

1986

Makromolekulares Kolloquium Freiburg

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Vogl, Otto and Cantow, Hans-Joachim, "Makromolekulares Kolloquium Freiburg" (1986). *Polymer News*. 13.
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Makromolekulares Kolloquium, Freiburg

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The Macromolecular Colloquium, which is held every year in the Spring in Freiburg, F.R.G., was held this time from February 28 through March 2, 1985. It was the 20th Macromolecular Colloquium and was attended by more than 400 scientists from all over Germany. Many graduate students from almost all German universities attended. Although the Macromolecular Colloquium is primarily a German meeting, this time a number of foreign scientists were also invited and participated. Twenty-five invited main lectures were given and about thirty papers were presented in poster form; the posters were introduced by one of the authors.

The Macromolecular Colloquium was co-chaired by Professors H.-J. Cantow and H. Finkelmann, University of Freiburg. Dr. Finkelmann has recently been appointed Professor in Freiburg and replaced Professor Gerhard Wegner, who has accepted the Directorship of the Max Planck Institute for Polymer Science in Mainz.

As the first lecturer, Professor H. Finkelmann of the University of Freiburg discussed "Transport Phenomena in Liquid Crystalline Elastomers." The author had prepared linear liquid crystalline polymers where the liquid crystalline

units are attached to an elastomeric polymer side chain, crosslinked the elastomers and studied the phase behavior of these polymers. The liquid crystalline elastomers show the characteristic phase behavior of low molecular liquid crystals and also the rubbery elasticity of conventional elastomers. The liquid crystalline units of these materials can be oriented



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by mechanical deformation; this type of polymer structure is useful for the study of gas transfer through the crosslinked polymers. Dr. H. G. Ohm of the laboratory of Professor S. G. Kirste discussed "The Structure of Liquid Crystalline Polymers by Neutron Scattering." The neutron small-angle scattering of mixtures of partially deuterated, and fully protonated liquid crystalline materials were investigated. It was shown that small changes in the polymer structure can give quite different polymers which may have nematic and smectic phases. In addition to the neutron scattering experiments, an investigation of the solution properties of these polymers was also carried out.

Professor G. Wegner now of the Max Planck Institute in Mainz, presented his most interesting work on "Cycloparaffins with Large Ring Members" (C_nH_{2n} ; $96 \leq n \leq 288$); these compounds are "models for partially crystalline polymers." Molecular uniform cyclic paraffins C_nH_{2n} ($n = 24, 48, 72, 96, 144, 288$) were synthesized as models for the study of the phenomena of chain folding. Crystallization behavior and solid-state properties of these mono-disperse cyclic oligomers were compared with the corresponding linear paraffins C_nH_{2n+2} . The syntheses were carried out by oxidative coupling of α,ω -diines, starting from 1,24-tetracosadiene. This reaction gave linear α,ω -diines which still have the triple bonds in the chain and at the ends. Linear oligomers were made by oxidative coupling in concentrated solution, while cyclic compounds were prepared in high dilution. The separation of linear and cyclic products had to be done at the point when the compounds still have their triple bonds. Quantitative hydrogenation gave the cyclic or linear paraffins. Spectral investigations allowed the identification of signals which are specific for the overall structure but also allowed the determination of conformer sequences in the fold area. Indication of "chain folding" was observed in linear paraffins with $n > 168$.

Professor G. Goldbach presented the work of his research group on the structure and properties of segmented polyamides from polyether and polyamide blocks; blocks of polytetrahydrofuran and polylactolactam provided technically interesting thermoplastic materials with a broad spec-

trum of properties. The primary reason for this combination of properties of these polymers is the existence of several phases and the possibility of readily varying the average lengths of each of the two block components. The three phases consist of: (a) an amorphous phase which forms the matrix consisting of lactolactam and tetrahydrofuran sequences, (b) a discontinuous amorphous phase which consists primarily of polytetrahydrofuran, and (c) a crystalline phase which consists of oriented lactolactam sequences. The first phase provides the internal plasticizer; the second, the internal impact resistor.

