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Conference Report

ICRIS '96: Controlled Organization and Molecular Dynamics of Polymers, Uji, Kyoto, Japan

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The first International Symposium organized by the Institute for Chemical Research of Kyoto University was held in Uji, Kyoto, Japan from November 7 to November 8, 1996. Uji is about 15 km south of Kyoto, it is famous for the production of Uji-cha, green tea of the highest quality. Uji was also famous as a resort of the Fujiwara clan, which held the real political power in the Heian period of Japan, about one thousand years ago.

The Conference in Uji was supported by Monbusho, the Ministry of Education, Science, Sports and Culture. The Symposium was organized by an organizing committee, chaired by Professor Takeaki Miyamoto.

The special purpose of this Symposium was to help celebrate the 70th anniversary of the foundation of the Institute. The meeting consisted of 16 invited papers and 21 papers which were presented in poster form.

The Institute for Chemical Research of Kyoto University was initially established in 1915 as a Special Institute of Chemistry, a satellite facility of the College of Science of Kyoto University (presently Faculty of Science, Kyoto University) to explore and manufacture medical drugs which were important during the first world war.

Based at this facility, the Institute for Chemical Research, Kyoto University was formally established in 1926, to undertake fundamental studies and their application to particular fields of chemistry. The Campus of the Institute for Chemical Research was initially located in Takatsuki, but moved later to Uji, its present location.

The Institute was reorganized in 1992, and now consists of 9 divisions and 2 satellite facilities. Each division, on the average, is made up of 3 laboratories, headed by a full professor. In all, there are 31 laboratories, including 3 laboratories for guest professors. The on-going research embraces a broad range of topics in chemistry: nuclear chemistry, and physics, physical chemistry, surface chemistry, organic and inorganic chemistry, polymer chemistry, bio-organic chemistry, protein and enzyme chemistry, molecular biology and human genome science. Currently there are approximately 110 full-time academic staff members of the Institute, 200 graduate students, and 30 visiting scientists working at the Institute.

The 31 laboratories of the Institute for Chemical Research, Kyoto University can be grouped into several fields of chemical sciences and each group has a high level of activity and also has the proper size for cooperative work which is highly encouraged and is functioning successfully.

This first Symposium was organized by the polymer research group under the title "*Controlled Organization and Molecular Dynamics of Polymers*" which was thought to represent best the thinking of the polymer community at the Institute. Over 150 scientists participated in the Symposium with several invited speakers from abroad.

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Accelerator Laboratory



Main Building of ICR

The conference was opened by Teruya Shinjo, the Director of the Institute, who outlined the objective of the Institute and the purpose of the Symposium. The meeting then reconvened for the scientific sessions with the invited speakers presenting their work and emphasizing the interrelationship between their interests and the interests of individual members of the Institute.

The following **Invited Lectures** were presented at the Symposium:

H. W. Spiess, Mainz, Germany, *Multidimensional Solid State NMR Studies of Molecular Dynamics*

Multidimensional solid state NMR yields unique information about the complex dynamics of polymers. By two dimensional (2D) NMR, e.g. of ^1H or ^{13}C , rotational and conformational dynamics can be monitored in real time. Moreover, the geometry of rotational motions was elucidated free of model assumptions. This information is equivalent to that of quasielastic, incoherent neutron scattering, albeit in orientational rather than reciprocal space.

Moreover, with 3D- and 4D-techniques, *memory effects* concerning the *orientation* and the *rate* can be studied by probing higher order autocorrelation functions involving selected groups along the chain. Even more desirable is information about the chain motion by probing dynamic order parameters for the carbon-carbon bond directions along the macromolecular chain. These are now accessible from measurements of residual dipole-dipole couplings between ^1H bonded to adjacent carbon atoms by 2D exchange NMR and the newly developed technique of

high-resolution solid state multiple quantum NMR spectroscopy. The different aspects introduced above were demonstrated by studies of the slow chain dynamics of polymers at the glass-transition.

U. Buchenau, Jülich, Germany, *Picosecond Dynamics of Polymers*

The picosecond dynamics of disordered matter, although extensively studied, is still poorly understood. There is much more low frequency motion than in the corresponding crystalline substances. This is not only true at low temperatures, where glasses exhibit tunneling states and localized low frequency vibrations coexist with the sound waves, but also at the glass transition temperature, where the undercooled liquid "freezes in" to form a glass.

