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Conference Report

International Symposium on "New Polymers"



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On November 30 and December 1, 1991, an International Symposium sponsored by IUPAC was held at the Miyako Hotel in Kyoto, Japan; it was entitled "New Polymers." It was organized to honor Professor Takeo Saegusa on the occasion of his retirement. The chairman of the organizing committee was T. Higashimura, Kyoto University, who was assisted by Y. Chujo, Kyoto University, and the chairman of the local committee, Y. Imanishi, Kyoto University. The meeting brought together about 210 participants, 130 from Japan. Two plenary and 15 invited lectures were presented and 87 papers were presented in poster form.

The meeting was opened with a plenary lecture by Walter Heitz. He presented his work on "Rodlike Polymers: A Challenge to Polymer Synthesis." Aromatic AB-polyesters can be obtained as soluble materials if both monomer units are statistically mono-substituted; lyotropic behavior is found at high concentrations. In the viscosity molecular weight relationship the exponent for aromatic polyesters is lower than 1, indicating flexibility in aro-

matic polyesters. Stiff macromolecules are differentiated from rodlike macromolecules. For example, polymers of norbornene are stiff due to restrictive conformational changes, but poly(*p*-phenylene) is rodlike. W. Heitz also discussed the preparation of poly(phenylene vinylene) and poly(phenylene ethynylene) as well as poly(phenylene) by palladium catalyzed synthesis. It was found that poly(phenyl-1,4 phenylene) is a thermotropic polymer and poly(1,4 pyridinium) salts are new classes of rodlike poly(cations).

The plenary lecture by Takeo Saegusa on "Organic/Inorganic Polymer Hybrids" was coauthored by Y. Chujo. It described the combination between organic polymer and inorganic substance which has been a useful approach in the developments of new materials having desirable mechanical properties. So-called "composite materials" represent a typical example in which an inorganic substance such as a metal oxide or carbonate is dispersed in the matrix of an organic polymer. New materials of another combination between organic polymer and silica gel were prepared.



Takeo Saegusa



Toshinobu Higashimura

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Miyako Hotel, Kyoto, Japan

by blending them at a molecular level dispersion. These materials are transparent glasses and are better called "hybrids." These hybrids were prepared by the sol-gel reaction of tetraethoxy-silane, the precursor of silica gel which is prepared by using a repeating unit of the polyoxazoline. These polymers are transparent glasses and homogeneous. Calcination of the transparent hybrid produces another material of highly porous silica gel with high surface area of nearly 1000 square meters per gram and a pore size diameter ranging between 20 and 100 Å.

George G.I. Moore (and Miguel A. Guerra) of St. Paul, MN described "Novel Perfluoropolyethers by Direct Fluorination." Oligomeric and polymeric fluorinated polyethers have been of great interest because of their low temperature properties and higher thermal stabilities. Each of these polymers are prepared by oligomerization reactions. The direct fluorination of hydrocarbon polyether analogs has recently been investigated. Fluorination of poly(ethylene oxide) yielded primarily a white solid insoluble in all liquids. It can be post fluorinated to a material of high thermal stability. Oxymethylene polymers and copolymers with ethylene oxide on fluorination gave oils with glass transition temperatures of -150°C . Polydiioxolane, polydiioxepane and polytrioxocane have also been fluorinated to give both oils and gummy solids. The fluorination of these materials is extensive but often not complete.

