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Conference Reports

Japan-U.S. Seminar on Polymer Synthesis

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Hiroyuki Nishide



Otto Vogl

A seminar on Polymer Synthesis entitled "Advanced Materials Based on Macromolecules" was held from October 29 - November 2, 1990 at the Tokyo Garden Palace Hotel which is located in the Ochanomizu section of Tokyo. The seminar was sponsored by the Japan Society for the Promotion of Science and the National Science Foundation, USA, and was under the cochairmanship of Professors Eishun Tsuchida and David A. Tirrell.

The seminar was the 5th of a series that was conceived over 20 years ago. The first meeting was held in Japan at the Fuji View Hotel on Lake Kawaguchi in Hakone in 1974; it was entitled "New Aspects of Ionic Polymerization" and was under the cochairmanship of Junji Furukawa and Otto Vogl. The second seminar entitled "Functional Polymers" was held in Pingree Park in the Rocky Mountains at the lodge of Colorado State University, 9,000 feet above sea level. It was under the cochairmanship of Joseph P. Kennedy and Takeo Saegusa and was held in 1979. The next seminar, the 3rd of the series, was held at the Shin Osaka Hotel in Osaka, Japan in 1983; it was under the cochairmanship of Koichi Hayashi and John K. Stille and was entitled "Synthesis and Reactions of Oligomers and End-Reactive Polymers". The last meeting was held in Yorkville in the Napa Valley in California and was under the cochairmanship of Eli M. Pearce and Hidefumi Hirai; it was entitled "Synthesis, Properties and Reactions of Specialty Polymers".

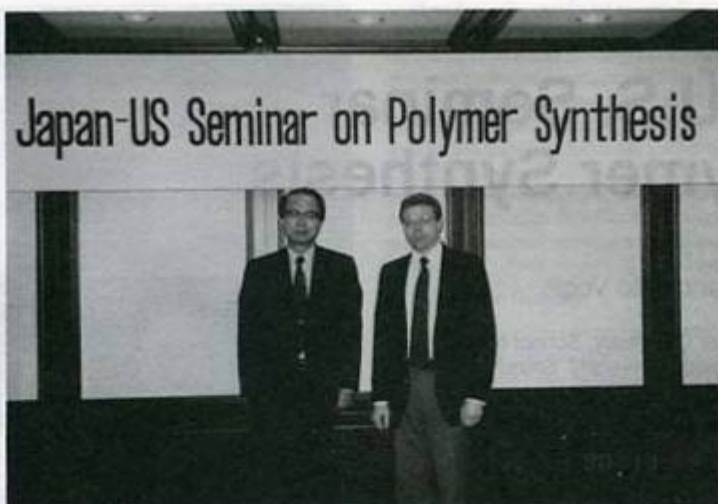
This most recent seminar in Tokyo consisted of 24 lectures. As in the previous seminars, attendance was by invitation only; it consisted of the speakers and about 20 observers from Japan and two from the United States.

The seminar started on Sunday night with the review of the program and the introduction of the participants followed by a welcoming reception. The actual seminar started with a lecture by

Robert H. Grubbs (California Institute of Technology) entitled "Applications of Organometallic Reagents in Polymer Synthesis". He mentioned that numerous reactions in organometallic chemistry in the past few years that are applicable to the synthesis of new polymers with controlled structures have been discovered. Many of the best defined systems involve catalysts for ring opening metathesis polymerizations (ROMP). These well defined catalyst systems can be used to polymerize a variety of monomers. An excellent route to polyacetylene was found in the bulk polymerization of cyclooctatetraene. This route provides a solution to many of the fabrication problems associated with the standard routes for the preparation of insoluble and infusible polyacetylene and allows



Tokyo Garden Palace Hotel, location of the seminar.

