Polymer Science in Croatia

Otto Vogl, *University of Massachusetts - Amherst*
Franjo Flajsman
Zvonomir Janovic
Helena Jasna Mencer

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Franjo Flajšman(a), Zvonimir Janović(b), Helena Jasna Mencer(b) and Otto Vogl(c)

(a) INA Oil Company, Zagreb, Croatia, (b) University of Zagreb, Zagreb, Croatia and (c) Polytechnic University, Brooklyn, NY 11201, U.S.A.

Introduction

Croatia is a country located in Central Europe; in the northwest it borders on Slovenia, in the northeast on Hungary, in the south on Bosnia-Herzegovina and in the east on Yugoslavia (Serbia and Montenegro). Croatia stretches from the slopes of the Alps deep into the Pannonian Valley and to the banks of the Danube and Drava rivers. Croatia also has a long coastline on the Adriatic Sea of nearly 1,890 km. Much of Croatia consists of islands and isles. When the islands (1,185 have been counted of which 66 are inhabited) are included the coastline is three times as long. This configuration makes Croatia a Mediterranean and central European country.

The shape of the country is unique and resembles a "croissant" or horseshoe as a result of the migration of the croatian (slavic) tribes in the dark ages. Croatia has a population of nearly 5 million people, a land area of about 57,000 sq. km and a territorial sea of about 30,000 sq. km. It is divided into 21 counties.

The capital of Croatia is Zagreb with nearly 950,000 inhabitants. There are a number of other important cities in Croatia: Split, Rijeka, Osijek, Pula, Zadar and the famous city of Dubrovnik.

For centuries, Croatia was an autonomous part of other countries, Hungary, the Austrian-Hungarian monarchy and Yugoslavia. Most of Dalmatia, the coastal provinces, excluding Dubrovnik, was until the Napoleonic period in the early 19th century part of Venice. In September 1991, Croatia proclaimed
written history of Zagreb. For some time Zagreb and Croatia were a bulwark against the Tatars and then against the Turkish invasions into the southern part of Europe.

UNIVERSITIES IN CROATIA

Scientific research activities in the Republic of Croatia are carried out in government-financed institutions. Croatia has four institutions of higher learning. The University of Zagreb, the University of Split, the University of Rijeka and the University (actually an agricultural University) in Osijek.

THE UNIVERSITY OF ZAGREB

The University of Zagreb is the oldest and largest university in the Republic of Croatia and one of the oldest universities in Europe. The beginnings of higher education in Zagreb are closely connected to the Jesuit Gymnasium established in 1632 for the teaching of moral theology. Thirty years later in 1662, the academy for a higher level of learning of philosophy was started. The actual history of the University of Zagreb began in 1669 when the then Jesuit Academy in the Royal Borough of Zagreb was granted university status and privileges in a document by the Holy Roman Emperor and Croatian-Hungarian King Leopold I of Hapsburg. The school was given the right to award doctoral degrees.

In 1861 the Croatian Sabor (Diet), at the initiative of Bishop Josip Juraj Strossmayer, passed legislation on the University of Zagreb. Emperor Franz Joseph signed a legal document on the University of Zagreb in 1869 which founded the modern University of Zagreb.

Today the University of Zagreb consists of 28 colleges, 3 arts academies with 48,000 students and 2500 graduate students. Branches of the University of Zagreb on the Adriatic coast are in Dubrovnik and on the Istrian peninsula.

The Faculty of Chemical Engineering and Technology

The Faculty of Chemical Engineering and Technology was founded in 1919, as the first
Department of Chemistry was created with the objective to provide education in Chemistry and Chemical Engineering. A number of distinguished scientists had been active in teaching and research in this department, for example Vladimir Prelog (Nobel Prize 1975) as professor of Organic Chemistry from 1934 to 1941. Ivan Murek, the first professor of Organic Chemistry from 1920-1933, who invented the famous "Murek's Furnace" for elemental organic analysis. Frenho Hanaman, the inventor of tungsten filament, was a professor of Inorganic Chemical Technology and Metallurgy from 1922 to 1944. Ivan Plotnikov, active in the field of photochemistry, was a professor of Physics and Physical Chemistry between 1920 and 1945 and Rikard Podhorsky was a professor specializing in unit operation and unit processes.

