

## Polish chemistry in the century of the discovery of polonium and radium by Maria Skłodowska-Curie and Pierre Curie

This is another in a continuing series of articles on chemistry in IUPAC National Adhering Organizations

### Historical

The beginnings of modern chemistry in Poland are connected with a great educational reform that was introduced by the Royal Commission of Education. That institution, which was founded in 1773, was in fact the first ministry of education in Europe. Under its auspices, the chairs of chemistry and natural history were established in 1782 at what was then known as Cracow University (now called Jagiellonian University). Jan Jaskiewicz (1749–1809), who was the first Professor of this chair, and his successor Franciszek Scheidt (1759–1807), introduced into their lectures the theories of Antoine Lavoisier. Jędrzej Sniadecki (1768–1838) became Professor of Chemistry at the University of Vilnius after completing his studies in Cracow, Pavia and Edinburgh, and in 1800 published the first Polish textbook of modern chemistry. This eminent scientist exerted a strong influence on the early stages of development of chemistry in Poland. At the present time, the Sniadecki medal is the highest distinction awarded by the Polish Chemical Society.

In 1795, Poland lost its independence for over 100 years, and the development of the experimental sciences was considerably hampered. The best situation in country was in the region that incorporated the Austro-Hungarian Monarchy, where the universities of Lvov and Cracow were able to continue their activities, and which was also where the Technical University at Lvov was organized. In 1883 in Cracow, Karol Olszewski (1846–1915) and Zygmunt Wroblewski (1845–1888) accomplished the first static liquefaction of nitrogen, oxygen and carbon monoxide. Olszewski became one of the founders of modern cryogenics. He also liquefied and solidified argon, and determined its critical properties. In about 1900, Władysław Natanson (1864–1937) Professor of Theoretical Physics in Cracow, published a series of papers on the problems of thermodynamically irreversible processes, becoming a pioneer in the modern thermodynamics of irreversible processes. Marian Smoluchowski (1872–1917) Profes-

sor of Physics at Vienna, Lvov and Cracow universities developed the theory of fluctuations in gases and, independently of Einstein, proposed the theory of Brownian motion. Subsequent experimental confirmation of the Einstein–Smoluchowski equation became one of the final proofs in the kinetic theory of matter.

Great achievements in organic chemistry were made by Alfred Freund (1835–1892, first synthesis of cyclopropane, 1881), Bronisław Radziszewski (1838–1931, Radziszewski's conversion of nitriles to amides with  $H_2O_2$  in alkaline solution, 1890), Stanisław Kostanecki (1860–1910, synthesis of flavonoids, 1899) and Stefan Niementowski (1866–1925, synthesis of 4-oxoquinazolines, 1895). In Cracow, Leon Marchlewski (1869–1946) was one of the founders in the field of chlorophyll chemistry. During the inter-war period (1918–1939), the study of organic chemistry developed at the chemistry departments of universities and technical universities. The particularly active centres were in Warsaw, Cracow and Lvov. From that period, the investigations performed by Tadeusz Milobędzki (1873–1959, organophosphorus chemistry), Wiktor Lampe (1875–1962, curcumin and light-sensitive dyes), Karol Dziewonski (1876–1943, work on synthetic dyes, decacyclene and other polycyclic aromatics), R. Malachowski (1887–1944, carbonyl cyanide) and Edward Sucharda (1891–1947, chemistry of pyridine) deserve to be mentioned.

Among the Polish scientists who were working in Warsaw, two names deserve to be mentioned here: Jakub Natanson (1832–1884), who was the author of one of the earliest syntheses of artificial dyes (fuchsin), and Józef Boguski (1853–1933), a pioneer in the field of chemical kinetics who also proposed the widely known equation which describes the kinetics of the dissolution of solids in liquids.

