Centers of Polymer Research; Polymer Science in Kyoto, Japan

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Centers of Polymer Research

POLYMER SCIENCE IN KYOTO, JAPAN*

by

Akio Nakajima

Department of Polymer Chemistry
Kyoto University
Yoshidahonmachi, Sakyo-ku
Kyoto 606, Japan

Kyoto was the capital of Japan for more than 1000 years until 1868, the beginning of the Meiji period; during this period Kyoto also enjoyed a long tradition of textile industry. Not surprisingly, a Department of Textile Chemistry was created in the Faculty of Engineering of Kyoto University in 1941 which then became the center of systematic polymer research. In the early years of the Department's existence, Emeritus Professors Ichiro Sakurada, Masao Horio, Kiyohisa Fujino and Seizo Okamura were responsible for the solidification of the new Department. Work on poly(vinyl alcohol) and VINYLON fiber directed by Professor I. Sakurada and on viscose rayon directed by Professor M. Horio brought significant success. In spite of the practical implications, the research objectives of the Department maintained emphasis on the basic nature of all investigations. The Department of Textile Chemistry was renamed the Department of Polymer Chemistry in 1961. At the present time it consists of eight Kozas, the name KOZA is used in Japanese universities for the basic unit of a research group. In addition to the Department of Polymer Chemistry, active work in polymer research at the Faculty of Engineering of Kyoto University is also carried out in part of the Department of Synthetic Chemistry and of the Department of Hydrocarbon Chemistry. The Department of Synthetic Chemistry was created in 1960 and had as one component the synthesis of polymers; Professor Ryohei Oda and Professor Junji Furukawa took responsibility for this area of research. The work on polymer science of the individual members of the Faculty is much more basic than might be expected from the name of the Faculty.

Polymer research at Kyoto University is also carried out at the Institute for Chemical Research located in Uji City, located in the immediate vicinity of the city of Kyoto. Four divisions in the Institute are concerned with polymer chemistry. The staff of the divisions also shares teaching responsibilities for the graduate students of the Department of Polymer Chemistry. A Division at the Institute for Chemical Research is similar in structure to the Koza but the staff members have no responsibility for undergraduate teaching.

The number of students in the Department of Polymer Chemistry is evenly divided between undergraduate [40] and graduate [40] schools. Of the graduate students, 30 are enrolled in the Masters Program and 10 in the Doctoral program.

The last twenty years have witnessed continued growth in various phases of all polymer research programs. Inevitably, the following professors have retired from the University: Professor Ichiro Sakurada, Professor Masao Horio, Professor Kiyohisa Fujino, Professor Waichiro Tsuji, Professor Seizo Okamura, Professor Keinosuke Kobayashi, Professor Ryohei Oda and Professor Junji Furukawa.

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Not only at Kyoto University, but also at Kyoto Technical University, scientists have been active in polymer research. Kyoto Technical University appeared as a university of the new system in 1949 in accordance with the National School Establishment Law, incorporating two State Colleges: Kyoto College of Textile Fibers and Kyoto College of Industry, which were established in 1900 and 1903, respectively. At the present time, the University has two Faculties, *i.e.*, the Faculty of Industrial Arts and Faculty of Textile Fibers. In the former, 3 professors and 2 associate professors and in the latter 3 professors and 4 associate professors are active in polymer research.

Kyoto University

Department of Polymer Chemistry:

Professor Norio Ise is exploring the fundamental aspects of the thermodynamic quantities of polyelectrolyte solutions, such as the mean activity coefficient, the heat of dilution, and the partial molar volume, *etc.* On the basis of these studies, the research interest of his group changed toward more biopolymer-oriented activities. Professor Ise in cooperation with Associate Professor Tsuneo Okubo, and Instructors Shigeru Kunugi and Hiromi Kitano have studied the influence of polyelectrolytes as catalysts of ionic reactions and found significant acceleration and/or deceleration effects; the experimental results have also been theoretically interpreted. Professor Ise investigated most recently small-angle X-ray scattering of dilute solutions of biological polyelectrolytes. It was revealed that an ordered distribution of ionic solutes appeared in dilute solution for sodium polyacrylic acid, poly-L-lysine and lysozyme. By using Zincke's reaction a novel method to obtain models of esterase has been developed by introducing functional groups into poly(vinyl pyridine) and its derivatives. Studies are also being done on the kinetics and mechanism of enzyme reactions to make a thorough analysis of the rate and equilibrium parameters of the catalysis by α-chymotrypsin and trypsin. His group also is getting involved in the investigation of bioreactors.