The appropriate tool for the study of this problem is inelastic neutron scattering. Polymers are often good glass formers and allow the switching from coherent to incoherent scattering on the same substance by using protonated and deuterated samples. In the paper, neutron scattering studies in the picosecond dynamics in polymers were reviewed.

T. Kanaya, Uji, Kyoto, Japan, *Local Dynamics of Amorphous Polymers*

Dynamics of amorphous polymers have been extensively studied using various kinds of techniques, such as mechanical relaxation, dielectric relaxation, NMR spectroscopy, dynamic light scattering, quasielastic neutron scattering and fluorescence depolarization. Recently much interest is focused on dynamics near the glass transition which is mainly governed by the intermolecular cooperativity. On the other hand, far above the glass transition temperature, the dynamics of a polymer chain is not much affected by the intermolecular interactions, but by the intramolecular interactions. At those higher temperatures, elementary processes for conformational transitions are dominated by the intramolecular connectivity in a polymer chain. The main mechanism of the elementary process has been examined by quasielastic neutron scattering measurements in a time range of 4×10^{-13} to 4×10^{-10} seconds.

Y. Tsunashima, Uji, Kyoto, Japan, *Dynamics and Structures of Polymers in Solution*

The dynamics of polymers in dilute solution is being now understood in more detail by using advanced methods of dynamic light scattering. For flexible linear homopolymers, the scattering is mainly due to the concentration fluctuations of the polymers whose segments undergo thermal motions. The diffusion coefficient, its first and second concentration-dependent coefficients, the internal motions, and the first cumulant give a revised understanding of the hydrodynamic interactions of the polymer chain.

For flexible AB-diblock copolymers, the scattering due to the A-B composition fluctuations take place in addition to the scattering due to the concentration fluctuations. When the polymers are dissolved in good solvents, the composition fluctuations are dominant in the single chain and emerge as the shift of the center of mass the A subchain, relative to that of the B subchain (the interdiffusion) and/or as the hydrodynamic heterocontacts between A and B subchain elements (the enhanced internal motions). These internal motions interact with the diffusion motion and retard the diffusion of an entire polymer molecule.

J. A. Kornfield, Pasadena, CA, USA, *Dynamics of Block Copolymer Nanostructures*



Julia A. Kornfield

Zhi-Quan Shen

Nanostructured block copolymers have potential applications in emerging technologies as well as in conventional fields, such as novel separation membranes, biomedical materials, optical devices and microelectronics. Recent discoveries of an array of fascinating morphologies in ABC triblocks motivated the study of their dynamics and flow alignment behavior since it may provide routes to functional nanostructures that are inaccessible through a block copolymer containing just two types of blocks. Like diblock copolymers, the form and size of the nanostructures of ABC triblock is amenable to rational control, and their local structure can be globally aligned using applied fields, especially flow.

Much of the previous work on flow induced alignment behavior has focused on A-B diblocks and A-B-A triblocks, the latter exhibiting characteristic alignment due to loop and bridge conformations of the polymer chains at the microphase interfaces. No study has examined the alignment of A-B-C triblocks; distinct behavior from the A-B and A-B-A systems can be expected. For example in a three-microphase ordered A-B-C triblock, only bridges exist, but no loops. To better understand the dynamics and alignment of A-B-C triblock terpolymers the author focused on model copolymers. The kinetics of flow-induced alignment was examined with rheo-optical methods, and the nanostructures and global orientation were detected by TEM and SAXS.

H. Watanabe, Uji, Kyoto, Japan, *Dynamics and Structure of Triblock Copolymer Systems*

Styrene-butadiene-styrene triblock copolymers, typical thermoplastic elastomers, often exhibit rubbery, plastic, and viscous behavior at low, intermediate and high temperatures. The rubbery response has been attributed to a network of glassy discrete styrene domains bridged by the middle diene blocks, while the viscous response was attributed to a disordered structure of the constituent blocks. The plastic behavior has been attributed to soft domain structures.

These conventional molecular pictures suggest that the rheology of triblock co- and terpolymers is governed by the motional freedom for the middle block ends. The validity of these models has been examined by studying the rheological and dielectric behavior of these triblock copolymers in selective solvents for the middle block.