At the same time, many talented Poles had been working in different laboratories abroad. Marcell Nencki (1847–1901), who worked in Russia and Switzerland, was the author of some important publications in the field of organic chemistry and biochemistry. He greatly contributed to an establishment of the structure of heme, obtained hemine from hemoglobine, and studied the mechanisms of formation of urea in animal organisms. Stanisław Kostanecki, who was also working in Switzerland, was renowned for his work on the structure and synthesis of flavonoids (Kostanecki synthesis). Bohdan Szyszkowski (1873–1931) published important papers on electrochemistry and surface chemistry.

Ignacy Moscicki (1867–1946), an outstanding specialist in chemical technology working in Switzerland, performed a technical synthesis of nitric acid from air.

Maria Skłodowska-Curie (1867–1934) and Kazimierz Fajans (1887–1975) are among the most famous Polish scientists who worked abroad, Mme Curie in France, and Fajans in Germany and then in the USA. There is no need to explain here their role in the development of modern chemistry and physics.

When Poland regained its independence in 1918, only just a few years of research and teaching had been organized at the old and new universities and technical universities. In fact, in the inter-war period, all the main branches of chemistry research had their representatives at Polish universities and laboratories. In inorganic chemistry Wiktor Jakob (1886–1971) and Bogusława Jezowska-Trzebiatowska (1908–1991) had been working on the coordination chemistry of transition metals and the chemistry of rhenium. Włodzimierz Trzebiatowski (1906–1982) began his work on the magnetic properties of alloys and intermetallic compounds. Alfons Krause (1895–1972) carried out studies on the structure and properties of amphoteric hydroxides and oxides, in particular of iron.

Important research was carried out in the field of organic chemistry. Osman Achmatowicz (1899–1988) was an eminent specialist in the chemistry of alkaloids and terpenes. Synthetic dyes were investigated by Waclaw Lesnianski (1886–1956) and natural dyes by Wiktor Lampe. Polycyclic aromatic hydrocarbons and alkaloids were the object of research carried out by Jerzy Suszko (1889–1972). Tadeusz Urbanski (1901–1985) had begun his work on nitrocompounds and explosives.

The field of Physical chemistry was represented by many investigators. Among the most notable were: Wojciech Swietoslawski (1881–1968) an international authority in the field of thermochemistry, ebulliometry and polyazeotropy. Antoni Galecki (1882–1962, chemistry of colloids), Mieczysław Centnerszwer (1874–1944, chemical kinetics, multiphase equilibria electrochemistry of fused salts), Alicja Dorabalska (1897–1975) a specialist in microcalorimetry who studied the heat of radiation of radioisotopes, allotropic transformations and corrosion of metals, Bogdan Kamiński (1897–1973, surface chemistry, flotation of minerals), Wiktor Kemula (1902–1985, electrochemistry, polarography), Antoni Basinski (1905–1990 colloids, polymers and chemical kinetics) and Jan Zawadzki (1866–1928, chemical kinetics). The physicochemical fundamentals of chemical technology were studied by Jozef Zawadzki (1886–1951, technology of sulfuric acid and Portland cement, thermal decomposition of solids). New methods of petroleum technology were developed by Stanislaw Pilat (1881–1941).

Zygmunt A. Klemensiewicz (1886–1963) working in the Fritz Haber laboratory in Karlsruhe, laid the foundations for membrane electrodes in potentiometry. After the First World War, several centres were created which carried out both research and practical applications of classical and technical analytical methods. The names of Tadeusz Milobędzki and Marcelli Struszynski (1880–1959) of the Technical University of Warsaw should be mentioned here.

All this highly successful development was suddenly interrupted by the outbreak of the Second World War in 1939, which resulted in great disruption to the whole country. After the war, those scientists who survived contributed to a reconstruction of the system of higher education in Poland. In the years 1945–1955, new centres of research in chemistry had been established. Besides the chemistry departments of the universities (Warsaw, Wrocław, Łódź, Cracow, Gdansk, Poznan, Torun, Lublin, Białystok, Katowice, Opole) and the technical universities (Warsaw, Wrocław, Łódź, Gdansk, Gliwice, Szczecin, Rzeszów, Lublin, Poznan), research institutes of the Polish Academy of Sciences (established 1951) were also created.