Professor Yasunori Nishijima has been conducting research on the supramolecular structure and physical properties of polymer solids, the structure and micro-Brownian motion of polymer molecules in solution and in the melt. The migration and relaxation of electronically excited energy of photochemical reactions in polymer systems is also under investigation in his research group, which includes Associate Professor Masahide Yamamoto, Lecturer Tokuji Fujimoto and Instructors Yoshihiko Onogi and Shinzaburo Ito. They have developed fluorescence methods for studying the micro-structure and specific functions of polymer molecules. In the studies on the structure of polymers, the emphasis has been placed on the understanding of specific functions of polymer systems in terms of molecular structure, molecular motions and inter- and intra-molecular interactions, especially in the time scales of nanosecond and sub-nanosecond ranges. The individual subjects which are currently being investigated are: molecular orientation behaviors in polymer solids and liquid crystals studied by fluorescence polarization methods; micro-Brownian motion of polymer molecules in solution by rotational depolarization of fluorescence; excimer emission of polymer molecules; excimer formation in micellar systems; infrared emission of polymer solids; photoconductivity of polymer solids and formation of electronically excited triplet state in polymer systems.

Department of Polymer Chemistry, Kyoto University, Kyoto.

Professor Toshinobu Higashimura has continued in his investigation of the cationic polymerization of vinyl compounds. His most important recent finding is a bimodal molecular weight distribution of polystyrenes made by cationic polymerization which demonstrated the presence of two independent propagation species in this type of cationic polymerization. This discovery led to his subsequent extensive work on the nature of the propagation species in cationic vinyl polymerization. His group, which also includes Instructors Toshio Masuda and Teruhiko Maegawa, is now utilizing stop-flow spectroscopy in their kinetic studies and has determined the propagation rate constants for the polymerization of a series of styrenes and provided supporting evidence for the multiplicity of the polymerizations; his concept of the "nondissociated" propagating species has resulted in the living cationic polymerizations of *p*-methoxystyrene and *N*-vinylcarbazole by iodine and the synthesis of novel block copolymers. The selective dimerization of styrenes and related monomers to their linear dimers has been achieved by careful selection of the catalysts. His current research is also concerned with the biodegradation of the linear styrene dimers by microorganisms. Another area of active investigation is the polymerization of acetylene derivatives catalyzed by WCl_6 and $MoCl_5$, and the study of the properties of the polymers. A coordination mechanism similar to that of the metathesis polymerization of cyclic olefins has been proposed for the propagation reaction.

Professor Hiromichi Kawai has been devoting his research to the study of the mechanical properties of polymeric materials in the solid state, especially as it involves supermolecular structures of polymer heterophases. The research subjects of his research group, which consists also of Associate Professor Sueo Kawabata and Instructors Takeji Hashimoto, Shoji Suehiro, and Hiroichi Hasegawa are as follows: By a combination of dynamic X-ray diffraction with dynamic birefringence and dynamic scattering, the deformation mechanism of crystalline super-structures, for example, spherulitic and row-nucleated crystalline textures is being studied in order to assign the alpha and beta mechanical dispersions of poly-α-olefins. Small-angle X-ray and polarized light scattering are being carried out in order to characterize the morphological and heterogeneity parameters of crystalline and heterophase polymer systems in the solid state in solution. Also studied are the mechanism of formation, the domain-boundary structures, and the bulk properties of block copolymers. Another important area of investigation of his group, mainly developed by Associate Professor S. Kawabata is the mechanics and fracture of solid polymers including composite systems and fiber assemblies, in which the mechanics of woven and knitted fabrics are also studied in close correlation with the mechanical properties of the constituent yarns.

