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31st International Congress of Pure and Applied Chemistry, Sofia, Bulgaria, 1987

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Conference Reports

31st International Congress of Pure and Applied Chemistry, Sofia, Bulgaria, 1987

BULGARIAN ACADEMY OF SCIENCES



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The 31st International Congress of Pure and Applied Chemistry was held from July 13 to 18, 1987 in Sofia, Bulgaria. It consisted of 10 plenary lectures and about 50 invited main lectures. The meeting was organized by the Organizing Committee under Professor L. Zheliazkov and was under the sponsorship of the Bulgarian Academy of Sciences.

The IUPAC Congress had 9 sessions and over 1,900 participants from 38 different countries came to Sofia for this meeting. Session 8 was devoted to "Polymers;" it consisted of 16 invited lectures and over 100 presentations in poster form.

Sofia, the capital of The People's Republic of Bulgaria is situated in the central part of the Balkan Peninsula. It is a natural crossroads between east and west, north and south and lies at an altitude of 550 meters at the foot of the Vitosha and Lyulin Mountains. Bulgaria was settled as early

as 6,000 years ago; during Roman times it was inhabited by the Thracians and Sofia was known as the city of Serdica in the Roman Empire.

The IUPAC Congress was held at the new Lyudmila Zhivkova Conference Center, a splendid, new building in the center of Sofia.

Takeo Saegusa of the University of Kyoto, Japan, opened the Polymer Session with a lecture on "Spontaneous Periodic Copolymerization via Zwitterion Intermediates." He mentioned the well known concept of electrophilic and nucleophilic monomer which had been used in his laboratory for alternating copolymerization of specific monomer pairs. An extended version of copolymerizations of oxazolines and related monomers with acrylic acid and propiolactone was presented. T. Saegusa also discussed the preparation and characterization of polymers based on 2-oxazoline involving such termonomers as carbon dioxide to form terpolymers of



Invited Main Speakers.

From left: Mihailov, Tudos, Marechal, Shopov, Saegusa, Plate, Kalai, Vogl, Borissov, Hogen-Esch, Jedlinski, Kennedy, and Penczek.

ABCABC structures. He also mentioned new so-called periodic copolymers ABBABBABBA based on 2-oxazoline as the B component.

Otto Vogl, Polytechnic University, New York, presented his work on "Helical Polymers." He pointed at the existence of helical structures in many natural polymers such as in poly(α -amino acids), poly(nucleic acids) and specific polysaccharides, but also the helical forms in the solid state of numerous isotactic synthetic polymers. Specifically designed polymers, polychloral and poly(triphenylmethyl methacrylate) can now be made that are essentially 100% helical. Because these polymers are completely helical it has become possible to prepare these polymers in onehandedness only; high optical rotations of $4,000^\circ$ for polychloral and 400° for poly(triphenylmethyl methacrylate) have been achieved. Stereospecificity of the initiation and the subsequent addition steps of the monomer leading to polymerization are essential for obtaining onehandedness and optical activity of the polymer. O. Vogl also compared helicity of these polymers with optical dissymetry in selected, especially isotropic inorganic crystals. The latter are based on ionic (sodium chlorate), molecular (benzil) and polymeric structures (quartz). A comparison of helicity and optical rotation in inorganic crystals, biomaterials and synthetic polymers was pointed out. This comparison has recently become possible because a precise method of measuring the optical rotation *in suspension* of solid powders of inorganic and polymeric materials has been developed and accurate determinations of the optical activity of many solids can now be carried out.

Hideki Shirakawa, Kazuo Akagi, Shintaro Katayama from the University of Tsukuba and Kataro Araya from Hitachi Limited, Akio Mukoh and Toshikazu Narahara, from Hitachi, discussed "Characterization and Anisotropic Properties of Highly Oriented Polyacetylene Films Prepared in Liquid Crystal Solvents." They have shown that highly oriented polyacetylene films can be prepared in a microscopically aligned nematic phase of a catalyst solution by two different methods: Orientation by gravity flow of the solution and alignment in a magnetic field. Films made by these two methods are highly oriented along the fiber axes as determined by polarized infrared and visible absorption measurements. They exhibit high electrical conductivities when

doped with iodine, arsenic pentafluoride and sulfuric acid. Conductivities of 1.2×10^4 S/cm were obtained which are similar to that of mercury.

Mircea Grigoras of the Institute of Macromolecular Chemistry in Jassy, Romania presented the talk of the work of Cristofer I. Simionescu and M. Grigoras "The Polymerization of Anthracene Monomers." The authors concluded that the high reactivity of anthracene monomers cause a peculiar behavior in polymerization processes. Polymerization of polymerizable anthracene containing monomers is accompanied by side reactions involving the anthracene ring; addition and substitution reactions may occur. Radical, ionic and coordination polymerization of vinylanthracenes are not simple processes. Anthracene derivatives can also be used in condensation polymerizations. Still, anthracene containing polymers are of interest for photo-chemical and photo-physical reasons.