## Inorganic chemistry and related fields

Coordination chemistry is one of the best developed fields of inorganic chemistry. Research in this direction is being carried out in Wrocław, Cracow, Poznan and Torun, and also in several smaller scientific centres elsewhere. The synthesis, structure and physicochemical properties of transition metal complexes using different ligands are being studied, including ligands of biological importance such as amino acids and nucleotides, forming models of metal-centred biological systems. Chemical and thermal stability, spectroscopic and magnetic properties, and the chemical and the photochemical reactivities of these complexes are also under investigation. Homogeneous catalysis, closely related to structural coordination chemistry, is represented in Poland in several centres which are specialising in inorganic (Wrocław, Poznan, Cracow), organic (Warsaw) and physical (Warsaw, Cracow) chemistry.

Separation of lanthanides, their coordination and structural chemistry, spectroscopy and chemiluminescence are being studied in Lublin, Wrocław, Łódź and Poznan.

Silicate chemistry is centred on the synthesis of old and new generations of zeolites, pillared clays (Cracow) and structure, as well as the properties of glass (Cracow, Gdansk).

Different aspects of solid state chemistry are under study in Poland. The physicochemical properties of simple and mixed oxides of transition metals are the object of investigations connected with heterogeneous cataly-

sis, the high temperature corrosion of metals, and materials engineering (Cracow). Defect structure and equilibria, diffusion, electrical conductivity, and the magnetic properties of transition metal oxides, as well as the segregation in solid solutions and reactions in solid state also being investigated.

Equilibria and binary and ternary diagrams of transition metal oxides are under study in Szczecin and Cracow, and those of alkaline earth phosphates in Wrocław. Investigations into the synthesis and structure of mixed oxide systems, important from the point of view of high temperature superconductivity, have been undertaken.

Physical and structural chemistry studies on solids are being carried out in Wrocław, where the crystal structure and magnetic properties of uranium compounds, intermetallic compounds, ferroelectrics and other solids are being investigated.

The synthesis and study of physical properties of nitrides, metal hydrides, intercalated chalcogenides and fullerenes are being carried out in several laboratories.

## Physical chemistry and related fields

Theoretical chemistry was founded in Poland at Cracow in the 1950s under the leadership of Kazimierz Guminski (1908–1983), and at the Jagiellonian University, and also in Warsaw under Włodzimierz Kolos (1928–1996). Both centres very quickly gained an international reputation, the Cracow centre for its studies of the electronic structure of  $\pi$ -electron molecules and transition metal complexes, as well as molecular vibrations; the Warsaw group in very accurate calculations of the electronic structure of small molecules (Kolos and his student Lutosław Wolniewicz, Torun). Meanwhile, other centres began research in theoretical chemistry (Torun, Wrocław, Poznań) as well in as smaller places (Lublin, Katowice, Łódź) and other scientific pioneers appeared (who were often the students of the above-mentioned founders). The results of the joint efforts often represented the state of the art in the following areas: the modern theory of intermolecular interactions and molecular properties, the most accurate calculations for small systems, including a determination of the mass of the neutrino, muon-catalysed fusion, electronic correlation in atoms and molecular vibrations, efficient algorithms for protein structure prediction, global optimization algorithms and the development of efficient methods in density function theory, etc.

Studies on the application of correlation analysis in organic chemistry (solvent and substituent effects on physico-chemical properties) should also be noted (Warsaw, Poznań, Cracow). Some contribution to the theory of aromaticity (Warsaw) should also to be mentioned here.

Equilibrium and nonequilibrium thermodynamics, as well as thermochemistry have been developed in Warsaw, Cracow, Łódź, Gdansk and Wrocław. These relate, among others, to diffusion in liquids, the theory of charge transport in metals, diffusion in adsorbed layers, the thermodynamics of associated liquids, and physical chemistry studies of metal hydrides under high pressure. This embraces both the synthesis of various hydrides and determinations of the thermodynamic characteristics of systems under high pressure. The results concerning the thermodynamics of solutions and fused salts which were obtained by means of electrochemical methods (ionic equilibria and acid-base interactions) should also be mentioned here.