Professor Akio Nakajima has maintained broad interest in the molecular properties of polymers as they relate to their structures and conformations with particular emphasis on polymers of biological interest. His group, which includes Associate Professor Fumiyuki Hamada and Instructors Toshio Hayashi and Hisao Hayashi has developed a small-angle X-ray scattering apparatus capable of measuring polymer solutions in the whole concentration range with high accuracy: By this method the chain conformation of flexible polymer and the conformations of polypeptides in helix solvents could be evaluated. Chain conformations and helix-coil transition of charged and non-charged polypeptides were also investigated in detail. Recent study on light scattering of polyelectrolytes in very dilute solution also gave important results. Another subject is the thermodynamic studies of concentrated polymer solution which provided data to improve greatly conventional theories. He is also carrying out research on the conformation and the micro-heterophase formation of novel blockcopolymers consisting of polypeptide block as one component and on the properties of membranes prepared from these blockcopolymers as biomedical materials. Professor A.Nakajima holds also a chair in the Biomedical Polymer Research Center which was recently founded within Kyoto University: he is assisted in his research activities at this institution by Instructor Hiroko Sato.

Theoretical investigations of polymer solution have been carried out by Associate Professor Hiromi Yamakawa who developed a statistical mechanical theory of wormlike chains with helical conformation arising from bending and torsional energies. The chain conformations, scattering functions, persistence vectors, angular correlation functions,

anisotropic light scattering, dipole momemts, electric birefringence and electric dichroism were elucidated in the framework of the theory.

Professor Shigeharu Onogi is making significant contributions in research concerned with the rheological properties of concentrated solutions, melts of polymers, the rheo-optical properties of amorphous and crystalline polymers and the flow properties of suspensions. Staff members of his group are Associate Professors Tadahiro Asada and Toshiro Masuda and Instructors Takayoshi Matsumoto, Akira Tanaka and Masaoki Takahashi. The main subjects which are now studied by the group are: The study of rheological properties of branched polymers and blockcopolymers; molecular weight and concentration dependences of viscoelastic parameters of star-branched polymers; extensional and fractural properties of these polymers and the relationship between the rheological properties and the internal structure of blockcopolymers. Studies on the non-linear viscoelasticity of liquid polymers and of crystalline polymers led to the elaboration of satisfactory constitutive equations for the liquid, and to the clarification of the relationship between morphology and deformation mechanisms of crystalline polymers. Another research area is concerned with liquid crystals. By means of a cone-plate type rheometer combined with a spectrophotometer of a polarized light system, a rheo-optical apparatus has been developed with which the relationship between the rheological properties and the structures of liquid crystal systems, including polymeric liquid crystals, could be invesigated. His research group is also extending its activities into work on the flow properties and the thixotropic and rheospectic behaviors of various disperse systems.

Professor Yukio Imanishi has been carrying out investigations in polymer synthesis, polymer reactions, radiation-polymer chemistry and biomedically interesting synthetic polymers. Recent work in cooperation with Instructor Masahiko Sisido covers the field of functional polymers and functions of polymers. Synthesis of functional polymers and membrane systems which can convert solar energy to high energy chemical substances are being studied: the elemental processes of these reactions are being investigated by fast-kinetic measurements in especially designed apparatus. Professor Imanishi's group synthesized multifunctional cyclic peptides and elucidated conformations, interactions with ions and catalytic effects of these compounds in ester enzymes, the intramolecular and intermolecular interactions of functional groups covalently attached to a polymer chain are being studied. Stereoselective polymerization of amino acid derivatives has been selected for the study as a model system for the optical-enantiomer specificity of biopolymers. This group also has interest in biomedical application of synthetic polymers and the syntheses of segmented hydrophilic-hydrophobic copolymers are carried out; the copolymers obtained are tested for their use as prostheses.

