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Centers of Polymer Research

Polymer Science in the Nagoya Area, Japan

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The Shinkansen "Hikari" (often referred to as the bullet train), on its way from Tokyo to Kyoto makes its first stop at Nagoya. Nagoya is a city of over 2,000,000, Japan's fourth largest city. It is the center of the Tokai district which consists of five prefectures (Shizuoka, Aichi, Mie, Gifu and Nagano), and is one of the major industrial areas in Japan. Various kinds of polymer industries are represented here including both large and small polymer manufacturers and utilizers. Examples of both types are the petrochemical industries in Yokkaichi City, and the automobile industries in Toyota City.

The polymer science activity in Nagoya is characterized by the close cooperation between polymer scientists in industry and in academic institutions. Nearly 10% of the polymer chemists of Japan live in this area with most of them belonging to industrial laboratories. Frequent seminars and meetings are held to foster understanding and cooperation between universities and industrial laboratories in different disciplines of polymer science. A typical example is the numerous panel discussions which are held biennially "to fill the gap between polymer synthesis and physics". The first such discussion was held in 1966 under the title of "Preparation, Characterization and Physical Properties of Block, Graft and Random Copolymers". Other meetings were held on "Membranes and Flocculants for Water Treatment", "Chemistry of Separation by Chromatography and Membranes", and "Stiff Chain Polymers" and sponsored by the Tokai Division of the Society of Polymer Science.

Efforts are continually underway to bring together basic science and technology in industry and universities. Regular meetings of younger polymer chemists in the Nagoya area are held now.

Academic research in polymer science in the Tokai district is being carried out in the following universities.

NAGOYA UNIVERSITY

Faculty of Engineering

Department of Synthetic Chemistry: Professor Mitsuru Nagasawa, Associate Professor Ichiro Noda, Instructors Yoshio Muroga and Yoshinobu Isono are interested in the conformation of polymers in dilute and

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concentrated solutions, specifically polyelectrolyte solutions. Their interest is focused on the preparation and characterization of polymers with well defined structures. Consequently, a great deal of attention is paid to samples used for studying the physical properties of polymers.

Dr. Teruo Fujimoto (now Professor at the Technological University of Nagaoka) has been working to develop the anionic polymerization technique for the synthesis of nearly monodisperse polymers. He and his coworkers have prepared linear polymers with narrow molecular weight distributions higher than 10 million, and star-shaped polymers whose branches have molecular weights higher than a million.

Professor Yuya Yamashita has broad interest in the organic chemistry of macromolecules. With Dr. M. Okada he has been studying ring-opening polymerization, with Dr. S. Iwatsuki, charge transfer complex polymerization, and with Dr. K. Ito, copolymer microstructures. More recently, he became interested in graft copolymers, using macromonomers for the synthesis of tailored graft copolymers which contain a structural and a functional segment. Surface accumulation of functional segment based on designed morphology is



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being studied with Instructor Yasuhisa Tsukahara. General molecular design of functional segments is being studied with Assistant Professor Yuhsuke Kawakami and Instructor Yoshiki Chujo. Dr. Kawakami is also interested in solid acid catalysts and polymer catalysts for organic synthesis.

Professor Shin Tsuge's research interests include the characterization of the microstructure of synthetic polymers by pyrolysis-gas chromatographic technique. He is also involved in the study of the thermal behavior of polymers by TGA, DSC and pyrolysis-mass spectrometry.

Department of Applied Chemistry: Professor Tamaichi Ashida together with Assistant Professor Takashi Yamane is studying by x-ray diffraction techniques the structure of biopolymers. He is especially interested in globular protein cytochromes, homo-polypeptides with hydrophobic side chains, and oligopeptides with secondary structures in the crystalline state. He is also investigating the molecular structures of cyclic oligomers of synthetic polymers, cyclic tetra- and pentamers from 6,8-dioxabicyclo[3.2.1]octan-7-one, and cyclic tris(ethylene terephthalate).

Professor Hajime Saito in cooperation with Instructor Meisetsu Kajiwara is working on the synthesis of phosphorus-nitrogen compounds and their properties. He is investigating the reactions of cyclic and polymeric phosphazenes with alkoxides, aryloxides and amines. He is also studying the polymerization behavior of cyclic polymers which were found to have excellent thermal and chemical stabilities and useful electrical properties. He also is interested in the synthesis of inorganic polymers which have also complementary properties to ceramics.