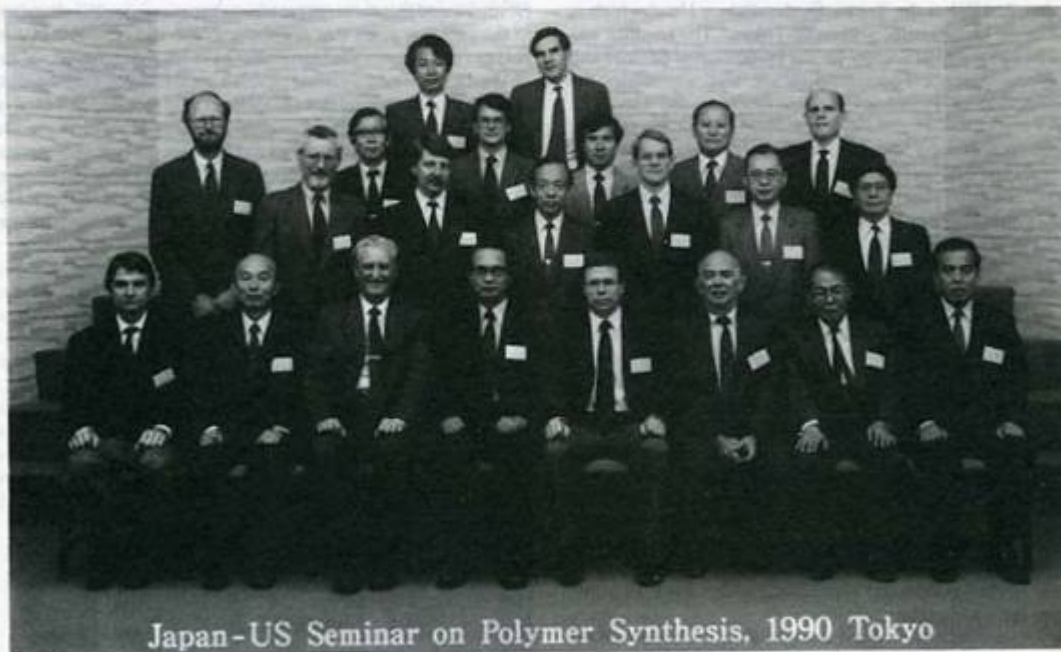


Eishun Tsuchida, David A. Tirrell, co-chairmen of the seminar.

the preparation of a variety of derivatives and copolymers to be prepared. Catalysts have also become available that are capable of polymerizing functional monomers and will even function for polymerizations in aqueous solution.

"Silica Gel-Organic Polymer Hybrid — Principle, Synthesis

and Applications" was discussed by Takeo Saegusa, Kyoto University. A polymer hybrid is defined as a blend of properties of two or more polymeric components at the molecular level. Specifically, hybrids between silica gel and organic polymers consisting of N,N-dialkyl or N-alkyl carboxylic amides were discussed. They



Japan-US Seminar on Polymer Synthesis, 1990 Tokyo

Speakers of the Japan-U.S. Seminar on Polymer Synthesis.



At the banquet.

were prepared from orthosilicate esters, a precursor of silica gel in a so-called sol-gel procedure. The original products are soluble in organic solvents, they are transparent glasses and the hybrids of silica gel with organic polymers with up to 50% silica have been prepared. On pyrolysis of these materials at 600 C highly porous silica gels with controlled pore size have been obtained.

"Design of Macromolecular Structures" was described by Otto Vogl (Polytechnic University), L. Steven Corley, William J. Simonsick, Jr. and K. Hatada. For the past decade the authors have been working on the development of rules that govern the synthesis of helical polymers and have used the polymerization of trichloroacetaldehyde and other perhaloaldehydes as the most promising examples. Most of these polymers form rigid helical structures. Discussed were the initiation of chloral polymerization and the oligomerization with achiral and chiral initiators, the detailed characterization of individual oligomeric species and the determination of their absolute configurations. Combination of GC, high resolution NMR spectroscopy at 500 MHz and K+IDS mass spectrometry as well as single crystal analysis of individual compounds allowed the determination of the structures of all stereoisomers of tertiary butoxide and bornyl oxide initiated, acetate

endcapped, fluoral, chloral and bromal oligomers up to the pentamers and in some cases to the decamers. It was found that the initiation was not stereospecific, but in the case of chloral and bromal polymerization, after the formation of the linear trimer, the oligomers are essentially stereospecific, are formed by exclusive meso addition and gives oligomers which already exist in the form of rigid helical structures.

