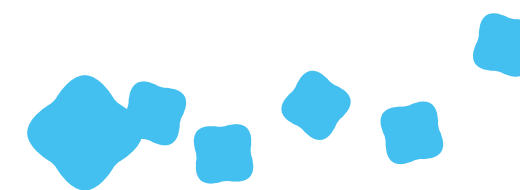
In February 2014, Sugiyasu and co-workers published an article in *Nature Chemistry*². It was a ground-breaking paper as it presented the point that living polymerization is applicable to supramolecular polymerization and that the technology can be used to precisely control the lengths of supramolecular polymers.



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Controlling self-organization by designing monomers

Aimi, who studies polymers, says, "We have been using conventional monomers such as styrene and methyl methacrylate." On the other hand, Sugiyasu, who studies supramolecular polymers, says, "The design of monomers is vital." That is because, in the case of supramolecules capable of self-organization, the structure of the monomer molecules virtually determines the nature of the assembly.

Figure 3 (a) shows a novel porphyrin molecule which is designed and synthesized by Sugiyasu to be ideal for use in supramolecular polymerization. In a normal self-organization process, there is only one pathway through which molecules transform from a monomer state into a supramolecular polymer (organized state). Monomers aggregate spontaneously and form chain-like polymers.

On the other hand, there is two pathways for this new porphyrin molecule to self-organize: one is leading to a particle aggregate, and the other to a supramolecular polymer.

When the porphyrin molecule is dispersed in a solvent as monomer, first, eight to 10 of them loosely assemble by hydrogen bonds, forming a nano-sized (about 10 nm in diameter) particle aggregate^{*3}. This is because nearly no energy is required for these monomers to form the particle aggregate while a certain level of energy is required for them to form into the supramolecular polymer. As such, monomers first form the particle aggregate. Since the aggregate is loosely bonded, it is suspended in solution as the molecule reversibly assembles and dissociates.

Then, a small amount of "seeds" of supramolecular polymers are added to the solution containing dispersed particle aggregates. These seeds are made of supramolecular polymers that are grown from the same porphyrin molecules, and fragmented into very short pieces. What happens next?

While individual monomers dissociates from the aggregate, they assemble at the ends of the seeds and grows into a supramolecular

polymer. This is because the energy level of a supramolecular polymer is lower than that of an aggregate, and porphyrin molecules ultimately transform into a supramolecular polymer with the aid of the seeds (the particle aggregate is a metastable state. Figure 3 (b)).

This means that the initiation of self-organization of a supramolecular polymer was successfully controlled, although such achievement had been popularly thought to be unlikely. It was found after examining the behavior of these molecules that the polymerization of porphyrin molecules involves a mechanism similar to that associated with living polymerization.

In fact, by changing the ratio between the amount of seeds added and the amount of particle aggregates, lengths of supramolecular polymers were controlled. As such, living supramolecular polymerization was realized for the first time in the world.

"The importance of living polymerization in academia and industry has been verified in the long history of polymer chemistry. I think that this research revealed the vast potential of supramolecular polymers. So far, we have ob-

served living supramolecular polymerization using only this porphyrin molecule. However, we are looking into other molecular designs with similar polymerization properties," says Sugiyasu.

New molecular design is expected to lead to the emergence of novel functions. It is also expected that many more new polymerization methods will be developed, and (supramolecular) polymers will be used to create new soft materials that no one has ever thought of before.

(by Akiko Ikeda)

Note
*1:Radicals: molecular or atomic species that have unpaired electrons. They are generally unstable, and most of them are impossible to isolate. They are often assumed as reactive intermediates in reactions and decomposition.
*2:Press release: <http://www.nims.go.jp/eng/news/press/2014/02/p201402030.html>
*3:Aggregate: state where two or more molecules of the same species congregate by relatively weak intermolecular forces of attraction.

