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Conference Reports

"Macromolecules 86" An International Conference on Functional Polymers and Biopolymers

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The MACRO GROUP UK, a joint association of the Royal Society of Chemistry and the Society of Chemical Industry in the UK, sponsored an international conference on "Functional Polymers and Biopolymers at the University of Oxford. This conference, "Macromolecules 86," was held at St. John's and Trinity Colleges of Oxford University from September 15 to 19, 1986. It was organized under the chairmanship of Professor R. Epton (Wolverhampton Polytechnic, UK) with his associate coordinators, Dr. R. Mortier (Castrol Research, UK), Dr. A. C. Finch (Pentafin Associates, UK), and Dr. S. M. Hoare (Boots Company PLC, UK). The organization of this meeting was also assisted by Jane C. Vogl, the business office manager of the Division of Polymer Chemistry, Inc., ACS, of the United States.

The Symposium consisted of two Plenary Lectures and 60 papers, of which 30 were Polymer oriented and 20 were concerned with Biopolymer subjects. In addition, 50 posters, equally divided between polymers and biopolymers, were presented.

Over 300 participants, of whom 40% were from the UK, 34% from continental Europe, and 13% from the USA, accepted the organizers' invitation to discuss problems of great current interest in polymer science from amongst the general subjects selected by the organizing committee; the two subtitles, especially, represent topics at the forefront of present developments in polymer science.

Many of the participants were housed at St. John's, Trinity, and Pembroke Colleges of Oxford University. The weather during the second week of September was excellent; the location and general atmosphere were most suitable for this symposium. The plenary lectures and a considerable number of the major lectures were held at the University Museum, surrounded by birds, dinosaurs, and unusual archaeological artifacts. Other parts of the symposium were held in the lecture rooms of the Department of Earth Sciences and at the Rhodes House.

On Monday evening, before the beginning of the conference, the participants met after dinner at the College for a reception in order to get acquainted with one another. On Tuesday



Geoffrey C. Eastmond



Otto Vogl

evening a recital was held at the Concert Hall at the University of Oxford, and on Wednesday evening the publishers of Butterworth Scientific, Ltd. invited the participants to a wine and cheese reception at the University Museum.

The highlight of the meeting was the banquet on Thursday evening at which Dr. Geoffrey Eastmond of the University of Liverpool, Chairman of the Macro Group UK, presented his views on the development of Polymer Science in Britain and on future development of science in general. In proposing the toast to the overseas visitors he expressed delight at the variety of polymer chemistry offered at the conference but concern that expertise in the fundamentals of polymer chemistry is not being sustained in the UK; Professors Frechet (University of Ottawa, Canada) and Challa (University of Groningen, The Netherlands) responded to the toast.

Technical sessions opened on Tuesday after an introduction by Dr. Eastmond. In his opening lecture, Otto Vogl of the Polytechnic University, Brooklyn, NY, discussed "Recent Developments in Functional Polymers." He pointed out that over the last few decades Polymer Science and Engineering has undergone frequent changes of emphasis since it evolved as a separate branch of science. He drew attention to the continuing vigorous growths of polymer science and of polymer



University College, Oxford



Court Yard, St. Johns College

development and utilization. These growths are a result of the increasing use of commodity plastic materials and, more importantly, of the recent thrust in sophisticated polymeric materials.

Many highly sophisticated polymers are functional polymers, whose effectiveness and, consequently, utilization are based not only on macromolecular properties but also, significantly or entirely, on functional groups. Tailor-making polymers of high effective functionality requires more than the incorporation of functionality alone. Often it is necessary to introduce flexible spacer groups into the main or side chain of polymers to facilitate fabrication. Interactions between polymer science and life sciences have become more important, and more recently, in microelectronic and space applications, there is a need of polymeric materials with properties that are in the interface of polymers and ceramic materials.

R. B. Merrifield of Rockefeller University, New York, presented his talk on "The Solid Phase Approach to the Chemical Synthesis of Biopolymers." Continued advances in understanding of the role of biopolymers in living systems have increased the demand for these materials. Chemical synthesis of natural materials can be achieved by classical solution methods or by the solid phase techniques which have been developed for use in peptide and protein synthesis. Much of the peptide chemistry needed for solid state synthesis was adapted and modified from reactions developed originally for classical methods. Very large numbers of small peptides have now been synthesized by this technique. Peptides with from 50 to 80 α -amino acid monomer units in the chain have also been prepared in high purity and in satisfactory yields. Another method for solid state synthesis is playing an important role in the preparation of oligonucleotides, decapeptides, and some oligosaccharides, which have however been prepared only with some difficulty.

