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Specialty Polymers -Present and Future

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An International Conference Celebrating the 25th Anniversary of the Journal "Polymer" September 18-20, 1984 University of Birmingham, Birmingham, UK

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An International Conference celebrating the 25th anniversary of the journal *Polymer* under the title "Specialty Polymers - Present and Future" was held September 18-20, 1984, at the University of Birmingham England, OK. Receiving its Royal Charter in 1900, the University of Birmingham was a most appropriate venue, being one of the older provincial British foundations and having strong traditions in macromolecular science. These stretch back to the milestone achievements of Professor Sir Norman Howarth and his School in polysaccharide chemistry, through those of the substantial high polymer research group built by Professor Sir Harry Melville and continued by Professor James Robb; down to the work of the present high polymer and materials team of which Dr. James Hay, the local coordinator of the conference, is a prominent member.

The Meeting consisted of two plenary lectures and 17 invited lectures; 12 other lectures were also presented. In addition, 35 papers were presented in poster format. The conference was attended by nearly 200 people from 13 countries.

After the opening on Tuesday, September 18, 1984, by Prof. J. C. Robb on behalf of the University of Birmingham, the Meeting was opened by Sir Geoffrey Allen, F.R.S., Unilever Research, who introduced the subject of the meeting with an overview on the theme "Speciality Polymers: Retrospect and Prospect." He gave a history of how specialty polymers have evolved on the basis of special needs, price, and performance of polymers. Specialty polymers have been known, prepared, and used for some time, but the significant growth and thrust in the development of polymers until recently was in commodity polymers. This emphasis is changing: as more and more highly sophisticated polymers are needed for special applications, such polymers have to be

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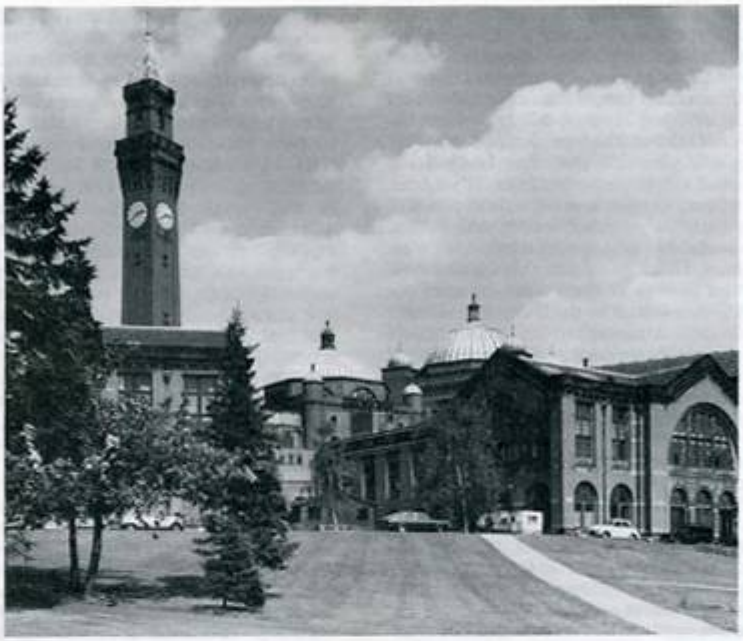

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tailormade. Sir Geoffrey pointed out the timeliness of this conference and mentioned that the vigorous growth of the field of specialty polymers will continue and increase as more sophisticated uses develop for polymeric materials.

In the second plenary lecture, Otto Vogl, Polytechnic Institute of New York, amplified the introductory lecture of Sir Geoffrey and pointed out that not only will the specialty polymer be based on the materials that are already made, but a substantial growth is expected in tailormaking polymers, especially by introducing functional groups into part of the polymer chain. Prof. Vogl pointed out that the thrust of the development of polymer science can again be seen in the vigorous growth of polymer chemistry and polymer synthesis on a highly sophisticated level, polymer synthesis with full understanding of polymer physics and polymer technology, but also with its important interaction with the life sciences. Specifically, he described the work of his research group on the synthesis of polymeric stabilizers, polymeric antioxidants of the hindered phenol type, polymeric flame retardants utilizing bromine-containing monomers, and the extensive work that has been done at the Polytechnic Institute of New York on polymerizable, polymer-bound, and polymeric ultraviolet stabilizers of the type of the 2(2-hydroxyphenyl) 2H-benzotriazoles.

