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Polymer Science in Milan, Italy

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Italy is in the center of the Mediterranean. Milan, the second largest city of Italy, with a population of nearly 2 million, is the hub of the Italian industrial north. The city has also been, for nearly two millennia, an important center for culture, for the arts and for science.

Polymer chemistry in Milan developed rapidly after World War II. It was one of the most vigorously growing scientific disciplines in Italy. Polymer science in Milan is concentrated in three important centers of research: at the Politecnico di Milano, at the University of Milan, and at the Institute of Macromolecular Chemistry of the National Council Research of Italy. About 15 senior professors and their students are active in research in polymer science in Milan; in addition, almost 50 scientists are active and permanently employed by the University or by the National Research Center. The highest concentration of the research activity is at the Politecnico, which has 10 professors.

At this time, it is probably appropriate to remember that after World War II when the research activities started at the Politecnico, there was only one professor's chair and this chair was in the Institute of Industrial Chemistry; Giulio Natta was the holder. Work in his group was primarily in catalysis and on carbonation reactions. He was joined in the late 1940s by a young graduate from Professor Qualico's group in Florence, Piero Pino. Pino brought organic chemistry, heterocyclic chemistry and inorganic chemistry to the Politecnico, and another assistant, Dr. Ercole, also joined the group. In 1952, Natta recognized the potential impact of Ziegler's "Aufbaureaktion" of ethylene with triethylaluminum and the subsequent discovery of linear polyethylene and coordination polymerization with transition metal complexes.

Natta recognized that the polymerization of propylene had a
tremendous potential. Under his leadership and with Pino's assistance, work on the polymerization of propylene started at the Politecnico and the first propylene was made by Paolo Chiril in March of 1954. After this discovery, explosive developments in polymer science followed at the Politecnico in close cooperation with Montecatini. A highly competent group of very young, vigorous, enthusiastic and highly competent students assembled around Natta and Pino and within a few years the entire field of olefin polymerization with coordination catalysts was opened up and worked out. In 1958 polypropylene was commercialized by Montecatini in Ferrara and in 1963 Professor Natta received the Nobel Prize.

The "Natta" school flourished; Italy and Milan became a center of polymer chemistry and polymer science.
Politecnico di Milano

A. Department of Industrial Chemistry and Chemical Engineering

Today 18 professors are engaged in this department in polymer chemistry, polymer characterization, theoretical aspects in polymer chemistry, polymer engineering and material science.

Lido Porti is Professor of Industrial Organic Chemistry in the Department of Industrial Chemistry and Chemical Engineering. His work involves the polymerization of hydrocarbon monomers with transition metal catalysts, particularly with Ziegler-Natta systems. Work in progress covers the following topics: a) Polymerization of ethylene with soluble catalysts based on group 4 metals. These studies include the influence of the catalyst structure on the activity and on the molecular weight distribution of the polyolefins. b) Evaluation of new catalyst systems for ethylene-propylene copolymerization. c) Polymerization of conjugated dienes; work in this field is mainly aimed at the identification of new catalyst systems and at the elucidation of the factors that determine stereospecificity.

Federico Santini is Professor of Applied Chemistry and Materials. His field of research involves the degradation of olefins in the environment, the modification of polyolefins with polar monomers, especially the preparation of graft copolymers useful as compatibilizers in polymer blends. Additional interests of Federico Santini involve the surface modification of high technology fibers and the improvement of interfacial adhesion in composites. The structure of humic acids and interactions of these materials with metals is also being studied. New polymers are being synthesized which can be used for the preparation of membrane suitable for use in gas separation.

The instrumentation and facilities available to Dr. Santini’s research group are excellent and include: a) facilities for differential thermal analysis, FT-IR spectroscopy, Braubender mixer, Instron dynamometer, instrumentation for potentiometric titrations and polarographic measurements.

Marta Carla Galli is a Professor of Industrial Chemical Technologies. Her interest is in Ziegler-Natta catalysis for diolefins polymerization, the metathesis reaction on cycloolefins and linear olefins, metalorganic complexes of transition metals and lanthanides.