The discovery of the hanging mercury drop electrode, stripping voltammetry and chromatopolarography (the first amperometric detectors for liquid chromatography) were made in the school of electrochemical studies founded by Wiktor Kemula in Warsaw. Electrochemical investigations have also been carried out in Łódź, Wrocław, Poznań, Cracow and Gdansk in the field of the structure of electrolyte solutions, including nonaqueous solutions and fused salts, both inorganic and organic, the structure of double layers, the kinetics and mechanism of electrode processes, corrosion, electrochemical sources of energy, modified electrodes (polymeric electrodes in particular), organic electrosynthesis and electroanalysis, as well as in the exploration of fused carbonate fuel cells and a recognition of the kinetics and mechanisms of electrode processes in the electrolysis of aluminium and magnesium. Polish physicochemists have a long and well-established tradition in the study of interfaces. A number of institutes at the universities and in the Polish Academy of Sciences have been founded (in Cracow, Warsaw, Wrocław, Gliwice, Poznań and Łódź). At the same time, five applied chemistry research institutes and four industrial laboratories have been organized (Warsaw, Kędzierzyn-Koźle, Puławy and Cracow). Fundamental and applied research has been developed which led to the industrial application of new catalytic processes. Amongst other subjects, the selective oxidation of hydrocarbons, the synthesis of sulphuric acid, synthesis of ammonia, hydrogenation, processes of refining, chemistry of zeolites catalysts, combustion of pollutants are being studied. Investigations into the applications of quantum chemical methods in catalysis have also been carried out. Novel efficient catalysts were developed for industry.

Research into surface and colloid chemistry is being carried out in Cracow, Lublin, Wrocław, Poznań and Łódź. The main achievements in this area are related to the development of the convective diffusion theory of colloid transport, the formulation of a new localized adsorption model for a description of the kinetics of ad-

sorption of macro molecules, development of a unified theoretical description of adsorption, description of the electrokinetic phenomena in disperse systems and the synthesis of a new class of biodegradable nonionic surfactants (dioxanes).

The rapid development of physicochemical studies in material science (Wroclaw, Warsaw, Poznan, Lodz and Gliwice) should also be mentioned here. This relates both to the search for new materials and studies on their physical properties important in practice. One should also mention here the results of investigations into the electrical and optical properties of molecular crystals and composite materials, novel photoactive materials, the recording of optical information, the spectroscopy of highly conducting organic materials and nonlinear optical properties. Results obtained from research on reticular doped polymers and plasmic polymers should also be mentioned here. In Warsaw, novel liquid crystalline materials were elaborated and applied in practice. A rich family of ferroelectric crystals were discovered which were based on halogenoantimonates and bismuthates, and important results were obtained in the field of magnetic materials (Wroclaw). This field embraces among other things semiconducting magnetics (Warsaw), permanent magnets based on rare-earth compounds, thin magnetic films (Poznan), and magnetic properties of a variety of uranium compounds which appeared to be interesting from the physical point of view (spectacular ferromagnetic properties of  $\beta$ - $\text{UH}_3$ ; Wroclaw). A contribution to the investigations into various types of intermetallic rare-earth compounds (Wroclaw, Cracow and Katowice) and magnetic nanomaterials (Warsaw and Poznan) should also be emphasized. Recently, a number of new molecular ferro- and antiferromagnetic materials were synthesized and explored with respect to their physical properties and low temperature magnetism (Wroclaw).

In structural studies, a special position is occupied by the hydrogen bond research which is being carried out in Wroclaw, Poznan, Warsaw, Cracow, Lodz, Gdansk and Szczecin. This relates to the theory of vibrational spectra, infrared continua, polarized transmission spectra, isotope effects, charge distributions and proton transfer in hydrogen bonded molecules, and numerical band shape analysis and dynamics of hydrogen bonded systems. Special attention is being paid to the strongest quasi-symmetric bridges such as those in protonated proton sponges. Resonance methods, namely NMR (Warsaw, Cracow, Poznan—structural application of nitrogen magnetic resonance, dynamic aspects, both theoretical and experimental) and ESR and NQR (Poznan, Wroclaw—application to hydrogen bonded solids in particular) have been developed.