Masaaki Yamabe of Yokohama, Japan presented his work on "A Challenge to Novel Fluoropolymers." Perfluorinated vinyl ethers are extremely versatile comonomers used for preparing functional perfluoropolymers. The hexafluoropropylene oxide chemistry was developed in the 1960s and opened a way for the industrial preparation of polyfluoro(vinyl ethers). The copolymerization of tetrafluoroethylene with various perfluoro(vinyl ethers) has also been investigated and commercialized. New novel fluoropolymers based on perfluoro(vinyl ethers) were also discussed. Carboxylated perfluoro(vinyl ether) can be copolymerized with tetrafluoroethylene to give perfluorinated ion-exchange membranes. Transparent perfluoropolymers were developed based on an extremely selective cyclopolymerization using specially designed difunctional perfluoro monomers such as perfluoroallyl vinyl ether. These copolymerizations proceeded smoothly and cleanly with radical initiators. The polymers have exceptionally high transparency and some solubility, with good chemical and similar electrical properties and a very low refractive index.

The "Functional Liquid Crystals: Phase-Induction and Photoreactivity" was discussed by Helmut Ringsdorf, Mainz, Germany. Doping of discoid compounds containing an electron rich core, e.g. triphenylene, with electron acceptors, e.g. trinitro-

fluorenone, leads to induction of liquid crystalline phases and functionalized charge transfer complexes. The investigation of photochemical reactions in synthetic organized media has found growing interest. Less attention has been paid to the influence of the photoreactive event on the structure of the medium. This contribution dealt with the synthesis and properties of multifunctional materials, containing both photoreactive and self-assembling units.

Ernest Marechal, Paris, France presented his work on the "Synthesis and Characterization of Thermotropic(Arylene Fumarates)—Block—Poly(Alkylene Fumarates)." The presentation discussed the crosslinking of mesomorphic polymers with special concern for lyotropic species and side chain thermotropic polymers, mainly polysiloxanes, and a few main chain polyesters. Some main chain thermotropic polyesters with fumaric acid groups as rigid units were described. Particular emphasis was paid to the direct polycondensation of the corresponding difunctional oligomer, interfacial polycondensation of an alpha, omega, dichlorocarbonyl oligoester. The polymers obtained were primarily block copolymers with rigid blocks and some that exhibit nematic phases. Curing of the products was carried out either by photochemistry or by radical crosslinking.

Roland Rubner of Erlangen, Germany described the "Dedicated Polymers for Future Progresses in Microelectronics." Continuous miniaturization in microelectronics requires advanced materials and processes. Novel anhydride-containing filmforming polymers, which spontaneously react with bisaminoalkyl-siloxanes, were synthesized for the use in photolithographic processes. This allows the modeling of photoresist patterns and thus enhancement of practical resolution. In addition, efficient polymeric dielectrics with improved solubility in environmentally safe solvents were developed.

Dotsi Y. Sogah of Ithaca, NY described "Design, Synthesis, Architecture Control and Surface Activity of Amphiphilic Oxazoline Polymers." Fluoropolymers are known to have excellent thermal, chemical resistance and low surface tension. Novel, partially fluorinated oxazolines were polymerized by living cationic ring opening polymerization techniques. These polymers were able to modify Nylon surfaces at a very low level of concentration. Water soluble block copolymers were prepared by sequential addition of 2-methyl-2-oxazoline and the desired fluorinated oxazoline. The polymers form stable Langmuir-Blodgett mono- and



Registration



Itaru Mita, President SPSJ

multilayers in thin film prepared by depositions of interest in electronic applications.

Daniel J. Brunelle of Schenectady, NY described his work on "Recent Advances in the Chemistry of Aromatic Cyclic Oligomers." Chemistry of cyclic oligomers has recently developed into new procedures for the preparation of cyclic oligomeric carbonates. These were prepared by pseudo-high dilution, hydrolysis/condensation reaction of Bisphenol A-bis-chloroformate conveniently in 90% yield. The cyclic oligomeric carbonates could be polymerized in solution or in the melt with a variety of catalysts and high molecular materials were obtained. Many types of bisphenols containing various functional groups have also been incorporated into cyclic oligomeric carbonates and then ring open polymerized to high molecular weight polymers. Additional improvements could be made by a) crosslinking of polycarbonates via incorporation of small amounts of bis-cyclics or b) by incorporation of monomers which lead to semi-crystalline regimes in the polymers.

