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Advances in Synthetic Polymer Chemistry: New Polymer Types and New Directions, The Sixth Carl S. Marvel Symposium

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Advances in Synthetic Polymer Chemistry: New Polymer Types and New Directions
The Sixth Carl S. Marvel Symposium

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On March 18 and 19 of 1985, the Carl S. Marvel Symposium was held on the Campus of the University of Arizona in Tucson, Arizona, under the title of "Advances in Synthetic Polymer Chemistry: New Polymer Types and New Directions." It was organized by Professor's James M. Mulvany and Henry K. Hall, with James Mulvany doing the lion's share of the organizing. The meeting was sponsored by the Southern Arizona Section of the American Chemical Society of the Department of Chemistry, University of Arizona, Tucson, Arizona, and was supported by sixteen companies.

This year's symposium was the sixth biennial symposium. The symposium series had been started in 1975 on the occasion of Professor Marvel's 80th birthday, several subject areas have been discussed, the first being on "Polymer Chemistry" followed by "Organometallic Catalysts in Organic Chemistry," "Synthesis of Natural Products," "Molecular Aspects of Catalysis: Metal Assisted Chemistry," "Polymer Surface Analysis and Conductive Polymers."

This year's symposium celebrated also, somewhat belatedly, Professor Marvel's 90th birthday (September 14, 1984) and marked the eve of his 25th year at the University of Arizona, following his retirement from the University of Illinois.

It might be recalled, that in honor of Professor Marvel, the Department of Chemistry of the University of Arizona on April 28th, 1984, dedicated its building as the "Carl S. Marvel Laboratories of Chemistry." The entire student body, faculty and staff of the Department of Chemistry, University of Arizona, and many of his friends, administration officials and the governor of Arizona participated in this tribute.

This sixth Marvel Symposium on "Advances in Synthetic Polymer Chemistry: New Types and New Directions" consisted of eleven invited lectures which was held over a period of two days.

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In the opening lecture on Monday morning, Professor Vogl described his work on "Optical Activity based on Macromolecular Asymmetry," work that had been pursued over twenty years with several coworkers. He disclosed that optically active polymers whose optical activity are entirely based on macromolecular asymmetry (helicity) can now be synthesized. The design of these structures, polyamide oxides, is based on polychloral, which exists only in diastereomeric configuration.

When prepared with chiral initiators, by anionic polymerization, polychloral with specific rotation of over 5000 degrees has been obtained. It was described that optical activity can arise when chiral centers are present in the main or side chain or by macromolecular asymmetry (helicity) alone. Another possibility exists where optical activity introduced by chiral centers forces the main chain additional macromolecular asymmetry, as it is well known in the case of proteins. Macromolecular asymmetry as the sole cause for optical activity has been relatively little studied, although cases exist in the crystalline inorganic salts or in quartz single crystals. The polymerization for the preparation of optically active polychloral was carried out with anionic initiators using the cationic polymerization technique. The chiral centers of the initiators were either in the anion or in the cation. The polymerization of chloral, where the chirality was in the anion was more extensively studied. Most recently the research group has studied the initiation mechanism, molecular linear oligomers with one, two and three chloral units were isolated and separated by gas chromatography and identified. This progress was decisive for the understanding of how to design optically active polymers based on macromolecular asymmetry.

"Polymer Architecture Control in Group Transfer Polymerization" was presented by Dr. O. W. Webster of the Central Research and Development Department of the DuPont Company. The desire to control the macromolecular architecture of polymer design has become of great importance in polymer chemistry. Group transfer polymerization provides a powerful tool for the controlled polymerization of acrylic
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monomers using organosilicon initiators. Because the polymerization proceeds as a living polymerization, monodisperse polymers with predetermined molecular weights have been synthesized by adjusting the monomer/initiator ratio. Because of the living nature of this polymerization, group transfer polymerization provides the means for the controlled design of the preparation of block copolymers and the design of block lengths and functionality.