Professor H.-J. Cantow of the University of Freiburg described his "NMR Studies on Model Compounds for Temperature and Solvent Influence on the Dimensions of Polar Macromolecules." In diatetic head-to-head polypropylene on the basis of spectroscopic studies, it was shown that the temperature dependence could be determined by measuring the analogous low molecular structural model compounds. Crystalline and glassy amorphous areas in polymeric systems could be analyzed. Head-to-head poly(vinyl chloride) also gave an interesting subject for investigation. From these studies, not only could structural information be obtained but also could the stereochemistry of the erythro and threo configurations be confirmed.

Professor G. R. Strobl of the Max Planck Institute in Mainz presented his "Molecular Motion Defect Structures and Phase Transition in Oligo- and Polytetrafluoroethylene." Polytetrafluoroethylene has three different solid-state transitions between 19 and 30°C. The corresponding oligomers, perfluoro-n-alkanes, show qualitatively similar behavior in their phase transition at lower temperatures. Because oligomers can be obtained as single crystals, the entire investigation could be carried out by characterizing these phase transitions. The investigation and determination of the x-ray parameters and defect structures of the individual modifications showed that the helix reversal defects of polytetrafluoroethylene consist of helical arrangements.

Professor K. Konnecke of Hoechst described "Partial Compatibility of the Interphases of Polymer Blends by IR Spectroscopy." He has found that knowledge of the properties of



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Picture of Freiburg made from the top of the Chemistry Building

polyblends and the improvement of these properties with respect to toughness and fabricability play an important role in the development of new polymeric materials. By an experimentally simple method, so-called intermolecular interactions could be identified by infrared spectroscopy as the first step of compatibility. From the change of the absorption behavior of characteristic groups in blends, one can identify the existence of the interactions and which functional groups are involved in these interactions. The author described model blends of polyoxymethylene with poly(methyl methacrylate) and polyoxymethylene with poly(butylene terephthalate), using ATR-IR spectroscopy. In all cases, the interactions between the ester groups of the polymers and the ether groups of polyoxymethylene were recognized as important.

Dr. H. M. Laun of the BASF, Ludwigshafen, described the "Molecular Orientation and Elastic Deformation in Polymer Melts." On the molecular basis, polymer molecules have only limited mobility because of the neighborhood of other molecules. The melt of these molecules can be oriented by deforming the neighborhood. Diffusion during fabrication by elastic deformations with small shear and stretching forces could be analytically analyzed and evaluated. A connection between molecular structure and elasticity of the melt could be established.

The next paper was given by Dr. W. M. Kulicke, Technical University of Braunschweig, who described the behavior of polymer solutions based on molecular parameters. The full gamut of the complex viscoelastic behavior of polymer solutions was investigated with particular emphasis on the microstructure. The objective of this work was to correlate transport, fabrication, and improvement methods in a more exact way. The investigations on rheology were primarily concerned with the relationship between shear viscosity and molecular weight; concentration of polymer solutions as a function of the shear rate could be developed which would be valid over a very large area of weight-average molecular weight range.

On Friday morning, Professor O. Vogl, Polytechnic Institute of New York, presented his new results on "Optical Activity Based on Macromolecular Asymmetry." He reported that optically active polymers have now been made whose optical activities are based entirely on macromolecular asymmetry (helicity). The example used was isotactic polychloral, which exists only in helical conformation. When prepared with chiral initiator by anionic polymerizations, polychloral samples with optical activities of several thousand degrees have been prepared. It is not certain, however, that this is the ultimate value of the specific rotation that may be expected for a 4_1 helix of polyoxymethylene structure consisting of only one screw sense. It was also mentioned that the possibility cannot be excluded that only preference has been obtained at this state of research, and the polymers are not exclusively helices of one screw sense. It was pointed out that the initiation step is now better understood and shows how the first few monomer units are added and in what stereochemistry. Stereospecificity of monomer addition, entirely meso(isotactic), ultimately seems to result in an exclusive conformation of a 4_1 helix.

