

1988

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Otto Vogl

University of Massachusetts - Amherst, vogl@polysci.umass.edu

Hiroshi Sumitomo

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Vogl, Otto and Sumitomo, Hiroshi, "U.S.-Japan Seminar: "Synthesis, Properties and Reactions of Specialty Polymers"" (1988). *Polymer News*. 180.

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Conference Reports

U.S.-Japan Seminar "Synthesis, Properties and Reactions of Specialty Polymers"

Hiroshi Sumitomo^a
and Otto Vogl^b

^aFaculty of Agriculture, Nagoya University, Chikusa, Nagoya 464, Japan

^bPolytechnic University, Brooklyn, NY 11201

The U.S.-Japan Seminar on Polymer Synthesis, now the fourth of the series, was held from July 20-July 24, 1987 at the Napa Valley Lodge, Yountville, CA 94599. It was organized by Professor Hidesumi Hirai, University of Tokyo and Professor Eli M. Pearce, Polytechnic University; the program consisted of thirteen speakers and nine observers from the American side and thirteen speakers and seven observers from the Japanese side.

The meeting place, the Napa Valley Lodge, provided a pleasant surrounding, which allowed, in addition to the excellent lectures, a congenial way for people to get ac-



Napa Valley Lodge

quainted, to exchange scientific and personal views and, generally speaking, to provide an atmosphere of inspiration.

The meeting was opened by Professor Pearce, who reviewed the program and discussed the rules of the meetings. With T. Saegusa as the session chairman in the morning of the first day on the subject of *Synthesis of Specialty Polymers* Shohei Inoue, University of Tokyo, presented his work "From Living to 'Immortal' Polymerization." In his laboratory it was found that living polymerization of cyclic but also of some vinyl monomers can be carried



Hiroshi Sumitomo



Otto Vogl

out with aluminum porphyrin initiating systems. They are excellent initiators for a variety of monomers such as epoxides, β -lactones, γ -lactones, ϵ -lactones and lactides. The alternating copolymerization of epoxide and cyclic acid anhydride or carbon dioxide gave polymers and copolymers with narrow molecular weight distribution. The most important new development in this area is the polymerization of methacrylic esters; it proceeds in the presence of radiation with visible light and at room temperature. This polymerization seems to have some similarities with the group transfer polymerization of methacrylates with silicone compounds as part of the initiating systems. The polymerization of methyl methacrylate with this initiating system proceeds via the (porphyrinato)aluminum enolate as the growing species; visible light is not only needed for the initiation reaction but is also necessary for every step of the propagation reaction (addition of the enolate to the methacrylate). Although the polymerization of the epoxide with this initiating system is of nucleophilic or anionic nature with (porphyrinato)aluminum alkoxide as the growing species, it is not easily

terminated in the presence of protonic compounds or hydrogen chloride. Regular and constant chain transfer is observed during this polymerization which gives this polymerization an immortal nature.

William J. Bailey described the work of his group on "Recent Advances in Free Radical Ring Opening Polymerization." Free radical ring opening polymerization is comparatively rare. Although certain ketene acetals are convenient for introducing an ester group into the backbone of an addition polymer, these acetals are not very reactive in copolymerizations. Various cyclic acrylates are highly reactive and can undergo nearly complete ring opening. W. Bailey also described polymerization of spirocyclohexadienes; the driving force for this ring polymerization is the formation of an aromatic ring. The resulting polymers are thermally very stable but exhibit greater solubility.

Takayuki Otsu of Osaka City University described the "Synthesis, Characterization and Application of Poly(Substituted Methylenes)." The polymerization of 1,2-carboxylate substituted carbon-carbon double bonds are relatively rare. Professor Otsu's group found that dialkyl fumarates homopolymerized with radical initiators. The yield and molecular weight of the polymers increased with the bulkiness of the ester substituents. Isopropyl and *tert*-butyl fumarate esters are prime candidates for these polymerizations and gave polymers that are rod like and have high stability against ultra-violet light and hydrolysis. The polymers have no glass transition temperature and have interesting properties as potential lens materials. It was found that maleates do not polymerize but can be isomerized during the polymerization procedures (Monomer-Isomerization Radical Polymerization) with such bases as morpholine; the fumarates initially produced are then the monomer for the polymerization. *N*-Substituted maleimides polymerize also readily with radical initiators and are also readily copolymerized with other vinyl monomers.

