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Conference Report

Second S.R. Romania-U.S.A. Seminar on Polymer Science

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The second S. R. Romania-U.S.A. Seminar on Polymer Science, supported jointly by the National Council for Science and Technology, Romania and the National Science Foundation, U.S.A., was held at the Institute of Chemical Research, ICECHIM, in Bucharest from September 11 to 15, 1983. The first Seminar had been held in Iasi on "Radical Blocks and Graft Polymerization."

This Seminar entitled "New and Modified Polymers" was under the cochairmanship of Dr. V. E. Dobrescu, Scientific Director of ICECHIM for Romania and Prof. J. Salamone, Dean of Science of the University of Lowell for the U.S.A. The Seminar was held immediately after the 29th IUPAC Macromolecular Symposium, which was held the week of September 5, in Bucharest. The S.R. Romanian-U.S. Seminar was under the overall guidance of Prof. Ioan Ursu, first Vice President of the Council of Science and Technology.

At this second Seminar there were twelve U.S. participants, two from industry and about twice the number of participants from Romania. A few Romanian scientists participated as observers on a temporary basis. This gave some people from the Institute (ICECHIM) who were experts on some specific subjects the opportunity to gain international experience.

On Sunday, September 11, 1983 the seminar was opened for Romania by Mr. M. Florescu, the Minister State Secretary of the Council of Science and Technology, Mr. N. Barbulescu, the Deputy Minister of the Chemical Industry and Mrs. Maria Ionescu, the General Director of ICECHIM, and for the U.S. by the Ambassador of the United States to Romania, Mr. D. Funderburk.

A total of 28 papers were presented at this 2nd S.R. Romanian-U.S.A. Seminar on Polymer Science; a significant amount of time was reserved for discussions. Presentations ranged from organic chemistry of polymers to characterization, characterization techniques and properties of new polymers.

In the opening paper, Elena-Gabriela Badea discussed Diene Rubber Modification using Thiol Type Antioxidants such as 4-(mercaptoacetamido)diphenylamine. With radical initiators this compound was bound to the polymer during the vulcanization process; the vulcanized rubber was found superior (before and after extraction) in air oven aging test, to polymers that had only low molecular weight antioxidant blended into the polymer. Otto Vogl described his work on the preparation of homo- and copolymers of ω -epoxyalkanoates for polyethers and ω -alkenoates for polyolefins

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whose terminal functional carboxylate groups are separated from the main chain by methylene spacers with up to 8 methylene groups. The preparation of head to head polyisobutylene by Grignard coupling of 2,2,3,3-tetramethyl-1,4-dibromobutane with copper complexes as catalyst was also discussed. The new development of optically active polymers whose optical activity is based entirely on macromolecular asymmetry was presented with polychloral as the example. This entirely isotactic and optically active polymer was found to have an $[\alpha]_D^{20}$ of 5000 degrees. Polymers with cycloaliphatic units in the polymer chain were discussed by Victor Bulacovschi. He presented data for the preparation of polyesters and polyamides with cycloaliphatic diacids particularly cyclopropane- and cyclobutanedicarboxylic acids with regular aromatic-cycloaliphatic condensation polymers and described some of their properties.

Vivian Stannett talked on his recent grafting work on cellulose which consisted of radiation and chemical (Ce-ion) radical grafting of acrylic and methacrylic acid. The polymers obtained were useful as ion exchange resins, and as polymers with high water absorbing capacity. M.M. Marinescu described transformation reactions of polyacrylamide obtained by inverse emulsion polymerization by redox initiators. E. J. Vandenberg presented his work on polyethers with reactive side chains; he discussed the definition of the various types of initiator systems which are based on modified aluminumalkyl initiators, particularly the cationic and the coordinative anionic systems and reported his most recent work on polyglycidol and poly(2,3-epoxybutanediol-1,4).

A. Caraculacu discussed his work on polymers with dibenzyl structures in macromolecular chains, polyurethanes, polyureas, polyimides and poly(parabanic acids). The polymerization of ion-pair comonomers was the subject of the lecture by Joseph C. Salamone. A new class of vinylic cations and vinylic anions was found to spontaneously polymerize to an alternating, ampholytic copolymer; this was demonstrated with the pair 4-vinylpyridinium p-styrenesulfonate or with 3-methacrylamidopropyltrimethylammonium 2-acrylamido-2-methylpropanesulfonate. The ampholytic behavior of these polymers in the absence and presence of salts were studied. The DuPont Company has recently disclosed a new type of polymerization, Group Transfer Polymerization. F. Peter Boettcher discussed the advantages of this polymerization, which works particularly well with methyl methacrylate as the monomer, with silyl ketene acetals as initiator and with HF_2 as the catalyst. Polymers of low, but also of high molecular weight could be obtained with narrow molecular weight distributions. Boettcher also presented the work of lower molecular weight telechelic poly(methyl methacrylates) of narrow molecular weight distribution of exact one or two functionality prepared by low temperature anionic polymerization. Mihail Ionescu presented work on new catalysts for oxidative coupling of phenols especially work involving traditional catalysts modified with mercaptans, and thiophenols. Donor-acceptor copolymers were discussed by Virgil Barboiu. He studied radical copolymerization of acrylate and/or methacrylate monomers substituted with electron-donor or electron-acceptor groups. Modifications of condensation polymers was the subject of William H. Daly's talk. Chloromethylation has become a very important reaction and significant improvements in the use of safe chloromethylating agents have now been made. The quaternization of chloromethylated polymers was then studied with tertiary

amines with special emphasis on the effects of steric hindrance, and chain flexibility of the polymers. The synthesis of poly(vinyl alcohol), made into beads by suspension methanolysis of poly(vinyl acetate), and the application of these polymers was discussed by Mihail V. Dimonie. James A. Moore described a new class of polymers, poly(enamino-esters), and vinylogous nucleophilic substitution as a route to new polymers. Starting from 1,4-dihydroxy-2,6-dicarboethoxy-1,4-cyclohexadiene and reacting his compound with aliphatic, benzylic and aromatic diamines, polymers were obtained which could further ring close to polyquinolones. An interesting method that seemed to give very high molecular weight polymers was described by Bogdan C. Simionescu. It involves plasma induced radical polymerization that was allowed to proceed very slowly to polymers in only low yields. Almost all the common monomers have been claimed to have been prepared to high molecular weight (up to 10^5) polymers or copolymers.