J. B. Rose described "Developments in the Synthesis of Polyarylethers." He mentioned particularly the routes available for the synthesis of polyarylethers which are actually polyethersulfones and polyetherketones. D. Y. Sogah, from the Central Research and Development Department of E. I. due Pont de Nemours and Company, described the synthesis of functionalized polymers by group transfer polymerization. This work was done in cooperation with W. R. Hertler and O. W. Webster. The newly developed group transfer polymerization technique can be used for the preparation of poly (methyl methacrylate) and other methacrylates with terminal hydroxyl, carboxyl, and nitrile groups. Polymers containing allyloxy and pendant methacrylate groups were also prepared. "Redox Catalysis by Polymer-bound Flavins" was discussed by G. Challa, State University of Groningen, The Netherlands. He had modified linear polystyrene chains with pendant flavin and quaternary ammonium salts to obtain water-soluble redox catalysts; a number of reactions with these materials were performed. G. Wegner, The Institute of Macromolecular Chemistry, University of Freiburg, West Germany, discussed "Structure and Properties of Polymers with Metal-like Conductivity." He described polymers where the metal-like conductivity was a property of the sublattice formed by the segments of the polymer in special valence state and showed that chain length does not seem to be an important parameter for the electrical properties.

P. Pantelis, British Telecom, Ipswich, UK, spoke about "Piezoelectric Poly(vinylidene fluoride)"; he pointed out that techniques for enhancing the response and for continuous production of piezoelectric properties are now available; he also discussed copolymers as piezoelectric materials. "Structure-Property Relationships in Liquid Crystal Polyesters" were described by R. W. Lenz, University of Massachusetts, Amherst, MA. Investigations have been carried out

on the structure-property relationship in main chain thermotropic, liquid crystal polyesters containing a variety of different types of mesogenic groups. Molecular factors appear to control the types of mesophases formed, either nematic or smectic, and their transition temperatures and behaviors. R. Srinivasan, IBM, Yorktown Heights, NY, presented his work on the "Modification of Polymer Surfaces by Far-Ultraviolet Radiation of Low and High (Laser) Intensities." Far-ultraviolent radiation is highly effective in modifying the surface of a variety of polymers because of its short penetration depth and high quantum yield for bond breaking. This process can be conveniently used for controlled etching techniques for polymers. "High Resolution Laser Addressed Liquid Crystal Polymer Storage Displays" was discussed by H. J. Coles, Liquid Crystals Group of the University of Manchester, UK. Smectic polysiloxane polymer liquid crystals with cyanobiphenyl side chains are capable of high-resolution laser writing on thin polymer films.

"Synthesis, Physico-Chemical Properties and Application of Poly(amidoamine)s" was discussed by P. Ferruti, University of Brescia, Italy. These polymers have been prepared by polyaddition of primary monoamines or bis-secondary amines to bis-acrylamides; they have application in the biomedical field. Another presentation on the use of polymers in the medical field was given by G. W. Hastings, Biomedical Engineering Unit, Medical Institute, Hartshill, UK. His talk was entitled "Structural Considerations and New Polymers for Biomedical Application." He discussed the preparation and use of polymers intended for surgical implantation. New polymers are used which might be oriented or might be composites, for example, with carbon fibers. Special structural order is an important consideration for biomedical applications. "Novel Hydrogels for Biomedical Applications" were discussed by B. Tighe, University of Aston, Birmingham, UK. Although water-swollen poly(2-hydroxyethyl methacrylate) is the best known and most widely used hydrogel, other polymers with a range of water-binding behavior, and thus mechanical, surface, and permeability properties, are now being developed. They are useful for contact lenses, artificial liver support systems, substrates for cell growth and adhesion studies, and permselective membranes for biosensors. J. N. Hay, University of Birmingham, presented his work on the "Generality of Plastic Fracture." A miniaturized materials testing rig has been developed which enables fracture parameters in plastic materials to be quantified—tensile, compression, fracture and toughness behavior of polymers in the glassy phase.