"Structure-Property Relationships in High Performance Thermoset-Thermoplastic Blends" was presented by P. T. McGrail of Cleveland, UK. Thermosetting resins are used for many applications including composites, molding compounds, high performance adhesives and surface coatings. A wide variety of such resins has been used. Blends of thermosets and thermoplastics may be prepared by dissolving the thermoplastic in the thermosetting resin precursors, with or without the use of a solvent, depending on the choice of thermoplastic or the thermoset. Particulate morphology can be determined, the type of morphology in the phase sizes dependant on a number of important parameters.

Eric J. Goethals, Ghent, Belgium presented his work on "New Block and Graft Copolymers Based on Cationic Polymerizations." The highly living character of a number of cationic ring opening polymerizations has been used to synthesize new, well defined, segmented copolymers. This has been achieved by sequential monomer additions, by grafting reactions, by macromonomer copolymerizations as well as by chain transfer to polymer. New examples of such polymers are based on such well known monomers as tetrahydrofuran, alkyloxazolines, cyclic amines, cyclic acetals and cyclic sulfides. Segmented copolymers containing polyelectrolyte segments and segmented star copolymers have been prepared.

A most interesting paper was presented by Henry L. Hsieh of Bartlesville, Oklahoma. The paper was entitled "Water Soluble Polymers for Hostile Environment Oil Recovery Applications." Contrary to popular belief, petroleum reservoirs are not underground cavities containing large pools of oil. Rather, the oil is

trapped in very small pores of rock, typically sandstone limestone. When a well is drilled into an oil-bearing format petroleum flows to the wellbore under natural pressure exerted water and/or gas surrounding the oil. In some reservoirs, the oil is also forced into the wellbore because of the release of natural gas dissolved in oil. Regardless of the source, the pressure is not enough to overflow the surface without an external energy source. In some reservoirs however, the oil has to be artificially lifted to surface. In a typical reservoir, combined production by natural forces and water or gas injection is expected to total about 1/3 the original oil in place. While water is effective in forcing the oil flow to wellbore in a producing well, there is a tendency to follow the least resistant path and bypass regions containing high amounts of unswept oil. Water soluble polymers can be added to injection water to increase viscosity and, as a result, reduce mobility. Polyacrylamides most frequently used in polymer flooding, hydrolyse at elevated temperatures producing carboxylates in the polymer backbone. Copolymers prepared with various ratios of acrylamide and N-vinyl-2-pyrrolidone, tested for thermal stability, showed good results. Increasing demand for higher temperature resistance for those polymers used in polymer flooding is required and temperatures as high as 150°C are needed. One method that is now being explored is *in situ* crosslinking polymer solutions in oil bearing formations which can produce gel type materials "in place" at the desired location.

Walter R. Hertler of Wilmington, Delaware described his work on "Synthesis and Application of Acid-Labile Acrylic Polymer." Group transfer polymerization is a useful process for the preparation of acrylic polymers with well-defined architecture and functionality. With functional monomers, such as hydroxyethyl methacrylate or methacrylic acid, protection of the functional groups is necessary. Alpha-Alkoxyalkyl esters of methacrylic acid, such as tetrahydropyranyl methacrylate can be easily prepared. Methacrylic acid with such vinyl ethers were found to behave well in group transfer polymerization. These polymers are useful for deep lithography because of the sensitivity of the tetrahydropyranyl methacrylate unit to ultraviolet light which decomposes to tetrahydropyrane and the polymethacrylic acid unit.



