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Second Euro-American Conference in Oxford on “Functional Polymers and Biopolymers”

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Second Euro-American Conference in Oxford on "Functional Polymers and Biopolymers"

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The Second Euro-American Conference in Oxford on "Functional Polymers and Biopolymers", also called "Macromolecules '89" was held at the University of Oxford at the College of St. John and Wadham from September 4 to 8, 1989. It was under the honorary chairmanship of Professor Roger Epton representing the RSC/NCI Macro Group U.K. and Professor Otto Vogl representing the ACS Division of Polymer Chemistry, Inc.

The conference organizers were assisted by an International Honorary Advisory Program Committee involving about 20 people and a local organizing committee. About 360 scientists attended the meeting from 23 countries around the world. Delegates came primarily from Europe and the United Kingdom with about 25% from the United States and a strong contingent from Japan.

A number of the papers presented at the conference are to be published in the British Polymer Journal Volume 23, (June/July 1990).

The conference consisted of 4 plenary lectures and about 70 additional lectures of which 25 were invited lectures; more than 70 posters were presented at the meeting.

The conference focused on the Design, Synthesis, Properties and Applications of Functional Polymers including Biomaterials. The first conference on "Functional Polymers and Biopolymers" was also held in Oxford in September 1986 - "Macromolecules '86".

Macromolecules '89 emphasized Biopolymers and the Synthesis and Properties of Macromolecules. Discussions on polymer blends and the synthesis and utilization of functional polymers also played a major role at the conference.

The first speaker of the conference, D.C. Sherrington of the University of Strathclyde, Scotland, outlined his view of the "Development of Functional Polymers and Prospects for Further Development in This Area". He pointed out two aspects of functional polymers, namely, that the definition of such polymers is either based on the fact



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that these polymers have functional groups in their macromolecular structure or that functional polymers are based on the function that they fulfill in their application.

M. F. Perutz of the MRC Laboratory of Macromolecular Biology, Cambridge, U. K., gave his presentation entitled "Proteins Made to Measure". Dr. Perutz, Nobel Laureate of Chemistry of 1982, described the development (over the last 25 years) of proteins. The detailed structure of a number of proteins had been worked out, especially by X-ray analysis; the complex with various transition metal analogues have provided a tremendous amount of information. For polymers with interesting catalytic properties, chemical Merrifield type synthesis is the reaction of choice to synthesize polyamino acids with up-to 100 amino acid units; gene technology allows us to proceed further. It is now possible to redesign active sites for a new substrate to change the optimal pH of an enzyme for catalysis. We are now able to leave it to the computer

of genetic engineering to produce the hemoglobin molecule in *E. coli* bacteria which may serve as a blood substitute.

H. Scheraga of Cornell University in Ithaca, N.Y. discussed the "Use of Polypeptides to Study Interactions in the Fundamental Structural Features of Proteins". Synthetic homo- and copolymers of amino acids can be used to obtain quantitative information about the tendencies of the 20 naturally occurring amino acids to adopt the α -helical, β -structure, and β -turn conformations.

J. H. Richards of the California Institute of Technology in California discussed "Synthetic Molecular Biology as an Approach to Novel Enzymatic Catalysts". A variety of techniques has been used to create proteins that now have properties that mimic natural proteins. The strategies include: synthesis of genes encoding proteins with amino acid sequences of interest; site-directed mutagenesis throughout the native proteins in a planned way; various techniques of random mutagenesis to provide families of mutants that can then be screened to find those that possess the desired property; the creation of protein hybrids that contain structural domains from different parents; the chemical synthesis of proteins and protein analogues that mimic the activity of the native proteins for which they are models. Much of this work in protein chemistry is involved with minimum energy calculations.

A. Abe of the Tokyo Institute of Technology had been asked to present his view on "Conformation and Conformational Ordering in Polymeric Systems". The interdependence of the bond rotations is a common feature of most chain molecules. The rotation of the state RIS analysis indicates that the orientational correlation more or less persists in the constituent bond of the chain. The chain conformations are also very much susceptible to external constraints. General examples of polymeric systems which exhibit certain characteristic conformational ordering have been discussed.