M. Doi, Nagoya, Japan, *Dynamics of Volume Transition in Gels*

Certain kinds of polymer gels immersed in a solvent exhibit a discontinuous change of equilibrium volume when external conditions such as temperature or solvent composition are changed continuously. This change is known to be a first order phase transition and is called the volume transition. In the early

investigations, the volume transition was interpreted in analogy with the gas-liquid transition of simple fluids.

However, recent studies indicate that such an analogy is incorrect. This is demonstrated by two experimental observations: a.) Hysteresis: the threshold temperature at which the collapsed phase of the gel transforms to the collapsed phase. b.) Anomalous dynamics: in the swelling process there is an incubation period during which the whole gel is swollen only slightly, followed by the process of large volume change.

The author has solved the complete equation for the swelling dynamics and showed that the phenomena are the results of the elastic effect.

J. S. Higgins, London, UK, *The Effect of Flow on Binary Polymer Blends*



Julia Higgins

The technological importance of polymer blends has long been recognized by polymer scientists. By mixing two or more polymeric species it may be possible to produce new materials with desirable properties possessed by neither of the constituent polymers separately. While blending technology relies on polymer-polymer compatibility, total miscibility in a thermodynamic sense is often not the aim. Nevertheless, the thermodynamics of mixing are crucial in understanding the miscibility of polymers.

It has recently become evident that another factor in the processing conditions can affect the phase separation—its rheological history. This surprising interaction of rheology and thermodynamics has been explored both experimentally and theoretically. It was found that the phase boundary can be either lowered or raised by different shear rates or more generally that the islands of immiscibility can appear separated from the main spinodal curve.

D. G. Gray, Montreal, Canada, *Controlled Organization of Chiral Structures in Cellulose and Cellulose Derivatives*

Cellulose is the most abundant polymer, it is indispensable as a renewable resource whose molecular structure is the basis of the useful mechanical, physical and chemical properties of wood, paper and a wide range of cellulose derivatives.

The main cellulose backbone has a chiral, relatively stiff structure, and therefore, cellulose and its derivatives may form chiral nematic (cholesteric) phases, both in solution (lyotropic liquid crystals) and in the absence of solvent (thermotropic liquid crystals). Such phases are characterized by pitch and handedness of the helicoidal arrangement of chain segments.

Chiral nematic phase separation was also observed for colloidal suspensions of cellulose rodlike crystallites. For these "chiral colloid crystals", the pitch may be controlled by changing the ionic strength, and the orientation of the chiral nematic direction may be controlled by application of a magnetic field.

K. Shimamura, Okayama, Japan, *Rigid Polymer Crystals*

Since the discovery of the polyethylene single crystal, chain folding has been recognized as one general form of conformation in crystalline polymers. Recent objectives in polymer synthesis have produced polymers with rigid structures. These liquid crystalline polymers exhibited high modulus and strength in film and fiber form. Some of these polymers are crystallizable but are too rigid to form folded chain crystals.

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One of the fabrication techniques to form crystalline structures of poly(*p*-phenylene benzobisthiazole) is dissolving the polymer in conc. sulfuric acid at about 100°C and quenching it to 0°C to form fibrillar crystals or by isothermal crystallization to form rodlike crystals. Reorganization of the rigid polymer chains in the rod crystals was achieved by annealing to 450°C.



Isao Ando

Akio Teramoto

I. Ando, Tokyo, Japan, *Structure of Polypeptides in the Solid State as Studied by High-Resolution NMR Spectroscopy*

The structural investigation of peptides, proteins, and other biopolymers in the solid state is being pursued increasingly by means of high-resolution solid state NMR. Most of the biopolymers consist of repeating sequences of peptide bonds with 20 different types of substituents at the α -carbon atom. The secondary structures of these biopolymers are classified as α -helix, β -sheet, ω -helix, and others, by means of a set of dihedral angles.

In solution, the NMR chemical shifts of biopolymers with internal rotations are often the average values for all internal rotations because of rapid interconversion by rotation about peptide bonds. In the solid state, however, chemical shifts are often characteristic of specific conformations of highly restricted rotation about the peptide bonds. The NMR chemical shift is affected by a change in the electronic state arising from the conformational change. NMR chemical shifts in the solid state, therefore, provide useful information about the electronic state and conformation of a biopolymer with a fixed structure. Solid state ^{13}C , ^{15}N , and ^{17}O NMR spectroscopy have been found to be extremely useful to study the details of the structures of proteins and peptides.