Poster session, M. Raetzsch

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Poster session

Shohei Inoue of Tokyo, Japan presented his work on "Precise Control of Polymerization Reaction with New Catalysts." In the precise control of the polymerization, the reaction of the monomer with a new catalyst in order to control the molecular weight of polymers (formed in addition or ring opening polymerization), is essential to regulate the reactivity of the active species at the polymer growing end. Some methylporphyrins are excellent initiators for the living polymerization of an unprecedentedly wide variety of monomers to give polymers with controlled molecular weight. This is due to the activation of the monomer by the coordination of an organoaluminum compound such as a Lewis acid. It is essential that no direct reaction occurs between the Lewis acid and the growing species. In this new system the porphyrin complex modified with di-*tert*-butylphenoxy-methylaluminum was found to be the best modifier for the high speed living polymerization of epoxides and lactones.

David A. Tirrell of Amherst, Massachusetts presented his work on "New Polymers From Artificial Genes." The advent of recombinant DNA technology has provided a basis for the development of polymeric materials characterized by essentially absolute uniformity of chain length, sequence and stereochemistry. Two aspects of this chemistry were discussed: i) the preparation of polypeptides containing unnatural amino acids, and ii) the synthesis of monodisperse populations of helical polymers. The strategy for incorporating unnatural amino acids uses as a host cell an auxotroph incapable of synthesizing one of the twenty natural amino acids. The host is transformed with a plasmid bearing an artificial gene encoding the sequence of interest, with the amino acid to be replaced, encoded in the normal fashion. The host is then grown on a medium containing the unnatural amino acid in places of its natural analogue. Using this strategy, it was possible to successfully prepare polypeptides carrying periodic selenomethionine residues and a broadly based exploration of this process. It was also possible to prepare monodisperse derivations of poly(glutamic acid) via artificial coding sequences, fused to the C-terminus of a 26-kilodalton fragment of glutathione S-transferase. Conversion of these polymers into poly(γ -benzyl-L-glutamate) and into oriented surface layers is presently being studied.

"Oligomers of Stereoregular Polymers" was described by Otto Vogl, Brooklyn, NY, in cooperation with Koichi Hatada, Charles M. Garner, Christoph Kratky, William J. Simonsick Jr. and Koichi

Ute. Many oligomers have been studied over the years; it among them are low oligomers obtained by oligomerizing methyl methacrylate at low temperatures. Tertiarybutyl magnesium bromide as the initiator gives almost exclusively isotactic (methyl methacrylate), while tertiarybutyl lithium complexed triethylaluminum as the initiator, gives essentially syndiotactic polymer; this has also been found for the oligomers. Some oligomers were characterized by ^1H NMR spectroscopy. Selected oligomers which could be crystallized by single X-ray analysis.

An even better example of the studies of oligomers: oligomerization of trihaloacetaldehydes, fluoral, chloral and bromal. These oligomerizations were more easily controlled because initiation could be carried out above the ceiling temperature. Subsequent oligomerization could be done by judicious schedules. Some of the oligomers crystallize easily and crystals could be grown. Oligomers of trihaloacetaldehydes: cases up to the undecamer were investigated by a combination of GC, capillary GC, NMR spectroscopy, K+IDS mass spectrometry and in over 10 cases by single crystal X-ray analysis. Some methods and combinations of these methods allowed us to establish beyond any doubt the structure of individual oligomers and their absolute configuration. Finally, the cooligomerization of chloral and bromal provided additional and interesting challenges as stereochemistry and competitive reactivity of the monomer under various conditions of cooligomerization were concerned.

In addition to the invited talks, some of the posters presented at this conference on "New Polymers" showed results of great interest. Of particular interest was the presentation by C. Hawker of Queensland, Australia, entitled "Novel Macromolecular Architectures Via the Convergent Growth Approach." The preparation of highly branched polymers, with branches at every repeat unit, has been until recently, a neglected subject. A new family of macromolecules has been synthesized which is characterized by high degree of branching which originates from a central point. As a result, the macromolecules appear to have a spherical shape, free of the sort of chain entanglement which is characteristic of most other high polymer systems. The nature of the monomer unit used to construct the macromolecules is



At the banquet
T. Saegusa J. Vogl W. Heitz



At the banquet
O. Vogl Ayako Saegusa T. Higashimura

significant role in determining the ultimate properties of the polymers. A variety of different approaches was carried out in attempts to design the properties of the dendritic macromolecules. Not only traditional dendritic macromolecules were used for the placement of functional group and monomer units at the periphery of the macromolecules, but also for the arrangement of monomer units in the interior of the spherical macromolecules. Comparison of the properties of these novel dendritic copolymers obtained by the stepwise convergent growth approach was presented.