Additional interests lie in phosphazene chemistry, cyclic and polymeric phosphazenes substituted with functional groups (-N=PR(R+)X), where R+ is alkyl or aryl. The applications of these materials are spread over different fields: functionalization, membranes for gas separation or for ionic transport, carriers for biological active substances and ligands for transition metals in catalysis. Conducting polymers and non-linear optical materials are also areas of research which include the chemical synthesis of polythiophenes with alkyl or alkoxy substituents, studies on the relation between the regiospecificity of synthesis processes, determined by NMR, IR and UV spectra of the polymers and the electro-optical properties of these materials.

Ferdinando Donnini, Professor of Macromolecular Chemistry for Engineers in the same department, works in a field of research which involves the synthesis of new specialty polymers or copolymers by step reaction polymerization and their characterization. Special areas of research involve the synthesis or functionalization of macromonomers with particular chain stiffness or flexibility, the selection and development of new base reactions, ability to link macromonomers with bridging atomic groups of particular stability and step synthesis of triblock and multiblock copolymers, combining soft-soft-hard-soft segments with different mutual affinity. Molecular, supramolecular, photosensitive and photochemical and physico-mechanical characterization of related oligomers and polymeric products is also being investigated. Of particular emphasis is also the study of structure-function relationship of polymers.

Excellent facilities and possibilities are also available for structural characterization to the group of Giuseppe Zerbi, Professor of Material Science. Professor Zerbi is also the Director of the School of Polymer Specialization “G. Natta” which is involved in education of young scientists in polymer science. Dr. Zerbi’s field of research
involves the main research themes of material science: it is focused	hon the understanding of the relationship between molecular structure
and macroscopic properties of polymers. The physical tools used
are mostly optical vibrational spectroscopies (infrared absorption
and reflection, Raman and neutron scattering) in their experimental,
theoretical and computational aspects.

Particular themes of Professor Zerbi's research are the dynamics
and spectra of structurally ordered and/or disordered classical organic
polymers (and of corresponding models). Phase transitions and
molecular mobility in polymers are also being investigated as are
the structures of polymers at interfaces. Generally speaking, structure-
properties relations and phase transitions of fatty acids, soaps,
phospholipids and biological membranes are being studied.

Additional investigations involve atomic charges, charge mobilities
from vibrational intensities and specific intermolecular interactions
in polymer blends. The structure and electrical conductivity of
polymerized polymers and oligomers for applications in photonics,
telecommunications, optical memories and molecular
electronics are also investigated. "Molecular Engineering" via
Quantum Chemical or Molecular Mechanics calculations for the
predictions of structures with improved electrical and non-linear
optical properties are particularly emphasized.

The laboratory is equipped with modern infrared interferometers
and with a multichannel Raman scattering spectrometer equipped
with a microscope. Fourier Transform Raman scattering
interferometers with infrared excitation can be used. Several IBM
personal computers and computer terminals for IBM, VAX,
UNIVAC, CONVEX are available.

Every year the laboratory offers an internal course on the
introduction to molecular dynamics and spectroscopy to Ph.D.
students and guests.

Institute Giulio Natta: Porri, Vogl

Giuseppe Tieghi is the Professor of Structure of Macromolecular
Materials whose interest is in the development of new methodologies
for the characterization of non-linear viscoelastic behavior of
polymeric materials. The investigation of non-linear effects is carried
out by analyzing the experimental results obtained from stress

Lido Porri at the former Natta Laboratory
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relaxation measurements in simple extension. In this way, methods for the measurements of mechanical properties on specimens of very small sizes are studied by microdynamometry. Also studied are the structure, morphology, physical and mechanical properties of new materials with segmented macromolecular structure, which can be obtained by polymerization of functionalized macromonomomers.

The instrument in this research group involved an automated microdynamometer for mechanical instrument measurements, automated X-ray powder diffractometer and an instrument for molecular weight measurements of polymers.