Department of Synthetic Chemistry:

Professor Takeo Saegusa has been working in polymer synthesis and in the exploration of new chemical reactions catalyzed by metal complexes. Associate Professors Yoshihiko Ito and Tetsuo Tsuda are responsible for the research in catalytic reactions and Instructor Shiro Kobayashi for the work in polymer synthesis. Professor Saegusa's group has discovered several new types of polymerization reactions and has successfully developed the new field of noncatalyst alternation copolymerization via zwitter ion intermediates and demonstrated more than 40 new types of copolymerizations. The new field of copolymerization of P(III) compounds as exemplified by "redox copolymerization" has been initiated. The polymers resulting from this study have potential for various applications in surface coating, fiber treatment and as adhesives and polymeric drug carriers. Another subject which is concerned with ring-opening polymerization is the synthesis of linear crystalline polyethyleneimine and its graft copolymers; this polymerization is based on the chemistry and polymerization of oxazoline. Super acid esters have also been used extensively as catalysts for ring-opening polymerizations. Of particular interest was the selective codimerization of ethylene oxide to dioxane.

Department of Hydrocarbon Chemistry:

Associate Professor Takeo Shimizu is involved in investigations of biologically interesting area: the template-directed synthesis of oligonucleotides, the catalytic action of polymers and the transport activity of synthetic functional polymers. Recently he

elucidated the interaction of positively charged polynucleotide analogs by studying the binding characteristics of nucleic acids with basic polymers, *e.g.*, poly-4-vinylpyridines and their derivatives with nucleotides. His group has also synthesized a series of lacton polymers and proposed a proton pump mechanism for the effective transport of alkali metal ions through membranes prepared from these polymers.

Institute for Chemical Research:

Professor Hiroshi Inagaki's research projects can be classified into four categories: a) separation and characterization of polymeric materials, b) fundamental aspects of block and graft copolymers, c) thermodynamic properties of polymer solutions and d) physicochemical properties of wool keratin and its derivatives. Associate Professor Takeaki Miyamoto and Instructors Hidematsu Suzuki and Takeshi Fukuda are collaborating in the specific research subjects which are in progress: Application of thin-layer and gel-permeation chromatography, ultracentrifugation to achieve polymer separation and characterization; higher-order-structure of wool keratin and its derivatives; thermodynamic properties of polyethylene in solution and chain conformation of block copolymers in solution.

Professor Ryozo Kitamaru's research interests include studies of polymer crystallization, fiber-formation and the crystalline and phase structure of polymers, chemical reactions on natural and synthetic polymers and the development of new polymer materials. He has extensively studied the phase structure of polymers in the solid state by a recently developed broad-line NMR and pulse ^{13}C NMR technique with high power ^{1}H decoupling. His research group includes Associate Professor Yoshito Ikada and Instructors Masao Hosono and Keisuke Kaji who also carry out research on the dynamics and molecular conformation of polymers by X-ray and neutron scattering techniques. Another project primarily investigated by Associate Professor Y.Ikada is concerned with biomedical materials for artificial blood vessels of small diameter. These investigations are now conducted in cooperation with the Faculty of Medicine.

Professor Kenichi Katayama is active in the field of structural and morphological studies of polymers in their solid state. Current research projects of his group, which includes Instructors Kaoru Shimamura and Akiyoshi Kawaguchi involve the observation of individual molecular chains with an ultra-high resolution electron microscope, which allows the detection of images of molecular chains forming a poly-p-xylylene single crystals. The crystallization mechanism and structure development under molecular orientation is also being investigated.

