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## Japan-US Seminar: Macromolecular Architecture and Engineering

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Conference Report

## Japan-US Seminar: Macromolecular Architecture and Engineering

Shin-Ichiro Shoda<sup>a</sup> and Otto Vogl<sup>b\*</sup>

<sup>a</sup>Department of Materials Chemistry, Graduate School of Engineering, Tohoku University, Sendai, 980, Japan; <sup>b</sup>Monbusho Professor, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan\*



Shun-Ichiro Shoda



Otto Vogl



Shiro Kobayashi Krzysztof Matyjaszewski Shohei Inoue

The US-Japan Seminar on Polymer Synthesis was held in Japan from October 28 to October 31, 1996; the location was Sendai, Miyagi Prefecture.

Since about 1600 A.D. the city of Sendai has flourished as the castle town of **Date Masamune** (1567–1636), the great feudal lord of the northern Japan region who reigned there supremely. The temple complex of the mausoleum of Date and his successors, called **Zuiho-den**, was built on Kyogamine, a beautiful ridge, covered with old cedar trees. It is now an extraordinary culmination of the architectural style of the Azuchi Momoyama period.

Today, Sendai, with a population of about one million inhabitants, is the political, economic and cultural center of Japan's Tohoku (northeastern) district. Sendai is known as the *City of Learning*. There are 8 universities in the city with about 40,000 students from Japan and abroad. Tohoku University is the major University; it has 30 research institutes and laboratories affiliated with it, including the Institute for Materials Research.

This U.S.-Japan Seminar on Polymer Synthesis was the 7th Seminar of the series and was held at the Washington Hotel in Sendai with **Shohei Inoue** and **Krzysztof Matyjaszewski** as the Co-Chairmen. Much of the organization was done by the upcoming Chairman of the Japanese side, **Shiro Kobayashi**, with the able assistance of Shin-Ichiro Shoda and Hiroshi Uyama. The meeting was sponsored by the Japan



Shun-Ichiro Shoda Hiroshi Uyama Richard Turner

Society for the Promotion of Science and the US National Science Foundation.

As in Seminars of similar kind, the attendance was by invitation only; there were 12 invited Japanese academic invited speakers, 8 US invited academic and 8 Industrial invited speakers, 8 Japanese and 2 US observers.

\*Permanent address: Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA.

*Head to Head Polymers* by **Otto Vogl**, Kyoto, Japan and Brooklyn, NY, USA

Pure head to head (H-H) addition polymers, such as H-H polyolefins, H-H acrylates and H-H poly(vinyl halides), have been of interest in the understanding of part of the structure/properties relationship of polymers. The polymer structures have provided challenges of synthesis, characterization and of the measurements of their mechanical and rheological properties. H-H poly(vinyl halides) were synthesized by improved halogenation techniques from poly(1,4-butadiene) and have made H-H poly(vinyl chloride) and H-H poly(vinyl bromide) easily accessible for a more extensive characterization of these polymers. Blends were prepared with polycaprolactone and poly(methyl methacrylate) and between the poly(vinyl halides). The thermal behavior and the thermal degradation behavior of these blends were investigated.

*Synthesis and Chiral Recognition of Helical Polymers*, by **Yoshio Okamoto**, Nagoya, Japan.

Many stereoregular polymers have helical conformation in the solid state and some of them can maintain the structure even in solution. A helical structure is chiral and therefore a one-handed helical polymer is optically active. Helical polymers are interesting because they show chiral recognition for enantiomers and several helical polymers, including polymethacrylates and polysaccharide derivatives, have been practically used as stationary phases to separate a wide range of enantiomers. Helix-sense-selective radical and anionic polymerization of various monomers were investigated.

*Atom Transfer Radical Polymerization as a Tool for Synthesis of Well-Defined Polymers*, by **Krzysztof Matyjaszewski**, Pittsburgh PA, USA

Atom Transfer Radical Polymerization is one of the most successful methods enabling control of radical polymerization of various monomers and allows the synthesis of polymers with new topologies, compositions and functionalities. Atom Transfer Radical Polymerization is based on the reversible atom transfer between propagating radicals and dormant macromolecular alkyl halides catalyzed by transition metals. It can be used for a large variety of monomers including styrenes, (meth)acrylics, dienes and acrylonitrile. Well defined (co)polymers with low polydispersities with reasonable molecular weights have been prepared.