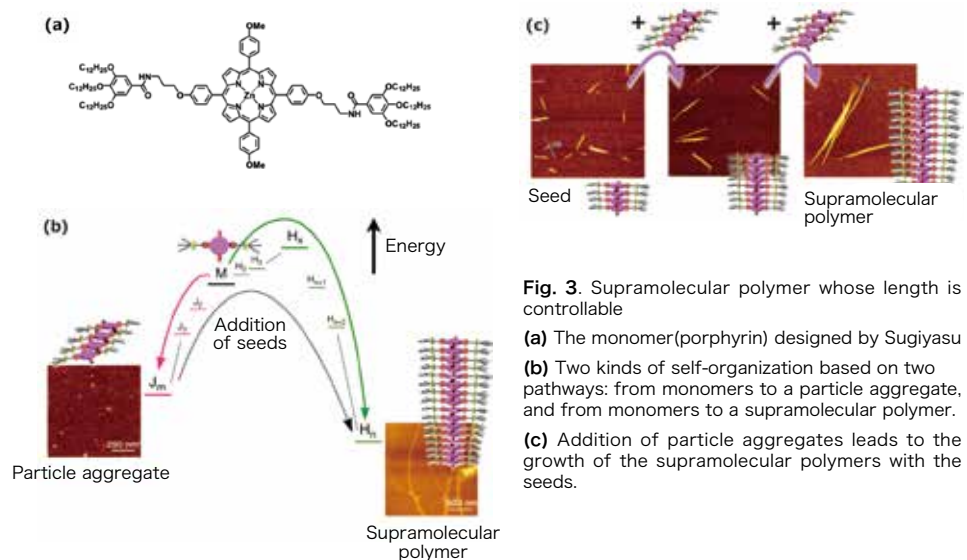


Fig. 3. Supramolecular polymer whose length is controllable
(a) The monomer(porphyrin) designed by Sugiyasu
(b) Two kinds of self-organization based on two pathways: from monomers to a particle aggregate, and from monomers to a supramolecular polymer.
(c) Addition of particle aggregates leads to the growth of the supramolecular polymers with the seeds.



Our research on the Living polymerization

Upon receiving the NIMS award 2014, Prof. Matyjaszewski and Prof. Sawamoto, sent us comments on their research on living radical polymerization.

--What inspired you to carry out this research based on which you won the NIMS Award?

My interest in radical polymerization grew in the early 1990s when the development of living cationic polymerization and the precision synthesis of polymers thereby appeared, at least to us, to begin maturing. Around at that time, as the general principle of "dormant-active species equilibrium" had been established in a variety of living polymerizations, we began to realize that a carbon-halogen bond, critical in controlling cationic polymerization, dissociates not only heterolytically into ions but homolytically into radicals upon catalysis, and this realization led us to seriously consider to apply the latter to developing living radical polymerization, which the peers also began to consider a "last frontier" in precision polymerization. So, we embarked to explore catalysts that

would not be Lewis acid catalysts but something different which induce the homolytic dissociation of carbon-halogen bonds. After some unsuccessful attempts, we came to consider late transition metal complexes as catalysts and eventually discovered the carbon tetrachloride/ruthenium complex initiating system.*

--What kinds of materials and fields do you think this polymerization method has been contributing or will contribute to?

Nature creates biopolymers (e.g., genes, proteins, and enzymes) that, from a polymer chemistry viewpoint, are mostly precision-controlled "condensation" polymers, namely, macromolecules with a heteroatom-based backbone. Then, we often ask to ourselves: "After billions of years of evolution, why did Nature not choose chain-growth polymerization for biopolymer synthesis?" Or, "Could we pioneer a new area of polymer science by creating similar artificial polymers and macromolecules of similar precision by a chain-growth process that, by definition,

gives carbon-chain backbone with pendent functionality?" We are now considering answers to these questions, particularly to sequence control.

In our view, the materials that our precision polymerizations may provide and possibly contribute to society include advanced sealants, polymer electrolyte solid films for lithium secondary batteries, pigment dispersants, surfactants, photoresists, high-performance adhesives, and core-functionalized star polymers for molecular recognition and hazardous chemicals separation. All these have been synthesized by us and others, while some being commercialized.

*This research was first published in *Macromolecules* in 1995 by us then in the group of Professor Toshinobu Higashimura (Professor Emeritus of Kyoto University), where Lewis acid-catalyzed living cationic polymerization has also been developed. The initial-phase experiments for living radical polymerization were carried out by Mitsuru Kato, then a second-year Masters student now working at Kuraray Company. Equally important contribution and leadership obviously came from Professor Masami Kamigaito (Nagoya University), then a JSPS research fellow in our group whose keen insight and devotion eventually led to the ruthenium complex.



Mitsuo Sawamoto

After graduating from the Department of Engineering, Kyoto University, acquired a Ph.D. from Kyoto University Graduate School. 29th president of the Society of Polymer Science, Japan. Currently a professor at Kyoto University. <http://living.polym.kyoto-u.ac.jp/sawamoto.html>

-- What inspired you to carry out this research based on which you won the NIMS Award?

After developing controlled/living ionic polymerization of various vinyl and heterocyclic monomers, we recognized the challenge of controlling radical polymerization to the same extent. The impact of realizing such systems could be enormous, since nearly half of all polymers are made by conventional radical polymerization, yet providing ill-defined polymers with uncontrolled molecular weight and broad molecular weight distribution. We approached this challenge by detailed kinetic analysis and decided to employ a catalytic process based on atom transfer radical addition, ATRA, a very selective reaction used by synthetic

organic chemists. We adopted this system to polymer synthesis and developed atom transfer radical polymerization, ATRP. Now ATRP systems employ thousand times less catalyst than ATRA and can be run at parts per million Cu-based catalysts in benign solvents such as water in the presence of sugars or Vitamin C as reducing agents.*

--What kind of material fields do you think that ATRP will contribute to in the future?