Maurizio Pegoraro, Professor of Polymer Science and Technology, is involved in polymer compatibilization; the preparation of grafted polymers as a means of glassy or semi-crystalline polymer toughening. Mechanical properties of those blends are being studied and compared with the mechanical theoretical viscoelastic models. Also being investigated are polymer surface energy measurements and theoretical predictions, including the interface properties and interphase adhesion; their theoretical and practical evaluation. Special attention is given to the composite polyimides/carbon fibers.

Gas and liquids transport properties of polymeric membranes are also being studied, which involves the investigation of permeability and diffusivity measurements. Theoretical predictions of transport properties in rubberlike and in glassy polymers include the preparation of special polymers for selective gas separation. Different classes of polyurethanes are being tailor-made for this purpose. Entropic elasticity in rubberlike networks, network crosslinks densities from mechanical properties and viscosity properties of high temperature resistant composite materials is also being investigated.

The instrument facilities of the group include dynamic rheometers with tools to measure moduli and dilatation, thermal analysis D.S.C., an instrumented impact tester, optical and electron microscopes, FT-IR analysis, a compression molding apparatus, a Brabender mixer, mechanical-dynamic property analyzers (Rheovibron and Rheometrics), and a Lysozyme gas permeameter.

In the department are also two professors responsible for teaching and research in polymer engineering: Andrea Pavan, Professor of Polymer Engineering and Maura Ronco, who is a Professor of Polymer Materials. The research activities of this group include research in physical and mechanical properties of polymer blends and of rubber-modified glassy polymers. Theoretical modeling and experimental characterization of yielding and fracture of polymers and composites showing viscoelastic behavior. A further field of interest of this group is the development of engineering designs of polymeric materials.

Facilities in this group include instruments for physical and molecular characterization of polymers, machines for processing and preparation of solid test specimens, instruments for rheological and mechanical testing, incluling creep and creep fracture, yield and fracture under different test configurations, fatigue and impact fracture. Ancillary optical microscopes and video-recording systems are used to analyze the mechanical phenomena.

Associated with the activities in Milan is Paolo Ferruti, Professor of Applied Chemistry at the Department of Mechanical Engineering at the University of Brescia. Dr. Ferruti has two special fields of research. The first is the synthesis of ionic polymers and macromonomers by Michael-type stepwise polyaddition processes; he uses intermediates for: a) obtaining crosslinked resins capable of complexing heavy ion metals to be used in industrial catalysis; b) surface modification of inorganic materials to render them suitable for the same purpose; c) preparation of surface-modified polymeric materials, as well as block and graft copolymers for biomedical use; and d) preparation of heparin complexing resins for achieving regional heparinization in extracorporeal circuits, especially during hemodialysis.

Another area of interest of Dr. Ferruti's group is the synthesis of end-functionalized oligomers to be used for preparing oligomeric derivatives of drugs and enzymes. In particular the following main lines of research are being followed: a) the introduction of original methods of reactive functions of already available oligomers, such as poly(ethylene glycols); and b) preparation of new end-functionalized oligomers of N-vinylpyrrolidone and substituted acrylamides by radical polymerization in the presence of functional chain transfer agents. This chemical laboratory headed by Dr. Ferruti is equipped for polymer, as well as for organic synthesis, and has an FT-IR spectrometer, a U.V. spectrometer, viscosimetry measuring devices, a IH NMR spectrometer and a differential scanning calorimeter.

Students at the Politecnico
University of Milan

Department of Organic and Industrial Chemistry

At the University of Milan there is one major group involved in the study of the stereochemistry of organic chemistry of polymers. Mario Farina is the Professor of Macromolecular Chemistry and Giuseppe Di Silvio is Professor of Industrial Chemistry. Another member of this research group is Piero Bazzani.

The research interest of this group involves stereochemistry, radical polymerization, the determination of kinetic parameters in homo- and copolymerization, the control of the molecular mass distribution as well as the synthesis of block and star copolymers.

Solid state polymerization in inclusion compounds is also being studied. It not only involves the analysis of the structure of clathrates containing monomers or polymers, but also their stability and reactivity. Another field of interest in Farina’s research group is anionic polymerization, where linear and branched homo- and copolymers containing functional groups are being synthesized.