A number of interesting aspects of the development of new drug control release systems were targeted and polymer conjugated drug systems were discussed. M. Wilchek (Weizmann Institute, Rehovot, Israel) discussed "Targeted- and Polymer-conjugated Drug Systems". The mechanism by which the complexes exert their activity is not yet completely understood. A major direction of research involving chemotherapy is the development of a means to suppress the toxicity of existing drugs without impairing their therapeutic activity. Such macromolecular drug derivatives, even if nonspecific, are expected to increase the efficacy of the drug through more effective distribution, retardation of chemical or metabolic degradation and maintenance of prolonged nontoxic levels of the drug due to its slow release. Some chemotherapeutic drugs such as daunomycin and methotrexate, were shown to be more effective when used in association with carriers such as DNA, dextran, proteins or polypeptides.

"Controlled-Release Model Systems" was presented by S. Polowinski of the University of Lodz, Poland. Systems for controlled release of biocides have become more and more sophisticated. Modifications have been realized such as development of carriers coated with polymer films, multilayer systems, impregnations, etc. The preparation of multicomponent systems is achieved by combin-

ing the systems mentioned above.

H. Kawaguchi of Keio University in Japan discussed the "Bio-interactions of Polymer Microspheres with Blood Components"; he found that when polymer latex particles are mixed with a suspension of blood cells, several interactions take place between particles and cells such as hemolysis from erythrocytes, phagocytosis of particles by granulocytes and aggregation of platelets. The extent of these interactions significantly depends on the properties of latex particles the size hydrophilicity and surface potential, and coexisting blood components. Of particular importance was the development of excellent measurements for phagocytosis.

"Soluble Functional Polymers for Human Haemoglobin Modification for Use in Blood Substitution" was presented by E. Dellacherie from ENSK-INPL Nancy, France. Fixation on soluble polymer of anionic groups such as carboxylates, phosphates or sulfates leads to macromolecular effectors of haemoglobin such as polymers which can mimic the role of natural effectors, DPG.

P. Hutchinson of Ciba-Geigy Pharmaceuticals discussed "Soluble Polymeric Carriers for Drug Delivery; the Accumulation of Poly(N-2 Hydroxypropyl) Methacrylamides in Mice Following Intravenous Administration".

Of significant interest was the presentation by T. Ouchi of the Kansai University in Japan describing "Design of Poly(Malic Acid)-5FU Conjugate Exhibiting Antitumor Activity". Poly(malic acid) is a biodegradable absorbable polyester having pendant carboxylic acid groups. It can be used as a polymer carrier to covalently attach both the parent monomeric drug and the target agent. Poly(malic acid) can now be very conveniently prepared by ring-opening polymerization of the corresponding benzyl ester. Malic acid dibenzyl ester can also be copolymerized with L-lactide. 5-Fluorouracil can now be attached very conveniently either directly or with appropriate spacer groups the linkage of which allows ultimately the degradation of the side groups from the polymeric backbone chain. The antitumor activity of conjugate of 5-fluorouracil/poly(malic acid) is significantly increased both by testing it against P-388 lymphocytic leukemia in vivo or in vitro.

C.H. Bamford of the Institute of Medical and Dental Bioengineering of University of Liverpool discussed "Study of Platelet-Membrane Permeability Utilizing Polymer-drug Adducts and Related Derivatives". Much effort has been spent on attempts to develop a synthetic non-thrombogenic surface, usually of a polymeric material, i.e., a surface which does not activate any of the three major coagulation pathways.

One section of the meeting was devoted entirely to protein synthesis. R.E. Offord of the University of Geneva, Switzerland gave a talk entitled "Protein Engineering or Protein Semisynthesis?" Modern biology and medicine have produced great demand for proteins having novel structures, not found in nature. Analogues are invaluable for the study of structure-activity relationships, and where questions arise of the importance of non-covalent interactions in protein structure and function. Existing knowledge of the underlying principles of protein action makes it possible to design analogues with tailored func-

tional properties, and is for example, sometimes responsible for the wish to incorporate within the protein chain non-polypeptide elements simulating one or the other of the natural turn motifs.