Professor Michio Kurata, together with Instructor Kunihiro Ozaki, is conducting a systematic study on non-linear viscoelasticity of concentrated polymer solutions by utilizing stress relaxation under large deformation and flow birefringence in non-steady flow. Data obtained proved most useful for the recent development of the Doi-Edwards theory of polymer entanglements. A new apparatus for dynamic light scattering measurements has been constructed at the Institute for Chemical Research, Kyoto University, Uji, by Instructor Toshio Nemoto and his group. The apparatus is based on the time interval counting among 2048 successive photons. Application of this technique to the study of molecular motions of extremly high-molecular weight polymers, cyclyzed polymers and of gels is now in

Institute for Chemical Research, Kyoto University, Uji.

progress. Diffusion and sorption of gases and their mixtures in heterogeneous polymer membranes are being studied by Associate Professor Hisashi Odani and coworkers with the objective of clarifying the nature of the permselectivity. Professor M.Kurata serves also on the graduate faculty of the Department of Industrial Chemistry, Faculty of Engineering.

Kyoto Technical University

Faculty of Industrial Arts:

Professor Taisuke Ito is investigating the strain behavior of polymer crystals under high pressure (8 kbar) and the diffusion of low molecular weight penetrants through polymers under high pressure (5 kbar). He measured the compressibility and its anisotropy for many polymer crystals and determined the activation volume for diffusion of low molecular weight organic molecules in Nylon 6 and poly(ethylene terephthalate).

Professor Shinzo Yamashita has a broad interest in rubber chemistry and technology, *i.e.*, synthesis and properties of reactive elastomers, structure and properties of liquid rubber vulcanizates, chemical reactions of rubber with silica, calcium carbonate and lignin *etc.*, and simple reclamation study for the reuse of scrapped elastomers. Associate Professor Shinzo Kojiya is studying the polymerization behavior of cyclic dienes, especially cyclopentadiene. He also has interest in the synthesis of reactive elastomers and their properties. With Professor S.Yamashita, he developed a new rubber based on polybutadiene which has chemically active chlorine groups and hydroxyl groups; they also developed a new vinyl ether-cyclopentadiene copolymer elastomer which is degradable.

Professor Nariyoshi Kawabata is interested in the purification of waste by polymeric adsorbents. Certain vinylpyridine-divinylbenzene copolymers were found to have an excellent adsorbing capacity for phenol and can be efficiently regenerated. Together with Professor Yamashita they studied the reclamation of scrap elastomers and found excellent reclamation reagents, in the phenylhydrazineferrous chloride and tributylamine-cuprous chloride systems.

Associate Professor Jun Nishimura is working on cationic copolymerization of 1,3-bis(p-vinylphenyl)-propane and its derivatives and found that a cyclopolymer containing highly-strained [3,3]paracyclophane units was obtained by cationic polymerization; radical or anionic initiators did not show any units in the polymer which could be attributed to a cyclopolymerization reaction.

Faculty of Textile Fibers:

Professor Nobuo Utsumi's interests are in fiber chemistry, especially the microstructure of high polymers. He has been investigating the submicrostructure of cellulosic materials and other polymers, and the photoviscoelastic properties of high polymers. Associate Professor Tsuyoshi Kiyotsukuri is primarily interested in the chemical modification of polyesters and polyamides and is studying the structure-property relationships of condensation copolymers in the presence and absence of halogens. His studies have resulted in the better understanding of the effect of polymerization solvent on the chemical structure and regularity and properties of copolyamides prepared by interfacial copolycondensation.

Professor Mikio Araki is interested in chemical modifications of cellulose; but also in the synthesis of functional polymers. Associate Professor Isoji Taniguchi is working on research and development of polyethylene, polypropylene and ethylene-propylene copolymers. He is also interested in the evaluation and characterization of the polymers as materials and in syntheses of inorganic polymers.

Professor Norito Uchino is working on the synthesis of cationic polymers and semiconduction polymers. He is also investigating the effects of molecular weight and charge density of cationic polymers on the flocculation properties of kaolin suspension.

Associate Professor Toshio Kitano has been working on melt spinning and film-processing of synthetic polymers. In collaboration with Professor M.Araki, he is now active in the synthesis and processing of fibers for medical use which are absorbable in the human