Eishun Tsuchida (Waseda University) presented his work on the "Synthesis of Polyphenylene Thioethers through Cationic Oxidative Polymerization". Polyphenylene ethers have in the past been prepared from p-halothiophenoxides and have now been commercially produced from p-ichlorobenzene and sodium sulfide. This polymerization is carried out under pressure and at elevated temperatures. It has now been found that diphenyldisulfide can be oxidatively polymerized to poly(p-phenylenesulfide) by cationic mechanism using electrical or chemical oxidations. Polymers were produced in high purity and high yield in the presence of equimolar amounts of oxidizing agents such as quinone or with catalytic amounts of vanadylacetylacetonate under oxygen atmosphere. From the mechanistic point of view it is likely that the polymerization proceeds via the phenylbis (phenylthio) sulfonium cation which is produced by oxidation of diphenyldisulfide in acidic medium.

Donald T. Dix (Dow Chemical Company, Midland, MI) described Dow's work on "Benzocyclobutenes: A New Class of High Performance Polymers". Benzocyclobutenes constitute the basis of a new and versatile approach to the synthesis of high performance polymers for applications in the electronics, adhesives, and aerospace industries. The basic technology involves a family of thermally polymerizable monomers which contain one or more benzocyclobutene groups per molecule. The polymerization consists of a thermally initiated ring opening of the benzocyclobutene to a o-quinodimethane intermediate. The subsequent fate of this intermediate depends largely on the type and number of other functional groups present in the monomer molecule. One example of the use of benzocyclobutene polymers is as a dielectric layer in multichip modules.

"Direct Syntheses of Poly(phenylene) and Poly(pyrolylene) using Catalysts" was discussed by Naoki Toshima (University of Tokyo). Poly(1,4-phenylene) and poly(2,5-pyrrolylene) are known as heat-resistant and electrically conducting polymers. They have in the past been relatively inaccessible because of the methods used



"Coffee break."

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Naoki Yoshioka, Kayoko Nemoto, and Hiroyuki Nishide.

for their preparation. A number of $\text{CuCl-AICl}_2\text{-O}_2$ catalyst systems have been developed for the preparation of these two types of polymers. Systems that contain as an additional component pyridine as well as a polar solvent were used for the polymerization which was found to be most effective; polymers with relatively high conductivity were prepared. "Advances in Anionic Synthesis of Functionalized Polymers" was described by Roderic P. Quirk (University of Akron). Alkylolithium-initiated anionic polymerizations of styrene-type derivatives, particularly those with protecting groups, can be performed without the incursion of spontaneous terminations or chain-transfer reactions. The poly(styryl)lithiums have stable carbanionic chain ends, which can be converted into a diverse array of functional endgroups, for example by such long established reactions as carbonation and amination. These polymers are useful for a variety of further reactions including chain extension, branching, and block copolymerization.

Hidefumi Hirai (Science University of Tokyo) discussed the "Sequence Regulation in Radical Copolymerizations of Methyl Methacrylate and Styrene". Radical copolymerization of styrene and methyl methacrylate produces sequence distributions according to first-order Markovian statistics. In the presence of metal halides, the radical copolymerization of polar vinyl monomers such as methyl methacrylate and acrylonitrile with electron-donating monomers such as styrene and butadiene gave 1:1 alternating copolymers. The authors undertook a study of a quantitative comparison between the alternation-regulating abilities of various metal halides as complexing agent for methyl methacrylate in the copolymerization of methyl methacrylate and styrene. Boron trichloride was found to have the largest alternation-regulating effect. It was found that by lowering the polymerization temperature from -60°C to -95°C the coherotacticity of these copolymers goes up from 70% to 89% which is the highest value of coherotacticity ever reported.