"Terminal Functional Polyolefins by a Novel Cationic Living Polymerization" was described by J. P. Kennedy of the University of Akron, Akron, OH. He had discovered recently that certain complexes of organic acids and Lewis acids efficiently induce the living polymerization of isobutylene and its copolymerization with isoprene at relatively high temperatures. This is the first example of a chain transferless, terminationless polymerization and copoly-

merization of isobutylene. The nature of the head and tail groups of the polymers can be controlled by suitably chosen initiators. Solvent and temperature effects on conversions have been investigated, and it is postulated that the living polymerization of isobutylene by ester/boron trichloride complexes proceeds by a novel two component group transfer type polymerization mechanism. "Group Transfer Polymerization: Control of Polymer Architecture by Silicon-Mediated Processes" was presented by D. Y. Sogah of the Du Pont Co., Wilmington, DE. He described the recently reported and fundamentally new method of preparing acrylic polymers: group transfer polymerization is catalyzed Michael-type addition of silyl ketene acetals to $\alpha\beta$ -unsaturated esters, nitriles, and arboxamides. Very recently, an extension of the concept of the sequential aldol condensation reactions was found and applications of the processes to the synthesis of polymers with well-defined structures were described.

"Functional Polymers via Furan Chemistry" was presented by A. Gandini of EFP, Saint Martin d'Heres, France. This work on the wider investigation of the behavior of furan monomers in polymerization and condensation processes included free-radical, electrophilic, and nucleophilic reactions, functionalization by oxidation, functionalization through the



Museum, Oxford University

Conference Reports

Diels-Alder reaction, and the photocyclo-additions of furan/acrylic functions. "New Fluorinated Polysiloxanes and Polystyrenes" were discussed by D. Teyssie of the College de France, Paris, who reported the synthesis of new fluorinated silicones and polystyrenes; one of the main interests of fluorinated polysiloxanes arises from their application in high-performance coatings. The author described the synthesis of new olefinic perfluoroethers and the subsequent hydrosilylation by linear poly(methylhydrosiloxanes) containing various proportions of SiH pendant groups; new fluorinated styrene monomers have been prepared and their free-radical polymerization and copolymerization with styrene was investigated. The "Synthesis and Copolymerization of Poly(dimethylsiloxane) Macromers" was described by G. Gordon Cameron (University of Aberdeen, Scotland). Macromolecular monomers have received much attention in the last ten years and many new types of macromers have been made, mainly with polymerizable olefin or vinyl groups. The authors reported the synthesis of poly(dimethylsiloxane) macromers of various chain length and their radical copolymerization with styrene and acrylonitrile. G. Martinez (Plastics Institute, Madrid, Spain) described the "Stereoselective Substitution on PVC Using Phase Transfer Catalysts." In the substitution reaction on PVC with sodium benzenethiolate in solution it was found that the reaction is stereoselective in that only the isotactic and the heterotactic triads are reactive, while the syndiotactic triads remain unreactive even at high temperatures. The authors concluded that this reaction is only possible through the highly reactive isotactic dyads. The substitution markedly improved the thermal stability of the PVC polymer in terms of degradation rate and discoloration.

The use of "Functional Polymers to Prepare Model Elastomeric Networks" was presented by J. E. Mark (University of Cincinnati, Cincinnati, OH). He mentioned that it is now possible to produce elastomeric networks of known structure by end-linking functionally-terminated polymer chains. Such networks are "model" networks in that the highly specific nature of the end-linking process permits control of junction functionality, average network chain length, chain length distribution, and numbers and lengths of dangling-chain irregularities. R. Greco (Institute of Technology and Rheology, Avcofille, Italy) discussed "EPR Bulk Functionalization: Kinetics and a Possible Application of the Modified Rubber." Polyolefin functionalization was achieved by attaching polar groups, such as esters of anhydrides, onto the polymer backbones by a solution reaction. Some properties of these materials and their use for further reactions were studied; maleated EPR especially was investigated. J. de Abajo (Plastics Institute, Madrid, Spain) presented his work on "Reactive Poly(diethyleneglycol terephthalate) Oligomers." The author has prepared oligomeric polyesters and then converted their terminal OH groups to other reactive groups which were then cross-linked. Maleimide and nadimide have proved to be very useful as end-capping functions in the preparation of high-temperature reactive oligomers and then the maleimide-terminated materials were cured with tertiary butylperbenzoate. Frank N. Jones (North Dakota State University, Fargo, ND) presented his work on "Synthesis of Oligoester Macromonomers having $M/M_c < 1.1$." He reported on research in his group which is aimed at the synthesis of monodisperse telechelic $-OH$ and $-COOH$ functional oligoesters. The authors reported a method for synthesizing telechelic oligoesters by treating diacids (or anhydrides) and sym-

