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Centers of Polymer Research; Polymer Science in Tokyo, Japan, Part II: Suburban Area

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CENTERS OF POLYMER RESEARCH

Polymer Science in Tokyo, Japan Part II: Suburban Area

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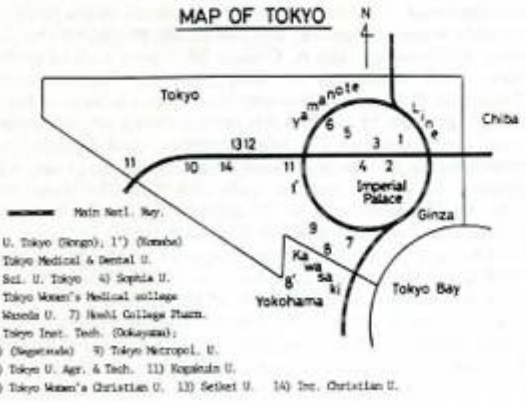
Metropolitan Tokyo now consists of twenty-three wards (the old Tokyo), three counties, twenty-six cities, and several independent towns and villages. A number of other cities belong to neighboring prefectures; Yokohama (pop. 2.7 million), and Kawasaki (pop. a million) are adjacent to Tokyo, forming the large urban megalopolis in Tokyo bay. The eastern and central part of the old Tokyo are connected by a national railway line called Yamanote (loop) line; it runs in a circular route with a diameter of about 10 km which connects several downtown districts. The polymer research activities in central Tokyo, i.e., inside the Yamanote line, have been reviewed in detail in Part I of this series. It is our objective to provide information regarding the research activities in academic institutions in the remainder of the Tokyo area.

Tokyo Institute of Technology

In the immediate vicinity of central Tokyo, i.e., just outside of the Yamanote line, are located Tokyo Institute of Technology, Tokyo Metropolitan University, and Hoshi College of Pharmacy. Tokyo Institute of Technology, located at Ookayama, is a national university established initially as Tokyo Technical College in 1881. It has two faculties; Science and Engineering; the Faculty of Science has five departments and the Faculty of Engineering has sixteen. The University also has a school of general education in natural science and a school of liberal arts. Research efforts in polymer science are in two departments in the Faculty of Engineering; the Department of Polymer Chemistry (founded in 1962) and the Department of Textile and Polymeric Materials (renamed in 1973). The research is mostly devoted to polymer chemistry and physics. Some of the research subjects in the Department of Chemical Engineering are also closely related to the chemistry and physics of polymers. Several years ago, Tokyo Institute of Technology opened another campus at Nagatsuda about 15 km northwest of the main campus to accommodate six laboratories. The Research Laboratory of Resources Utilization (originally founded in 1939) has achieved a high level of activity in the field of polymer chemistry. Professor Emeritus Kisou Kanamaru has been primarily responsible for this pioneering work in research as well as education in polymer science at the Tokyo Institute of Technology.



Faculty of Engineering

Department of Polymer Chemistry—Associate Professor Takuhei Nose is studying thermodynamic properties of polymers in the glassy state and in solution in a wide range of concentrations. The pressure dependence of the cloud point for mixtures of two polymers or two oligomers was investigated. The process of phase separation of polymer solutions or polymer blends is also of interest to his group. Light scattering experiments were performed for polymer-solvent systems near the critical so-

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lution temperature. Also investigated in this temperature range was the variation of the interfacial tension of phase separated polymer solutions as a function of temperature and molecular weight of the polymer. The time-dependent properties of polymer solutions were also investigated by dynamic light scattering. Instructor Tadashi Komoto, a former coworker of Professor Toru Kawai, continues to study the crystallization of polypeptides as the polymerization of α-amino acid NCA proceeds. Conformational aspects involved in the interaction between basic poly(amino acids) and synthetic polymers are studied as a model for biopolymers in the connective tissues. In an effort to find a substitute for the articular cartilage materials, Dr. Komoto is now studying morphological changes of high density polyethylene caused by the wear from an applied frictional force.