Samuel I. Stupp (University of Illinois at Urbana-Champaign) described the "Synthesis of Materials with Self-Ordering Chiral and Functionalized Macromolecules". He mentioned that the molecular construction of homologous linear polymers with translational polar symmetry reveals 3D structures ranging from glasses to liquid crystals to crystals. These transformations are observed with remarkable subtle changes in structure such as the disordering

in the handedness of chiral dipoles appended to a molecular backbone or the removal of 3 methylene groups in a 45-atom repeat unit. The ordering of functionalized monomers and their combopolymers has also been discussed. Combmacromolecules can ally the molecule properties of their stems and teeth and are also potential precursors for the dimensionality of the macromolecules in linear polymers. If the teeth had anisometric self-ordering behavior it is possible that "functionalized" versions of these polymers may serve to spatially organize chemical functions.

"Novel Synthesis of Polyimides and Model N-Substituted Phthalimides" was described by S. Richard Turner (Eastman Kodak Company) and Robert J. Perry. Polyimides are perhaps the most important class of commercial thermally stable high temperature polymers. A large effort has been made in research and development and continues to be made for the synthesis, characterization, and structure/property relationships of these technologically important materials. They are basically prepared by reactions of dianhydrides and diamines or from the reactions of diisocyanates and dianhydrides. The authors have found that o-dihaloaromatic compounds react with primary amines in the presence of a suitable palladium catalyst, carbon monoxide, and base to give N-substituted phthalimides in high yields. This reaction can also be used for the preparation of polymers using tetrahaloaromatic compounds and aromatic diamines.

"Synthesis of Various Types of Condensation Polymers by Using Organosilicon Monomers Having Specific Reactivity" was presented by Yoshio Imai (Tokyo Institute of Technology). Specific silicon chemistry and functional silicon-based polymers was described. New synthetic methods of the preparation of polyamides and related condensation polymers by using N-trimethylsilyl-substituted diamine monomers were described. Particularly mentioned was the synthesis of new disilane-containing condensation polymers, the preparation of new silicopolyimide hybrid materials, and the synthesis of new siloxane-based starburst polymers. Highly branched polysiloxane based, starburst polymer were synthesized starting from the initial generation of tris[(phenyldimethylsiloxy)dimethylsiloxy]methylsilane and the building block of bis[(phenyldimethylsiloxy)methylsiloxy]di-methylsilanol where the phenylsilane moiety was a synthetic equivalent of N,N-diethylaminosilane, a

suitable electrophilic silicon species.

"Synthesis and Characterization of Polysilanes" was also discussed by Krzysztof Matyjaszewski (Carnegie Mellon University). Polymerization of disubstituted dichlorosilanes with alkali metals via reductive coupling has the character of a chain reaction process. Copolymerization of various dialkyl substituted dichlorosilanes by reductive coupling gave statistical copolymers. Macrooligomers of cyclooligosilanes are by-products of this reductive coupling reaction. Polymers of molecular weights from 10,000 to 100,000 have been prepared via anionic ring opening polymerization of cyclotetrasilanes. Poly (di-n-alkyl)silylanes show intriguing UV absorption properties but the adsorption behavior depends strongly on the first link in the side chain; phase transitions are believed to be responsible for this behavior.

Seiichi Nakahama (Tokyo Institute of Technology) described "Synthesis of Block Copolymers with Hydrophilic and Hydrophobic Segments". He described the synthesis of block copolymers containing hydroxy groups, as for example, in 4-hydroxy, 3-hydroxyethyl and 2-hydroxymethyl-styrenes. The monomers were prepared by protecting the hydroxyl group with trialkylsilyl groups. The synthesis of block copolymers containing amino groups with very narrow molecular weight distribution of the individual blocks were also described.

"Stereospecific Polymerization with Group 4-Metallocenes" was presented by R. Waymouth (Stanford University). Cyclopolymerization of 1,5-hexadiene with homogeneous Ziegler-Natta catalysts gave primarily poly(methylene-1,3-cyclopentane) with very small amounts of uncyclized monomer units present. Molecular weights are in the range of 40,000. Under similar condition, 1-hexene gave only oligomers.

