2009 Kyushu-Seibu Busan-Gyeongnam

# Joint Symposium on High Polymers (14<sup>th</sup>) and Fibers (12<sup>th</sup>)



October 25-27, 2009

The Inamori Auditorium, Kagoshima, Japan



# Kyushu-Seibu / Busan-Gyeongnam Joint Symposium on High Polymers (14th) and Fibers (12th)

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#### Co-organized by:

Kyushu Branch of the Society of Polymer Science, Japan, Pusan-Kyeongnam Branch of the Polymer Society of Korea Seibu Branch of the Society of Fiber Science and Technology, Japan Pusan-Kyeongnam Branch of the Korean Fiber Society

#### Chairman:

Prof. Koji Yoshinaga, Kitakyushu Institute of Technology, Japan

#### Local committee:

Prof. Koji Yoshinaga, Kitakyushu Institute of Technology, Japan Prof. Keiji Tanaka, Kyushu University, Japan Prof. Katsuhiko Fujita, Kyushu University, Japan Prof. Junichi Kadokawa, Kagoshima University, Japan Prof. Masashi Kunitake, Kumamoto University, Japan

#### Secretary General:

Prof. Masashi Kunitake, Kumamoto University, Japan Prof. Nam-Ju Jo, Pusan National University, Korea

# Preface

It is our great pleasure to welcome you to the '09 Kyushu-Seibu/Busan-Gyeongnam Joint Symposium on High Polymer (14<sup>th</sup>) and Fibers (12<sup>th</sup>) in Kagoshima. We believe that this symposium will set the stage for successful continuation of the Joint Symposium.

The First Pusan-Kyushu Joint Symposium was held at Pusan National University in Korea on November 2 in 1984, to stimulate the research activities among the polymer scientists in both the Kyushu branch members of the Society of Polymer Science, Japan and Pusan-Kyeongnam branch members of Polymer Society of Korea. The first Joint Symposium, initiated from informal talks between one of editors (Tisato Kajiyama) and Prof. Sung Chul Kim of Korea Advanced Institute of Science and Technology at the winter Gordon Conference in 1983, signified much to provide a forum for polymer scientists in the Pusan-Kyeongnam area of Korea and Kyushu area of Japan. One of reasons why the first symposium gained a big success is due to the neighborhood between the two branches in the geographical sense. Thanks to the big success of first symposium, the second symposium was also successfully held in Fukuoka, Japan in 1985. Two branches of the fiber societies in Korea and Japan, located at the same area, joined from the third joint symposium, held in Cheju, Korea in 1987. At that time, the name of the joint symposium was the third Symposium on High Polymers and the first Pusan-Seibu Joint Symposium on Textiles. The branches are the Busan-Gyeongnam branch of the Korean Fiber Society and the Seibu branch of the Fiber Science and Technology, Japan. The present name has been employed from the joint symposium held in Kumamoto in 1997.

This symposium provides topics and information on recent development in fields of polymers and textiles in Kyushu-Seibu area of Japan and Busan-Gyeongnam area in Korea.

October 25, 2009

Kohji Yoshinaga Symposium Chair

# Symposium Schedule

# October 25, Sunday

17:30 - 18:30 **Registration** 

18:30 – 20:30 Welcome Party in Kagoshima University

# October 26, Monday

8:40 – 9:30	Registration
9:30 - 9:40	Opening Address by Prof. Koji Yoshinaga from Japan
9:40 - 10:30	Invited Lecture from Japan
	" Chemistry of Soluble Carbon Nanotubes - Fundamentals and Applications - "
	Prof. Naotoshi Nakashima (Kyushu University) Chair: Prof. Seung Kook An (Pusan National University)
10:30 – 11:20	Invited Lecture from Korea
	" Organic Syntheses and Properties of Novel Conjugated Polymers for LED "
	Prof. Hongsuk Suh (Pusan National University)
	Chair: Prof. Katsuhiko Fujita (Kyushu University)
11:20 – 12:30	Lunch break
12:30 – 13:50	1st. Poster Session (PA) in Presentation Room
14:00 - 15:20	2nd. Poster Session (PB) in Presentation Room
15:30 – 16:20	Invited Lecture from Japan
	" Synchrotron Small-Angle X-Ray Scattering from Drug Delivering Nano-Particles in Solutions: Pharmacological Efficiency and Particle-Inner Structures "
	Prof. Kazuo Sakurai (The University of Kitakyushu)
	Chair: Prof. Ildoo Chung (Pusan National University)
16:20 – 17:10	Invited Lecture from Korea
	" Dye-Cyclodextrin Rotaxane: Synthesis, Characterization and Promising Application "
	Prof. Jong Seung Park (Dong-A University) Chair: Prof. Masashi Kunitake (Kumamoto University)
17:30 – 19:30	Banquet (Kagoshima University COOP)