Polymers research at the Faculty of Chemical Engineering and Technology started immediately after its establishment. Initially by investigations of natural polymers particularly cellulose. Today there are several research groups covering the whole field of polymer science and engineering. Much of the work is devoted to synthesis, characterization, processing, polymer blends and composites and the degradation and stabilization of polymers. This department also possesses good facilities for the study of conducting polymers.

In addition to the standard equipment for organic synthetic work, a number of specialized equipment used in the research programs in polymer science and engineering, such as: IR, UV, H-NMR spectroscopy, thermal analysis equipment for measurement of mechanical properties, and a substantial number of computers. The faculty also has good access to laboratories with a large number of instruments, which are used in the research activities of the Department.

Degradation and Stabilization of Polymers: Degradation, aging and stabilization of polymers plays an important role in the research activities of the Department of Chemical Engineering and Technology. The aging of different rubbers and thermoplastic elastomers is being studied by Professors Vladimir Brvar and Jasenka Jelenčič. This work is devoted to investigation of the peroxide degradation of natural rubber latex film in inert media or in the presence of oxygen. These materials had been vulcanized with different accelerators which gave polymer networks of different structures and crosslink densities which, in turn, causes different behavior to UV irradiation.

Copolymerization and Copolymers of Brominated Vinyl Monomers:

Professor Zvonimir Janovič is investigating the properties of structural adhesives of polymeric composites, elastomers and adhesives. Professor Vladimir Rek is studying the interrelation between processing, structure and properties of polymeric materials, particularly of polyurethane's (PUR). The research is focused on: stability, degradation and annealing processes and of new PUR materials. It was found that structure and composition of PUR effect significantly the course and the degree of the chemical, photooxidative and thermo-oxidative degradation of these materials. The degree of the structural changes, especially of the change in the morphological structure of PUR and its mechanical and thermal properties was determined. Annealing/quenching processes influence the morphological structure of PUR. Segments reordering, mechanical properties and viscoelastic function was found to be interrelated. Novel PUR materials, particularly PUR foams based on polyols and PUR with high thermal stability using a polylvinyl monomer in the polyl component has also been studied.

The research group of Professor Branko Kunst is primarily...
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interested in polymer membranes. The formation, structure and the properties of asymmetric reverse osmosis and ultrafiltration membranes are being investigated. The mechanism of the formation of the asymmetric structure during the precipitation process of passing the thick polymer solution into the non-solvent and the phase separation that occurs during this process is being studied. The experience from the more traditional processes has been applied to the membrane preparation from various polymeric materials. The porous structure of the membrane’s skin has been carefully examined and the exact structure has been related to the membrane’s performances.

The research of the group of Professor Helena Jasna Mencer, the Vice President of the University of Zagreb, is concerned with:

1) **Hydrodynamic and thermodynamic properties** (solvability, miscibility, phase separation) of polymer solutions; the mechanism and the efficiency of some polymer separation methods (GPC, fractionation methods); the correlation between molecular weight distribution of polymers and their macroscopic properties.

2) **Kinetic analysis of polymerization reaction** of thermosetting resins (epoxies and unsaturated polyester-resin) and their composites, the rheology of thermosetting resins and modelling of their curing kinetics.

3) Studies of the correlations of the process parameters in solution and emulsion copolymerizations and their product properties (molecular weight distribution, composition drift, thermodynamic behavior).

Faculty of Mechanical Engineering and Naval Architecture

The beginning of the education in polymer processing at the University of Zagreb started at the Faculty of Mechanical Engineering and Naval Architecture. Polymer processing curricula started back in 1971, and, by now 220 Dipl.-Ing. have been granted. The students in the Departments of Production, Industrial and Material Engineering are also educated in this field. Education in Polymer Processing provides a profound knowledge in designs using polymeric materials, in testing of polymers, in the production of polymeric parts, in understanding equipment, mold design, reactive processing and other important functions of polymer fabrication.

Scientifically, Polymer Engineering and Processing is covered by the Chair of Polymer Processing and Materials Engineering. The Chair of Polymer Processing was established in 1974 and is now headed by Professor Igor Catić. He is assisted by Associate Professor M. Sercer and three assistants.

The main fields of scientific interest of Chair can be summarized as follows: Calculation of mold elements, heat exchange in molds for injection molding of thermoplastics, rubber compounds, thermoset, PS-E and thermoforming, design of runner systems for injection molding of rubber compounds, trend regulation of injection molding processes, development of expert systems for the elimination of visibly faults in the moldings, CAD in mold design, recovery of polymeric parts, development of new injection molded polymeric products, reactive cyclic polymer processing with the mold as a batch reactor, systemic analysis of injection molding of polymeric materials, compression molding of thermosets, thermoforming, extrusion coating and coextrusion, film extrusion and welding of polyethylene films.