James McGrath of the Virginia Polytechnic Institute and State University described the work of his group on "New Polymerizations for New Polymeric Materials." One of the gate through a covalent ester species, while with methyl of multiphase copolymers, primarily via living polymerization or step reaction copolymerization. Considerable work is also devoted to polydimethylsiloxane. Various aspects of anionic group transfer, coordinated anionic and coordinated ring-opening polymerization, the (polymerization that had been described earlier by S. Inoue) were also presented.

Three subjects were discussed Wednesday afternoon. The first presentation was by Takeo Saegusa of Kyoto University. He described "Polymerization of 2-Oxazolines and Functional Polymers Derived From Them." The polymerization mechanisms of 2-oxazolines were discussed, especially the polymerization of 2-perfluoroalkyl-2-oxazolines. With methyl tosylate as the initiator these monomers propagate through a covalent ester species, while with methyl triflate through ionic species. The difference of the nature of the propagating species is ascribed to the difference in the nucleophilic reactivity between the counter anion and the monomer. In addition, several other systems of polymerization have been found, in which the propagation proceeds via electrophilic covalent species. Some important examples of polymerization reactions of other kinds of monomers were mentioned which were expressed neither by the scheme of the conventional "cationic" nor "anionic" polymerization.



Participants: U.S.-Japan Seminar.

On the bases of the reexamination of these observations a new concept of schematization of the so-called "ionic polymerization" reactions has been proposed which involves ionic/ionic, ionic/dipolar and dipolar/dipolar interactions of monomer and growing species. Functionally substituted poly(2-oxazolines) and crosslinked polymers have also been prepared. The polymers from 2-oxazolines have excellent blending properties because they have the "dialkyl amide" group as part of the polymer chain.

Koichiro Hayashi of Osaka University discussed "Reaction Mechanism of Enzymes Studies by Pulse Radiolysis Technique." The reduction mechanism of biopolymers such as hemoproteins and flavoproteins were elucidated by the use of fast observation techniques such as pulse radiolysis. Particularly investigated were the radiation induced reduction mechanism of myoglobin, hemoglobin, earth worm hemoglobin and horse radish peroxidase. It was found that this technique is useful for investigating electron transfer reaction in a variety of biological systems.

In the last presentation of the afternoon, Otto Vogl of the Polytechnic University discussed "Helical Polymers: Optical Activity Based on Macromolecular Asymmetry." Increased sophistication in polymer synthesis has allowed some optimism and thoughts that it might be possible, at least in some cases, not only to control a) configuration during the synthesis (stereospecific polymerization) but also control or at least influence b) conformation during the synthesis of the macromolecular chain. With better understanding of the conformation of the macromolecules and with higher sophistication in polymer design and synthetic skill it has become feasible to plan the synthesis of macromolecules in their secondary structure. It has been known for a long time that much of the biological activity of some macromolecules depends not only on the proper arrangement of the monomer sequences but also on the correct conformation of the macromolecules and the tertiary structures. Helical conformations are common in nucleic acids and in stereoregular isotactic polymers of olefins and aldehydes.

A number of optically active polymers have been measured in the solid state as films. Inorganic materials such as sodium chlorate, sodium bromate, quartz, sodium periodate, benzil and other solids have been measured as single crystals. O. Vogl's laboratory has now developed a method to determine reliably the optical activity of solids in suspension. He described the comparison of the measurements of inorganic solids as crystals and in suspension and two types of helical polymers in suspension and solution. The values in the optical rotation in the single crystal and suspension of the

Conference Reports

inorganic materials were the same. In polymeric systems, the values in suspension and solutions were also identical.

Using chiral initiators for the initiation of chloral polymerization, polychloral samples with high optical rotations have been obtained. The numeric value of the optical rotation of these polychloral samples depended on the stereospecificity of the addition of the first monomer or the first few monomer units on to the chiral initiating anion. Confidence was expressed that complete stereochemical control will be achieved in the not too distant future which would lead to the synthesis of perfect helices of one handedness with high optical rotation.