ATRP is very well suited for synthesis of precisely designed and constructed polymers with complex architecture. New opportunities are offered by covalently linking synthetic (co)polymers made by ATRP with inorganics and natural products. The resulting hybrid materials, with properties

not available before, can find many new applications from very efficient dispersants, antifouling and very low friction surfaces to drug and gene delivery systems. ATRP can link various organic polymers to proteins and nucleic acids. It can be used for synthesis of intelligent, stimuli responsive materials with self-healing and shape memory properties. We have signed 16 commercial licenses and production of polymers by ATRP started in Japan by Kaneka Corp. in 2004.

*The first paper on ATRP published in 1995 has been cited 3447 times (ISI Web of Science, 01.01.2015)



Krzysztof (Kris) Matyjaszewski

After graduating Technical University of Moscow, he received his doctorate from the Polish Academy of Sciences, and completed a postdoctoral fellowship at the University of Florida. He is now professor at the Carnegie Mellon University. <http://www.cmu.edu/maty/matyjaszewski/>

Diverse applications of Soft Materials

Soft materials are used in a wide range of situations.

The challenge of soft material researchers, in addition to meeting the basic requirement of making materials soft, is to come up with how to add required functions to their materials.

In this section, the current research on soft materials will be presented in terms of five usage categories: electronic function, biomaterials, optical function, adhesives and separation function.

1 Electronic function

Creating electronic devices based solely on soft materials

Organic materials are light-weight and inexpensive. They are flexible and combustible. Taking advantage of such characteristics of organic materials, innovative electronic devices have been developed. Organic materials, however, normally do not conduct electricity. So, research had been carried out to find out how to run electric current through organic materials. So far, doping has been found to be effective in making organic materials electrically conductive as with inorganic semiconductors. However, the conventional doping method has had a problem of making the materials chemically unstable.

To deal with this problem, Yuka Kobayashi at NIMS discovered a totally different doping technique. Her method not only may allow the creation of highly stable electronic devices using organic materials alone, but also may allow for devices to be operational

using extremely low power.

“The key is a salt bridge,” says Kobayashi. Salt bridges refer to ionic hydrogen bonds, which are frequently observed in biological macromolecules such as proteins. Kobayashi found that if certain organic molecules are bound together by salt bridges, and a salt bridge network is formed, then protonic defects spontaneously occur in the network, which give rise to the same effect as a conventional doping reagent do (Figure 1). She also found that using this phenomenon, electric current can run through this organic molecule with only very low voltage.

Kobayashi is considering developing a large-screen, power-saving and flexible display by using this organic molecule as a material to generate transparent electrodes.

To make the display flexible, it is also indispensable to develop electric wiring that

will not break when the display is bent and unbent repeatedly. Metal wiring is currently used for this purpose in the conventional rigid devices. However, there is a concern that it might break or come off if the display is subjected to repeated bending and stretching. Consequently, Jin Kawakita at NIMS developed a material for wiring that has electric conductivity in a metal level and can tolerate bending.

The material is made of conductive polymers that are coated with fine metal particles (Figure 2). The organic polymer called polypyrrole was used as a conductive polymer, and silver was used as fine metal particles. This combination improved electric conductivity by two orders of magnitude compared to commercial polypyrrole alone.

Kawakita explains, “This wiring material is strong against bending because the silver

that covers the surface of the polypyrrole is in the form of fine particle aggregates. These particles respond well to the shape-changing polypyrrole.”

Another advantage of this material is that it can be manufactured quickly. “This technology is still in the study phase, but I would really like to develop it as electrode technology, which is one of the keys to next-generation electronics,” says Kawakita enthusiastically.

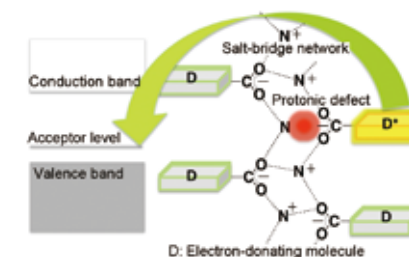


Fig. 1. When a salt bridge network is formed, protonic defects occur in the network, working as a dopant.