Polymers are subjected to molecular characterization by SEC and LLS and by structural characterization in solution and in the solid state by NMR. Thermal characterization of amorphous and crystalline polymers is being carried out by DSC, the solid state characterization by CP MAS NMR.

The facilities in the department include high-vacuum and inert-gas polymerization set-ups for regular and for high pressure reactions. Instruments include also exclusion chromatographs equipped with RI and UV detectors, laser light scattering instruments (Wyatt Technology, type DAWN F) with batch and flow cells for simultaneous measurement at 15 different angles. A Methot TA 3000 thermal analyzer is also available; 200, 300 and 900 MHz NMR spectrometers for solution studies are accessible as are 300 MHz spectrometer equipped with a solid sample probe.

The School of Specialization in Polymer Science “Giulio Natta”

The research groups involved in polymer science in Milan cooperate in a School for Specialization in Polymer Science, named after Giulio Natta. It is an advanced school of education which is based at Politecnico.

Polymer science developed after Natta and his collaborators contributed very significantly to its vigorous growth over a period of many years. Continuing the tradition, the Specialization School was started at the Politecnico di Milano in 1978 for the purpose of preparing new young specialists in various branches of polymer science to be employed by industries, universities or by national laboratories.

The preparation of the young specialist develops in two main directions. It begins first with tutorial courses on different subjects in polymer science and provides a general, more comprehensive knowledge of polymer science, which normally cannot be given during the university curriculum. Secondly, the student has to spend two full years working in a laboratory on an original scientific research project in a field of specialization of his choosing. During the second year of research, the student is exposed to various aspects of modern polymer science, thus testing and practicing what he has learned during the tutorial courses.

The structure of the school’s two-year curriculum is organized in the following way: During the first year, four introductory general courses are offered to all students in an attempt to provide a common

B. Department of Chemistry

Giuseppe Allegre is a Professor of Chemistry. His field of interest includes statistical conformational studies on macromolecules; macromolecules in solution adsorbed onto surfaces and confined within tubular cavities. Branched polymers are studied in good and bad solvents as are macromolecular collapse with micellar aggregation. The evaluation of the persistence length and of the isotropic-nematic transition temperature of aromatic polyesters and polyamides is also being investigated.

In Allegre’s research group, macromolecular structure determination by X-ray diffraction is being carried out. The main techniques of investigation consist of X-ray diffraction from oriented fibers and from crystallized powders applying the Bragg’s method; polyolefins, polydiolefins, and polyesters are currently under study. Dynamic studies involve branched and rigid linear polymer chains in solution at different concentrations. Other fields of interest are: a) the theoretical evaluation of 

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and of the monoclinic coefficient of different macromolecules; and b) the diffraction studies on incipient crystallization of polymers including iso- and syndiotactic polypropylene, iso- and syndiotactic polystyrene, polyoxazolides.

The instruments and facilities of this group include single-crystal X-ray diffractometer of the Comitato Diffrattometrico Milanese; a single-crystal diffractometer of the Instituto di Chimica delle Macromolecole, C.N.R.; photometric, wide angle X-ray diffraction camera; a small-angle X-ray diffraction camera; a powder X-ray diffractometer with a recording device; a graphic system for conformational energy calculation and three-dimensional display of molecular systems; several personal computers and a computer terminal for IBM, UNIVAC, and DIGITAL computing facilities.
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background for all of them coming from different fields and from different universities. For the second year the students do research under the direction and in one of the professors' laboratories. At the end of the two years, the results of the research are collected in a thesis which is then presented and discussed by a committee of the professors of the school.

A final diploma of specialization is given by the Politecnico after the final thesis has been discussed and accepted by the committee. The diploma has legal value in Italy. Some fellowships (for the duration of two years) are available to students chosen by the school through a selection which will be made in Milan before the start of the academic year.

Titles of the regular courses of the School of Specialization in Polymer Science "Giulio Natta" are: First year: Principles of Polymer Chemistry, Structure of Polymers, Characterization of Polymers. The second year consists of the following curriculum divided into the three major disciplines:

1. Polymer Chemistry Curriculum: Methods of Polymer Synthesis, Ziegler-Natta Catalysts and Polymerization; Modification of Polymers; Advanced Methods of Polymer Characterization; Functional Polymers.