"Design, Synthesis and Conformations of Polypeptides with Specific Topographical Features" were described by V.J. Hruby of the University of Arizona in the United States. Most peptide hormones and neurotransmitters are relatively small, conformationally flexible molecules. In order to determine their "biologically active" conformation, a number of approaches have been developed to conformationally constrain these polypeptides. However, surprisingly little has been done to examine the side chain conformational properties in peptides, the factors which determine specific preferred side chain conformations, and the relationships of those conformations to the overall topography and biological activity. A number of specific polypeptides have been synthesized and studied for their specific behavior.

"Construction, Cloning and Expression of Synthetic Genes Coding for Completely New Nutritionally Rich Artificial Proteins" was the subject of a lecture by H. Koster of the Bioresearch Division of Milligen, Burlington, MA, U.S.A. Synthetic genes coding for artificial proteins with predefined and nutritionally valuable amino acid compositions have been constructed and cloned in *E. coli*. It has been shown that completely novel, not naturally occurring proteins which have not been optimized during the evolution process could be developed and synthesized.

"New Star-Branched Polypeptides" so called "Fuzzy Rods" have been synthesized by W.H. Daly. He started with poly-functional primary amines and carried out N-carboxyanhydride polymerization to form living polymers of a degree of polymerization of 10 to 20. These star arms were connected with a primary amine groups to the primary central organization. Polybenzyl- and poly(phenyl glutamate) were used as examples. The polymers prepared were very unusual in their physical properties, including molecular weights and molecular weight distributions.

K. Matsuzaki of Shinshu University in Tokyo, Japan talked on the "Structure and Antiviral Activity of

Sulphated Polysaccharides" These were prepared using piperidine/S03 complexes on soluble polymeric carriers.

"Soluble Polymeric Carriers for Drug Delivery using Poly-N(2-hydroxypropylmethylacrylamide)" was presented by K. Petrak of the Ciba-Geigy group in Hershham, U.K.

The Design of Structures of Functional Polymers was the subject of a number of important lectures.

G. Wilke of the Max Planck-Institute of Coal Research in Muhlheim, F.R.G, described the "Stereochemistry of Catalysis and Initiation" and described a number of catalyst structures that are becoming important for highly specific catalytic reaction polymerizations.

"Design and Synthesis of Functional Organic Macromolecules and Group Transfer Polymerization on Solid Support Utilizing Organosilicone Reagents" and the "Group Transfer Polymerization on a Solid Support" were reviewed by W.R. Hertler of the Du Pont Company in Wilmington, Delaware. He described group transfer polymerization that was shown to be a valuable method for controlled synthesis of acrylic polymers. Very recently his group has been able to carry out the synthesis of silyl ketene acetals on crosslinked polystyrene supports and has found that efficient GTP of MMA and AN can be performed with initiators bonded to swellable crosslinked polystyrene supports. Graft copolymers can also be obtained when polymer-supported chain transfer agents are present during solution GTP of MMA.

"The Polyampholytes from Charge Transfer Polymerization of Ion Pair Comonomers" was discussed by J.C. Salamone of the University of Lowell, Lowell, MA.. He pointed out that, for several years, the spontaneous polymerization of vinylpyridinium salts with special emphasis of the search for polymerizable strong acids and their copolymerization with vinylpyridinium styrenesulfonate acid have been carried out. Recently, a most efficient copolymerization was carried out with 4-vinyl-N-methylpyridinium, methylsulfate, with α -methylstyrene or p-methoxy styrene. Kinetic studies of this polymerization indicate that the propagation has been predominantly by monomer pairs, using the kinetic scheme derived by Hall.



Oxford skyline.



High Street Frontage, University College.



University of Oxford.

G. Wegner discussed "Self Assembly and Control of Order in 2D and 3D Polymer Systems". The "Controlled Synthesis of Functional Polymers by Living Cationic Polymerization" was presented by M. Sawamoto of Kyoto University, Japan. Living cationic polymerization of vinyl monomers provides a way to prepare by new controlled syntheses cationically prepared functional polymers for new monomers. Sawamoto discussed new initiating systems and functional polymers with narrow molecular weight distribution based on vinyl ether monomers including star shaped polymers and sequence controlled functional oligomers. R. Quirk presented his ideas on "Anionic Synthesis of Chain-End Functional Polymers".