metrical diols with dicyclohexylcarbodiimide. More recently, oligomers were prepared with symmetrical diols in the center and unsymmetrical diols to build up the polymer chain.

Wednesday morning opened with a main lecture by N. Ise (Kyoto University, Kyoto, Japan) entitled "Ordering Phenomena of Ionic Polymer and Biopolymer Solutes in Dilute Solutions." Years ago it was recognized, on the basis of x-ray scattering experiments, that tobacco mosaic virus particles were distributed equidistantly in the wet and dry gel states and in concentrated solutions. A similar conclusion was subsequently reached for proteins. Recent developments allow the approach to the studies at much lower concentrations of ionic polymers than earlier studies. A single broad diffraction peak, consistent with a distorted ordered structure, when the molecular weight was high and the salt concentration was low was achieved. It seems very clear from the study of a variety of macrolons, including ionic biopolymers, that they form ordered structures in dilute solution. The structure is highly distorted and results from electrostatic interactions between particles through intermediary counterions. Edward D. T. Atkins (University of Bristol, Bristol, U.K.) presented his work on "Chain Folding in Polymers: Its Occurrence and Importance in Synthetics and Biopolymers." Regular chain folding occurs in synthetic polymers such as polyethylene, polystyrene, and polysiloxane. Chain folding is also very common in nylons, in polysaccharide-protein complexes including insect silk, in gas vesicles walls, and in the polysaccharide-protein present in insect ovipositor fibers.

Three interesting talks had to do with new approaches to high-temperature polymers. The first, by H. D. Stenzenberger (Boots-Technologie, Dossenheim, F.R.G.) described "Aspects of the Chemistry and Applications of Bismaleimide Based Resins." He pointed out that polyimides have been known for a long time; totally aromatic linear polyimides are now used as coatings. However, thermosetting imide resins currently being tested for many applications are polyimides prepared by polymerization of monomeric reactants, acetylene-terminated polyimides, and bismaleimides. The author described particularly the technology that has been developed in the areas of bismaleimides. Bis maleimide resins are obtained from a variety of bismaleimide building blocks, using several reactions: vinyl-type copolymerizations with allyl-type reactive diluents, Diels-Alder copolymerization, ene-type chain extension reaction employing allyl-phenyl-type comonomers, copolymerization with reactive elastomers and Michael addition-type chain extensions. The authors discussed, in particular, the Diels-Alder-type copolymerization and ene-type chain extension to give new cross-linked polymers whose balance of properties, especially as filled compositions, is desirable to open new fields for such materials. "Cross-Linkable Polyester-Imides" was presented by J. G. de la Campa (Plastics Institute, Madrid, Spain). His work involved preparing polyesters and polyesterimides with pendant imide groups. Polymers modified with maleimide, tetrahydrophthalimide, and nadimide pendant groups, when heated, presented an exotherm corresponding to the cross-linking reaction through the double bonds. "New Acrylic-Functional Oligomers and Their Industrial Applications" were discussed by W. R. Dunnivant (Ashland Chemical Co., Columbus, OH). Several different types of acrylic-functional urethane and ester-based oligomers have recently been developed and are finding use in the manufacture of metal

castings and high performance composites. The oligomers, the processes in which they are used, and the industrial advantages of both the chemistries and fabrication process technologies involved were discussed. These materials, used in foundry and composite applications, involve acrylate or methacrylate functional urethane oligomers in the manufacture of structural fiber-reinforced composites. For foundry applications, functional acrylic oligomers have polymerizable carbon-carbon double bonds; the compounds include acrylated esters and ether resins, vinyl ester resins, and a number of commercially produced acrylic-capped, isocyanate-terminated prepolymers.