Department of Chemical Engineering: Professor Yutaka Miyahara is interested in the applications of ultrasonic relaxation in polymer solutions and also the study of the physical chemistry of aqueous solutions of non-electrolytes. With Assistant Professor Fumio Kawazumi, he is studying the heat capacity of aqueous solutions of polysaccharides. With Associate Professor Hiroyasu Nomura he is studying molecular relaxation processes, such as rotational and vibrational relaxation of molecules in the liquid state and in solution by ultrasonic absorption spectroscopy, Rayleigh-Brillouin scattering and Raman scattering. He is also investigating the dynamics of bound water of solutes in aqueous solutions.

Faculty of Agriculture

Professor Hiroshi Sumitomo is active in the field of polymer synthesis. He is investigating mechanisms of polymerization and copolymerization and is studying the preparation of new polymers. With Associate Professor Masahiko Okada and Instructors Kazukiyo Kobayashi and Kazuhiko Hashimoto, the investigations of the polymerization of cyclic acetals and bicyclic acetals, oxalacetone, and oxalacetam are being carried out. He is also interested in the synthesis of new classes of specialty polymers, especially bicyclic monomers, the mechanisms of their formation, polymer structure and properties: (1) Dextrantype synthetic polysaccharides with potential physiological activities, (2) 10-, 20-, and 25 membered cyclic oligoesters, macrolides, which show

interesting complexation and transport behaviors for metal ions, and (3) hydrophilic perm-selective membrane of polyamide consisting of the alternating arrangement of an amide group and a tetrahydropyran ring. Stereospecific ring-opening polymerizations of optically active hetero bicyclic monomers have given stereoregular optically active products whose formation mechanisms, structures and properties are being investigated.

Faculty of Science

Department of Chemistry: Professor Shoichi Ikeda is investigating the association of molecules and macromolecules in solution, including micelle formation of surfactants, self-association of polypeptides and binding of dye molecules onto polypeptides and polynucleotides. The association of biopolymers is often accompanied with conformational changes. These behaviors are observed by light scattering, viscosity, circular dichroism and infrared absorption spectra. Associate Professor Hiroshi Maeda is interested in electrolytic and kinetic aspects of conformational changes of polypeptides.

NAGOYA INSTITUTE OF TECHNOLOGY

Department of Polymer Technology: Professor Akira Takizawa is investigating the sorption, diffusion, permeation and separation of small molecules through polymer membranes, particularly synthetic polypeptide membranes, of poly(*n*-alkyl *L*-glutamate), poly(γ -benzyl *L*-glutamate), poly(glutamic acid), poly(β -benzyl *L*-aspartate), poly(*L*-methionine) and poly(*L*-leucine). In these membranes, polypeptide molecules show helical conformation and the side chain influences the equilibrium and kinetics of the membrane processes and can be used for the design of membranes with good water permeability and separation of aqueous solution. With Associate Professor Yoshiharu Tsujita, he is working on the relationship between structure and physical properties of solid polypeptides with stacked benzene in the side chain and helix-coil transition in dilute and concentrated polypeptide solutions of poly(β -benzyl *L*-aspartate).

Professor Kazuichi Tsuda is investigating the polymerization of vinylsulfonium salt monomers and the polymer reactions of poly(vinyl sulfide). He is also working on the polymerization initiation mechanisms with sulfur radicals and the initiation of radical polymerization of α,β -unsaturated carbonyl compounds with *N,N*-dimethylaniline. Associate Professor Shuji Kondo is interested in the synthesis of new sulfur containing polymers: poly(sulfonium ylides), poly(azasulfonium salts) and poly(imino sulfuranes).

Associate Professor Yasuo Yuki is working on the synthesis of thermally stable polymers containing 1,3,5-triazine rings in the main chain. He is also interested in functional polymers containing heterocyclic rings in the side chain. He is investigating the radical polymerization and thermal polymerization of isopropenyl-1,3,5-triazines.