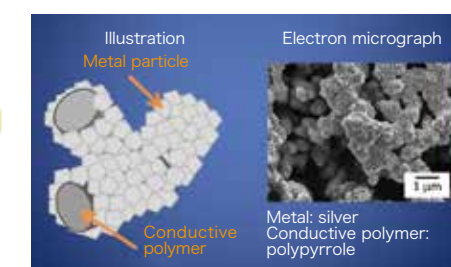


Fig. 2. Conductive polymer covered with fine metal particles

Next-generation material for realizing multi-color electronic paper

Electronic paper is expected to serve as an alternative to printed materials such as newspapers and books. It is currently available only in monochrome display. Colorization research has been carried out, but full-fledged commercialization has yet to be achieved. The “metallo-supramolecular polymer” which Masayoshi Higuchi at NIMS developed exhibits excellent electrochromic property (Figure 3). Electrochromism refers to the phenomenon where color change occurs when electric current is passed through a material. A metallo-supramolecular polymer is a polymer consisting of organic ligands and metal ions. By applying a voltage to the polymer for a few seconds to change the amount of electric charge in the metal ions, charge

transfer occurs from the metal ions to the organic ligands, generating a color. Unless voltage is applied again, the color remains the same. The color can be adjusted by the kinds of metal ions used. The use of iron, copper and ruthenium generate blue, green and red, respectively. Moreover, by adjusting the voltage applied, the color intensity



Fig. 3. Colors produced by metallo-supramolecular polymers

and tone can be changed.

Using metallo-supramolecular polymers containing several metal ion species, Higuchi demonstrated the potential of thin, multi-color electronic paper.

“I hope that application of this material will help reduce environmental impact and energy consumption.” (Higuchi)

Yuka Kobayashi
Organic Materials Group, Polymer Materials Unit, NIMS

Jin Kawakita
Semiconductor Device Materials Group,
Nano-Electronic Materials Unit,
Nano-Materials Field, MANA, NIMS

Masayoshi Higuchi
Group Leader, Electronic Functional Materials Group,
Polymer Materials Unit, NIMS

2 Biomaterials

Soft human tissue is potentially a perfect niche for soft materials

As a branch of advanced medicine, regenerative medicine has been receiving increasing attention. However, “Surprisingly, much remains still unknown about cell micro-environment that promotes tissue formation. Cell micro-environment has been a hot research topic for biomedical scientists around the world,” says Naoki Kawazoe of NIMS. He has been developing scaffold materials to efficiently guide cells into functional tissues (Figure 4). He is using collagen, a naturally-occurring polymer as

a raw material of scaffold. This scaffold material features a precise pattern of pores that accommodate cells. Such a scaffold material has not developed until recently because it was difficult to fabricate a pattern of pores on sponge-like soft materials.

To prepare the scaffold material, an arbitrary pattern of water droplets is firstly drawn on a cooled copper plate and is frozen. Then, collagen solution is poured on the pattern and the construct is freeze-dried. It seems easy, but when the collagen

solution is poured, strict control of temperature is required to prevent the pattern of ice from melting. “We have successfully prepared a collagen sponge with controlled pore size and arrangement. This scaffold material can be used to examine the effect of pore size and arrangement on tissue formation,” says Kawazoe. Additionally, his group also succeeded in controlling a vascular network by using a scaffold in which proteins that promote the growth of vascular cells are patterned. This scaffold

material is expected to be useful in regenerative medicine.

“Smart polymers” exhibit various functions in response to stimuli such as temperature and light. Mitsuhiro Ebara at NIMS has recently been attracting attention after he developed a sheet material for cancer treatment which responds to alternating magnetic field. His next major project is to create artificial organs that will take full advantage of the characteristics of soft materials. (Figure 5) “I will use biodegradable smart polymers. By the time that the material positioned in a human body is about to completely break down, somatic cells gradually enter the scaffold polymer and develop into a new organ.”

In this procedure, the hardness of the scaffold polymer needs to be adjusted as the regeneration of the organ progresses, to maintain suitable environment for cell growth. To achieve this, Ebara says that he will use smart polymers that fulfill various functions in response to an external stimulus. In addition, if a drug needs to be administered to a target organ, it can be placed in the smart polymers before applying the polymers into the body. The drug can be released with precise timing by sending a stimulus to the smart polymers from outside.

To create the kinds of artificial organs that Ebara is envisioning, there are still issues to overcome such as developing biodegrad-

able polymers that are as soft in texture as real organs. However, all necessary technologies are steadily becoming available, and the creation of such artificial organs is no longer a distant dream.

Naoki Kawazoe
Tissue Regeneration Materials Group, Tissue Regeneration Materials Unit, Nano-Bio Field, MANA

Mitsuhiro Ebara
Smart Biomaterials Group, Biomaterials Unit, Nano-Bio Field, MANA

