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Polymer Science in Romania I: "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

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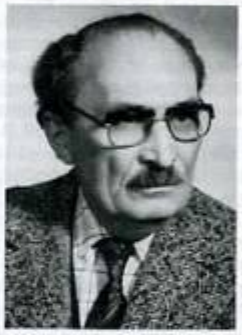

Cristofor I. Simionescu

Most of the polymer research in Romania is done in Bucharest, the capital of the Socialist Republic of Romania, and in Iaşi. Some polymer research is also carried out in research centers in Mediaş, Piteşti, Săvineşti, Timişoara, and Rîmnicu-Vîlcea; the primary objective in these activities is applied polymer research. The present article is concerned with the research in macromolecular science which is carried out in Iaşi.

Situated in the northeast of Romania, Iaşi, the old capital of Moldavia, was already established at the beginning of this millennium. When first mentioned in a document in 1408, the settlement was already an economically important local center. It is here that Prince Michael the Brave sanctioned the unification of the three Romanian principalities (i.e., Moldavia, Wallachia, and Transylvania) in 1600. In Iaşi the signal was given for the 1848 Revolution in the Romanian countries, and it was here that Prince Alexandru Ioan Cuza was elected ruler of Moldavia (1859). These actions were the prelude of the historical act of the formation of the Romanian national state by the unification of Moldavia and Wallachia.

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Besides the early events ofRomanian history, one can trace in Iasi also the beginnings of Romanian culture and higher education. As early as the first half of the 17th century, a school of higher learning, the *Vasilian Academy* in Greek, was set up in Iaşi, almost at the same time that the first print started functioning. In 1814 the first school of engineering was opened in Iaşi. In 1835 the first modern institute of higher learning in Romania, the *Michaílen Academy*, and one year later, the *Philharmonic-Drama School Conservatoire* were established. The first *Romanian University* was founded in 1860 by Prince Alexandru Ioan Cuza; it is still called by his name today.

Iaşi is today a city of about 400,000 inhabitants, spread over seven hills; it is full of vitality in spite of its 500-year history. With its University, the Polytechnic Institute, the Medical School, School of Agriculture, and the Conservatoire, Iasi is full of academic life in spite of its increasing importance as an industrial center. The chemical industry is represented by an antibiotics factory, a complex synthetic fibers works, and a plastics processing company. Since 1948 Iaşi has been the seat of the Academy of Sciences of the SR Romania, Branch of Iaşi.

"Petru Poni" Institute of Macromolecular Chemistry was established in 1964 at the initiative of the President of the Academy, Branch of Iaşi by separating it from the Institute of Chemistry. The Institute of Chemistry had been founded

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in 1951 by Professor Radu Cernătescu (1894-1958), member of the Academy. Professor Cernătescu was the first Director of the Institute. He was followed until 1963 by Dr. Ilie Matei (1895-1969), professor at the Polytechnic Institute, and Dr. Ioan Zugrăvescu, professor at the University, both corresponding members of the Academy. Since 1970 the leadership of the Institute has been in the hands of Dr. Cristofor I. Simionescu, professor at the Polytechnic Institute, President of the Academy, Branch of Iaşi between 1963 and 1974.

The name of Professor Petru Poni (1841-1925) was given to the Institute of Chemistry in 1956. Petru Poni was professor of chemistry at the University in Iaşi and is considered the founding father of chemical research in Romania. Twice he was elected President of the Romanian Academy of Sciences.

In the period 1951-1970 the Institute functioned under the auspices of the Academy of SR Romania and between 1970 and 1975 under the sponsorship of the Ministry of Education. In 1975 it was incorporated into the Central Research Institute of Chemistry of the Ministry of Chemical Industry along with all other specialized institutes and centers devoted to basic research in chemistry, formerly units of the Academy of Sciences of the SR Romania.

The "Petro Poni" Institute of Macromolecular Chemistry is currently concerned with both fundamental and applied research in chemistry and technology of polymers. Considerable effort is devoted also to the investigation of the relationship between chemical structure and characterization of macromolecular compounds, especially new or modified polymers. The Institute cooperates with other institutes of the Central Research Institute of Chemistry as well as with other academic institutions. Cooperation includes research and supervision of graduate and undergraduate students in chemistry and technology of macromolecular compounds. Several members of the Institute are also instructors or lecturers at the Polytechnic Institute of Iaşi. The Macromolecular Institute has its own Ph.D. program and more than 50 Ph.D.s have graduated since 1969 when the program was started.

The Institute has also close cooperation with industry, assisting, on a contract basis, in solving specific problems.

The Institute has over 150 graduated employees (chemists, chemical engineers, physicists, and mathematicians); 40 have doctoral or doctor-engineer degrees; an equal number are technicians. The Institute is divided into five research laboratories, each with at least 20 graduates; one section consists of a research laboratory and a research group which is concerned with analysis. The laboratories are subdivided into research groups.