Shohei Inoue of the University of Tokyo, Japan presented his work on "From Living to 'Immortal' Polymerization." He described the preparation of aluminum porphyrin initiators and their uses in the living polymerization of epoxides, or lactones, the alternating copolymerization of epoxides and cyclic acid anhydrides or carbon dioxide, the living polymerization of methacrylic esters and the 'immortal' polymerization. The presence of certain protic compounds for example methanol, does not interfere with the polymerization of lactones to high molecular polymers.

Joseph P. Kennedy of the University of Akron, USA presented his work on "Macromolecular Engineering by Living Carbocationic Techniques." He demonstrated the cationic living polymerization of isobutylene, the preparation of telechelic polyisobutylene, the preparation of linear tert.chloro-telechelic polyisobutylene, the living polymerization of 2,4,6-trimethylstyrene. The use of certain esters and ethers in conjunction with boron trichloride causes rapid, living polymerization of isobutylene at relatively high temperatures; when lactones instead of regular esters are used, the isobutylene polymerization proceeded by a ring expansion polymerization. This type of cationic living polymerization is very similar to the group transfer polymerization of methyl methacrylate by silicon compounds, which is a coordinative anionic process.



Convention Center: "Lyudmila Zhivkova."

Conference Reports

The paper by Takayukio Otsu of Osaka City University in Osaka was entitled "Block and Graft Copolymer Syntheses by Iniferter Technique." Otsu described the concept of the iniferter technique, a model for living radical polymerization in homogeneous system, and the apparent use of such systems for the synthesis and design of block copolymers. It was concluded that the iniferter technique is a novel synthetic method for the design of the chain end structure of polymers by radical polymerization. Monomers such as styrene and methyl methacrylate have been used, but vinyl acetate or vinyl chloride also polymerize well, when dithiocarbamate activated by photochemical means is used as the radical initiator.

Thilo E. Hogen-Esch of the University of Florida presented his work on "Stereochemical Aspects of Anionic Vinyl Polymerization." He discussed the careful analysis of end groups in oligomers and the polymerization of asymmetric monomers where the "E" and "Z" configuration of the monomer plays an important role in the reactivity of the monomers and the stereochemical arrangements of the monomers in the polymer.

Ivan M. Panayotov, D. K. Dimov, R. P. Stamenova, C. B. Tsvetanov of the Bulgarian Academy of Sciences, Sofia, discussed the "Complex Forming Properties of Linear and Crosslinked Poly(Ethylene Oxide)." The structure of the solvation shell of the complex forming properties of poly(ethyl oxide) of the cation was determined spectrophotometrically using alkaline-earth derivatives of fluorene. Radiation crosslinked poly(ethyl oxide) gave three dimensional structures of much greater size than the solvation cages of macrocyclic compounds. The effectiveness of crosslink solvations, as exemplified of alkali picrates is not different from linear polymers. Crosslinked poly(ethylene oxide) offers the opportunity to estimate the binding capacities of different ligands (solvents, monomers, polymers) for alkali metal cations with the aid of the competition method.

Zbigniew J. Jedlinski of the Polish Academy of Sciences in Zabrze, Poland, presented his work on the "Recent Development in Anionic Polymerization of Lactones." He discussed the ring opening polymerization of four, six, seven membered lactones as a convenient and flexible way of preparing specialty polyesters. With substituted β -propiolactones, using solutions of potassium and other alkali metals in THF as initiators, very high molecular weight homopolymers and block copolymers were obtained. Solutions of alkali metals also initiate polymerization of simple oxiranes.

"Various Catalytic Problems in Step Growth Polymerization" was discussed by Ernest Marechal and P. J. Madec of the University of Paris, Paris, France. E. Marechal discussed side reactions that have been encountered in the hydrosilylation on allylic monomers, particularly allyl ethers. His group found that both *t*-butanol (which was used as the solvent) as well as the catalyst chloroplatinic acid, caused side reactions. One side reaction is the rearrangement of the allyl ether group used for the hydrosilylation. Another side reaction is caused by the free hydroxyl group of the oligomer. A third side reaction is the hydrogenation in the presence of the catalyst which caused the formation of a saturation of the double bond. The authors also described the addition of carboxylic acids to epoxides to give β -hydroxy-substituted polyesters. A new chromium containing catalyst was found to eliminate the side reactions which are normally caused by catalysts such as ammonium salts or acids.