# October 27, Tuesday

Excursion to Kagoshima City

# **Access Map**



# Abstracts

# Chemistry of Soluble Carbon Nanotubes - Fundamentals and Applications -

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#### **INTRODUCTION:**

CNTs are central nanomaterials in the fields of nanoscience and nanotechnology due to their remarkable electrical, thermal, optical, and mechanical properties<sup>1</sup>. The electrical properties of CNTs, which range from semiconducting to metallic depending on their chirality, cause them to be excellent materials for nanowires, rectifying heterojunctions, field-effect transistors, and electronic devices.<sup>1-2</sup> High Young's modulus and aspect ratios of CNTs make possible to use them for the reinforcement of fibers. The use of SWNTs in biological applications such gene delivery, cancer therapy and biosensors is also being exploited. These potential applications are, however, often limited because of their insolubility in many solvents due to strong intertube van der Waals interactions. Therefore, strategic approaches toward the solubilization of CNTs are essential for the applications of CNTs.<sup>2</sup> The study may open doors in the areas of chemistry, materials science, electronics, biochemistry, biology, pharmaceutics, and medicine (Fig. 1).

#### **CNT/POLYMER COMPOSITES**

Addition of of CNTs to polymers is expected to reinforce their intrinsic properties of the matrix polymers and to create additional functionalities. Strategic approaches for the homogeneous dispersion of SWNTs are very important in the fields of CNT/polymer composites. We report in the meeting: i) the fabrication of the CNT/polymer composites by in situ solvent-free photo-polymerization using a UV-curable monomer, ii) the structural and electrical properties of the films obtained by the UV curing of the composites,<sup>3</sup> iii) newly polymer synthesized gels composed of poly(*N*-isopropylacrylamide) (PNIPAM) and single-walled nanotubes exhibiting a volume phase transition between shrinkage and swelling by ON/OFF near-IR laser irradiation<sup>4</sup>, and iv) the formation of self-assembly of conducting CNTs with a honeycomb structure on polymer films and on silicon wafer from solution casting of a CNT/lipid conjugate <sup>5-6</sup>.

#### **REFERENCES**

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Fig. 1. Soluble carbon nanotubes and their applications.

#### **Organic Syntheses and Properties of Novel Conjugated Polymers for LED**

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#### **INTRODUCTION**

Conjugated polymers have been incorporated as active materials into several kinds of electronic devices such as transistors,<sup>1</sup> and organic light-emitting diodes<sup>2</sup> (OLEDs) including flexible displays. Most of the research in the field of polymer-based electroluminescent devices has been focused on main-chain conducting polymers such as poly(plenylenevinylene) (PPV),<sup>5</sup> poly(p-phenylene) (PPP),<sup>6</sup> poly(thiophene),<sup>7</sup> poly(fluorene).<sup>8</sup> their copolymers and soluble derivatives, because of the prospective application as large-area light emitting diodes (LEDs). New electroluminescence (EL) polymer utilizing new back-bone, poly(2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenant hrene)) (PCPP), with stabilized blue emission is reported. РСРР synthesized from was 4*H*-cyclopenta[*def*]phenanthrene over 5 steps.

#### **RESULTS AND DISCUSSION**

New electroluminescence (EL) polymer utilizing back-bone, new poly(2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenant hrene)) (PCPP), with stabilized blue emission is reported. PCPP was synthesized from 4H-cyclopenta[def]phenanthrene over 5 steps. The photoluminescence (PL) spectra of PCPP did not show any peak in the long wavelength region even after annealing for 18 hours at 150 °C in air. The OLED with the configuration of ITO/PEDOT:PSS/PCPP/Al generates EL emission with maximum peak at 400 nm, low turn-on voltage (6.0 V), and excellent CIE coordinates (x = 0.17, y = 0.12) for the blue color without any filtering. The maximum brightness of the OLEDs using PCPP was 1500 cd/m<sup>2</sup> at 14 V. The maximum luminescence efficiency of the polymer LEDs with PCPP was 0.70 cd/A at 180 mA/cm<sup>2</sup>. In addition to this, PCPP displays stabilized blue EL emission without any low energy emission band in the region of 500-600 nm even after annealing for 18 hours at 150 °C or operation of the device for 40 minutes in air. Figure 5g illustrates the pictures of the PL color changes of PCPP and PF 2/6 as a function of annealing time. Both films are pure-blue in the beginning,



Fig 1. Pictures of the PL color changes of PF 2/6 and PCPP as a function of annealing time. The CIE coordinate evolution diagram of the PF 2/6 and PCPP devices as a function of operating time in air.

without any green emission. As the annealing time becomes longer, however, the color of the PF 2/6 film gradually changes from blue to green. This change corresponds to the change in its CIE coordinates from x = 0.20, y = 0.18 to x = 0.24, y = 0.35. In contrast, there is no change at all in the PL color of PCPP, with almost fixed CIE coordinates through the whole annealing process, clearly demonstrating the superior color stability of PCPP.