The Meeting was continued on Tuesday evening at the Lake Hall residence. A session devoted to wine tasting was followed by an International Forum on "Future Developments in Polymer Science" with a panel chaired by Sir Geoffrey Allen, FRS; it was concluded that one of the most important aspects in the trend of polymer science is the development of education and particularly the type of education that is necessary to prepare the new scientists for the needs of the 1990s in polymer science.

"Elastomeric Emulsion Interpenetrating Networks (IPNs)" was presented by M. Narkis of Technion City, Haifa, Israel. His group prepared IPNs by swelling a crosslinked polymer with a second monomer and polymerizing the second monomer, a commonly applied technique; the incompatibility of the two polymers caused domain formation by phase separation. Another contribution from Technion, "Polyblends Containing Liquid Crystal Polymers," was presented by A. Siegmann. Blends of thermoplastic polymers in which thermotropic liquid crystalline polymer particles were prepared at elevated temperatures and isotropic and anisotropic specimens were prepared by compression and injection molding. These thermoplastic/thermotropic polymer blends exhibit unusual behavior similar to that of short-fiber-reinforced systems. I. K. Partridge of the Cranfield Institute of Technology, Cranfield, UK, described the "Effects of Particle Size, Volume Fraction and Particle-Matrix Adhesion upon Mechanical Properties of Rubber-Toughened Plastics." It was concluded that the fracture resistance of the rubber-toughened polymers is governed by the post-yield behavior.

P. J. Lemstra of the DSM Central Laboratory, Geleen, The Netherlands, presented "Speciality Products Based on Commodity Plastics." He noted that a distinction is often made between the mass-produced commodity polymers, which currently represent over 90% of the total polymer volume, and the speciality polymers. He found, however, that the distinction is not always clearcut, since novel preparation techniques for bulk polymers are now increasingly used in speciality applications. N. H. Ladizesky of Prof. Ward's laboratory at the University of Leeds, UK, discussed "New Developments in Ultra High Modulus Polyethylene Composites;" he found that the adhesion of highly oriented linear polyethylene to polymers can be increased by plasma treatment, and composites of various strengths have been prepared using these materials. D. R. Moore, ICI Petrochemicals & Plastics Division, UK, described "Mechanical Properties for Engineering Applications of Poly(ether-ether-ketone)." Poly(ether-ether-ketone)s are a versatile, high technology plastic which has important applications because of their stiffness, strength, and toughness.

A number of additional presentations were given in the areas of Polymer Synthesis and Chemistry including a presentation by E. Roerdink, Dutch State Mines Laboratories, Geleen, The Netherlands, on the "Preparation and Properties of High Molar Mass Stanyl*, a New Development in Nylon Polymers," and by G. C. Alfonso, The Institute of Industrial Chemistry, Genova, Italy, entitled "Synthesis, Morphology and Properties of Rubber-Modified Poly(ε-caprolactam) by Fast In-Situ Polymerization."

About biomedical polymers, we heard from R. M. Ottenbrite, Virginia Commonwealth University, Richmond, Virginia, USA, on "The Effect of Hydrophobic Groups on Polyanionic Polymer Activation of Macrophages," and "On the Hydrolytic Stability of Resorbable Biomaterials" by P. Tormala, Tampere University of Technology, Finland. Physical properties were discussed by R. Simon on "Side-Chain Polysiloxane Liquid Crystals and Their Behavior in Electric Fields," and by R. J. Young of Queen Mary College, London, England, on "Molecular Imaging in Polydiactylene Crystals."

Engineering polymers were discussed by G. W. Calundann, Celanese Research Company, Summit, NJ, USA, who talked about "Anisotropic Polymers, Their Synthesis and Properties," and by T. Cotgreave of the Shell Research Ltd., Chester, England, who presented a paper on "MFRE—An Engineering Polymer Composite," which means a milled-

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fiber-reinforced epoxy resin composite developed for low-temperature use.