2. Polymer Physics Curriculum: Statistical Thermodynamics of Polymers (Solutions, Melts, Rubbery State, Crystallization); Scattering Methods in Polymer Physics; Molecular Dynamics, Mobilities and Phase Transition in Chain Molecules; Dielectric, Electric and Optical Properties of Polymers. Special seminars are conducted in Polymer Surfaces and Interfaces; Numerical Simulations of Structural and Physical Properties of Polymers; Advanced Methods of Characterization of Polymers.

3. Polymer Engineering Curriculum: Processes of Industrial Polymer Production; Fundamentals of Polymer Processing; Principles of Polymer Engineering, Technology and Properties of Polymer Composites; Recycling and Recovery of Industrial Polymers.

A series of seminars on special topics are presented every year; the subjects are continually updated.

National Council for Research

Institute for the Chemistry of Macromolecules

After the discovery of isotactic polypropylene by G. Natta and his group, the subsequent vigorous progress in the polymer research led, in 1961, the Italian National Council of Research to create a Center of "Chemistry of Macromolecules." The Center was located in the Politecnico di Milano; in 1968, this center was enlarged into an Institute with its own autonomy and a new location.

Guido Audi is the director of the Institute. At the present time, 20 scientists and 12 technicians work in the Institute. The scientific research of the Institute has four major themes: a) Ziegler-Natta polymerization; b) Specialty polymers; c) Biopolymers; and d) Development of new methodologies for the characterization of macromolecules.

Paolo Lucchetti, Maria Carmela Saccu, Domenica Tinti, and Fabrizio Piccinini are involved in the study of the stereochemistry of Ziegler-Natta catalysts. This is done by NMR analysis of the microstructure of the polymers obtained by these investigations.

The group has contributed significantly to the understanding of the mechanism of isospecific polymerization with traditional and supported high yield Ziegler-Natta catalysts. Their studies include:

a) NMR analysis of isolated steric defects and of isolated ethylene units in propene-ethylene copolymers.

b) Determination of the stereochemical structure of selectively labeled chain end groups.

c) Synthesis of model compounds, selectively labeled monomers, and co-catalysts in order to interpret the NMR spectra. Recently, reactions between catalyst components and successive polymerization steps have been directly followed by NMR.

Giovanni Ricci is interested in the polymerization of diolefins with Ziegler-Natta catalysts based on transition metals and lanthanides. His current research involves the following topics:

a) Synthesis of new catalysts and characterization of the polymers obtained from these polymerizations.

b) Study of the mechanism of the formation of stereoregular polydiolefins.

c) Studies of the organometallic compounds of the synthesis of lanthanides and their use as catalyst components.

Silvia Daini, Mariella Catellani, and Alberto Bolognani are members of a research group which studies polymers for electronics applications. Their interest is focused on the synthesis of macromolecules having an extended π-system. They are mainly interested in the characterization of their structure and their electrical and spectroscopical properties. This group is also involved in the synthesis of different thiophene derivatives: oligomers, structures with condensed thiophene rings, poly(3-thiophene). Both traditional and electrochemical polymerizations are carried out. Some of these materials have shown interesting electrooptical properties and are now under investigation for possible applications in information transmissions and for optical switches. Interesting phenomena, such as electrochromism or thermochromism, are also being studied. The polymers are also being spin coated onto thin films with improved order or are being investigated for their behavior when fabricated by Langmuir-Blodgett techniques. William Porzio is responsible for the X-ray diffraction studies of these polymers in powder form, or in the form of spin coated or LB films. This study is carried out at varying temperatures with a computer controlled Siemens D-500 diffractometer.

Silvia Luziani is in charge of the Vibrational Spectroscopy Laboratory. This laboratory is equipped with a Bruker FT-IR instrument with a Raman attachment for the analysis of the near IR. Raman
facilities with different laser sources and a Cary 2400 spectrometer are also available. Photo-induced absorption measurements are also carried out; the laboratory is especially equipped to study the resonant Raman scattering of conjugated systems.