A rapid development of almost all branches of crystallographic studies began in the 1970s. This relates to structural studies on such systems as

intermetallic alloys, metalloorganic and complex compounds, organic and biologically active compounds (including proteins). The results that were obtained in studies of disordered structures, phase transitions, liquid crystals and hydrogen-bonded systems should be mentioned here. These achievements were made possible due to, among others things, the development of modern facilities (e.g. the KUMA automatic four circle diffractometer with CCD detector).

In the field of radiation chemistry which was developed in Lodz, Warsaw, Wroclaw and Siedlce, results were obtained concerning the description of excited states and migration processes in irradiated materials, including quantum mechanical electron tunneling, low temperature pulse radiolysis, the radiation chemistry of polymers and free radicals, computer simulations of radiation and modelling of the solvated electron.

During the inter-war period, three important names in the field of photochemistry and photophysics should be mentioned: Wiktor Kemula, and the physicists Stefan Pienkowski (1883–1953) and Aleksander Jablonski (1898–1980). At Warsaw University, Pienkowski set up a well-known school of photoluminescence studies where a number of significant discoveries were made: independence of luminescence spectra of excitation energy, the concept of the fluorescence centre, an exploration of the anisotropy of adsorbed molecules and above all, both the discovery of the metastable excited state and the publication by A. Jablonski of a subsequently well known energetic diagram which described spectra and photoluminescence kinetics.

In Gdansk, a solvatochromic method of dipole moment determination in excited state was elaborated, in Warsaw donor-acceptor (CT) complexes in gas phase and the kinetic rules of photophysics of CT complexes were discovered. The presence of twisted conformations in the excited state (TICT states) was explained for molecules containing electron donor and acceptor fragments. The existence of such states was confirmed in a number of experiments. In other studies, direct excitation to the triplet state in the presence of heavy atoms or paramagnetic compounds was demonstrated. The phenomenon of photoinduced double proton transfer was discovered. In Cracow, the theory of electron transfer and the kinetics of elementary photophysical processes was extended. In Poznan, studies of photochemical reactions for biologically important molecules are being carried out. In Wroclaw, B. Jezowska-Trzebiatowska initiated intense studies on the spectroscopy and luminescence of coordination compounds. Among other things, several new laser-active materials based on lanthanide compounds were discovered. The recent contribution of Polish physico-chemists to the spectroscopy of single molecules, arising from close international cooperation, should also be noted.

## Organic chemistry

Early research maintained links to the pre-war studies. Jerzy Suszko (1895–1972, Poznan: quinine alkaloids), Osman Achmatowicz (1899–1988, Lodz, later Warsaw: strychnine, Lycopodium alkaloids), and Zofia Jerzmanowska (Lodz, flavanoids) were all involved in the isolation and structure of natural products, Edwin Plazek (Wroclaw) was involved in the chemistry of pyridine and Tadeusz Urbanski (Warsaw) developed the chemistry of nitrocompounds and explosives. New researchers gradually took the lead: Jan Michalski (Lodz) extensively developed the chemistry of organophosphorus compounds, Henryk Kuczynski (1909–1991, Wroclaw) and Witold Zacharewicz (Torun) led the foundation of terpenoid chemistry and Maciej Wiewiorowski (Poznan) developed the field of lupin alkaloids.

The next generation, currently active, has broadened further the fields of research. This has been connected to the rising interest in scientific investigations in general and with the growing availability of new instrumentation. In addition this has also been connected with an expansion in international cooperation. As a result, new ideas and new subjects have been developed.