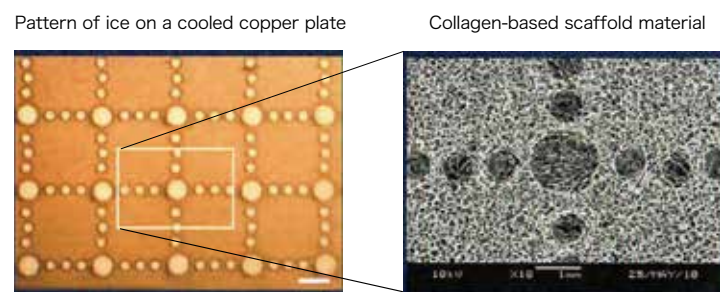


Fig. 4. Scaffold material used for tissue regeneration

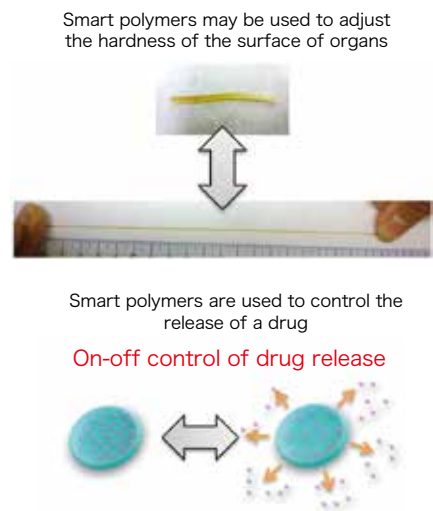


Fig. 5. Concept of smart polymers applicable to artificial organs

3 Optical function

Soft materials that control light

The development of optical devices, such as organic EL displays that use light-emitting organic materials, has been advancing. Conventional organic materials are unstable and short-life time. In addition, the molecules that constitute the coloring materials commonly aggregate causing discoloration. To address these issues, Takashi Nakanishi at NIMS developed a new organic material. His end product was a luminescent organic material made by connecting branched alkyl chains of organic soft-hydrocarbon molecules (Figure 6). Oligo *p*-phenylenevinylene (OPV) molecules and anthracene molecules were used as the source of luminescence. These luminescent molecules are protected from aggregating by covalently attaching bulky and soft alkyl chains to them. As a

result, the intrinsic luminescent properties of the molecules can be expressed, and the material’s durability against light and heat was greatly improved. Furthermore, attaching alkyl chains to these luminescent molecules converted the material from a solid to liquid state, which is quite environmental friendly solvent-free liquid state when one can consider its further fabrication processing. Liquid OPVs and anthracenes emit blue light. By mixing existing phosphors to this liquid, you can easily formulate luminescent liquids that emit various colors including white (Figure 6). “Many applications of luminescent liquids are possible, such as using them as lighting devices and displays, by coating ceilings and walls with them. In cooperation with industries, we would like to

come up with practical applications of this technology as early as possible.” (Nakanishi) NIMS researchers are focusing on light and color. Colorful subjects as opals, jewel beetles and kingfishers have in common. They don’t possess pigments per se, but they do possess so-called structural color, which means that their fine surface structure reflects only light of certain wavelengths. Hiroshi Fudouzi in NIMS developed a photonic rubber sheet made of structural color materials. The rubber sheet changes color as deforming the shape as shown in Figure 7. To create this material, he coated a suspension containing fine particles of about 0.2 microns in diameter on a thin substrate plate. This process produces regularly-spaced layers of the fine particles in a

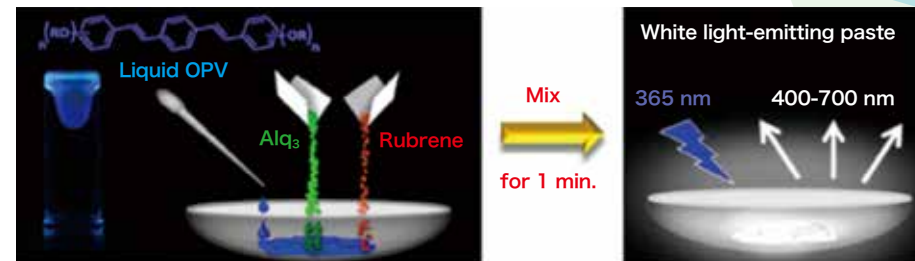


Fig. 6. Luminescent color tuning in a luminescent liquid



Fig. 7. Photonic rubber sheet

self-assembling manner. The gaps between the fine particles are filled and fixed by polymers. The resulting layers with about 5 microns thickness reflect light of only certain wavelengths thereby showing structural colors.

The wavelength of the reflecting light changes with the distance between the fine particles, so if the substrate plate is made of

easily deformable materials such as plastic or rubber sheet, the surface color changes only on the deformed part of the plate. “For example, if these photonic rubber sheets are glued onto the surfaces of metal or concrete, you would be able to clearly identify where deformations occurred in these structures,” says Fudouzi. He is currently carrying out joint research with Public Works Research

Institute and Hiroshima University to achieve commercialization of the rubber sheet.