Dr. Shalaby W. Shalaby of Ethicon, Inc. described the present status of “New Synthetic Polymers of Biological Importance.” He discussed approaches which are used to synthesize new chain molecules for biologically absorbable and non-absorbable sutures, using ring opening and/or step reaction polymerization processes. He analyzed strategies to modulate the physico-chemical and biological properties of novel thermoplastic and elastomeric polymers with special attention to the design of intrinsically radiostable and sequentially isomorphically absorbable polymer chains.

Dr. D. Tomalia of the Dow Chemical Company, presented his thoughts and experimental approaches for “A New Class of Polymers: Starburst/Dendritic Macromolecules.” Although the basic principle of looking at highly branched polymer structures had been discussed and contemplated in the past, it seems that the author is the first to describe synthetic approaches by which this new class of topological macromolecules which he calls “starburst polymers” could be prepared. The fundamental building blocks for this new class of polymers are referred to as “dendrimers.” These dendrimers differ from classical monomers/oligomers/polymer structures by their high functionality which causes high branching because of the maximized “telechelic” terminal functionality. “Reactive end groups” will allow a) controlled molecular weight development (monodispersity), b) controlled branching (topology), and c) versatility in design and modification of the terminal end groups. The dendrimer synthesis can basically be established by a variety of strategies involving “time sequence propagation” techniques. The author described the progress of this polymerization technique similar to the evolution of an onion where layers of monomers are added forming the macromolecule which ultimately leads for practical purposes to about eight layers. These polymer structures are spherically symmetric and have cavities in the center. The primary approach of the author was to prepare “starburst” polyamides by this polymerization technique.

“Synthesis and Characterization of New Radiation Sensitive Polymers” was described by C. Grant Wilson of the IBM Research Laboratory in San Jose, California. Radiation sensitive polymers have found a wide range of applications in photoinaging technology because of the high resolution which such systems can afford. However, polymer based imaging systems have greatly improved in sensitivity, especially caused by “chemical amplification.” The initial event creates a catalytic site and this catalyst can be used to initiate the polymerization or depolymerization sequence, consequently, resulting in making or breaking of very large number of bonds. A new sensitive imaging system has been identified, based on photosensitized, interfacial, cationic polymerization. High resolution relief images are grown on
the surface of a polymer film, rather than etched into the materials.

Prof. Robert W. Lenz of the University of Massachusetts, described the "Preparation, Characterization, and Properties of Thermotropic Liquid Crystalline Polymers." Thermotropic liquid crystalline polymers, particularly polyesters, were discovered about fifteen years ago in Tennessee Eastman's laboratories, but have now been widely studied in the last decade in many laboratories throughout the world. Nevertheless, relatively little is known about the structure-property relationship of thermotropic liquid crystalline polymers. A wide variety of polymers based on aromatic ester mesogenic units, with and without flexible or rigid spacers, have recently been prepared and characterized. Flexible spacers have a profound influence on the properties of such polymers which have been recognized from research on other polymer systems; this work amplified the importance of spacer groups in polymer chemistry. Flexible spacers reduce both melting and clearing temperatures; type and length of the spacer can determine whether either nematic, cholesteric or smectic phase is formed. Polymers were described where the mesogenic group is either in the side chain or in the main chain of the polymer: a number of applications for the polymers are suggested.

"Polymers of Hydrophilic Backbones with Pendant Functionalities" were described by Prof. C. G. Overberger, of the University of Michigan. He described the preparation of synthetic polynucleotide analogs having linear poly(ethylene oxide), poly(vinyl amine), and poly(ethyleneimine) as backbone in place of phosphate-ribose, and chiral nucleic acid base derivatives as analogues. Ordered conformations were observed as determined by hypochromicity. The polymers and the appropriate model compounds were characterized and identified by UV, CD and NMR spectroscopy.