The subject *Polymers for Advanced Application* was introduced in a talk on "Recent Advances in High Performance Polymers" by C.E. Sroog from the Du Pont Company in Wilmington, DE. New monomers were discussed which have broadened the understanding of the proper arrangements of polyimides and represented new challenges to theoretical concepts regarding polyimide properties. Polyimide esters with thermotropic polyester segments, as well as flexible polyimides were discussed. Polyetheretherketones (PEEK) derived by nucleophilic aromatic of a Friedel-Crafts type condensation of the corresponding acid chloride was also discussed. Crosslinking procedures can be applied to either of these polymers to prepare new polymeric structures. Thermal and Mechanical Properties of Aryl Ketone Polymers and Their Composites" were discussed by J. N. Hay of the University of Birmingham U.K.

Liquid Crystalline Materials were discussed by R. A. Gaudiana of Polaroid Corporation of Cambridge, MA. His talk was entitled "Non-Crystalline Rod-Like Polymers - Optical, Spectral and Morphological Properties". He pointed out that incorporation of non coplanar biphenols in the backbone of three classes of main chain aromatic polyesters significantly alters many of the properties of rod like polymers. They are colorless, substantially soluble in organic solvents and showed, in the X-ray diagram, diffuse halos, typical of amorphous materials. They have low glass transition temperatures and exhibit ex-

tremely low nematic low temperature solid/nematic transition temperatures. Most importantly they are highly refractive and birefringent.

A.S. Hay of McGill University in Montreal, Canada presented his paper on "Polymers from Arylphenols and Arylbiphenols". He discussed the polymerization of highly hindered bisphenols, tetraphenylbisphenols or hindered diphenyl-quinones, the preparation of a new class of redox polymers.

Solid state properties and morphology developments in the solid state were discussed by several people. I.M. Ward presented his view on "The Structure and Properties of Orientated Thermotropic Liquid Crystalline Polymers". The primary thrust in this research has been to gain structural understanding of the low strain mechanical behavior of a range of oriented thermotropic liquid crystalline polymers. The relaxation processes by dynamic-mechanic and dielectric relaxation was studied by NMR spectroscopy. It involved the quantitative study of the mechanical anisotropy and an attempt to understand the temperature dependence on the Young's modulus at a quantitative level. Thermal conductivity measurements and X-ray studies also supported this investigation.

"Polymeric Alloys From Functional Polypropylene" was presented by T. Simonazzi of Himont, Ferrara, Italy. Copolymerization of propylene and 1,3-butadiene in liquid propylene in the presence of superactive Ziegler-Natta type initiating systems allows the production of random copolymers having unusual microstructures. These magnesium chloride supported titanium catalysts with electron donors have proven to produce an important category of new materials based on polyolefins. For example, a polystyrene grafted on reactive copolymers of butadiene and propylene was produced. These polymers were used as compatibilizers for PP/HIPS blends based on the general concept of polymer/polymer miscibility. The particle size of the dispersed phase is very dramatically reduced and the interfacial adhesion of the phases of the blends is strongly enhanced by the graft copolymers.

Z. Janovic of INA-OKI, Zagreb, Yugoslavia discussed "Copolymers of Bromine Containing Vinyl Monomers".

He pointed out the important function that these polymers play in the reduction of flammability, particularly of polystyrene. Copolymers involved not only vinylbromide and brominated styrene derivatives but also brominated poly(meth)acrylates and brominated maleimide derivatives as well as phosphorous-bromine containing vinyl monomers.

"Novel Active Polymers Containing Cinnamate Groups" was presented by G.R. Mitchell and M.J. Whitcombe of the University of Reading, U.K. This paper presented the strategies for the synthesis of liquid crystalline polymer systems containing photoactive units based on the cinnamate ester functionality. These novel materials possess liquid crystalline phases which may be influenced by the action of an external light source. Photoactive groups were incorporated into the main chain or in the side chain.