The poster papers provided a wide variety of interesting topics: these are mentioned here only by their titles, in order of their appearance in the program: "Novel Monomers of Polydiacetylenes," "Synthesis of Poly-3,4-Diaminostyrene—A Precursor of Catalytic Polymers," "Radiation Induced Graft Polymerization of Vinyl Monomers and Mixed Vinyl Monomers onto Poly(vinyl alcohol)," "Electronic Properties of Some Polymeric Quinones," "Polymerization of Acrylamide Initiated by Copper(II)-Aminoacid-Chelate/CCl_4 Systems," "Comparative Evaluation of Thermal Stabilities of Novel Sulfonic Acid Resins from Anhydride Modified Polystyrene with Commercial Styrene Based Resins," "Thermal Degradation of Polyphenylquinoxalines," "The Structure of Sulfonated Phenol Formaldehyde Novolacs," "Polymers with Photosynthetic Function," "New Developments in Macroinorganics-Thermodynamics of Basic Polymers," "Highly Stable Photopolymer Networks," "Mechanical Properties of Fiber Reinforced Biodegradable Polymers," "Surface Grafted Heparinizable Materials," "Conformation of Sequential Polypeptide (Leu-Leu-D-Phe-Pro) and Formation of Ion Channel Across Bilayer Lipid Membrane," "The Thermodynamical Equilibrium State of Microparacrystals in Polymers," "Structures and Defects in Crystals of PTFE," "Liquid Crystalline Polymers as Additives to Enhance the Device Properties of Low Molecular Mass Liquid Crystals," "Dynamic Light Scattering Studies of Thermotropic Mesomorphic Polymers in Dilute Solution," "A Study of the Viscoelastic Properties of Side-Chain Liquid Crystalline Polymers in Low Molar Mass Mesogens," "Gradient Polymers(II)—Mechanical Behavior of Polystyrene/Poly(methyl methacrylate) System," "Optical Recording and a Possibly Reversible Storage Material," "Photoregulated Adsorption of Dyes to Polymers," "Epoxy Adhesives: The Possible Improvement of the Properties of Boundary Layers," "Shrinkage Behavior of Modified PAN Precursors During Thermal Stabilization and Subsequent Pyrolysis to Carbon Fibers," "Anomalous Decay/Generation of Defects Around the Glass Transition Temperature," "Optical Waveguiding in Doped PMMA," "Laser Light Scattering Characterization of Kevlar in Concentrated Sulfuric Acid," "Time Dependent Refractive Index Changes in PPMA," "Three Dimensional Analysis of Phase I and Phase II Poly(vinylidene fluoride)," "Elastic Modulus Measurements in Shocks Between a Rigid Sphere and Sport Shoes on Synthetic Playing Surfaces," "Composites of Polypropylene and Fibrous/Plate Organic Fillers," "Acrylic Terpolymer Modified by Blending with Polyorganosiloxane Polymer or Reinforcing," "Quantitative and Qualitative Constitutive Effects in the Linear Theory of Binary Polymer Composites," "Cementing in Oil and Under Water," and "Isothermal Volume Dependence of Thermodynamic Gruneisen Parameter of Fluorocarbon Fluids."

On Thursday evening, the International Conference was closed with the expression of a great deal of satisfaction by the organizers and participants. In the not-so-distant future another meeting on Specialty Polymers will be again sponsored by *Polymer*. The focus of this future meeting will be on different aspects of specialty polymers depending on the scientific development immediately following and sparked by this meeting. Provisional arrangements have been made to hold the meeting at Johns Hopkins University, Baltimore in June 1986. Professor Ron K. Eby, Department of Materials Science, Johns Hopkins University, Baltimore, Maryland is responsible for the organization.

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 hinderance, 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(enaminoesters), 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 10^8) 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 iso-$C_4H_{11}^+$ 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: Nonclassical 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 quarternary 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.