The characterization of polymers requires a number of techniques. Stanley C. Israel convinced the participants that direct pyrolysis-chemical ionization mass spectroscopy should always be included as one of the most important methods, now that selectivity can be readily achieved by using CH_5^+ , NH_4^+ and $\text{iso-C}_4\text{H}_{11}^+$ ions, as the ion source. Many regular and more exotic polymers have been studied; this technique is now being investigated for use in forensic applications.

Polybutadiene modifications by halogenation and reaction of the halogen-containing polybutadienes with alkyl lithium were discussed by Radu D. Bordeianu. Reactions involved in this type of modification, can now easily be controlled. Raphael M. Ottenbrite gave the U.S.-Romanian Seminar on Polymer Science a slightly different direction; he demonstrated the importance of interactions of polymer science with life science, by discussing the biological activity of polycarboxylic acids. A considerable amount of data has now been accumulated in this area of research. Polymer structure and molecular weight have been related to biological activity. Synthetic polyanions exhibit a large number of interesting biological responses. Of major interest are antiviral, antitumor and immunological effects by eliciting macrophage cell activation. Maria Bruma gave an account of her work on heterocyclic polymers, which use as their important features the following heterocycles: oxadiazoles, benzoxazinones or benzothiazoles. Mihail Dimonie then presented his view of the ring opening polymerization of cycloolefins by metathesis reaction with special emphasis on the further elucidation of this mechanism. Thomas St. Pierre is interested in polyamines; he is studying the structure and characteristics of poly(vinyl amine) and poly(ethylene imines). Ultimately he would like to investigate all polymers with amino groups as part of the polymer chain especially those where the amino groups are directly attached to the polymer backbone and where the amino groups are spaced at various distances from each other. He presented a rather complete NMR structure study of some of these polymeric amines. Olga Butufei presented some work of her ICECHIM group on polymeric catalysts for hydrogenation, particularly poly(aminochloroquinones) complexed with palladium (II), with palladium (II).

A more applied work was presented by George I. Brode of Union Carbide Corporation; he described Phenolics: Non-classical routes to solid and liquid binders; this new process is based on the specific preparation of phenolics dispersions;



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from these dispersions, thermoplastic and thermosetting phenolic powders have been prepared. A suspension polymerization was used for making dispersions and free flowing powders with precise control of molecular weight; this process is much less energy intensive than the usual processes for obtaining phenolic resins.

Adrian Carpov discussed some new aspects of the syntheses of polymers with quaternary ammonium groups and Dan Donescu presented a technique of semicontinuous emulsion copolymerization of vinyl acetate and dibutyl maleate; this work is of a more applied nature and was done in cooperation with Romanian industry.

For the Romanian colleagues of considerable interest because of the oil production in Ploesti, about 40 miles north of Bucharest was the presentation by Charles L. McCormick. In his talk on polymers for enhanced oil recovery, McCormick addressed such problems as oil recovery technology, polymer flooding, economic considerations, technical problems, and the complex problems of fundamental and applied research for the search of polymers suitable for these applications. Particularly the polyacrylamides and some copolymers of acrylamide, especially of those with 2-acrylamido-2-methylpropanesulfonic acid as the monomers, and dextran, grafted with acrylamide and other comonomers, were discussed.

Changing somewhat the main subject of the seminar some developments in rheology were also discussed. A long standing and unsolved problem is the question of liquid-liquid transitions in polymers. Some new developments in attempts to solve unequivocally these problems were presented by Viorica Dobrescu. Evidence was given for the existence of

the liquid-liquid transition phenomenon with the suggestion of favored packing in the regions of the liquid-liquid transition. Conjugated polymers, particularly polyacetylene and substituted polyacetylenes and their geometrical changes were presented by Ioan Negulescu. Especially the isomerization of polyacetylenes in the solid state and in solution from the cis-rich to the trans-rich form of conjugated polyenes was discussed.

Polymers of dienes and their modifications are very important in the research efforts of ICECHIM and consequently the last talk by Valentin Gruber was concerned with this subject. This research group was also investigating the reinforcing effects of rubber modifications with nitroso derivatives, with important practical implications.

In conclusion, this U.S.-Romanian Seminar on Polymer Science was very successful, with much new and significant work presented. It was particularly refreshing to see a larger than normal number of younger people taking part in this Seminar.

It is expected that some cooperative work will result from this meeting between U.S. and Romanian research groups, as preliminary talks were being held during the meeting, and assurances to strongly support these efforts were given by Romanian authorities. It was agreed that another S.R. Romania-U.S.A. Seminar on Polymer Science, but with a somewhat different theme could be held in 1986. All participants of the S.R. Romania-U.S.A. Seminar on Polymer Science left the meeting with a great sense of satisfaction of accomplishment.