"Gelation/Crystallization of Synthetic Polymers," presented by P. J. Lemstra (University of Eindhoven, The Netherlands), involved the study of chemical crosslinking performed during or after polymerization which results in the formation of nonreversible permanent polymer networks. Thermoreversible gels were obtained when the crosslinks were of a physical nature. In some cases of synthetic polymers, processing in the melt is not feasible due to thermal degradation, while solution processing is not desirable. Interesting thermoreversible gels which are formed on subsequent cooling and/or coagulation are quite interesting; processing for membranes and gel spinning for polyethylene have been successful and have given new and unusual structures.

Liquid crystalline polymers have become of great interest in recent years, and H. J. Coles (University of Manchester, U.K.) described "The Liquid Crystalline Behavior of Side-Chain Polymer Liquid Crystals in Low Molar Mass Mesogens." Low molecular weight liquid crystalline compounds had an important impact on the nonemissive electro-optic display industry over the last decade because such displays use low operating voltages and are essentially nonconducting; their very low power requirements led to their widespread use in calculators, watch and computer graphic displays. A particular material suitable for a specific application is normally chosen because of its thermal, elastic, viscous, dielectric, and refractive index properties. For any application, the material used will normally be a mixture of several low molecular weight compounds chosen to make a compromise of the various properties. The authors used 4-cyano-4'-pentyl-biphenyl and connected it via a spacer group to a polysiloxane having approximately 50 siloxane units. The "Synthesis and Properties of Liquid Crystalline Elastomers" was described by F. J. Davis (University of Reading, U.K.). His group used polymer systems similar to those described by Coles. The potential of such materials for these various applications depends on the combination of the properties of monomeric liquid crystalline materials with those of macromolecular structure. The properties of monomeric crystalline materials are well defined. Polymeric systems show a number of additional properties. One of their advantages is the ability to form elastomers and consequently materials with various degrees of crosslinking. Acrylate monomers where the mesogen is connected to the polymerizable unit by means of a flexible spacer group were also synthesized. Homopolymers and structures with low crosslink density showed marked birefringence and textures typical of a nematic liquid crystalline phase. In highly crosslinked samples (25%), no liquid crystalline phase was observed.

On the afternoon of Wednesday, F. E. Karasz (University of Massachusetts, Amherst, MA) presented his lecture on "Highly Conducting Polymers Based on Poly(arylene

Vinylene)." Polyphenylene vinylene is conveniently synthesized via a precursor sulfonium salt polyelectrolyte; the latter can be thermally treated to yield polyphenylene vinylene in film or fiber form of substantial orientations. When doped with arsenic pentafluoride, materials with conductivities of $2 \times 10^3 \text{ S cm}^{-1}$ have been obtained. "Molecular Organization of Electrochemically Prepared Conductive Polymer Films" was presented by G. R. Mitchell (University of Reading, U.K.). He pointed out that a wide range of conducting polymers based on heterocyclic rings can now be produced by electrochemical deposition. He studied particularly polypyrrole/p-toluene sulfonate films and investigated their individual characteristics and morphologies. The materials were investigated for their molecular anisotropy; a detailed x-ray study and other characterizations were made. A number of unconjugated polymers are capable of forming electroconducting materials on doping with electron acceptors. B. Gordon III (Pennsylvania State University, University Park, PA) has synthesized derivatives of poly(p-phenylene pentadienylene) and found that "Proton Abstractions. A New Route to Electrically Conductive Polymers" can be carried out with, for example, n-butyllithium. He found, in preliminary examinations, that conductivities of up to 10^3 S cm^{-1} could be measured.

The "Influence of Tacticity on the Initiation Mechanisms of PVC Degradation" was presented by C. Mijangos (Plastics Institute, Madrid, Spain). The nature of defect structures such as polymer unsaturation, branching, head-to-head structures, and structures obtained by autooxidation were thought to be responsible for thermal instability of PVC, even though the content of the defect structures is as low as from 0.2 to 2.5 per 1000 monomer units. "New Approach to the Mechanism of PVC Stabilization in Solution" was discussed by B. Ivan (Central Research Institute of Chemistry, Budapest, Hungary). The extent of free hydrogen chloride evolution as a function of time for PVC solutions containing several stabilizers (for example, lead stearate) showed that considerable induction periods of hydrogen chloride evolution are observed as the stabilizer content is increased.