*Metal Complex-Mediated Living Radical Polymerization*, by **Mitsuo Sawamoto**, Kyoto, Japan



**Virgil Perčec**      **Mitsuo Sawamoto**

One type of living radical polymerization is based on transition metal-mediated radical formation from alkyl and related halides. A combination of a ruthenium(II) chloride complex with a *n*-alkyl halide in the presence of an aluminum alkoxide has proven to be most effective. The features of these living radical polymerizations include: a.) wide range of initiators; b.) use of metal complexes of ruthenium, iron and nickel; c.) tolerance of water and other protic agents; d.) feasibility of precision synthesis of block, random and end-functional polymers.

*From One-Dimensional to Three-Dimensional Polymers*, by **Virgil Perčec**, Cleveland, OH, USA

Flexible polymer chains exhibit statistical 3-dimensional shapes which are based on a random-coil conformation in solution and in the amorphous state or a lamellar structure in the crystalline state. Rigid-rod like polymers display a worm-like shape in solution, in the amorphous, in the crystalline or in the liquid crystalline state. If the molecular weight of the polymers is lower than their persistence length, they exhibit a one dimensional shape. The design of rigid-rod one dimensional polymers and icosahedral three dimensional polymer structures were discussed.

*Preparation of New Types of Block Copolymers by Radical/Cation Transformation Polymerization*, by **Mikiharu Kamachi**, Toyonaka, Osaka, Japan

Radical polymerization is the most utilized method in industry for the preparation of high polymers from vinyl and diene compounds. Sequence control and structure control are difficult in radical polymerization. Radical-promoted cationic polymerization, carried out in the presence of electron transfer agents can transfer certain propagating radicals to the corresponding cations. This technique allows the preparation of homo and block copolymers from vinyl monomers and cyclic compounds by radical/cation transformation polymerization.



**Mikiharu Kamachi**      **Joseph Wirth**

*Olefin Polymerizations and Copolymerizations Using New Pd(II)- and Ni(II)-Based Catalysts*, by **Maurice S. Brookhart**, Chapel Hill, NC, USA

A series of Pd(II) and Ni(II) complexes serve as initiators for the polymerization of ethylene and  $\alpha$ -olefins as well as the

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copolymerization of ethylene and methylacrylate to high molecular weight polymers. The polymerization is influenced by the structure of the initiator and type of metal, ligand structure, monomer concentration and temperature. The polymerization of  $\alpha$ -olefins with nickel initiators has living character and di- and triblock polymers have been prepared. Not all the polymer structures have the structure of the linear structure based on the monomer but extensive rearrangements can occur which lead to highly branched structures from ethylene and copolymers of the  $\alpha$ -olefin with ethylene even though no ethylene is present in the polymerization.

*Anionic Polymerization of N,N-Dialkylacrylamides in the Presence of Diethyl Zinc*, by **Seiichi Nakahama**, Tokyo, Japan

Anionic polymerization of *N,N*-dimethyl, *N,N*-diethyl- and *N,N*-diisopropyl acrylamide were carried out with *sec*-butyllithium/diphenylethylene in the absence and presence of diethyl zinc. In the absence, the molecular weight is generally broad because of slow initiation and extensive transfer reaction. In the presence of diethyl zinc the molecular weight is predictable. Similar results were obtained in the anionic polymerization of methacrylates. Diethyl zinc seems to coordinate with the growing anion and control side reactions.

*Alternating Copolymers of 3,4-Epoxy-1-butene and Derivatives with Maleic Anhydride*, by **S. Richard Turner**, Kingsport, TN, USA

3,4-Epoxy-butene was prepared by selective oxidation of butadiene. It contains two different polymerizable groups. Cationic initiators readily ring open the epoxide to form polyethers with pendant vinyl groups. Free radical homopolymerization is sluggish because of the allylic monomer structure but gives readily alternating copolymers with maleic anhydride with both 1,2 and 1,4-enchainment of the 3,4-epoxy-1-butene in the copolymer structure.