### What are the main lines of organic chemistry research in Poland now?

New methods of organic chemistry: nucleophilic substitution in aromatic nitro compounds (Warsaw), two-phase reactions (Warsaw), oxidation of organic compounds (Wroclaw), and new stereoselective syntheses (Warsaw, Lodz and Wroclaw). The chemistry of natural products: isoprenoids (Warsaw, Bialystok), carbohydrates (Warsaw, Gdansk) amino acids, peptides (Wroclaw, Gdansk, Warsaw, and Opole), alkaloids (Warsaw, Poznan), antibiotics (Gdansk), porphyrins (Wroclaw). Nucleic acids (Poznan), nucleotides (Lodz), organo-phosphorus and -sulfur chemistry (Lodz, Wroclaw and Lublin), organoboron chemistry (Torun), organosilicon chemistry (Lodz, Poznan and Gdansk), chemistry of heterocycles (Gliwice, Lodz and Cracow), supramolecular chemistry (Warsaw). High pressure methods are studied in the synthesis of organic compounds (Warsaw).

Two large projects are underway in Warsaw: reactions in catalytic two-phase systems and 'vicarious nucleophilic substitution' have been carried out. The chemistry of the thioacids of phosphorus (thiopyrophosphates, substitution reactions of thiophosphates) was developed in Lodz, where substantial contributions have been made to the chemistry of phosphorus(III) compounds and to optically active sulfur(IV) acids. Organic syntheses based on amino acid-derived aldehydes were expanded upon in War-

saw. New oxidation methods of aromatic compounds have been introduced in Wroclaw. New syntheses of amines based on phosphoamidites were studied in Lodz. The structures and syntheses of the first sulfur atom-containing alkaloids were studied in Warsaw. The structures of several complex polyene macrolide antibiotics (Gdansk) have been disclosed. Several significant results have also been achieved in the synthesis of natural products: new approaches to marine sterols and vitamin D-type compounds (Warsaw), new porphyrins (Wroclaw), two general (*de novo*) approaches to monosaccharides (Warsaw), and  $\beta$ -lactam synthesis (Warsaw). In nucleoside chemistry, the contributions of Łódź (chemistry of nucleoside esters with phosphorus thioacids, synthesis of enantiomeric phosphoric acid containing isotopes of oxygen) and Poznan (Markiewicz's reagent in nucleoside chemistry) should be mentioned.

## Analytical chemistry

The reconstruction of educational institutions and industry after the Second World War promoted the development of modern analytical techniques. Wiktor Kemula (Warsaw), developed different variants of voltammetry, in particular pioneering work on chromatopolarography (1953), and anodic stripping voltammetry (1958). Janina Swietoslawska (Warsaw) introduced mathematical methods into spectrophotometry (1952), long before the importance of chemometry was recognized. Bogdan Kaminski (Cracow), Janina Opienska-Blauth (1895–1987) and Andrzej Waksmundzki (Lublin) created a basis for the further development of chromatography. Jerzy Minczewski (1914–1995) (Warsaw) introduced modern approaches to inorganic trace analysis. Zygmunt Marczenko (Warsaw) developed the application of organic reagents for the separation and spectrophotometric determination of metals and metalloids. All of these scientists have created scientific schools that are still active and are well recognized abroad.

The development of analytical chemistry exerted a considerable influence on research topics in Poland. In chemical techniques, research on organic reagents continues, including derivative spectrophotometry and separation by flotation and multicomponent complexes in spectrophotometry (Warsaw). The original technique of thiomercurometry was developed by M. Wronski (1926–1996) (Lodz). The iodine–azide reaction was applied in many methods which are of theoretical and practical significance (Poznan).

Significant achievements were noted in stripping voltammetry, the application of ultramicroelectrodes, ion-selective electrodes (Warsaw, Poznan and Lublin). New electrochemical instrumentation was developed (Cracow). Biosensors based on electrochemical detec-

tion have been developed (Warsaw).