N.A. Plate of the Karpov Institute of the Academy of Sciences in Moscow, USSR presented his work on "Order in Liquid Crystalline Polymers"; he showed new approaches to this problem. A most important contribution was by M.M. Coleman of Penn State University, PA, U.S.A. on "Design of Polymer Blends Involving Strong Intermolecular Interaction". Trends in the phase behavior of polymer blends can be predicted using a very simple concept. The basic idea is derived from a natural extension of previous work on theoretical and experimental studies of the mixing of polymers; these considerations involve relatively strong intermolecular interactions (hydrogen bonds) where the free energy of mixing is described by a simple equation. A good example is given for styrene copolymers with a small amount of vinylphenol incorporated; these copolymers which give excellent miscibility with polymethacrylates, and generally, with acrylic polymers.

"Two Phase and Other Polymer Particles: Preparation, Structure and Properties" was discussed by B. Torvell of the University of Lund in Sweden. Heterogeneous free radical polymerization gives polymer particles of widely different size, composition and structure. New developments for the preparation of large monodisperse particles by seeded emulsion polymerization or by the formation of small particles by polymerization of monomers solubilized in microemulsions make it possible to design processes for the preparation of polymer particles of almost any size in the range from a few hundred Angstrom to about 500 microns in diameter.

"Synthesis and Study of Stilbenic-Unit Containing Polyacrylates" was presented by E. Marechal of the University of Paris, France. Monomer units derived from carboxylic acids having stilbene units as part of their structure exhibit interesting mesogenic properties when they are part of low or high molecular-weight liquid crystals. Stilbenic units are self-mesogenic which means that they can lead to thermotropic or lyotropic polymers without performing mesomorphic blocks.

C. Eisenbach of the University of Bayreuth, F.R.G. discussed "Ordered Structures in Multiblock Copolymers" with special emphasis on the isocyanide groups as basic units.

"Local Dynamics in Liquid Crystalline Polymers" was presented by F. Lepretre of ESPCI, Paris, France. The authors discussed particularly polymers with the si-

loxane backbone with the mesogenic unit attached through a flexible spacer to the polymer chain. For temperatures below the melting of the crystalline regions, premelting phenomena have been shown to occur. Above the melting temperature, the carbon atoms of the methylene groups of the spacer are involved in large amplitude motions.

"Properties and Applications of Ferroelectric Liquid Crystalline Polymers" was also discussed by H.J. Cole of the University of Manchester, U.K.

A number of biological synthetic and natural polymers were discussed in the talk entitled "New Families of Multifunctional Polymers", by Professor P. Ferruti of the Polytechnic Institute of Milan, Italy. He reported the synthesis and property of new families of ter-amino polymers containing nitrogen and sulfur atoms in their main chain. They are obtained by the copolymerization of ethylene sulfide and diamines. "Poly(Alkylene Phosphate): Bioanalogous Synthetic Polymers" was discussed by S. Penczek, of the Academy Institute in Lodz, Poland. He mentioned that the backbone of both nucleic and teichoic acids is composed of diesters of phosphoric acid; thus these polymers belong to the class of poly(alkylene phosphate). The step-by-step synthesis, particularly of nucleic acids has been mastered. The preparation of analogs of nucleic acids was attempted by synthesis of simple poly(alkylene phosphate) chains, poly(alkylene phosphate) with sugars or its analogs in the chains and poly(alkylene phosphate) with bases in the main chain.

"Synthesis and Applications of Polyamino Acids With Nucleic Acid Bases" was discussed by K. Takemoto of Osaka University, Osaka, Japan. He discussed continuous systematic work concerning the preparation and properties of polyamino acids with nucleic acid bases together with their applications. Interaction between poly-L-lysines containing thymine and deoxine units can be observed in DMSO and seems to give the structure of a double helix.

J. H. Murdoch of the Central Research and Development Department of Du Pont in Wilmington, DE described the "Stereochemical Control of Poly(lactide) properties" particularly the preparation of poly(lactide) acids of high optical purity but also the preparation of compound DL lactide acid.

F. Sundholm from the University of Helsinki in Finland described the "Solution Properties of Copolymers of Poly(vinylacetate-co-vinyl alcohol) and the Crosslinking of Polymers with Vinyl Cinnamate Groups". In solution, inter- and intracatenary crosslinking reactions compete; thus a thermally forbidden polycycloaddition performed at varying temperatures should yield information about the polymer as a whole, as well as of the association of the hydrophobic groups.