*Theoretical Study on Reactivities of Ti-Methyl Bonds in  $d^0$  Methyltitanium Complexes for Insertion of Ethylene: Analysis by "Paired Interacting Orbitals"* by **Akinobu Shiga**, Tsukuba, Japan

Highly active catalysts have modernized the manufacturing process of polyolefins. Even higher sophisticated catalysts are expected to be developed to control molecular weight, and its distribution, copolymerization ratios, regio- and stereospecificities to develop polymers with ultimate properties. To

develop such sophisticated catalysts it is indispensable to clarify the relationship between the structure of the active site and the catalyst performance on the basis of the precise and quantitative understanding of the polymerization mechanism.

*N-Vinylformamide—Building Block for Novel Polymer Structures*, by **Robert K. Pinschmidt Jr.**, Allentown, PA, USA

*N*-Vinylformamide, the lowest member of the *N*-vinyl amide family, offers a unique mix of physical and chemical properties which make it highly attractive as a precursor for amide and amine functional polymers and for other monomers, oligomers and functional polymers. *N*-vinylformamide has been known for 30 years but only recently has a commercially feasible synthesis been developed. *N*-Vinylformamide has attractive physical and toxicological properties and high reactivity. It polymerizes and copolymerizes readily to water soluble polymers of very high molecular weight. The formamido group is easily hydrolyzed to the amine function.

*Simple Lanthanoid Compound as Initiator for the Polymerization of Polar Monomers*, by **Shohei Inoue**, Tokyo, Japan

Lanthanoid oxides are very active initiators for the polymerization of heterocumulenes such as isocyanates, ketenes and carbodiimides. Polymerization of ketene gives the polymer with the polyester structure as reported previously for the polymerization with anionic initiators. It is believed that the polymerization proceeds through an enolate structure as the growing species.

*Synthesis, Characterization and Syndiotactic Styrene Polymerization Results of a Titanium (III) Complex, Cp\*Ti(OMe)<sub>2</sub>: Mechanism Implications* by **Thomas H. Newman** and **Michael T. Malanga**, Midland MI, USA

Syndiotactic polystyrene is a semi-crystalline engineering plastic synthesized via a homogeneous Ziegler/Natta catalyst. The actual catalyst is a titanium(III) metallocene Cp\*Ti(OMe)<sub>2</sub>, which is prepared by reduction of Cp\*Ti(OMe)<sub>3</sub> with *tert*-butyl lithium and, for the polymerization of styrene, it is activated with methylalumoxane. The results support the polymerization mechanism involving a Ti(III) as the active site.



Akinobu Shiga Jane C. Vogl



Welcoming Banquet



At the Reception

*Aromatic Polymers: Synthesis via Nickel Catalyzed Coupling of Aryl Chlorides*, by **George T. Kwiatkowski**, Naperville IL, USA

A new polymerization technique for the formation of high molecular weight aromatic polymers via the nickel coupling of aromatic dichlorides has been discovered. The polymerization proceeds in a dry aprotic solvent such as DMAc using catalytic amounts of zero-valent nickel, triphenylphosphine or bipyridyl ligands and an excess of zinc metal. To obtain high molecular weight polymers, the reaction conditions must be rigorously dry using small amounts of nickel, a high triphenylphosphine nickel/ratio and moderate temperatures. The type and amount of ligand is critical.

*Novel Catalyst Systems for the Polymerization of Substituted Acetylenes*, by **Toshio Masuda**, Kyoto, Japan

Polymerization of substituted acetylenes by group 5 and 6 metal catalysts proceeds with metal carbenes as the propagating species like ring-opening metathesis polymerization of cycloolefins. Two types of catalyst systems were proven to be very efficient for the polymerization of substituted acetylenes: a.)  $\text{MoOCl}_2$ -cocatalyst-EtOH and b.) metal carbonyl-based catalysts. Cocatalysts for the first systems were *n*-Bu<sub>4</sub>Sn, Et<sub>3</sub>Al, Et<sub>2</sub>Zn and *n*-BuLi.

*Specialty Polymers vs Enabling Technologies*, by **Joseph G. Wirth**, MenloPark, CA, USA

Specialty polymers are allowing technology to design novel component systems or processes. Without such materials many of these novel systems do not work reliably and in a useful manner. These types of applications are very different from those for which high volume commodity or engineering polymer are used. In such cases, performance is the overwhelming concern and the materials are highly specialized to achieve optimum performance. Cost is of minor concern because the material is used in small quantities and the value it adds to the end use is exceedingly high.