#### **REFERENCES**

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# Dye-Cyclodextrin Rotaxane: Synthesis, Characterization and Promising Application

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Supramolecular chemistry covers intermolecular interactions where non-covalent interactions are involved, and many of them are based on host-guest interactions. Cyclodextrins (CDs) are cyclic oligosaccharides consisting of 6-, 7- or 8-glucose units, which are called  $\alpha$ -,  $\beta$ - or  $\gamma$ -CDs, respectively. They have hydrophobic interior and hydrophilic exterior, and are widely being used as hosts for various organic molecules. The formation of CD inclusion complexes with a variety of dyes has continuously drawn our interests, largely due to the ability of the CDs to alter the physical properties of the dyes.

This presentation covers the study of inclusion complexes of CDs and chromophore dyes. The stable rotaxane structure can be achieved with the synthesis of dye rotaxane. The introduction of CD ring around azo chromophore provides a simple way to improve the solubility and stability of azo dye. We have shown that by incorporating proper compounds as a coupler, azo dye rotaxanes can be used as pH indicators and metal ion sensors. We have described the synthesis of fluorescent acetylene dye rotaxane using the Pd-catalyzed reaction of Heck-Cassar-Sonogashira-Hagihara type. Its fluorescence properties in the solid state as well as in solutions are examined and compared with those of free dye. Free dye, which has tetra-carboxylic groups, is found to be highly sensitive to various metal ions, exhibiting high Stern-Volmer constants,  $K_{SV}$ . On the contrary, acetylene dye rotaxane exhibits much less quenching against various quenchers.

CD inclusion complexes in the form of pseudo-rotaxane, and their structural nature will be shortly mentioned as well. Some dyes are observed to exhibit an anisotropic structure by the formation of inclusion complex with CD. We have tried to understand and identify its structure by various characterization techniques, including photoluminescence, polarized optical microscope, differential scanning colorimeter, and laser scanning confocal microscope.



**Figure 1.** Synthetic schemes for dye rotaxane (a) by threading and capping (left), and (b) Heck-Cassar-Sonogashira-Hagihara reaction (right).

#### Synchrotron Small-Angle X-Ray Scattering from Drug Delivering Nano-Particles in Solutions: Pharmacological Efficiency and Particle-Inner Structures

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#### **INTRODUCTION**

A series of aromatic cationic lipids having amidine, amine, or diamine headgroups were synthesized for a DNA transfection reagent.[1] Structures of the DNA/lipid complexes were explored with synchrotron small-angle X-ray scattering (SAXS) with Spring-8 BL40B2 including ultra-diluted solutions (c.a., 0.08mM, approximately 0.01- 0.05 wt%), which are in the comparable range with those used for gene transfection in vitro and vivo experiments. In order to measure SAXS from such dilute solutions, we constructed a vacuum chamber to eliminate obstructing scattering (Figure 1). By use of this instrument, the S/N ratio increase by one order of magnitude.

#### **RESULTS AND DISCUSSION**

Figure 2 shows how the SAXS profiles change upon mixing with pDNA to a cationic micelle (DOTAP/DOPC/pGL3). The profile for the micelle can be fitted with a core-shell spherical model with the radius of 4 nm. The addition of DNA induces structural transition from spherical to lamella. The transition completed when the all cations were neutralized with the DNA phosphate anions. Combining with fluorescence and micro-calorimetry measurements, the present SAXS changes can be rationalized in terms of the type (b) model instead of (a) model as presented in Figure 3.



Figure 1. Optical arrangement of a vacuum camera equipment for SAXS experiments at Spring-8 40B2.



**Figure 2**. SAXS profiles changes upon mixing with a cationic micelle and pDNA, form a spherical to lamellae transition.



**Figure 3.** Two possible structures for the DNA/lipid lamellae complexes.

Additionally to the cationic lipid/DNA complexes, I will present SAXS from polymeric micelles that can delivery hydrophobic drugs. Furthermore, I will present the contrast variation technique that is a powerful tool common in neutron small angle scattering to elucidate structures for complex scattering objects. In X-ray scattering, sucrose or polyethylene oxide may be added to the solution to tune the solvent electron density so as to match a particular scattering object. These compounds show a larger electron density than water, since they contain oxygen atoms which have a relatively larger scattering length than carbon and hydrogen atoms. In this paper, we applied the sucrose contrast variation technique to a wormlike micelle system consisting of sodium lauryl ether sulfate (LES) and coconut fatty acid amido propyl betaine (AMPB). We added sucrose to the NaCl/water solution to adjust its electron density to match that of the shell and elucidated the scattering only from the core. By use of this technique, we examined the cross-sectional structure of the micelle and the salt concentration dependence of the scattering from the low q range and discussed the flexibility. Furthermore, we could observe that polypropylene glycol chain is included in the micellar core to induce the morphological transition of the entire micelle.

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