The next three papers were all concerned with various aspects of vesicle structures, their formation, characterization, and use. In the first talk, Dr. Martin J. O'Brien of the Eastman Kodak Company discussed "Polymerized Vesicles: New Materials and Directions for Chemistry and Biology." Recently several research groups had reported the synthesis of polymerizable amphiphiles and their polymerization into bilayer membrane vesicles. Polymers of these reactive lipids can be obtained in a self-organized array of several thousand lipids (vesicles). Lipid systems with incorporated diacetylene, methacrylates, or dienyl groups were described with emphasis on the characterization of the vesicles before and after polymerization. Vesicles are used for membrane models and polymerized vesicles are of interest as substitutes for monomeric vesicles in circumstances that require enhanced membrane stability.

Prof. S. L. Regen of Marquette University discussed his work on "Polymers of Vesicles and Some of Their Ghosts." Polymerized vesicles represent a new and unique class of organic polymers that are of interest in areas of membrane biochemistry, drug delivery, biotechnology and even in the solar energy conversion. The author discussed four classes of polymerized vesicles which have been developed in his laboratories: vesicles bearing a polymer backbone in the core of the bilayer, vesicles that can be depolymerized as well as polymerized, lipid bilayer vesicles which are encased within polymeric counterions and "ghost vesicles" formed via the use of vesicles as templates.

Prof. D. A. Tirrell of the University of Massachusetts presented his most recent thoughts on "Biological and Biomimetic Properties of Synthetic Polymers." The variety of uses that nature finds for macromolecules presents enormous challenges for the synthetic polymer chemist who is also familiar with biological applications and wishes to reproduce some of the characteristic biological functions. Exciting synthetic polymers have been prepared which approach catalytic efficiencies and even exceed those of natural enzymes. Several laboratories have produced synthetic polymers which possess some of the essential features of nucleic acids. In the author's recent work, membrane-mediated events which are under macromolecular control have been discussed. Synthetic polymers which form bilayer membranes which respond to environmental stimuli have been prepared. By presenting recent work and using speculative ideas and imagination, the author discussed some possible applications for such membrane systems.

In the last of the lectures, Prof. William J. Bailey of the University of Maryland, discussed the "Free Radical Ring-Opening Polymerization." Free radical ring-opening polymerizations are relatively very rare, although ionic ring-opening polymerizations are very common. The author found that introducing an oxy water atom into an unsaturated cyclic monomer permitted free radical ring-opening polymerization to occur. Thus, it was shown that cyclic ketene acetics, cyclic ketene imines, cyclic vinyl ethers, unsaturated spirothiocarbonates and unsaturated spirothioesters underwent such polymerization. In addition, the polymers also copolymerized with a wide variety of vinyl monomers with the introduction of functional groups, such as esters, thioureas, amidines, ketone, and carbonates, into the backbone of the additional polymer. This copolymerization makes possible the synthesis of biodegradable polymers, functionally terminated oligomers, polymers with enhanced thermal stability and monomer mixtures which expand upon polymerization.

In addition to the scientific presentations which were highly regarded by the over two hundred people who attended this meeting, other activities were associated with the Marble Symposium.

The meeting was opened by Dr. Nils Haaseltine, Senior Vice President of Academic Affairs and Provost at the University of Arizona. He brought the warm greetings of the University and the high regard that the polymer activities have on the campus of the University. At the banquet, on Monday evening, at the Plaza International Hotel, the introduction by Prof. J. E. Mulvaney, the chairman of the event, greetings of welcome were presented by Prof. Jeanne Pemberton, the chairperson of the Southern Arizona section of ACS and by Prof. George Atkinson, the head of the Chemistry Department of the University. Dr. Owen Webster of the DuPont Experimental Station, presented an interesting, amusing and witty presentation entitled "Breakthrough Research Results—Increasing the Odds for a Hit." Prof. Marvel thanked the speakers and the people present for coming to help him celebrate his 90th birthday.