M. Hosoda described "The Reaction of Optically Active Poly(triphenylmethyl methacrylate) in Solution." Optically active isotactic poly(triphenylmethyl methacrylate) represents one of the very few examples in which optical activity arises from atropisomerism phenomena. On heating of the polymer at 100°C in acetone solution, the optical activity disappeared slowly. It was shown that a quantitative amount of triphenylmethyl ether was isolated from the solution and in addition carboxylic acid groups and anhydride groups were formed during the heating. It was suggested that this reaction started at the end of the chain with a triphenylmethoxy fission and then proceeded along the chain with the formation of block copolymers consisting of one block of poly(triphenylmethyl methacrylate) and one block of a random methacrylic anhydride-methacrylic acid copolymer.

M. Kaku of Wilmington, Delaware described "Oxazoline Polymers: Synthesis, Monolayers and Multilayer Films." Ultrathin films prepared by transferring molecular layers from the air-water surface onto the solid substrates have received much attention. They have been designed and prepared and have provided novel polymers which involve polymeric hydrophilic backbone chains, for example, poly-oxazoline and a NLO active group in its hydrophobic tail. The hydrophobic tail which provide in any case the appropriate alignment of the NLO groups in the desired layer structures.

Y. Ito of Kyoto University, Kyoto, Japan described an exciting new development in "New Living Polymerization of 1,2-Diisocyanarenes via (Quinoxaliny)palladium Complexes: Synthesis of Helical Poly(2,3-quinoxalines)." Isocyanides are known to be polymerized by transition metal catalysts, especially by nickel salts to afford poly(N-substituted iminomethylenes). The polymerization reaction proceeds via consecutive insertion reactions of coordinated

isocyanides to a propagating organo transition metal complex. This method has now been modified to carry out a new living polymerization of 1,2-diisocyanarene giving poly(2,3-quinoxaline) via (quinoxaliny)palladium complexes. By this method, new living polymerization of 1,2-diisocyanarenes was described using trimethylsilane groups as substituents. The synthesis of novel liquid crystalline polymers on this basis has also been presented, as has been the 'screw sense selective polymerization.'

3,6-p-Tolyl-1,2-diisocyanarene was treated with palladium complexes with chiral phosphine ligands. The quater(quinoxaline)Pd complex was obtained as a diastereomeric mixture, which was separated and isolated by HPLC. There was no longer any conformational equilibrium between the opposite screw sense helical structures, therefore one compound could be separated chromatographically in the two diastereomers, which exhibit opposite specific rotations.

The meeting at the luxurious and famous Miyako Hotel gave the participants the opportunity to enjoy the old imperial city of Kyoto, which is now a living, up-to-date metropolis. It was wonderful to visit the many temples steeped in culture and beautiful garden and other sites of Kyoto and surrounding areas. The Conference on 'New Polymers' not only provided exciting scientific results but its highlight, the Symposium Banquet, provided the necessary elegance, so characteristic for the Miyako Hotel and Kyoto. Its focal point was a most unusual entertainment by a group of Kyoto musicians (Rokusai Nembutsu).

The participants expressed their enjoyment at being in Japan and having the opportunity to be part of the meeting on 'New Polymers' in Kyoto, in this cradle of polymer science of Japan.



Rokusai Nembutsu at the banquet

Polymer Science and Technology for the 21st Century **A symposium in honor of Otto Vogl on his 65th birthday**

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