Professor Ichitaro Uematsu devoted his early scientific activities to the investigation of solid state properties of synthetic polymers. His contributions are in a wide range of research areas covering polymer crystallization, glass transition, viscoelastic behaviors, and mechanical properties of polymers. His recent interests include the study of structure, physical properties, and transition phenomena in solution and in bulk of synthetic polypeptides. With instructors Shintaro Sasaki and Junji Watanabe they are studying lyotropic cholesteric liquid crystals formed from poly(γ-benzyl L-glutamate) or poly(γ-alkyl L-glutamate) (PBLG); for the first time they saw the inversion of the helical twisting sense with temperature and solvent composition. Solid state properties, the structure of various crystalline modifications of PBLG and the thermal phase transition have been systematically investigated. Associate Professor Akihiro Abe, who joined the group about three years ago, has been investigating conformation and configuration dependent properties of macromolecules.

Professor Riichiro Chujo is one of the pioneers of the use of high resolution NMR in the field of polymer chemistry. He studied the configuration of polymers and is trying to relate their structure with polymerization mechanisms by which the polymers were formed. His research in NMR covers polypeptides, biopolymers, and synthetic polymers. Instructors Isao Ando and Yoshio Inoue, working with Professor Chujo, are investigating the advent of helix-to-coil transition of polypeptides in solution by chemical shift measurements of the side chain atoms. The conformation of Retinal, known as one of the substances responsible in the chemistry of vision, is now under investigation. Professor Chujo is also active in theoretical work and is applying the catasrophe theory to various physical phenomena such as transition, vibration and critical point.

Professor Noboru Yamazaki has studied the copolymerization of olefins and diene monomers by using Ziegler-type catalysts. His contribution is also noted in the field of polymerization of vinyl monomers initiated by electrochemical methods. Recently his group, including Associate Professor Seiichi Nakahama, and Instructors Akira Hirao and Kazuo Yamaguchi, prepared biomimetic active phosphorus compounds and applied them to polycondensation reaction, particularly the preparation of aromatic high molecular weight polyamides. Other biomimetic compounds, which resemble naturally-occurring polyether-type ionophores, were investigated. In this work, more than thirty model compounds were found to exhibit remarkable ability for the active and selective transport of K^+ over Na^+ through a liquid membrane. The other subjects of the group include syntheses of inorganic-organic complex polymers, and asymmetric reduction of ketone with complexes prepared from $NaBH_4$ and saccharides.

Professor Toshio Kakurai has been investigating chemical reactions of polymers with functional groups. In collaboration with Instructor Toshihiro Seo, the polymerization behavior of vinyl monomers carrying polyazacompounds such as dicyandiamide, guanylurea, or substituted triazine groups as functional groups was studied. Their research also includes preparation and characterization of polymers which have groups in the side chain which show characteristic photochromism in solution as well as in bulk (film). The preparation of trifunctionally crosslinked polymers by cyclotrimerization of cyanamide groups appended to the chain terminals is also being studied; triazine crosslinks are formed which are very thermostable. Associate Professor Takashi Fukutomi and Instructor Koji Ishizu are carrying out kinetic studies on (1) the chain scission reaction by an applied mechanical force, and (2) the coupling reaction between polymers carrying reactive groups at the end of the polymer chain or in the side chain. This research has led to the preparation of soluble three-dimensional polymers by copolymerization of vinyl and divinyl monomers in the presence of a telogen under vigorous stirring, and the synthesis of a triblock copolymer comprising hydrophobic, anionic and cationic sequences. The ultimate objective of their research is the design of polymeric materials with domains with very different properties.

Professor Toshiro Iijima is exploring the characteristic feature of the interaction between macromolecules and simple molecules. Research carried out in cooperation with Instructor Jiro Komiyama, is in the following areas: counterion binding and conformational change of polyelectrolytes, preferential solvation of polypeptides from polar solvent mixtures, absorption of aqueous polyelectrolyte solutions, and interaction of dyes with water soluble polymers. Molecular aspects involved in these interactions are multimodal and co-operative binding of solvent molecules or ions with a macromolecule. Another area under active investigation includes study of sorption, reaction with and diffusion of simple solutes through polymeric membranes. Molecular design for a highly functional membrane such as permselective dialysis membrane, reverse osmosis membrane, or immobilized enzyme membrane is the ultimate object of this research.