One of the research laboratories of the Institute is the *Laboratory of Fibers and Natural Macromolecules* headed by Dr. Viorica Rusan. It is concerned with the separation of natural polymers from a biomass; these polymers are then modified by chemical, biochemical, or thermomechanical methods, and their utility as specialty fibers is being investigated. A new method was developed for an upgrading of the phytomass in a sequence of steps which can be adjusted according to the origin of the raw material and utilization of the final products. The method is based on the separation of the primary components (cellulose and lignin) after the extraction of other byproducts (pigments, alkaloids, oils, inulin, terpenes, proteins, polyphenols, and hemicelluloses). Efforts are being made to convert the byproducts into different useful products such as resins, organic fertilizers, sugars, and biologically active compounds. Cellulose is modified by esterification or grafting. Lignin separated as lignosulfonate is a byproduct in papermaking: it is investigated as a potential starting material for adhesives, soluble organic fertilizers, and surfactants. Investigations are being carried out to develop specialty fibers, especially new versions of carbon fibers. Investigations are also being carried out for the design of new adhesive compositions and composites (interpenetrating networks) based on cellulosic fibers and synthetic fibers in the principal of nonwoven materials. The scientific results of the laboratory are published primarily in "Cellulose Chemistry and Technology," an international journal founded by Professor Cristofor Simionescu in 1965; it has an international editorial board (A. Bjorkman, H. F. Mark, B. Rånby, K. Kratzl, T. E. Timell, et al.) and is published by the Academy of Sciences of the SR Romania.

Alexandru Ioan-Cuza University, Iaşi.

The *Laboratory on Semiconducting Polymers and Plasma Research* headed by Dr. Ioan I. Negulescu is involved in two areas of research: (a) synthesis and characterization of macromolecular compounds with specific electric properties and (b) synthesis and/or modification of polymers by means of electric (glow) discharges.

The investigation of polymers with special electric properties is focused on (i) polymeric materials with (semi-)conducting characteristics and (ii) photoconducting polymers. Conjugated polyenes, obtained by polymerization of various acetylenic monomers, are used as model compounds for the investigation of conducting polymers. Special attention is being paid to the relationship between chain configuration and electric or magnetic properties. Modification of polymers, such as the dehydrochlorination of PVC in the presence of phase transfer catalysts, is used as one way to obtain macromolecular compounds with blocks of conjugation along the polymer chain.

Polymeric photoconductors are being synthesized from monomers with anthracene, phenanthrene, or carbazole groups and their derivatives in the molecule. Macromolecular charge transfer complexes, formed between polymeric donors such as polymers with carbazole groups, and macromolecular acceptors such as fluorenone-containing polymers are also being studied as photoconducting materials.

Reactions in glow discharges (cold plasma) are being investigated in order to obtain thin films of polymers from a great variety of organic compounds, usually labeled as unpolymerizable substances. Efforts are also being made to impart new characteristics to existing polymeric materials. Part of these activities is concerned with the origin of life. A new theory has been proposed, i.e., a cold theory of the origins of life (C. I. Simionescu and F. Dénes) which states that the functional protobiopolymers appeared on cold surfaces under the action of electrical discharges through recombination of active species generated from methane, ammonia, and water.

In the *Laboratory of Polycondensation* under the leadership of Dr. Florin Popescu is concerned with the synthesis of polymers by polycondensation processes. The products have improved thermostability or they are materials with low flammability and with good adhesive and dielectric properties.

Direct polycondensation using phosphorus intermediates is being investigated for the synthesis of aromatic polyamides under mild conditions. Reaction conditions are carefully investigated in order to achieve optimum yields and high solution viscosities. Thermostable polymers (aromatic polyimides) are being synthesized starting from aromatic diamines and anhydrides of aromatic tri- and tetracarboxylic acids. Poly(amidimide)s, poly(esteramide)s, and poly(amino-bismalemide)s are also being synthesized from heterocyclic diamines with benzimidazole or benzotriazole units and aromatic dicarboxylic acid chlorides.

Heterocyclic diamines are also being used as chain extenders for obtaining heterocyclic polyurethanes which decompose at a somewhat higher temperature than classical polyester- or polyetherurethanes.

The synthesis of aromatic polysulfones is being studied by polycondensation of the corresponding intermediates in order to obtain engineering plastics with good thermal and dimensional stability.

Polycondensation of monomers containing phosphorous and halogens is being investigated from the point of view of obtaining new ion exchange resins, polyelectrolytes, and flame-retardant or fire-extinguishing polymers. Reactions of the phosphorous atoms on the backbone or side chains are studied to form amides or esters of various oxygenated phosphorous acids.