Takashi Nakanishi
MANA Independent Scientist, MANA, NIMS

Hiroshi Fudouzi
Applied Photonic Materials Group,
Photonic Materials Unit, NIMS

4 Adhesives

Coating agents that mimic the system of sessile organisms, and adhesives that are applied to human tissues

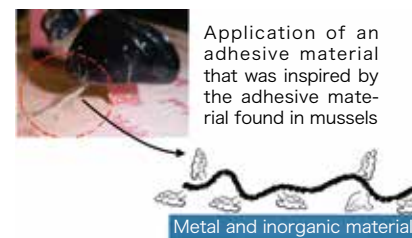


Fig. 8. Concept of coating agent developed by NIMS. Theoretically, this coating agent can be used even if the thickness is less than 10 nm. It has a great potential to improve adhesives and antifouling paint.

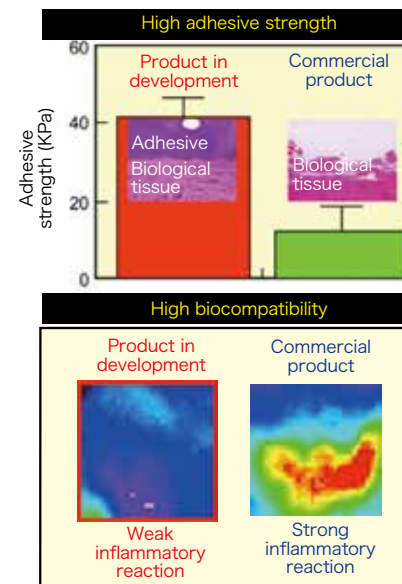


Fig. 9. Biological adhesive with high biocompatibility and high adhesive strength

The bodies of living creatures and materials are generally soft in texture. Inspired by a sessile organism, a coating agent that adheres to various materials was created. Masanobu Naito at NIMS developed this coating agent. He previously developed a coating material that prevents attachment of mussels to the hull of a ship by incorporating a mussel-repelling material into resin. Naito said, “This time, I came up with the idea by changing my way of thinking 180°.” He used the adhesion mechanism of mussels as a model (Figure 8).

Naito says, “Through my research, I intend to build a bridge between soft materials and hard materials.” The coating agent he invented has a property to adhere to a variety of materials. This is because, as illustrated in the figure, this adhesive has a residue that bind to both with hard materials such as metal and inorganic materials, and soft materials. So, this adhesive is expected to have a broad range of applicability for diverse combination of materials.

Adhesives have already been used to close wounds in clinical field. However, their performance is not fully sufficient. “The requirements of such adhesives are high adhesive strength and high biocompatibility,” says Tetsushi Taguchi at NIMS. He developed an adhesive that meets such requirements using collagen extracted from marine organisms as a main ingredient (Figure 9). He successfully fulfilled both requirements by integrating a hydrophobic group into collagen, which facilitated the infiltration of the adhesive into extracellular matrix and cells. “But this adhesive is still not good enough for actual medical treatment use.” Thus, further study was conducted to make the adhesive solidify more quickly without causing severe inflammatory reactions, and to make the adhesive more absorbable by the human body as wounds heal. As a result, an improved adhesive was created by using collagen with a lower melting point, which was obtained from marine

organisms. This helped clinicians spend less time heating and melting adhesives before using them. Also, the addition of a polyethylene glycol-based cross-linker

allowed the adhesive to solidify within three minutes. These were major accomplishments that made more prompt medical treatment possible.

Masanobu Naito
Catalytic Materials Group, Environmental Remediation Materials Unit, Environment and Energy Materials Division, NIMS

Tetsuchi Taguchi
Smart Biomaterials Group, Biomaterials Unit, Nano-Bio Field, MANA

5 Separation function

Membrane materials that separate impurities

The group led by Izumi Ichinose has been engaging in research and development of polymeric materials that are used to purify water by separating impurities.

Group members, Yoshihisa Fujii and Sadaki Samitsu, successfully developed a separation membrane which has holes of 10 nm diameter and is only 35 nm thick. A separation membrane is a filter made of a polymeric material called a diamond-like carbon. In a chemistry sense, this material stands between diamond and graphite. When polluted water is filtered through this membrane, which prevents impurities greater than 1 nm from passing, pure water can be attained (Figure 10).

Making smaller holes in a separation membrane will allow separation of even smaller impurities. However, this modification will decrease the processing rate per unit of time. The challenge of developing separation membranes was to come up with a technology with which polluted water can be filtered without compromising the processing rate. Due to its thinness and toughness, diamond-like carbon was the ideal material for addressing such challenge.

“The thinner the separation membrane, the faster liquids pass through it. Diamond-like carbon membranes are thin and strong. In addition, unlike conventional plastic separation membranes, they are resistant against petroleum, chemical agents and high temperatures. For this reason, we also thought that diamond-like carbon membranes would be useful in processing the large amount of water produced with crude oil,” says Fujii.