Department of Chemical Engineering—Since 1960 Professor Tominaga Keii has had research activities in the kinetics of Ziegler-Natta polymerization. His group has also explored catalytic reactions with zeolites and hydrogenase. Recent research on coordination polymerization involves investigation of support high yield catalyst and the living coordination polymerization of propylene with soluble Ziegler catalysts. Professor Keii found by short (seconds) polymerization studies of propylene that the high activity of the initiator was based on a high value of the propagation rate constant but not on a high concentration of active polymerization centers. He also showed that soluble vanadium containing initiating system provides a living polymerization system of propylene at low temperatures. He also presented experimental evidence for the bimetallic mechanism for the propylene polymerization with heterogeneous Ziegler catalysts. Instructor Yoshiharu Doi, who has been a coworker of Professor Keii in the field of polymerization, carried out ^{13}C-NMR analysis of polypropylene chains and found that the stereochemistry of the sequence distributions of propylene units obey the first-order Markov statistics.

Department of Textile and Polymeric Materials—Professor Kinzo Ishikawa has broad interest in studying the structures and properties of crystalline polymers, particularly the drawing of crystalline polymers and the plastic deformation of the crystalline phase. Drawing of polyethylene single-crystal mats is carried out in collaboration with Professor K. Miyasaka and the material is a useful model for the high modulus fibers. Professor Ishikawa is interested in the crystallization kinetics of polymer samples kept under a biaxially stretched condition and the morphology of such polymers. His group, including Instructor Masao Sumita, is also studying the mechanical properties of particle-filled polymer composites, especially when the matrix polymer is oriented, and the effect of the particle size on the yield stress of these polymer composites. Professors Ishikawa and Miyasaka are also jointly exploring the structure and properties of polyacetylene.

Associate Professor Munenori Sakamoto is working on the synthesis of model polymers and chemical modifications of natural polymers. With Instructors Takuma Teshirogi and Harue Watamoto, they study: application of the GC-MS technique to the study of chemical modification of proteins, synthesis of heparin-like polymers from cellulose, synthesis of poly(amino acids) with monosaccharide side chains, and prevention of photodegradation of natural polymers.

Professor Jiro Shimizu is interested in the open-end spinning of wool and the melt spinning of synthetic polymers, particularly at high speed with a take-up velocity of up to 10,000 m/min. Another research area includes the development of a new method for continuous measurements by laser light scattering of the diameter and birefringence of the spin line during the melt spinning process. With Associate Professor Akira Takaku, and Instructors Norimasa Okui and Toshimasa Hashimoto, the group is carrying out research on the melt spinning of polymer blends, preparation of selectively gas permeable hollow fibers, studies of the transition of polymeric materials by means of the thermally stimulated current, and production of carbon fibers from acrylic filaments and their use for fiber reinforced plastic application.

Professor Keizo Miyasaka is studying the properties of the nylon-6 and has found a new phase transition induced by stress. His research with Instructor Masao Sumita has resulted in the better understanding of the effect of chain orientation in the amorphous phase on various polymer properties. Professor Miyasaka has also been working on the structure of filler-dispersed polymer composites with varying degrees of filler content especially the critical value of filler content and its variation with individual polymers. He has also been engaged in the small angle x-ray analysis of crystalline polymers and with Instructor Akihiko Tanioka is investigating chemically modified hard elastic polypropylene films which exhibit anisotropy in the permeability of gases.

Professor Eiichi Kuze is carrying out investigations in the field of mechanical and thermal properties of composite materials, and electrical and optical properties of composite substances including semi-conducting polymer films and liquid crystals, especially the photoconductivity in the poly(vinyl alcohol) or polyacrylamide films containing metal ion (Cu^{2+} or Fe^{3+}) complexes. His group, which includes Associate Professor Atsuo Fukuda and Instructors Hideo Takezoe and Ryuichi Akiyama, is now utilizing laser light scattering in the determination of the Frank elastic constants and Leslie viscosity coefficients of nematics by observing the angular dependence of the scattered intensity and spectral width. The current subjects of the group include ferroelectricity of chiral smectic liquid crystals, optical and luminescent properties of cholesterics, filled-induced birefringence of isotropic fluids, photoconductive and photovoltaic effect of semi-conducting polyacetylene films, and formation of silver-based thin films, showing metallic electrical conductivity, from the polyacrylamide-Ag^{+2} complex solution.

Professor Tetsuya Sakai is studying various physical properties, including thermal, optical and electrical properties, of polymers and composite materials. They include: thermally stimulated current of extended chain crystal of polyethylene, and viscoelastic thermal expansion of glass-epoxy resin composites.