The newest field of this research is the application of the conception of the factual entrepreneurial culture in the field of polymer processing, particularly in injection molding shops.

The chair for Material Engineering with emphasis on the field of Engineering of Polymeric Materials was created in 1959. At the present time, it consists of two Associate Professors, J. Indof and Z. Smolčič-Zordik and three assistants. The main areas of interest are: Characterization of polymeric materials and polymer-based composites and correlations between structure and properties, mechanical, chemical and thermal properties.

THE UNIVERSITY OF SPLIT

The University of Split, established in 1974, is based on the foundations of the cultural, educational and scientific heritage of Dalmatia, which represents 25% of Croatia’s territory and has a population of around one million. Academic instruction in Dalmatia has a long tradition, reaching back into the middle ages. In 1396 a school of theology and philosophy was founded in the Dominican monastery in Zadar, with the right to give the title of Doctor Philosophiae. This Academy functioned until 1811.

Today, the University of Split consists of 9 Schools, including a school of Philosophy in Zadar, of Natural Sciences, Mathematics and Teacher Training in Split and of Electric and Electronic Technology, Engineering and Shipbuilding, Technology, Construction and Law also in Split.

The University of Split has about 10,000 students. It has a regional and multi-center structure with branches in Split, Zadar and Dubrovnik.

Faculty of Technology

This Department of Organic Chemical Technology was established in 1960. Polymer research started in 1963, when Dr. Urban Roje was appointed Professor. Today Professor T. Kovačić is the head of the Department assisted by Dr. I. Klarić.
This research team is mostly involved in the investigation of the effectiveness of the actions of plasticizers, specifically on the mechanisms and kinetics of plasticizers action in PVC, and the thermal stability of those mixtures. In addition, a number of PVC blends with other polymers, particularly those of more practical interest such as ethylene-vinyl acetate copolymers, chlorinated polyethylene, thermoplastic polyurethane, ABS, graft copolymer of methylmethacrylate-co-styrene onto polybutadiene are being investigated. Thermal degradation processes of some of these blends are being studied by isothermal and nonisothermal thermogravimetry and by applying different kinetic models for the mechanisms of degradation.

The Universities of Rijeka and Osijek

The University of Rijeka, established in 1973 consists of ten schools, a School of Medicine, a School of Technology, a School of Economics and the Hotel Management College. The University has about 10,000 students. The Josip Juraj Strossmayer University of Osijek, established in 1975 has now 6,500 full-time and 1,000 part-time students enrolled. Neither of these two Universities has any research or teaching in Polymer Science and Technology.

SCIENTIFIC INSTITUTIONS IN CROATIA

There are currently 23 scientific institutes and 55 colleges in Croatia. In the natural sciences there are 3 institutes with about 300 scientists; in the technical sciences there is one Institute with about 350 scientists.

The Institute Rudjer Bošković

The Institute Rudjer Bošković IRB is the largest scientific institution in Croatia which is engaged in basic natural sciences. The IRB was founded in 1950 by Professor Ivan Supek; today the General Director of IRB is Dr. Mijola Zovko. Since 1953 the Institute is committed to graduate studies. At present, the Institute employs 730 people, 390 of these are research scientists and 105 are graduate students in all areas of research. The Institute consists of 5 departments: Department of Physics, Department of Chemistry, Department of Biology and Medicine, Center for Marine Research and Center for Laser and Atomic Research and Development covering the following areas of research: theoretical and nuclear physics, nuclear chemistry, solid state physics, atomic and molecular physics, laser physics, preparative organic and inorganic chemistry, theoretical chemistry, biology and medicine, spectroscopy, physical and structural chemistry, marine sciences and computer sciences. Forty percent of all scientific output in Croatia comes from the IRB. Polymer sciences is a small part of the overall research activities and involves 10 scientists.

Polymer research at the Institute began in 1964 in the field of radiation chemistry and was followed with the application of spectroscopic methods to natural and synthetic polymers with the objective of determining structure and dynamics of polymers.

The investigation of polymers at the IRB is predominantly of a fundamental nature but the existing experience and the instrumental capabilities are also utilized for applied problems. The current research activities are described in the following sections.