In the session on *Biomedically Related Polymers* the first speaker on Wednesday morning, Hiroshi Sumitomo described the "Oligosaccharide-Carrying Styrene-Type Macromers. Polymerization and Specific Interaction Between the Polymers and Liver Cells." Convenient high-yield synthetic methods have been developed for oligosaccharide-substituted styrene type macromers and their polymers. The oligosaccharide carrying polystyrenes were found to function as specific recognition markers for proteins and cells. Especially, galactose-carrying polystyrene strongly enhanced adhesion and the viability of liver cells (hepatocytes) in culture, which was attributed to the galactose-specific interaction between the polymer molecule and hepatocytes. Carbohydrates, especially oligosaccharide chains play basic roles in information, recognition and regulation of living organisms. Synthetic polymers endowed with informational oligosaccharides, even with commercially available samples are of interest and importance in connection with pharmacological and biomedical applications.

"Synthesis and Properties of Novel Ion-Containing Polymers" were described by Joseph C. Salamone of the University of Lowell. The preparations, solution properties of unusual ion containing polymers were described. These polymers include polyampholytes derived from ion-pair comonomers and polyaminimides with bipolar ions in either the main chain or in the side chain. In addition, ampholytic ionomers derived from the polymerization of an ion-pair comonomer with a neutral comonomer were also discussed. Of particular interest was a new charge transfer polymerization from an ion-pair comonomer. This latter system is believed to have implications for the understanding of the mechanism of initiation of charge transfer polymerization.

"Design and Synthesis of Biocompatible Polymeric Materials" was described by Yukio Imanishi of Kyoto University. Two important approaches have been considered in designing biocompatible polymeric materials. One is to acquire the biocompatibility by controlling interactions with the living system through the control of surface properties of polymeric material. The other is to attain the biocompatibility of the hybridization of polymeric materials with biologically active substances or living cells. Imanishi's group synthesized a new class of polyetherurethaneureas to which heparin was bound by electrostatic interaction or by covalent bonding. The authors also grafted on various surfaces appropriately synthesized polyallylamine spacer containing polymers and connected the tetrapeptide Arg-Gly-Asp-Ser to a polydimethylsiloxane film blended with polydimethylsiloxane carrying primary amino groups.

David A. Tirrell of the University of Massachusetts described "Macromolecular Signaling Processes in Synthetic Bilayer Membranes." In his laboratory functionalized poly-

electrolyte chains have been prepared that can be anchored irreversibly onto the surface of synthetic bilayer membranes. By control of the conformational states of these surface-bound chains, Tirrell's group was able to manipulate the structural and functional properties of the membrane as a whole. This approach allows to mimic some of the most interesting characteristics of natural bilayer membranes, and to formulate vesicular systems that will release their contents rapidly and quantitatively in response to selected chemical and physical signals. The preparation, properties and potential utility of this system has been discussed.

Wednesday afternoon was left for open discussions and excursions in the neighboring towns in the Napa valley including visits to some local wineries to taste their produce.

On Thursday morning the session started with a talk on *Conductive Polymers* by Hideki Shirakawa, University of Tsukuba, entitled "Synthesis, Characterization and Properties of Aligned Polyacetylene Films." Polyacetylene is the simplest conjugated polymer consisting only of CH units in which each carbon atom has one π -electron forming a linear chain of π electrons. Large electrical conduction along the polymer chain has been observed due to the large anisotropy in electrical properties. Study of the intrinsic one-dimensional properties of oriented polyacetylene film by uniaxial stretching or direct polymerization of the monomers in the aligned form are essential. The author described the direct synthesis of aligned films by polymerization of acetylene in a matrix of nematic liquid crystals. Partial alignments of the fibrils have been observed and conductivities of 1.2×10^4 S/cm were obtained.

Yoshiyuki Okamoto of the Polytechnic University described "Recent Investigations of Electroresponsive Polymers: Structure, Characterization and Properties of Poly(carbon dichalcogenides)." He described polymers of carbondiselenide and carbondisulfide. Depending on the polymerization conditions the products show various electronic properties; insulators, semiconductors, and metallic conductors. The polymerization process under various conditions was investigated; it was also found that the initial polymers upon heating sometimes decompose into various polymeric and composite materials.