Professor H. W. Spiess of the Max Planck Institute of Polymer Science in Mainz discussed "Molecular Motions in Solid Polymers with Deuterium NMR Spectroscopy." Deuterium

NMR spectroscopy could open new possibilities for the characterization of molecular motion. Particularly important for the understanding of the mechanical properties of solid polymers, motion mechanisms can be differentiated and followed over an enormous dynamic range of 12 orders of magnitude. Some of the molecular motions and glass transitions, the characterization of correlation distributions, and the relationship between mechanical properties, molecular dynamics and structure, and the dynamics of new polymeric materials (for example, liquid crystalline polymers and polymeric membranes) can be investigated.

Dr. W. Gronski of the Institute of Macromolecular Chemistry in Freiburg discussed "Topospecific Deformation Mechanisms in Elastomers." These measurements were made by a combination of deuterium NMR spectroscopy and rheo-optical experiments. On the example of selectivity crosslinked 1,4-polybutadiene networks, it was shown that the deformation of the crosslinked chains is inhomogeneous. Furthermore, it was shown that considerable insight into the molecular deformation mechanism in chemically and physically crosslinked elastomers can be achieved, especially when topospecific deformation orientation behavior in well-defined positions of the networks are investigated.

Dr. L. A. Kleintjens of the DMS, The Netherlands, discussed "Polymers and the Lattice Gas Model." Using the pressure dependence of thermodynamic properties, a relatively simple mean field lattice gas model was found to be useful even in comparison to more extensive theories. This model can be used for polymer solutions near the critical condition and in polymer melts.

Professor B. A. Wolf, University of Mainz, mentioned new and very efficient techniques for (continuous) fractionation. Usually it is important to have a considerable amount of material if a polymer is to be fractionated into fractions of narrow molecular weight. New techniques are now being worked out, especially for poly(vinyl chloride)s, which allow the preparation of a considerable amount of fractionated material in a reliable way. It was possible to fractionate the polymers by a continuous countercurrent extraction. It is necessary that the system be selected in such a way that during the entire extraction the system remains in two phases.

Dr. A. Sanner of the BASF, Ludwigshafen, described the "Structure and Complexes of Poly(N-vinyl pyrrolidones)." Poly(N-vinyl pyrrolidone) in the form of soluble homo-, copolymers and also as insoluble crosslinked networks are used in pharmaceutical, cosmetic, and other technical products. Polymers of molecular weights from 2,500 to 1,000,000 are used which are prepared by radical polymerization in solutions. Poly(N-vinyl pyrrolidone) forms complexes with a number of compounds, particularly hydrogen donors and carboxylic acids. Especially important are the complexes with iodine which are used as disinfecting agents.

Dr. H. Albers of the Central Laboratory at Bayer A.G., Leverkusen, spoke on "Graft Copolymers of Cellulose Esters and Ethylene/Vinyl Acetate Copolymers." Ethylene/vinyl acetate copolymers with more than 70% vinyl acetate are known polymeric plasticizers for cellulose esters. This is possible only because, at this level of vinyl acetate in the copolymer, they are compatible with cellulose esters. By additional grafting of vinyl acetate onto the ethylene/vinyl acetate component, the miscibility with cellulose esters can be further improved. Particularly interesting is the decrease of the

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glass transition temperature of these mixtures and the fact that the polymer blends are transparent, although the blends are apparently phase-separated systems.

Dr. E. Sackmann of the Technical University of Munich described "Polymerized Liquid Double Layers and Their Possible Use as Model Biological Membranes." The combination of polymerizable amphiphiles with conventional phospholipids opens new possibilities for the building of models of biological membranes or for the preparation of two-dimensional macromolecular solutions. Partially polymerized vesicles show interesting analogies to cell membranes in their mechanical and elastic properties.

Professor G. Allegra of the Polytechnic Institute of Milan presented his work on the "Coil-Globular Collapse in Dilute Solution" and reported that the long-range attraction experienced by polymer chains in poor solvents is in contrast to the screened and three-body interaction. While the formulae for effective chain thickness are especially important for relatively short chains, the latter arise from interdependence among the two-body attractions prevailing for long chains.