Research Laboratory of Resources Utilization

Professor Akio Yamamoto and Associate Professor Takakazu Yamamoto are concerned with fundamental aspects of organotransition metal complexes, some of which are capable of initiating the coordination polymerization of vinyl monomers. Throughout their study, in collaboration with Instructors Sanshiro Komiya and Fumiyuki Ozawa, the prime attention has been centered on the key elementary steps involved in the polymerization by transition metal alkyls and hydrides, namely the activation process of transition metal alkyls and hydrides on interaction with various vinyl compounds. Novel types of polycondensation reactions catalyzed by transition metal complexes, leading to polyphenylene, polythiophene, polyferrocene, and polymethylene, have also been developed. Associate Professor T. Yamamoto has been independently engaged in the preparation of polymer-metal complexes (e.g., nickelated poly(vinyl chloride) and the application of polymer-iodine adducts for cathodes of batteries.

Professor Shuichi Suzuki and his group, including Associate Professor Isao Karube, have been devoting their research activity to the study of modification, im-

mobilization, and applications of biopolymers. They have developed an electrochemical method for immobilizing biopolymers and cells in collagen membranes. The enzyme electrodes with use of enzyme membranes have been prepared for the determination of total cholesterol, neutral lipids, and phospholipids in sera. The microbial electrodes have been constructed for the determination of BOD (biochemical oxygen demand), glucose, acetic acid, alcohol, ammonia, antibiotics, vitamins, and amino acids. The microbial electrodes consist of bacteria membranes and electrochemical devices. Immuno and enzyme-immuno sensors also have been developed for the determination of syphilisis, immunoglobulin G, human chorionic gonadotropin and α-fetoprotein. Biochemical energy conversion systems consist of the immobilized microorganisms and a hydrogen-oxygen fuel cell. Continuous hydrogen production was obtained by immobilized hydrogen producing bacteria and blue-green algae. Immobilized enzymes and microorganisms have been used for the production of bioactive substances such as antibiotics, enzymes, peptides and carotenoides. Recently, they have started the study on cell engineering and genetic engineering for improving biological functions of microbial cells. Photo- and sonic control of enzyme-membrane activities is also being studied.

Associate Professor Kazuo Soga has been devoting his research efforts to the study of coordinated anionic polymerizations. His group recently found that isotactic polymerization of propylene easily proceeds over titanium containing zeolite ion exchange catalyst without any additives. Based on this result, the development of a new type of highly active supported-catalysts is now in progress. Another area of investigation involves the syntheses of various copolymers involving simple oxide molecules such as CO_2, SO_2 as one of the components. The synthesis of conducting organic polymers has also been studied in this laboratory. A convenient way of preparing polyacetylene films was found and a method of determining the molecular weight of insoluble polyacetylene was developed.

Professor Makoto Okawara has contributed significantly in the field of syntheses and reactions of functional polymers, especially the development of new organosulfur and organotin compounds. In his research group, under the guidance of Instructors Takeshi Endo and Yoshio Ueno, a variety of polymers carrying functions such as electron transfer, oxidation-reduction, high reactivity, chelate formation, electroconductivity, photosenaitivity, biomimetic and other catalytic activities have been synthesized by the chemical modification of commercially available polymers or by the polymerization of functional monomers. An enthusiastic effort has been made on the synthesis and utlilization of the electron transfer catalyst as exemplified by alloxan, viologen, nitroxyl radical, lipoic acid, and polymers carrying these groups. His group has also studied the organic synthetic methods using polymer supports in connection with the peptide syntheses.

Professor Shigeo Tazuka has strong interest in the molecular design of various functional polymers with special reference to photoresponsive polymers. His approach is to interpret various functions of polymers on the basis of inter- and intra-molecular interactions which should be closely related to the polymer structure. For this purpose, he has designed and synthesized polyesters, poly(ester-urethanes), polyurethanes, polyionenes, and polymethacrylates bearing aromatic and heteroaromatic groups. Absorption and fluorescence spectroscopy have provided important information on the specificity of polymer effects in relation to the chemical structure of polymers, degree of polymerization, solvent, and temperature. Recently Professor Tazuka found allosteric association for some exciplex forming polymers in extremely dilute conditions. He has used this information to prepare photoconductive polymers, photo-crosslinkable polymers, photochromic polymers, and polymeric photosensitizers. For surface treatments of polymers he has developed a technique of thin layer photografting to introduce special functions, such as hydrophilic properties, to originally inert polymers. In collaboration with Research Associate Noboru Kitamura, he has succeeded in photofixation of carbon dioxide, mimicry of the antenna chlorophyll, and has produced materials with an efficient photoinduced charge separation.

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