Research in this laboratory is also being done in attempts to obtain aliphatic copolyamides intended as thermoadhesives in industrial processes which require the assembly of different items by thermocollage.

The activity of the *Section of Polyaddition and Structure of Polymers* with Dr. Adrian Caraculacu as its head involves the synthesis of polymers through addition reactions of isocyanates, studies of the fine points of the structure of PVC, thermal degradation (pyrolysis) of polymeric wastes, and the analysis of polymers.

The main problem in the group involves the study of the reactions of 4,4'-dibenzyldiisocyanate for the synthesis of different types of polyurethanes. This monomer was synthesized in the early 1960's by Professor Ilie Matei and industrialized in the 1970s. The Romanian polyurethane industry is based on 4,4'-dibenzyldiisocyanate. Reaction of the isomers of this monomer and of the corresponding diamines, i.e., 2,2'-, 2,4'- (or 4,4'-) diaminodibenzyl, are also being investigated for the synthesis of aromatic polyamides, polyimides, polyurethane ionomers, or other heterocyclic macromolecular compounds, such as poly(urethane-parabanic acid)s or poly(parabanic acid)s.

The relationship between the thermal stability of PVC and the types and amounts of structural defects in the PVC chains is also being investigated in this Section. Efforts are being made for the improvement of the thermal characteristics of PVC by introducing reactive groups during its synthesis followed by modification of the polymer chains through reactive groups in order to obtain stable graft copolymers or block copolymers.

Thermal degradation of polymers is also being investigated with the objective of upgrading polymeric wastes of various types (polyolefins, vulcanized rubbers, etc) through pyrolysis.

The activity of the research group of Polymer Structure and Physics within the Section is led by Dr. Virgil Bărboiu; it is involved in studying several aspects in the following areas of spectroscopy: NMR, IR, and UV-Visible spectroscopy for the determination of molecular structure; elemental analysis and analysis for functional groups; applications of mathematical and electronic computation methods; electrical and thermal properties of polymers; polymer photochemistry and photophysics (photopolymers applied as photoresists and photoconductivity in polymers).

The *Laboratory of Chemical Reactions on Polymers* under Adrian Carpov is concerned with the modification of polymers as adsorbants, hydrophilic acrylic ion exchangers, macromolecular supports for enzyme immobilization and for chromatography; water-soluble polymers are developed as flocculants, coagulants, protective colloids, additives for filtration processes and tertiary oil recovery, antifouling agents, additives for drug formulations and anticorrosive agents, as well as for microcapsulations of insecticides or pesticides (malathion, disulfoton).

Styrene-divinylbenzene matrices with large-size and super large-size pores are currently prepared using a mixture of diluents as porogenic agents. The effects of dilution, degree of crosslinking, and the effect of diluents on the porosity and on the coefficients of uptake, the specific surface area, and the average pore diameters are being studied in order to elucidate the manner in which inert compounds contribute to the formation of porous networks.

Various reactions are also being carried out on these crosslinked matrices. Especially studied are chloromethylation with monochloromethyl ether or 1,4-bis(chloromethoxy)-butene followed by amination in order to produce strongly basic anion exchanger resins. Morphological transformations which occur as a result of these reactions are also being analyzed by determining the porosity and the surface area by SEM.

Crosslinked acrylic copolymers bearing amino or carboxylic acid functional groups are being synthesized and used as supports for biologically active proteins.

The main interest of the *Laboratory of Elemental-Organic Polymers* with Dr. Mihai Marcu as its head are organohalogensilanes and the synthesis of polyorganosiloxanes (silicones). Both alkyl- and arylhalosilanes are the starting monomers for a series of technical products, i.e., oils, emulsions, and elastomers for which the technologies are being established. Another area of investigation is the synthesis and characterization of macromolecular chelates. Attention is

being given also to various organoaluminum derivatives which are being tested as polymerization initiators for vinyl or acetylenic monomers.

The Macromolecular Institute participates in international cooperations coordinated by the Academy of Sciences of SR Romania. Many distinguished scientists active in polymer science worldwide have visited the Institute in the past 25 years.

The Institute has organized or cooperated in the organization of significant national and international scientific meetings in the field of natural and synthetic polymers, such as the 29th IUPAC Macromolecular Symposium, MACRO '83, which was held in Bucharest. International symposia in Iaşi have been held under the title "Cellulose Chemistry and Technology."

The Institute of Macromolecular Chemistry in Iaşi and the Academy of Sciences of the SR Romania, Iaşi Branch, were the host of the first U.S.-Romania Seminar on Polymer Chemistry in 1976 and participated in the second U.S.-Romanian Seminar which was held in 1983 in Bucharest.

Several scientists from the Institute are members of foreign academies and scientific societies. Members of the Institute are also represented on editorial boards of journals on macromolecular science.