Excursion to Rila Monastery

"Phosphorous Containing Monomers, Oligomer and Polymers" was the subject of a talk by G. Borissov of the Bulgarian Academy of Sciences, Sofia, Bulgaria. He described the preparation of phosphorous containing polymers as fire retardant compositions by reacting polymers with selected reactive groups with alkyl phosphites and hypophosphorous acid as phosphorous intermediates. The introduction of phosphorous into polymers leads to the improvement not only of the fire resistance of the polymers, but also to improvement of adhesion, dyeability, water absorbance and aging resistance.

Stanislaw Penczek of the Polish Academy of Sciences, Lodz, Poland presented the work of his group on "Models of Biopolymers and Bioanalogous Polymers with Phosphate Units in the Chains." Polymerization of polyaddition of cyclic compounds have been used to prepare polymers modeling biopolymers with a poly(alkylene phosphate) backbone chain, such as it is known in nucleic acids and telichoic acids. Polyaddition of diepoxy compounds to phosphorous acid led to a new method of poly(alkylene phosphates). The thermodynamics of polymerization of ring opening polymerization of various phosphorous compounds as well as kinetics of the polymerization of five, six and seven membered monomers was studied. Polymer reactions are necessary to transform the initially formed polyphosphites, polyphosphoramidates and polymeric triesters to the required structure, the poly(alkylene phosphates).

Jaroslav Kalal of the Czechoslovak Academy of Science, Prague, Czechoslovakia presented a most interesting review: "Synthetic Polymers Today and in the Future in Medicine and Pharmacy." J. Kalal pointed out that drugs are rarely administered to patients in an unformulated state. The effect of the active drug depends very much on the way it has been formulated. J. Kalal discussed sustained release and prolonged delivery methods for drugs, microspheres and nanoparticles, targeting and prodrug approaches, magnetic particles, transdermal, buccal and gingival delivery systems, bioadhesive polymers, and artificial cells. Some polymers used in oral sustained release dosages have been and are being manufactured on an industrial scale and have been applied for years; others are in the beginning of their development.

Pierre J. Carreau of the Ecole Polytechnique of Montreal, Canada discussed his work on "Modelling of the Rheological Behavior of Polymers." Various approaches were illustrated

for the rheological modelling of polymer solutions and melts. The emphasis has been on concepts and theories which are based on a molecular description of the polymer molecule but which are expected to lead to reasonable predictions and descriptions of the flow properties for engineering applications. The theories to date can give a correct description of the relaxation spectrum of the macromolecules as one can determine from linear dynamic experiments over a large range of frequencies. Models were introduced which describe the shear thickening effects observed in polyelectrolyte solutions.

F. Tudos, A. Nagy, T. Foldes-Bereznich of the Eotvos Lorand University in Budapest, Hungary and the Central Research Institute for Chemistry, Hungarian Academy of Sciences described the work of Tudos' group on "New Results in Radical Polymerization Kinetics." Studies on the kinetics of radical polymerization by photochemical initiation had been carried out. Using intermittent illumination, the effects taking place at the beginning of illumination and the effects at the end of illumination can be multiplied. If, in addition to photo-initiation, some thermal initiation takes place, the effect is also modified. Calculations and attempts to decrease the errors have also been accomplished particularly at the beginning of the measurements. The kinetics of styrene polymerization in benzene using benzoin as the photo-initiator was measured at 50°C and up to 5% conversion. Similar measurements were carried out with methyl meth-

acrylate polymerization. Kinetic studies of the copolymerization of styrene and methyl methacrylate were also carried out and interpreted. All parameters were carefully measured, calculated and interpreted based on the Kelen-Tudos copolymerization equation and the "hot radical" theory.

The opening ceremony on Monday, July 13, 1987 was at the Zhivkova Conference Center. The opening remarks were given by the representative of the president of Bulgaria, the president of the Bulgarian Academy of Sciences and the president of IUPAC, Professor Rao, India. Professor Rao gave also the opening plenary lecture.

On Sunday evening, a reception was held at the Convention Center, sponsored by the Organizing Committee. Monday evening there was a concert by the Sofia Festival Symphony Orchestra and Tuesday evening a reception organized by the Bulgarian Academy of Sciences.

On Wednesday the conferees took an excursion to the famous Rila Monastery (first founded in the 9th century) which is located at an elevation of 5,000 feet in the mountains 100 miles southwest of Sofia.

The 31st IUPAC Congress and, for the polymer oriented scientists, the "Polymer" session was a great success. The Bulgarian Academy of Science and the organizers of the polymer session, are to be congratulated for their excellent programming on interesting subjects, good speakers and generally providing a congenial atmosphere for scientific discussion and inspiration.