*Preparation and Characterization of Microcrystals of Polydiacetylenes*, by **Hachiro Nakanishi**, Sendai, Japan

Compared to microcrystals of inorganic compounds and metals, those of organic materials and polymers have not been

extensively investigated. Microcrystals of a variety of organic compounds can easily be obtained by simple reprecipitation methods from their solution. Preparation of diacetylene microcrystals, their solid state polymerization behavior and the properties of the polydiacetylene microcrystals thus obtained by UV or  $\gamma$ -ray irradiation have been found to have highly interesting and unexpected properties.

*Rare Earth Metal Initiated Living Polymerization of Polar and Nonpolar Monomers*, by **Hajime Yasuda**, Higashi-Hiroshima, Japan

Rare earth metal initiated polymerization of methyl methacrylate was found to give high molecular weight polymers with extremely low polydispersity. The polymerization behaves like a living polymerization. At low polymerization temperature, highly syndiotactic polymers were obtained. The mechanism was elucidated by studying the oligomerization of methyl methacrylate with  $\text{SmH}(\text{C}_2\text{Me}_5)_2$ . Rare earth metal complexes such as  $\text{SmMe}(\text{C}_2\text{Me}_5)_2$  and  $\text{YMe}(\text{C}_2\text{Me}_5)_2$  and their THF complexes also initiate the living polymerization of alkylacrylates.

*Dendrite Metalloporphyrins: A Challenge to Nanoscopic Chemistry*, by **Takuzo Aida**, Tokyo, Japan

Dendrimers are hyperbranched macromolecules with well-defined three-dimensional shapes and can serve as building blocks to explore nanoscopic chemistry. A new dendritic structure has been developed in which the metalloporphyrin functionality is covalently encapsulated by an aryl ether dendritic framework. The zinc porphyrin dendrimers with one to 4 generations of arylethers have been synthesized and characterized. The characterization of the higher generations indicated an egg-like property where the molecular motion of the exterior dendrimer surface is frozen, while the interior environment remains flexible.

*Formation of Organized Structures through Variation in Molecular Architecture and Chemical Composition*, by **Coleen Pugh**, Ann Arbor MI, USA

Chemical anisotropy of amphiphilic molecules can be used to control both solution and solid state behavior and therefore enables the synthesis of unusual molecular architecture. Two systems were studied: polyrotaxanes and the smectic mesophase behavior in side-chain liquid crystalline polymers.

*The Functionality of Precise Molecular Assemblies on the Basis of Precise Synthesis*, by **Yukio Imanishi**, Nara, Japan

Functionality of proteins is exhibited on the basis of specific tertiary structures, in which a polypeptide chain folds into a specific structure or several polypeptide chains which associate to form ordered assemblies. Template-assisted synthetic proteins can construct a helix-bundle structure. Bilayer membranes or monolayer membranes consisting of chromophoric amphiphilic compounds can be synthesized where the chromophoric groups are placed based on the regular arrangement of the amphiphilic compounds.

*Reactive Processing of Polymers: a.) Reactive Processing of Engineering Thermoplastics and b.) Reaction Injection Molding of Polyurethanes*, by **H. Georg Schmelzer**, Pittsburgh, PA, USA

Engineering thermoplastics have enjoyed phenomenal growth. The capital investment required to develop and introduce a new engineering thermoplastic has increased dramatically. Engineering resin producers have increased their efforts to improve the performance of existing resins. One approach is to

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**Matsushima Islands**

move the chemistry from reaction vessel into processing equipment often referred to as reactive processing. One fertile area that allows flexibility and a wide range of materials is in the area of polyurethanes.

*Recent Advances of High Performance Plastics—Liquid Crystalline Polyesters*, by **Toshihide Inoue**, Nagoya, Japan

Liquid crystalline polyesters have some very excellent and unusual characteristics. New approaches at Toray under the guidance of the MITI program has produced a new polyester called SIVERAS.

*Biorecognizable Polymers: Synthesis, Structure and Bioactivity*, by **Jindrich Kopeček**, Salt Lake City, UT USA

The evaluation of the structure-property relationship of biorecognizable polymers requires an interdisciplinary approach, consisting of tailor-made synthesis, detailed analysis of polymer structure, and characterization of physicochemical and biological methods. The principles of this approach to polymer design, synthesis and characterization is demonstrated in the following examples: a.) targetable water-soluble carriers of bioactive compounds; b.) supramolecular structure and biorecognition and c.) soluble polymers as tools in analyzing biological processes.