Donald N. Schulz (Exxon Research and Engineering Company) discussed "Synthesis and Properties of Associating Polymers Systems". He described the preparation and properties (especially in solution) of some hydrocarbon and water soluble functional polymers that develop their properties primarily by self or inter chain associations. The hydrocarbon associating polymer systems were based on functional alpha-olefins. The polymers were prepared by special Ziegler-Natta polymerization methods that overcome catalyst poisoning by using Lewis acid precomplexed ester monomers. Another method revolves around monomers and polymers with organoborane structures. Polymers with hydrocar-

bon backbones require H-bonding, polar and anionic interaction for associations, water soluble polymers can associate via hydrophobic groups and zwitterionic groups.

Shohei Inoue (University of Tokyo) described the "Synthesis and Properties of Novel Graft Copolymers Containing Photoresponsive Polypeptides". Conformational change of a polypeptide controlled by external stimuli is known to govern biological functions such as transport properties across a membrane or the mechanism of vision. It was found to be of interest to construct a system in which a change in permeability across a membrane was achieved by conformational change of the polypeptide in the membrane induced by the photoisomerization of the chromophore attached to the polypeptide. The authors have investigated the circular dichroic and photoresponse properties of graft copolymers composed of the polyaspartate branch with the pendant azobenzene group attached to the poly(2-hydroxyethyl methacrylate) backbone in solution and in the membrane.

"Genetically-Directed Syntheses of New Polymeric Materials" was described by David A. Tirrell (University of Massachusetts). Recent advances in the synthesis and expression of artificial genes have established a viable route to the preparation of structurally homogeneous polymeric materials. A critical process in macromolecular design, the selection of an amino acid polymer that is expected to exhibit superior properties provided a target polymer as sequence that is then in coded into complementary sequences of DNA. This sequence is then in turn assembled through the combination of automated solid phase synthesis and then enzymatic ligation. Insertion of the artificial coding sequence into an expression vector and transformation of an appropriate host organism then provides a basis for the synthesis and then for the isolation of the target. The state of the arts is such that gram quantities of the target material can be isolated from laboratory-scale fermentations. Much of the recent effort is focused on the design and engineering of macromolecular crystals. It was of particular importance to design polypeptides with a structure that consists of a beta sheet portion of the chain which are expected to assemble into regular arrays of crystalline stems linked at the extrema by short β -turns. This strategy then leads to chain folded lamellar crystals of predictable thickness and surface functionality.

"The Preparation of Electro-Driven Chemomechanical Systems Using Polymer Gels" was described by Yoshihito Osada (Ibaraki



Excursion to Hakushu, Nagano Prefecture.

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University). It was found the polyelectrolyte gels undergo shape changes by applying DC current. The velocity of shape change is proportional to the charge density in the gel. This appears to be the first model of an electrically activated artificial muscle working in aerobic and aqueous medium systems because the gel contracts and dilates reversibly by an electric stimulus under isothermal condition. The electrical control makes use of crosslinked polyelectrolyte gels. The system is quite simple, and consists of a water-swollen polymer gel which is inserted between a pair of electrodes which is connected to a DC source. Particularly studied was a poly(2-acrylamido-2-methyl-1-propanesulfonic acid) gel. Electro-activated chemomechanical devices studied were artificial muscles, chemical valves, drug delivery systems and gel actuators.

Virgil Percec (Case Western Reserve University) discussed "Molecular Engineering of Liquid Crystalline Polymers". Thermotropic and lyotropic low molar mass and polymeric liquid crystals are responsible for the structure and function of many biological systems. Molecular engineering of main chain, side chain and branched polymers containing either flexible or calamitic and disc-like mesogenic groups were discussed. The design of main chain liquid crystalline polyethers which do not contain rigid-rod like mesogens demonstrate avenues to produce the nematic, smectic and columnar meso phases. The molecular design of side chain liquid crystalline polymers containing conventional rod-like mesogens and/or crown ethers obtained by living cationic polymerization and cyclopolymerization of functional vinyl ethers was also discussed.