M. Tsuji, Uji, Kyoto, Japan, *Fine Structures in Crystalline Polymer Solids Studied by High-Resolution TEM*

Scanning probe techniques such as scanning tunneling microscopy and atomic force microscopy are now routinely used in the field of material science to clarify atomic and molecular-scale surface structures. These techniques are, however, not adequate for investigation of internal structures such as lattice effects in the crystallites, unless such structures come out directly on the specimen surfaces and/or affect the surface structures to be detectable by these techniques.

To study the internal structures of crystallites, high-resolution observation by transmission electron microscopy (TEM) is the most appropriate technique. It has been used to study ultra-fine structures in crystalline polymer solids.

The following crystalline specimens were used to demonstrate the utility of high-resolution TEM: 1.) uniaxially oriented thin films of flexible-chain polymers such as isotactic polystyrene, poly(aryl-ether-ether-ketone), polyethylene and poly(4-methyl-1-pentene); 2.) whiskers of poly(*p*-

hydroxybenzoate) which are extended chain crystals. For some of the specimens which are vulnerable to electron irradiation at room temperature, the high-resolution images were taken at 4.2 K by cryogenic TEM.

K. Tashiro, Osaka, Japan, *Structural Changes in the Isothermal Crystallization of Polyethylene as Viewed from the Molecular Level*

Crystallization phenomena of the blend of deuterated high-density polyethylene with regular polyethylene with various degrees of ethyl branching were investigated. Depending on the degree of branching as well as the D/H ratio the cocrystallization and phase separation were observed. The origin of these phenomena was studied both from the thermodynamic as well as from the kinetic point of view, and also was studied by traditional thermal analysis as well as by time-resolved FT-IR and small-angle X-ray scattering measurements during the isothermal crystallization process. It was concluded that cocrystallization occurs for the polymers characterized by a similar crystallization rate.

E. L. Thomas, Cambridge, MA, USA, *Control of Interface Structure in Block Copolymer Systems*

The classical phases of block copolymers are the lamellar, cylindrical and spherical microdomain structures. The interface between the domains in each of these classical structures is of constant curvature. In recent years a number of novel microdomain structures have been discovered. These include the double diamond, double gyroid and lamellar-catenoid structures, in AB diblocks. For these structures the partitioning surfaces, called the intermaterial dividing surface is well approximated by surfaces of constant mean curvature.

ABC triblock copolymers also exhibit other novel structures, including various cylinder and cylinder phases as well as the highly unusual "knitting pattern" morphology. In certain cases the intermaterial dividing surface is a highly non constant mean curvature. Synthesis of block copolymers where one of the blocks is liquid crystalline also affords the possibility of new microdomain structures. In the instance of a liquid crystalline block, an additional feature of the morphology is the preferred orientation of the mesogenic units with respect to the intermaterial dividing surface.

The most recent development is the modification of these unusual structures where the usual composition-microdomain structure relationship of flexible coil copolymers was modified by chain architecture, block sequence distribution or by the presence of a liquid crystalline block.

E. T. Kang, Singapore, *Surface Structures and Dynamics of Functionalized Electroactive Polymers*

Surface modification of polymers via molecular design is one of the most versatile means of incorporating new functionalities into existing polymers. The surface modification and functionalization of some conjugated conductive polymers were explored. The conducting polymers were polyaniline and polypyrrole for the dielectric polymers, while polytetrafluoroethylene was the nonconducting polymer. The new functionalities incorporated as a result of surface modification include surface conductivities, surface biological activities, and enhanced adhesion characteristics.

S. Miyata, Tokyo, Japan, *Functional Polymers with Controlled Refractive Indices for Phase-Matched Second Harmonic Generation and Retardation Film Applications*

Two applications of functional polymers with controlled refractive indices were carefully studied for: a.) bulk phase-

matched second harmonic generation, and b.) retardation in film applications. The bulk phase-matched second harmonic generation was realized in a stretched polymer where the polymer contains urea linkages in the main chain. The urea polymer was synthesized from 4,4'-diphenylmethane diisocyanate and 4,4'-methylene bis(cyclohexylamine). The spin coated film has an initial positive birefringence. Drawing increased the birefringence, and the film can be used for phase matching just as in biaxial single crystals.