Department of Synthetic Chemistry: The research of Professor Ryuzo Asami covers a wide area of synthesis of macromolecules. His primary interests are in anionic



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polymerization and the synthesis of functional monomers and their polymerization. He is studying the anionic and cationic polymerizations of alkylbutadienes and phenyl substituted butadienes and the radical polymerization of phenylbutadienes, particularly that preparation of poly(2,3-diphenylbutadiene) which gave head to head polystyrene. Professor Asami's interests are now focused on the anionic equilibrium polymerization of isopropenylbenzenes, such as diisopropenylbenzene and triisopropenylbenzene. He is also interested in the synthesis of star and comb polymers by coupling reaction of living polymer of polystyrene or poly(tetrahydrofuran) and the synthesis of macromers. Functional monomers were synthesized by the reaction of vinylbenzyl chloride with nucleophiles and by the S_N reaction of p-hydroxystyrene as the nucleophile. Vinylstilbene and its aromatic homologue were synthesized from chloromethylstyrene and polymerized by radical, anionic, and cationic initiators.

Materials Research Laboratory

Professor Hisatsugu Kashiwabara is interested in the radiation chemistry of high polymers. Assistant Professor Shigetaka Shimada, Instructor Yasuro Hori and Dr. Masato Sakaguchi (Assistant Professor of Ichimura College) are working with him. Their interests are in the relation between physical properties and relaxation processes of solid polymers and structure of trapped free radicals by magnetic resonance (ESR and Broad Line NMR), dynamic mechanical measurement and optical spectroscopy. Work is also done on the oxidation of irradiated polymers (crystalline and amorphous phases), relaxation spectrum obtained from NMR and ESR data, and molecular motion of polymeric chain in urea-polyethylene inclusion complex.

Professor Kenji Yokota is investigating the field of radical polymerization with emphasis on the propagation step which is studied by kinetics and nuclear magnetic resonance. With Instructor Tadamichi Hirabayashi he is now working on the chemical modification of alternating copolymers and the use of derivatized polymeric materials.

TOYOHASHI UNIVERSITY OF TECHNOLOGY

School of Materials Science: Professor Koichi Ito is investigating the synthesis and characterization of surface-active polymers with known architecture. In collaboration with Professor Y. Yamashita at Nagoya University, he prepared amphiphilic graft polymers via copolymerization using methacrylic macromonomers, and is characterizing their bulk and surface properties by inverse gas chromatography.

Associate Professor Toshiaki Kitano is interested in the conformation of polyelectrolytes in water. He is exploring living anionic polymerizations for preparing well-defined polyelectrolytes [poly(methacrylic acid) and poly(glutamic acid)] with narrow molecular weight distribution.

AICHI INSTITUTE OF TECHNOLOGY

Department of Applied Chemistry: Professor Hiroshi Okamoto is working on many aspects of rubber chemistry and rheology. Such aspects include rubber elasticity under large deformation by uniform stress principle, molecular consideration of the C₂ term of the Mooney-Rivlin equation, rheological consideration of vulcanization curves with an oscillating disk rheometer, synthesis and properties of liquid elastomers with reactive fillers, and chemical modification of polyurethane elastomers. He is working on a simple reclamation process for scrap tire and polyurethane foam with thiol-amine complexes and metal oxides.

With Associate Professor Shinji Inagaki he is also working on the synthesis of reactive oligomers for liquid elastomers and adhesives. The interaction between rubber and fillers is explained by a reinforcing mechanism model of pseudo crosslinks.

MIE UNIVERSITY

Faculty of Engineering

Department of Industrial Chemistry: Professor Akira Takahashi is interested in the surface chemistry of polymers. The emphasis is on the studies of adsorption of polymers onto solid surfaces, surface chemistry of polymer monolayers and modifications of polymer surfaces. He is also investigating dilute solution properties of polyelectrolytes and sol-gel transitions of non-ionic polymers and polyelectrolytes. Associate Professor Tadayo Kato is studying dilute solution properties of polymers and lattices by quasi-elastic light scattering and gel permeation chromatography of macromolecules and polymer colloids.