Guido Audisio, the director of the Institute, is responsible for the laboratory of characterization of macromolecules. The facilities available in the laboratory include instruments for Gel Permeation Chromatography operating up to 150°C with UV, diffraction index and viscosity detectors, High Performance Liquid Chromatography, Differential Scanning Calorimetry and Thermogravimetry for thermal analysis. Gas-Chromatography coupled with Mass Spectrometry, and FTIR Spectroscopy are also available. Polymer characterization in solution is the responsibility of Raffaello Masnaghetti, and thermal characterization, of Fabio Bertani. The laboratory functions as analytical support for all the problems of the research groups of the Institute. It is also responsible for research in the following areas: a) Characterization of polymers by means of pyrolysis GC-MS. This work is presently concentrated on the distribution of the pyrolysis products as a function of the molecular weight of the polymer, b) Catalytic degradation of the polymers, as a possible future tool for recycling of the polymers, is carried out with the objective of finding some selectivity to produce some interesting new compounds. c) Synthesis and characterization of polymers with a flame retardant incorporated in its structure. These polymers, synthesized by polycondensation reaction or by grafting copolymerization, can be blended with polyolefins. It gives them high flame retardancy while retaining good mechanical properties.

d) Study of the degradation of some biological material by radicals which might be involved in the aging process of human tissue (collagen).

The influence of some "radical scavengers" to retard the aging process is being studied in attempts to stabilize some of the material.

The group of conformational analysis (Dino R. Ferro, Massimo Ragnoli and Augusto Provasoli) is interested in the development and the application of computational techniques to elucidate the conformation of synthetic and biological polymers. This activity, mainly based on molecular mechanics, quantum chemistry and molecular graphics, provides the theoretical interpretation of different physico-chemical properties. One of the current research lines concerns the refinement of the structure of microcrystalline polymers by combining energetic criteria (simultaneous minimization of intramolecular and intermolecular energy) with crystallographic techniques (Rietveld's whole profile method). This work allows for a deeper understanding of polymorphism and of the impact of lattice forces on the polymer chain conformation for several important polymer systems: trim-1,4-poly(penta-1,3-diene), poly(vinylalcohol), cis-1,4-poly(2-methyl-penta-1,3-diene) and last, but not least, polypropylene.

A second major research objective is involved in the elucidation of the structure of sulfated polysaccharides (mainly heparin and related glycosaminoglycans). Their properties are related to the understanding of the origin of their biological properties. This work is substantially based on the interpretation of the NMR data of these compounds (vicinal coupling constants and nuclear Overhauser effects) by means of molecular mechanics calculations. The calibration of a refined force-field for carbohydrates is another current effort of the group.

Lucia Zetta is responsible for the NMR laboratory; her closest coworker is Roberto Costamagna. Their field of interest involves the structural characterization of macromolecules in solution and in the solid state by means of high resolution, photo-CIDNP, MAS and microimaging NMR spectroscopy.

The main themes of their research in the biological field are: protein folding, peptide-protein and protein-protein interaction, and structure-function relationships. Structural information is derived from a variety of multidimensional homo- and heteronuclear NMR experiments, using paramagnetic or transient radical probes. NMR parameter constraining techniques are also used in the generation of molecular dynamics and chemical structures. Studies "in vivo" on the muscle physiology are also carried out by microimaging.

In the area of synthetic polymers, the defects known to be present in semicrystalline polyolefins are studied. The structures of conducting polymers are also investigated in the solid state by magic angle spinning techniques.

The instruments available to the laboratory are: a Bruker AM-500 NMR spectrometer for all nuclei, also suitable for reverse detection; a Bruker AM-700 for high resolution proton and carbon NMR spectroscopy, equipped with an argon laser for photo-CIDNP spectroscopy; a Bruker AM-200 WB for all nuclei, equipped with MAS and microimaging accessories; a Silicon Graphics computer system.

The laboratory also offers internal courses on the "Introduction to NMR Spectroscopy" for young scientists of the School of Polymer Specialization "G. Natta," and generally, for Ph.D. students and for guests.