Radiation chemistry of polymers. F. Ranogajec—The investigations involve the studies of the chemical and physical effects of ionizing radiation in polymers, radiation modification of polymers by grafting to increase the resistance of a stabilizer
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or other additives by bonding them chemically to the polymer chain. Radiation induced crosslinking and radiation polymerization is also carried out. Calorimetric investigation of high conversion polymerization aims to better understand the polymerization mechanisms in heterogeneous media and/or in the cases where the gel effect is involved. This data is important for the control of industrial processes.

Characterization of Polymers. Z. Veksli, M. Andreis, M. Topić—The investigation of polymer structures and relaxation processes in polymer structures is being studied by combination of spectrscopic methods: magnetic resonances (NMR, ESR), IR Raman spectroscopy, X-ray methods, dielectric and thermally stimulated depolarization current measurements. At present, the research is primarily concerned with the matrix morphology of polymers and polymer mixtures, phase separations in the glassy state and in solutions of copolymers, local orientation of block copolymers and the investigation of the compensation phenomena in the relaxation processes in order to understand property-structure-dynamic relationships. A potential of the double modulation ESR (DMESR) method recently developed in the Institute is being investigated in the range of slow molecular motion of polymers and copolymers. The method appears to be very sensitive to small free volume changes imposed by degradation, local orientation and phase separation.

The scientists at the Institute are extensively involved in international cooperation, have good collaboration with the industry and universities and participate in the graduate programs in the field of polymers.

THE CROATIAN ACADEMY OF ARTS AND SCIENCES

The Croatian Academy of Arts and Sciences is the highest-ranking scientific and artistic institution in the Republic of Croatia. It is the legal successor of the Yugoslav Academy of Arts and Sciences, established in 1866 as the highest-ranking scientific institution of the Southern Slavs. The Croatian Academy of Science initiates and organizes scientific activities and it is responsible for the implementation of their results. The Sabor (Parliament) of the Republic of Croatia controls the legality of the Academy’s activities. The Academy has regular, honorary and corresponding members, as well as associate members. The maximum number of regular members is 160.

The Academy cooperates also with great interest with its foreign counterparts.

THE CROATIAN INDUSTRY

Much of the production of the petrochemical and polymer chemistry is in the largest company of Croatia, Industrija Nafta D.D. Zagreb (INA). In addition, there are smaller production capacities of polymer latexes based on vinylacetate and acrylic copolymers in two chemical companies, “Karben” and “Chromos” both located in Zagreb. In fact the history of polymer industry in Croatia started in 1946 at Chromos by the production of phenolic resins.

INA Industrija Nafta D.D. Zagreb (INA)

INA Oil Company is a conglomerate company and the largest Croatian company. The value of its products and its financial potential make up almost one third of the national economy. INA, with its 26,000 employees is involved in the production of oil and gas, in processing of crude oil and trade and in transport of oil products in Croatia and abroad. The company produces petrochemicals, petrochemicals and mineral products. INA is among the ten largest petrochemical companies in Europe.
In 1992 the organic petrochemical industry exported over 80% of its annual production volume all over the world. The value of foreign trade transactions amounts to 1.3 billion US dollars.

INA is basically an oil company and consists of about 30% in refining, about 40% of oil exploration and production and about 30% in petrochemicals and polymer industry.

Polymer production in INA includes polystyrene, low density polyethylene and PVC by suspension, emulsion, and bulk polymerization. The total production amounts to 530,000 tons/year. In addition there are simpler production capacities for polyester fibers of about 16,000 tons/year and styrene ester copolymers as viscosity index improvers for motor oils at about 8,000 tons/year.

The research activity in polymer chemistry is entirely related to the production programs but some special fields are also being studied. The polymer research group, consisting of 25 scientists and technical staff, is located in the central research organizations INA-Research & Development in Zagreb, which employs 155 researchers, 55 are University graduates.

INA-R&D was founded in 1963 by Dragotin Fleš and Franjo Flajšman as the Research Institute for the first petrochemical complex in this part of Europe.

Prior to the establishment of this Institute there was some individual activity in the polymer field in Croatia on cellulose, based on the good tradition in organic and physical chemistry at the University of Zagreb. Although most of the activities in the early phases of the existence of the Institute was related to production problems including the detailed characterization of polymers, fundamental research was also carried out by D. Fleš, Z. Janović, V. Jarm, V. Čeke, R. Vuković, V. Kurešević. It involved the synthesis of optically active polymers of optically active compounds such as stereo-isomers of biopolylactones.