Dr. M. Mutter of the University of Basel spoke on "Artificial Proteins and Enzymes; a Future Prospective." The preparation of artificial proteins, for example, of globular polypeptide chains with unnatural amino acid sequences still has not been done. Based on the present knowledge of a secondary structure topology and folding mechanism, a new strategy for the formation of artificial proteins was developed which includes oligopeptide blocks with stable secondary structure which are then used as nucleating centers by segment condensation to topically significant units. Especially important is the development of a tertiary structure and the formation of hydrophobic clusters.

On the last day of the conference, Professor J. B. Lando of the Case Western University discussed work on the "Conduction of Polymerized Polyfunctional Diacetylenes." He has studied the dimer in 1,11-dodecadiene which can be crystallized and polymerized into semiconducting polymers. The materials process sheetlike structures with parallel polydiacetylene chains bridged by methylene groups. Polymeric forms of these dienes have also been prepared and crosspolymerized. Spectroscopic data indicate that the polymerized dimer has a band gap of 0.4 eV which can be compared to an activation energy of 0.18 eV for conduction. Electrochemical properties of layers of polymers of phthalocyanines and their low molecular analogs were described by Professor D. Wöhrle of the University of Bremen. He has investigated low molecular weight and polymeric phthalocyanines and studied their redox properties in solution, their activity in photoredox processes, their catalytic, electrocatalytic, and electrochemical properties, the electronic conductivity, and their photovoltaic properties. He has worked particularly with phthalocyanines which also have eight cyano groups attached to the rings. It was pointed out by the chairperson

that Dr. Wöhrle's presentation was particularly intriguing because he actually conducted an experiment during his lecture to show a very simple and convincing way the change into the conductive form.

Dr. M. Burkhard of the University of Freiburg then described his work on the "Cross-Linked Styrene Networks." This paper was substituted for a paper by Y. Shahab of Iraq, who was unable to come to the Symposium. "Highly Conductive Fluoranthrene Cation Salts" were described by Dr. E. Dormann of the University of Bayreuth. He used polymers which have been doped with a common doping agent. Of particular interest for these radical cation salts is their narrow ESR line width and a correspondingly long electronspin relaxation time. The one-dimensional stacking of aromatics causes the anisotropy of the static magnet susceptibility. In spite of the good quality of the single crystals, the defects limit the one-dimensionality and the electronic conduction.

Dr. K. P. Hofmann of the University of Freiburg presented "Light-Induced Interactions of Proteins on Photoreceptor Membranes." He mentioned that the retina of the eye has the outside segment of a specific detector; he described in detail the interaction and the protein transfer through these membranes. He believes that the transient protonation is an indicator for the specific conformation of occluded groups.

As the final presentation, Dr. M. D. Lechner of the University of Osnabrück presented the work of his group on "Photopolymers for Optical Reservoirs and Wave Guides." He showed that optical methods continue to gain in importance in retention, transport, and the use of information. For retention, holographic methods are of special interest because in this way very high intensities can be obtained; they are all-important because under the influence of light the reflective index can be changed. In addition to electrooptical crystals, photopolymers have been suggested recently for the optical retention; wave guides were proposed for the reflective index which is changed via the density. From what we know now, the various materials desired for the optical systems can be better defined. Photopolymers can also be used as components for integrated optics.

In addition to the primary lectures, nearly thirty posters were also presented. On Thursday evening a party with dinner was held at the Student Union. The general set-up of the meeting, which was held in the Chemistry Building of the University of Freiburg, was most convenient. Many ideas were exchanged, modified, and improved. Vigorous discussions took place in the lecture rooms, more at the post-sessions, and in the corridors. Excellent organization provided easy access for intercommunication among the participants. Most attendees are looking forward with increased interest to the next meeting in Freiburg.

Acknowledgments: We would like to express our appreciation to Mrs. E. Cary for her assistance during the preparation of this manuscript.