Concurrent with the project involving diamond-like carbon membranes, the research group is also developing polymeric porous materials (Figure 11). This is a

plastic material with numerous holes of 10 nm diameter. About 50% of the porous body consists of empty space and it has an extremely high specific surface area. Due to its property of absorbing oil, this plastic material can be used to filter the wastewater produced at oil refineries. This material can also be used for pre-treatment of polluted water before the water is filtered through a diamond-like carbon membrane, in order to improve treatment efficiency.

“The challenge was to figure out how to create numerous holes of 10 nm diameter in plastic materials,” says Samitsu. The research group eventually decided to use a technique called the phase separation method. Specifically, they dissolved a plastic material in a solvent of dimethylformamide, and quickly cooled it down. To acquire the right-sized holes, the key was

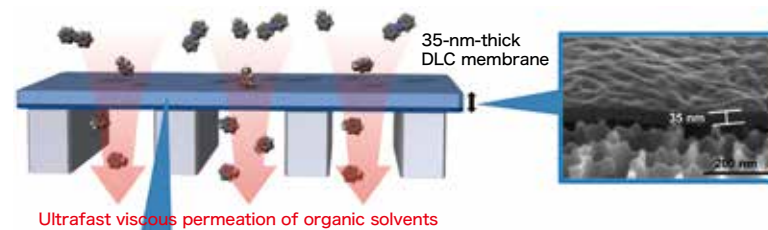
to determine the rate of cooling and final cooling temperature.

Samitsu says that the advantage of using soft materials as filters is their good reusability. The plastic absorbs oil from wastewater at room temperature, but when the material is heated to about 80°C, it softens and oil begins to come out. By removing the separated oil, the material can be used repeatedly.

“The market needs for separation membranes are expected to rise even further. We will continue to develop separation membranes incorporating the advantages of soft materials.”

Yoshihisa Fujii
Separation Functional Materials Group, Polymer Materials Unit, NIMS

Sadaki Samitsu
Separation Functional Materials Group, Polymer Materials Unit, NIMS



Ultrafast viscous permeation of organic solvents

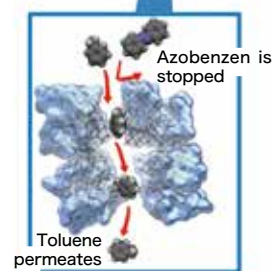


Fig. 10. Schematic diagram of a separation membrane made of diamond-like carbon

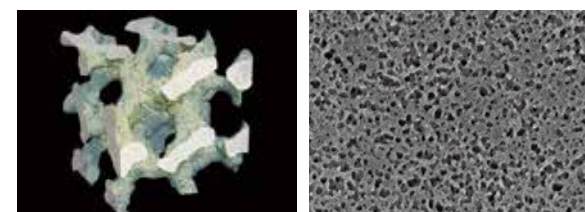


Fig. 11. Schematic diagram of polymeric nanoporous material and Scanning electron micrograph of a polymer porous material made of polystyrene (cross section)

Science is even more amazing than you think (maybe...) 3

Electronic paper: display device that works like real paper

Written by Akio Etori

Title lettering and illustration by Shinsuke

I recently went to see the China's National Palace Museum's treasure exhibition in Ueno, Tokyo. It was a wonderful exhibition where I could get a glimpse of the thousands of years of Chinese culture. Along with pottery, porcelain, paintings and hanging scrolls, I unexpectedly saw many penmanship works. I believe that writing characters on paper is a remarkable invention of mankind among many other cultural heritages.

In ancient times, men tried to convey their thoughts and experiences to their neighbors by means of cave paintings. Eventually, men invented characters by symbolizing the paintings.

The culture of writing reached its high point when paper came into existence. The printing technology invented by Johannes Gutenberg popularized the method of communicating using characters printed on paper. Printing technology enabled mass-production of printed materials including books, and the development of distribution systems helped spread information communication technology (i.e., media).

In 1946, the world's-first computer was built. Since then, the advancement of new information processing and communication technology has rapidly changed our lives. Today, an enormous amount of information can be distributed across the world in the blink of an eye, and that information can be saved on a storage device

and easily searched whenever you want. But that is not all. With the advancement of information processing and communication technology, display devices that act like real paper are about to be born.

Electronic paper, as the name suggests, is an extremely thin display device that can be used like real paper, and is light-weight and portable. Under sunlight, electronic paper is easier to read than liquid-crystal displays since electronic paper allows external light to reflect off it like ordinary paper while liquid-crystal displays are illuminated by a backlight. In addition, since electronic paper uses electricity only when pages are changed, the amount of power consumption is very small. So, once recharged, the device remains operational for a very extended time period. As such, electronic paper is an excellent display device that possesses a real paper-like quality compared to liquid-crystal displays.