A similar method of the controlled refractive indices of polymer was also used for other types of films. A series of side-chain functionalized polymers using *p*-nitrophenylcarbamate were imbedded into a phenoxy resin backbone. Poling and drawing can control both the in-plane and out-of-plane birefringence using the functionalized side chain polymer with large dipole moment and linear molecular polarizability.



At the Poster Session

The following poster presentations were presented by members of the Institute for Chemical Research, to a considerable extent in cooperation with other laboratories world-wide.

T. Kobayashi, S. Isoda, H. Kurata and S. Moriguchi. Elemental and Chemical Mappings of Electron Energy-Loss Spectroscopy

T. Ogawa, S. Hashimoto, K. Kuwamoto, S. Moriguchi, S. Isoda and T. Kobayashi. Structure Analysis of Thin Crystals by Electron Crystallography

S. Isoda, S. Irie and T. Kobayashi. The First Layer in Epitaxy of Organic Molecules; Point-on-line Coincidence

M. Tosaka, M. Tsuji and S. Kohjiya. Quantification of Stacking Faults in Syndiotactic Polystyrene Single Crystals

K. Urayama and S. Kohjiya. Ultra-high Extensibility of De-swollen Polydimethylsiloxane Networks in Supercoiled State

S. Murakami, K. Shimamura and S. Kohjiya. Deformation Morphology of Extruded and Blown Polyethylene Films

K. Osaki. Molecular Rheology, oops!

H. Watanabe. Molecular Rheology of Suspensions

T. Inoue. Molecular Rheology of Glassy Polymers

K. Kaji, M. Imai, G. Matsuba, T. Kanaya and K. Nishida. Structure Formation of Polymers During the Induction Period of Crystallization—Crystal Nucleation Process—

H. Takeshita, Y. Nishikoji, T. Kanaya, K. Kaji and K. Nishida. Structure and its Formation Process of Polymer Gels

K. Nishida, K. Kaji, K. Kiriya, T. Kanaya, H. Urakawa, J. S. Higgins and B. Gabrys. Salt can Control Electrostatic Structure in Polyelectrolyte Solutions.

T. Kanaya, M. Miyakawa, T. Kawaguchi and K. Kaji. Dynamics of Amorphous Polymers near the Glass Transition Temperature

F. Horii, H. Kaji, H. Ishida, K. Kawabara and K. Masuda. Structure and Dynamics of Polymers in the Different States as Studied by Solid State NMR Spectroscopy

H. Kaji, Y. Shen, T. Tai, and F. Horii. Solid State ^{13}C NMR Analyses of the Medium-Frequency Molecular Motion of Solid Polymers

Y. Tsunashima. Polymer Chain Dynamics in Dilute Solution under Couette Flow

A. Hirai, F. Horii, M. Tsuji, J. Sugiyama and H. Yamamoto. *In Situ* Formation of Organized Structures of Bacterial Cellulose

T. Miyamoto, T. Fukuda, Y. Tsuji, M. Minoda and N. Donkai. Controlling Molecular/Material Structures for New High-Performance Polymeric Materials

T. Fukuda, Y. Tsuji and T. Miyamoto. Application of Nitroxide-Controlled Free Radical Polymerization

Y. Tsuji, M. Minoda, T. Fukuda and T. Miyamoto. Synthesis and Interfacial Properties of Amphiphilic Block Copolymers with Pendant Glucose Residues

T. Kokubo, F. Miyaji, M. Minoda and T. Miyamoto. Apatite Formation on Organic Polymers



At the Banquet

Tsunehisa Kimura Derek G. Gray Takeaki Miyamoto

The poster session and the banquet were held at the Kyoto Daigo Plaza Hotel at nearby Rokujizo. The participants found the Symposium most stimulating. Many new and some rather advanced ideas were presented and invited extensive discussions. The participants are looking forward to the next conference, organized by the Institute of Chemical Research, Kyoto University, which we understand, is anticipated in 2-3 years time.

Acknowledgement

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Invited Speakers