"Chemical and Electrochemical Synthesis of Soluble Electro-Conducting Poly(2,5-Thienylene) Derivatives" was presented by Hideki Shirakawa (University of Tsukuba). In order to prepare soluble electro-conducting poly(2,5-thienylene) derivatives with functional 3-phenylalkyl and 3-phenylalkylthiophene groups were synthesized by Grignard cross-coupling reaction of 1-bromo-*o*-phenylalkane with 3-bromothiophene in the presence of dichloro[1,3-bis(diphenylphosphino)propane]-nickel II. They were studied from the viewpoint of electrochemical and chemical polymerizations. The chemical, electrochemical and electronic properties of these polymers were discussed including initial characterization, spectroscopy and electrochemical cyclic voltammetry.

Hiroyuki Nishide (Waseda University) described the "Synthesis and Magnetic Property of Conjugated Stable Polyradicals". For an organic molecule containing plural radical moieties, a magnetic interaction among them could be expected. The strength of the interaction is believed to depend on the chemical structure connecting the radical moieties. π -Conjugated phenoxyradicals bearing a polyene backbone were chemically stable and their spin concentration reached nearly Avogadro's number. While the bulk magnetism has not been realized, the profile of the magnetic interactions could be described as polyradicals with chemically elucidated structure. Two types of polyradicals, one with a delocalized and one with a spin localized radical were discussed. An antiferromagnetic and a weak ferromagnetic interaction were observed for the former and the latter polyradical, respectively. Mixing of both types of spins in one polymer chain seems to lead to a cooperative magnetic phenomenon.

Yukio Imanishi (Kyoto University) discussed "Biocomposite Materials for Promotion of Adhesion, Growth and Differentiation of Cells". Living bodies maintain and develop their life with specific recognition of external and internal signals with the aid of



Visit to JEOL Research Laboratories and Production Facilities, Akishima, Tokyo.

highly organized signal-accepting and signal-transmission systems in which many kinds of proteins and peptides take part. The design of composite materials composed of synthetic polymer membrane and biosignal molecules for enhancement of the signal transmission function was investigated which involved peptides with immobilized polymer membranes. Fibronectin with arginyl-glycyl-aspartyl-seryl sequences as the core peptide was investigated as receptors. Imanishi also described future prospects of biocomposite materials.

"Studies on and with Functionalized Polystyrenes" was presented by Eli M. Pearce (Polytechnic University). A variety of useful functionalized polystyrenes having fluoroalkyl ketone and fluoroalkyl carbinol functionalities have been prepared and studied as components that provide strong hydrogen bonding which provides the basis for miscible blends with a variety of H-bond accepting polymers. Hexafluoroisopropanol-polystyrene copolymers have been used as compatibilizers for polystyrene blends with polyethylene oxide and polyamides. Polymers have also been studied for their capability of providing high char forming systems to reduce flammability.

"Synthesis of Wood Plastic Composites by Radiation" was described by Koichiro Hayashi (Osaka University). The polycondensation of trimethylolmelamine by ionizing irradiation was discussed. For the polycondensation, an additive such as chloral hydrate is needed because it forms a convenient radiolysis product, namely a proton which is the catalyst for condensation of the trimethylolmelamines. The formation of the proton and their yield is proportional to the radiation dose. Hayashi also described the use of this reaction for the preparation of composite materials.

As it was the tradition in previous seminars on the third day of this meeting an excursion was undertaken that took us to the JEOL research laboratories and their production facilities in Akishima, Tokyo. The bus tour took us also to the Suntory Distillery in Hakushu, Nagano and one of the most famous vineyards of Japan, to Katsunuma in the Yamanashi Valley. This bus trip allowed extensive interaction of the individual scientists. They became more acquainted with one another as people changed seats during the trip to interact with another scientist while they exchanged their scientific views and opinions. The evening was spent in a Japanese restaurant in the country side in Takao, Tokyo. The banquet was held on Thursday evening at the Tokyo Garden Palace Hotel.

The meeting participants came away from the seminar with a great deal of satisfaction and feeling of accomplishment. The next meeting on Polymer Synthesis between scientists of the U.S. and Japan is planned in 3 years time in the United States.

One important factor became apparent during this meeting; the

average age of the participants was significantly lower than in past meetings which was found to be a very desirable situation. Selected people were also invited this time to present their work which they had done during the early period of their career.