The "Photochemistry and Energy Balance in Ultraviolet Laser Ablation of Polymers" was discussed by R. Srinivasan (IBM Watson Research Center, Yorktown Heights, NY). In a strong absorber of UV radiation, photoacoustic studies show that ablation begins long before all of the photons in one pulse are absorbed in the polymer. A quantitative correlation of the response to UV laser radiation of a polymer to its chemistry, its UV absorption as well as to the pulse energy is still a problem. Attempts have been made to work out a theory which can be tested experimentally. "New Polymers for Microlithography, the Chemical Amplification Approach" was given by Jean M. J. Frechet (University of Ottawa, Canada). New materials for applications as photoresists have been vigorously investigated and have produced materials of greatly improved properties through new concepts using polymers with pendant epoxy groups. The presently favored approach is the amplification of photoinitiated chain or catalytic reactions. Photoinitiation was used to initiate chain reaction or to generate a catalyst in localized areas within the resist film. The following problems were investigated: (a) photoinduced changes in the physical properties of polymers, (b) photoinduced multiple molecular rearrangements, (c) photocatalyzed depolymerization or chain degradation reactions. R. A. Pethrick (University of Strathclyde, Glasgow,

Conference Reports

Scotland) presented his work on "Electron Beam Lithography." He concluded that polymers are used extensively for the generation of patterns for fabrication of semiconductor circuits. Copolymers of methyl methacrylate and styrene have shown either positive or negative behavior depending upon the proportions of the two monomers present; various derivatives of methyl methacrylate and styrene have been investigated. The performance of any polymer resist depends critically upon the solvent used to generate the pattern.

On Wednesday afternoon, the part of "Synthesis and Characterization of Functional Polymers" of the meeting "Macromolecules 86" was concluded with three important contributions. R. Simons (University of Manchester, U.K.) discussed "Electrically Induced Storage Effects in Smectic Polysiloxanes-Controlled Optical Transmission." Comblike or side chain polymeric liquid crystals belong to a relatively new class of thermotropic liquid crystalline compounds. Numerous investigations have revealed nematic, smectic, and cholesteric polymers with properties analogous to their low molecular weight counterparts, with the added complication of a glass transition at temperatures below the range of the mesophase stability. This glassy phase was used to advantage by early researchers, and electrically or thermally induced optical textures were durably stored below the glass transition temperature indicating the possible use of these materials for data storage. The most widely studied materials are polysiloxanes onto which mesogenic groups are attached via flexible spacer groups.

"Ultra High Resolution Laser Addressed Liquid Polymer Displays" was discussed by H. J. Coles (University of Manchester, U.K.). He mentioned that a class of materials has been recognized that exhibit intermediate and mobile structures (i.e., mesophases) between the crystalline (or glassy)

phase and the isotropic melt. Polymer mesophases have recently been observed in the absence of solvents as a function of temperature only. Such thermotropic mesophases are very similar to those well known in low molecular weight liquid crystalline materials. The liquid crystalline to isotropic phase transitions of the polymers have been studied by optical microscopy and thermo-optical analysis. W. Driemeier (University of Osunbruck, F.R.G.) presented his work on "High Resolution Photorefractive Polymers for Integrated Optics." New photorefractive polymers allow the easy fabrication of passive components for integrated optics by simple illumination with ultraviolet light; no wet processing is needed. The polymers are reactive acrylate systems with a high content of radical generating compounds. Planar optical waveguides are prepared by solution deposition or by spin coating techniques; photorefractive properties are investigated holographically. The mechanism of refractive index change can be understood as a light-induced fixing of the high-index dopant to the low-index polymer (photofixing). Additional cross-linking hardens the film, providing for high resolution and stability. "Photopolymerization in Ceramic Processing," by P. D. Calvert (University of Sussex, U.K.), showed that multilayer ceramics (ML) processing is widely used in the production of capacitors and in packaging for large integrated circuits. Efforts have been made to extend the type of processing applicable to ceramic sheets by using photopolymerizable binders in analogy to photolithographic processes used in printed circuit boards and integrated circuit manufacture. Two types of processes are described. The first aims at the production of patterns in free-standing green tapes; the second considers the production of thin ceramic layers on silicon integrated circuits.