"A New Class of Polyconjugated Systems, Synthesis and Properties of Polymethylenecyclophanes" was described by Shigeyoshi Mizogami, of the Idemitsu Kosan Company. Polyconjugated systems so-called polymethylenecyclophanes having [2,2]-metacyclophane skeletons in the polymer chains have been designed and synthesized. Oxidative coupling of dihydroxy-[2,2]-metacyclophane catalyzed by ferric chloride easily yielded polymethylenecyclophane. The conductivity of these materials is low, but when doped with sulfuric acid vapor, the conductivity was enhanced by seven orders of magnitude to about 10^{-1} S/cm.

"The Synthesis of Organic Polymers Potentially Possessing Electrically Conductive, Piezoelectric and Nonlinear Optical Properties" was discussed by Henry K. Hall. Various polycondensation polymers based on anthraquinone and heterocyclic quinones were prepared and examined for their electrical conductivity. Multiazobenzene polymers were synthesized by oxidative coupling of aromatic diamines. Some of the materials were found to be borderline in conductivity. Piezo-active polymers from poly(vinylidene fluoride) macromers were synthesized by telomerization of vinylidene fluoride with methanol. Films of poly(bicyclo-

Conference Reports

" γ -Benzyl-L-Glutamate Graft Copolymers of Cellulose and Poly(arylene ether sulfone)" was described by William H. Daly of the Louisiana State University. Macroinitiators with primary amino substituents were synthesized but one of the following techniques: cyanoethylation of cellulose followed by reduction; nitration then followed by lithium aluminum hydride reduction to produce poly(arylene ether sulfone); phthalidmethylation followed by hydrazinolysis using molar ratios of γ -benzyl-L-glutamate ranging from 1 to 100 relative to the amine concentration; grafting is effected in anhydrous THF at room temperature. The reactivity of these derivatives was discussed.

The last two papers in the afternoon could be related to *Separation Processes*. Tisato Kajiyama of Kyushu University discussed "Polymer/Liquid Crystal Hybrid Thin Films With Unique Permselective Characteristics." A polymer/liquid crystal hybrid film is a blend of a thin film cast from a polymer solution in a nematic liquid crystals. Nematic liquid crystals have the characteristics of very low viscosity and high orientation of the liquid crystal molecules under an imposed electric field. The hybrid thin film can control solubility and diffusivity of permeating molecules, depending on chemical structures and/or physical properties of the liquid crystalline material, the characteristic of such hybrid systems to liquid membranes. Polycarbonate and poly(vinyl chloride) were used as matrix polymers and various nematic compounds as liquid crystalline materials. When an electric field was applied during evaporation of the solvent, the liquid crystalline molecules were oriented preferentially

along the direction of the imposed electric field. UV¹ and VIS light irradiation facilitates or activates permeation of potassium ions. This was believed to be the first report of a photo-induced active transfer of a metal cation through an organic thin films.

The last paper of the meeting presented by Samuel J. Huang of the University of Connecticut was entitled "Recent Advances in Biodegradable Polymers." The presence of hydrolyzable and/or oxidizable linkages in the polymer chains, the presence of suitable substituents correct stereo-configuration, balance of hydrophobicity and hydrophilicity; conformational flexibility contribute to the biodegradability of synthetic polymers. The morphology of the polymer samples also greatly effects the rate of biodegradation. The biodegradation of hydrolyzable polymers proceeds with the degradation of the amorphous region prior to the degradation of the crystalline regions. Linear and crosslinked polymers containing one or more hydrolyzable functional groups have been synthesized and found to be biodegradable; they showed promise in applications in biomedical and agricultural areas.

The symposium was closed by Professor Hirai who thanked the speakers, the discussion leaders and the observers. This vigorous and lively meeting was a demonstration of cooperation between the polymer scientists especially in the synthetic area between the United States and Japan. It was concluded that a great deal had been learned from each other and it was hoped that another meeting of a similar kind would be held before long.