Polymer synthesis was an active part of these investigations. It included the stereospecific polymerization of olefins copolymerizations based primarily on styrene monomer with the objective of developing commercially interesting and useful copolymers (SAN, ABS, copolymers with α-methylstyrene). The synthesis of alternating copolymers based on derivatives of styrene with donor monomers with electron acceptor monomers like maleic acid anhydride and N-substituted maleimides was investigated by D. Fleš, Z. Janović, R. Vuković and V. Kurešević. These studies also included the synthesis of functional polymers, specifically, the preparation of hydroxy- and carboxy-terminated polybutadiene by anionic and free radical polymerization carried out by F. Flajšman, T. Kovač and B. Jermain.

Most of the research activities of INA R&D was related to production problems. Such work included suspension polymerization of styrene with the emphasis on the stability of the polymerization system and the control of particle size distribution. As an important practical problem, the study of the flammability of the polystyrene foam was of special interest. It resulted in the development of resins with substantially decreased flammability which complied with the highest standards regarding the application of material in civil engineering particularly in housing construction by Z. Janović and K. Šarić.

Investigation on polyethylene was the subject of extensive studies including UV-stabilization, controlled thermooxidative degradation to produce polyethylene-waxes, and the modification of polyethylene with starch for UV biodegradable material.

The degradation of polymers were studied by gas chromatography, by mass spectrometry and other specific methods by J. Dureš Pittar, V. Šovob and F. Flajšman.

Extensive studies were carried out at INA-R&D for the development of new polymeric materials based on polymer-polymer mixtures. Mixtures of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide), ABS/PVC—and others blends were studied. Polystyrene was used as the base blending polymer with various other polymers to prepare mixtures to produce polymer blends with new and useful properties. The effect of the structure of the component polymers on the miscibility and the phase behavior of polymers was investigated. The entire research activity at INA-R&D over the last 30 years resulted in about 380 publications and patents and a number of innovations were introduced in the production plants.

Chromos—Chemical Industry Research, Zagreb

Polymer research and development work in these industrial organizations started some 50 years ago, proceeding the first industrial production of plastics in this part of Europe. A group of young engineers, coming straight from the Technical Faculty of the University of Zagreb, without any industrial experience and with scarcely available technical or scientific literature and instruments immediately after the second World War started this enterprise: the first domestic production of synthetic plastic materials, namely phenolic resins and molding materials. In later years, always hiring the best young graduates and promoting team-work, but under the supervision of the best professionals (A. Kostial, V. Doerner, T. Dobronić), other synthetic polymers were produced. They included alkyd resins, urea-melamine-formaldehyde resins as adhesives, coating resins and molding materials, unsaturated polyester resins, aqueous polymer dispersions of vinyl acetate and acrylic monomers and their copolymers, polyurethane coatings and adhesives, epoxide resins.

In the beginning, the main objective for this kind of polymer research was to follow, as closely as possible, the developments in the known fields of direct interest for the industrial production of paints, adhesives, molding materials, binders, etc. Later, starting in the middle seventies, it appeared as obvious, that the

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next step forward in the R&D work should be, not only to follow its advancement, but to be a creative part of it on the international level.

To achieve such a goal, a special organizational unit had been formed, namely Chromos—Chemical Research Center was established by Dr. Zvonimir Katović. The main objective for such an industrial institution was to bridge the gap between applied and fundamental research, so characteristic for that time and especially for countries on a similar level of development. This was tried through the purchase of the most modern instrumentation, hiring established scientists from the universities, and similar scientific institutions and very close cooperation with these institutions. At that time the cooperation with scientists of the Institute Rudjer Bošković (M. Topić, Z. Vekli) was very fruitful. This was achieved by the development of a more or less informal permanent interaction and an exchange of scientific and technological information by engaging the research scientists in professional international organizations in scientific meetings, conferences and exhibitions.

The research topics covered included work on phenol-formaldehyde resins (the role of hydrogen bonding in the curing processes and miscibility with other polymers); on epoxies (the chemistry and the mechanisms of resin formations, modification and co-reactions with other monomers and resins, on polyesters (the influence of the microstructure of unsaturated polyester and alkyds on their properties and performance). Of special attention was the synthesis, separation and characterization of oligomers formed during resins formation, like phenolic, amines, polyesters and epoxies, using various chromatographic methods, thermal analysis, SEM and spectroscopy techniques.

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