Biodegradation of Polymers was the subject of several papers, the first by A.C. Albertsen of the Royal Institute of Technology, Stockholm, Sweden who reported on "Polycarbonates and Polyamides as Degradable Biomaterials". Degradable materials are of great interest since they can be utilized in medical and agricultural applications and also as disposable packages. The most successful class of polymers has been shown to be the aliphatic polyester. These polymers undergo backbone hydrolysis at rates depending on their structures. Polyamides have been

prepared either by condensation or ring opening polymerization of the cyclic anhydrides; polyesters either from lactones or from glycols and dicarboxylic acid. The use of ketene for polyanhydride formation has also been studied.

F. Mares of Allied Signal Inc., Morristown, NJ presented a paper on "Novel Bioresorbable Polymers for Surgical Implants".

"Synthesis and Properties of Bio-erodible Aliphatic Polyesters" was described by J. Dahmann of the Institute of Polymer Science, Teltow-Seehof, G.D.R. Homo polyesters of lactic and glycolic acid had been prepared by mass polymerization of their cyclic esters with Sn-II-octoatas initiators. High conversion and molecular weights have been obtained by high polymerization rates. The application of these polymers in parenteral drug-release systems was found to be dependent in the very complex manner from the specific properties of drug component and polymer.

"Poly(N-Vinylacetamide) and Poly N-Methyl-N-Vinylacetamide" were described by S. Aalto of Enschede and his group from the University of Twente, The Netherlands. The hydrogels studied had relatively good blood compatibility. The adhesion of human endothelial cells on NVA and VIMA grafted films of silicones and poly ethylene was investigated; reduced cell adhesion was found for both modified over unmodified in silicone rubber and polyethylene films.

"Solution Properties of Pullulan" was discussed by P.A. Williams of the North East Wales Institute, Deeside, U.K. Pullulan is a microbial polysaccharide and consists of α -1,6 linked maltotriose. It is a linear polymer without branching and is easily water soluble. Pullulan molecules are slightly stiffer chains than the flexible random coils proposed earlier, below a molecular weight of 50,000.

D.M. Wiles of the National Research Council, Ottawa, Canada presented his work on "The Measurements of the Oxidative Degradation of Polymers" FTIR spectroscopy has proven to be highly successful for the characteriza-

tion of solid polymer samples because of the inherent specificity of vibrations spectroscopy and because of the unique capabilities to collect, store and manipulate data, built in a modern spectrometers. Oxidation of polyolefins leads to the mixture of hydroperoxides, alcohols and carbonyl products but detection of several of the species in EVOH copolymers by FTI spectroscopy is complicated by overlap of the strong OH absorption with the OH of the underreacted SEC alcohol groups. Spectral subtraction of non-oxidized film from that of oxidized sample is not especially informative but the prior use of gaseous NO and SF₄ derivatization is quite informative.

P. Hodge, University of Lancaster, U.K. discussed the "Preparation and Application of Langmuir-Blodgett Films from Pre-formed Polymers". "Self-assembling Monolayers: Building Blocks for Future Organic Materials" was presented by A. Ulman of the Eastman Kodak Company, Rochester, NY. "Electrical and Optical Properties of Novel Langmuir-Blodgett Thin Films of Poly(3-alkylthiophene)s" was discussed by I. Watanabe of MIT, Cambridge, MA. "Functional poly(aniline)s" were discussed by P. Kathirgamanathan of the Cookson Group, PLC, Greenfort, U.K.

The conference Macromolecules '89 in Oxford provided opportunities for several editorial boards of polymer related journals to meet, for committees to meet and plan for future polymer oriented meetings, and to enjoy the traditional atmosphere at Oxford University.

The organizers have concluded that the next meeting, the Third Euro-American Conference on "Functional Polymers and Biopolymers" entitled Macromolecules '92 will be held in 1992. Burton Anderson was selected as the American chairman, with the selection of the British counterpart to be decided soon. Macromolecules '89 was a very productive meeting; it allowed us to reestablish old friendships, to develop new ones and to hear the exchange of research results and opinions of the highest scientific quality.