Electrophoretic display using microcapsules is a typical operating principle adopted in commercial electronic paper. A sheet of electronic paper consists of microcapsules that contain black and white particles having electric charges. Upon applying voltage, black particles with a negative charge approach the positive electrode, while white particles with a positive charge are attracted to the negative electrode. The manipulation of positive and negative electrodes enables

displaying black and white characters. According to this method, only black and white displays are available, but attempts to apply different operating principles are made to realize color displays. For example, researchers at NIMS are studying and developing an electrochromic method using supramolecular polymers. Electrochromism is the phenomenon where application of voltage induces a reversible electrochemical redox reaction, which in turn causes materials to change their colors. This principle has been tested on many different materials.

The majority of types of black and white electronic paper in the market are covered in hard cases. However, I expect that new products to be commercialized in the near future will be capable of displaying full color and very thin so they can be rolled like real paper. In digital signage displays, liquid crystal is currently the mainstream technology and an enormous amount of electricity is consumed. These displays might eventually be replaced by electronic paper that consumes a small amount of electricity.

Visual communication means continue to change through inventions as time progresses, from the days of cave paintings to Chinese penmanship works, and to the present time of electronic paper.

While I am excited about the new electronic paper, I personally wish to preserve the old tradition of handwriting on paper.

I'm still waiting to receive the manuscript from you.

It was in my electronic paper... but the wind took it all...



Akio Etori: Born in 1934. Science journalist. After graduating from College of Arts and Sciences, the University of Tokyo, he produced mainly science programs as a television producer and director at Nihon Educational Television (current TV Asahi) and TV Tokyo, after which he became the editor in chief of the science magazine *Nikkei Science*. Successively he held posts including director of *Nikkei Science Inc.*, executive director of *Mita Press Inc.*, visiting professor of the Research Center for Advanced Science and Technology, the University of Tokyo, and director of the Japan Science Foundation.

1 NIMS researcher awarded the Sir Martin Wood Prize

(Oct.5, 2014) Dr. Masamitsu Hayashi, senior research scientist of NIMS, the Magnetic Materials Unit, was awarded the Sir Martin Wood Prize at the Millennium Science Forum held at the British Embassy in Tokyo. The Sir Martin Wood Prize is sponsored by the British company Oxford Instruments and is named after Sir

Martin Wood, Founder and Honorary President of Oxford Instruments. The prize is awarded to young scientists who have made an outstanding achievement in condensed matter physics. Dr. Hayashi was awarded the prize for his study of "Effective field measurements and spin torque dynamics in magnetic nanostructures".



British Ambassador to Japan, Mr. Tim Hitchens (left) awarding the Sir Martin Wood Prize to Dr. Hayashi (right).

2 Inauguration Ceremony Held for the Establishment of UMI-LINK

(Oct. 28, 2014) An opening ceremony was held at NIMS to commemorate the launch of a new international joint research unit called the Laboratory for Innovative Key Materials and Structures (UMI-LINK) where advanced materials studies will be conducted in collaboration among the French National Center for Scientific Research (CNRS), Saint-Gobain, headquartered in France, and NIMS. Such figures as French Ambassador to Japan Thierry Dana attended the ceremony. At the ceremony, representatives of the joint research participants, including Director of the CNRS Institute of Chemistry Dominique Massiot, Vice President of R&D and Innovation for Saint-Gobain Didier Roux, and NIMS Presi-

dent Sukekatsu Ushioda, made speeches about the significance of and expectations for UMI-LINK. Integrating the strengths of the participating institutions, the newly formed UMI-LINK aims to carry out academic

research with the goal of identifying physical and chemical properties of materials with novel nanostructures, and to perform applied research with the goal of pursuing the practical use of the nanostructures in industrial society.



Guests and representatives of the participating institutions at the opening ceremony

Hello from NIMS

“Oost West Thuis Best”, an expression in Dutch for “Home Sweet Home”. Those words pop up in my head every time I come back from business trips or holidays abroad. Although I have lived in many places and travelled even more, Japan has won my heart and stomach (awesome food!!). The paradox of strong traditions in the general society and the crazy trends among young people have made Japan an intriguing place to visit and live. No other place I want to be for the moment. No need to say that NIMS strongly contributes to these feelings. The opportunity to work in an environment where interactions between scientists from different nations are encouraged and the freedom to carry out your own ideas is accepted, is the most powerful stimulation

for every researcher to reach for the top. My encounters with scientists outside of NIMS have led to many invitations, not only invitations to their research groups, but also my invitation toward them to come to NIMS

and see how working in science can be different, fun, and motivating. As my research interest covers several fields like magnetic nanowire and molecular switches, this is the place to be.



 NGO Huynh Thien
Belgium
Sep. 2013 – present
ICYS-MANA

A scene from Matsuri (festival) in Tsukuba.