*Preparation and Application of Monodisperse Polyion Complex Micelles Formed through the Self-Association of Charged Block-Copolymers*, by **Kazunori Kataoka**, Noda, Chiba, Japan

Polymeric micelles from amphiphilic block copolymers have received much attention as powerful drug carriers. It has been shown that polymeric micelles that are stable in aqueous medium can incorporate hydrophobic anti-cancer drugs in their inner core, allowing their delivery to the tumor in high efficiency. These micelles are in the size range of natural particulate carriers including viruses and lipoproteins and are not restricted to the oligomer region. Even plasmid DNA and enzymes can be used for the formation of associates with block copolymers of opposite charge.

*The Direct Polymerization of Vinyl Alcohol and Vinyl Alcohol Derivatives*, by **Bruce M. Novak**, Amherst, MA, USA

A new approach has been made for the "direct synthesis" of poly(vinyl alcohol) from the fleeting intermediate vinyl alcohol, the unstable tautomer of acetaldehyde. While the homopolymerization has not been accomplished, copolymers with electro deficient comonomers, such as maleic anhydride, have been prepared.

*Choro-selective Enzymatic Polymerization for Polysaccharide Synthesis*, by **Shiro Kobayashi**, Sendai, Japan

Nucleic acids, proteins and polysaccharides are three important families of naturally occurring macromolecules. Polysaccharides, such as cellulose, xylan, chitin, and amylose are conceptionally much more difficult to synthesize and were a challenge to polymer chemistry. Very recently, the first synthesis of cellulose has been accomplished by polycondensation of  $\beta$ -cellobiosyl fluoride substrate monomer with the catalysis of cellulase, an extracellular enzyme. By applying this enzymatic polymerization technique, xylan and chitin have also been synthesized for the first time. A new concept "choroselectivity" concerning the spacial direction in the ordering of a macromolecular chain during polymerization has been proposed.

*Using Biology to Control Molecular and Supramolecular Structure in Polymeric Materials*, by **David A. Tirrell**, Amherst, MA, USA

Two recent developments using biology for polymer preparation were discussed: i.) use of protein engineering techniques to prepare thermally reversible, pH-sensitive gels; and ii.) the fabrication of nanometer-scale patterns and devices based on biomembrane templates. The design of reversible gels is based on the controlled association of helical protein domains related to natural coil structures. Such domains have been incorporated as end blocks in triblock copolymers bearing central polyelectrolyte domains of controlled charge density. On the other project, long nanotubes of fluid-lipid bilayers can be used to create templates for photochemical polymerization into solid state conduits and networks.



**At the Banquet**

This meeting provided an unusually good mix of the presentation of exciting and new scientific developments, but it also provided an opportunity for excellent personal and social contacts.

Sunday evening the Welcoming Mixer was held in the traditional Japanese style, at the Washington Hotel. Monday evening the academic invited speakers were invited to the Japanese restaurant "Nakajima" for a superb get-together with the local cuisine.



At the Banquet

On Tuesday afternoon an excursion trip was scheduled. This excursion had been a tradition of US-Japan Seminars on Polymer Synthesis in the past. The attendees were taken to the main attraction in this part of Japan, **Matsushima**, the Pine Islands, Matsushima is known as one of the "three most scenic places in Japan". Over 260 uniquely shaped isles which were formed as the result of erosive actions of waves and winds are scattered in the **Matsushima Bay**. Most isles are only rocks covered with Japanese pine trees. In the bay many varieties of sea-weed, delicacies in many Japanese dishes, are also grown. The participants of the meeting also visited **Zuigan-ji** a famous Japanese Temple complex which was first built in the year of 828, belonging to the Tendai sect; it was then called *Enpuku-ji*. It is the family temple of the Dates and flourishes as the most famous Zen temple in the Tohoku region, with many screens, scrolls and other exquisite objects of oriental art.



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| 2. Virgil Percec           | 15. Toshio Masuda     | 28. Tomohiro Yoritsue         |
| 3. Mikiharu Kamachi        | 16. Yoshio Okamoto    | 29. Robert J. Kumpf           |
| 4. Otto Vogl               | 17. Kazunori Kataoka  | 30. Yasuo Tsunogae            |
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