Professor Shouji Iwatsuki is working on the behavior of highly polar monomers, the synthesis of new strong acceptor donor monomers and their polymerization behaviors by alternating copolymerization of their charge-transfer complexes. He is also investigating reclamation of industrial polymer waste. Assistant Professor Akihiro Kondo is studying the polymerization of cyclic monomers with electron-donating functional groups and the preparation of the surface active fluorine-containing polymers.

SHIZUOKA UNIVERSITY

Faculty of Engineering

Department of Industrial Chemistry: Professor Kakuji Katsuura is working on the flame-retardation of fabrics and plastics including cotton, polyester and polyester-cotton blend fabrics, and thermoplastics such as polystyrene and ABS. With Associate Professor Norihiro Inagaki, their main interest is to clarify flame retardancy and the thermal degradation of polymers containing the flame retardants. They are also active in glow discharge polymerization (plasma polymerization) of compounds containing fluorine, and silicon, germanium, and tin for the modification of polymer films and polymer surfaces to prepare new electronic materials.

GIFU UNIVERSITY

Faculty of Engineering

Department of Textile Engineering: Associate Professor Ryuichi Sakamoto is working on the properties of synthetic polypeptides, dilute and concentrated solutions (including the liquid crystal phase) and the mechanical properties of fiber and films. He is also interested in solution properties of polysaccharide for clinical use.

SHINSHU UNIVERSITY

Faculty of Engineering

Associate Professor Masayasu Tasaka is working on the physical chemistry of charged membranes, especially the analysis of membrane phenomena with non-equilibrium thermodynamics, and is also interested in polymeric flocculants.

Faculty of Textile Science and Technology

Professor Nobumasa Hojo and Associate Professor Hirofusa Shirai are chiefly interested in the coordination chemistry of polymer metal complexes; the synthesis, coordination and chemical behavior of polymeric ligands with transition metal ions, and the polymer effects on complex formation. Understanding of chemical functions, unusual chemical behavior and catalytic properties of polymer metal complexes are studied as a function of ligand exchange reaction. They also are studying the synthesis, catalytic and electric functions of metalloporphyrins and their polymers, and the mechanisms of polyaddition and polycondensation reactions by metal complexes.

MEETING ANNOUNCEMENT

Transitions and Relaxations in Plastics and Rubbers May 1983, Melbourne, Australia

A three day workshop will be held in early May, 1983 on the measurement and analysis of transitions and relaxations in polymers with particular reference to industrial problems. The workshop format will include reviews of basic theory, hands-on practical sessions, laboratory demonstrations and problem solving discussion periods. Comprehensive notes will be issued with the workshop sessions.

The workshop will discuss in detail the techniques of differential scanning calorimetry, dynamic mechanical testing and dielectric spectroscopy. The advent of microprocessors and microcomputers has produced a quantum jump in the ease of use of these techniques and in the quality of the data. Instrument manufacturers are invited to display their equipment and to give presentations. There will also be a research session for papers associated with these techniques and the interpretation of data, and for case studies on the use of these methods in solving industrial problems.

The co-ordinator of this workshop is Dr. D. R. G. Williams, Chemical Engineering Department, Adelaide University, G.P.O. Box 498, Adelaide, 5001.

29th IUPAC International Symposium on Macromolecules September 8-9, 1983 Bucharest, Romania

Topics covered: (i) Polymer Chemistry; polymer synthesis by new chemical routes, methods of controlling polymer structure and properties, mechanochemical synthesis and other methods, chemical modification of polymers. (ii) Polymer Technology; new processes for the manufacture of established polymers, manufacturing processes for new monomers and polymers, scientific aspects of the unit processes in polymer manufacture. (iii) Polymer Processing; theoretical and technological aspects of polymer processing (elastomers, plastics, fibers) solid state processing, new additives for polymer processing. (iv) Structure and Properties; constitutive and configurational order in polymers, polymer properties in solutions, emulsions and dispersions, melts and solid state. (v) Degradation and Stabilization; theoretical aspects of polymer stabilization, new stabilizers, new methods for the evaluation of stability, relation between natural and artificial ageing, flame retardation, utilization of wastes. (vi) Polymer Modifications; chemical and radiation modification, polymer composites. (vii) Polymer Utilization; in communication, electronics, energetics, health, engineering, thermoplastics, etc. All the above include both theoretical and technological works.

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