Thin-layer chromatography, both gradient and pressured techniques, was developed (Lublin, Warsaw and Katowice). In HPLC, various stationary phases were investigated (Lublin). Fundamental theoretical studies on the relationship between retention data and the molecular structure of the chromatographed substances are being carried out (Gdansk, Torun and Lublin). Novel results have been obtained in trace analysis using ion-exchange chromatography with a theoretical approach to resolution, as well as in the modification of anion exchangers with sulphonated organic reagents (Warsaw). Students of Edmund Kozlowski (1932–1995, Gdansk), where head space analysis was studied, have been carrying out extensive investigations on the determination of organic pollutants in the environment, in particular on sampling and sample treatment. Liquid crystals were applied as stationary phases (Warsaw). New types of detectors have been developed (Cracow).

Atomic spectroscopy has been intensively applied to trace analysis (Warsaw). Particular achievements were associated with the study of interference effects and with correcting them by methods of standard addition and subsequent dilution, as well as with the application of chemical modifiers to atomic absorption spectrometry. Research on the use of microwaves in analytical spectrometry is also ongoing (Poznan). Spectroscopic techniques are being also applied to the study of metal speciation (Warsaw and Poznan).

Flow methods, with various detection methods and on line sample pretreatment methods are being developed for speciation, environmental and clinical analysis (Warsaw). Chemical sensors, including potentiometric, amperometric, piezoelectric, ISFETs and semiconductors are being developed for various methods of routine chemical analysis (Warsaw). Numerous chemometric methods have been developed for structural analysis, multicomponent analytical procedures, the optimization of analytical procedures and for data processing (Cracow, Rzeszow). The environmental monitoring of air and water pollution is being developed and carried out (Warsaw, Poznan). Research has been initiated into cooperation with the Environmental Specimen Bank (Warsaw). Several certified reference materials have been developed on the basis of international interlaboratory studies (Warsaw, Cracow).

## Polymer chemistry and technology

Polymer chemistry and polymer technology in Poland have their roots in the early 1930s, when the basic research on polyaromatic compounds (Wojciech Swietoslowski and Dyonizy Smolenski) and applied research on plastic and rubber technology was developed. This area includes the original technology for

synthetic rubber production (KER) which was later transferred to the USA.

After World War II, a number of centres for polymer science emerged. In Lodz, the physical chemistry of synthetic fibres was developed (Antoni Boryniec, Eligia Turska) as well as the chemistry of polyamides and polysiloxanes (Stanislaw Chrzczonowicz, Zygmunt Lasocki). Ion-exchange resins were studied in Wroclaw (Tadeusz Rabek, J. Lindeman), whereas the Warsaw Technical University group (S. Porejko) concentrated on polymer synthesis. In the University of Torun (Antoni Basinski), research in the area of the physical chemistry of polymers and colloids was carried out. In the early 1950s the Institute of Plastics was created (M. Wajnyrb, J. Pochwalski), which later became a part of the Industrial Chemistry Research Institute. In the latter, several new technologies were developed, including an original process for polyacetal polymer production.

Lodz remains the major centre for polymer chemistry and technology in Poland with its Center of Molecular and Macromolecular Studies of the Polish Academy of Science, Institutes in Lodz Technical University and several industrial laboratories. These groups cover a broad range of research fields, including theories of ionic ring-opening polymerization, the electric properties of polymers, and elastomer properties. In the Warsaw Institute of Technology, polymerization with metalloorganic catalysis and solid polymer electrolytes are being studied. The theory of fibre formation has been formulated by a group from the Polish Academy of Science Institute. In Gliwice, Szczecin, Wroclaw and Zabrze, degradable and biomedical polymers are under study, while in Opole, olefin polymerization is being investigated. Applied research in the area of polymer technology is being carried out, not only in the Industrial Chemistry Research Institute in Warsaw, but also in a number of industrial laboratories, namely in Plock, Osiecim, Blachownia and Tarnow.

## Chemical technology

The Polish chemical industry has a long history, dating back to the beginning of the 19th century. Parallel to its formation and growth was the development of chemical technology—a science which studies the processes and the products. Many outstanding Polish scientists have made significant contributions to its progress.

Initially, the chemical industry in this region was based exclusively on local raw materials, such as the rock salt used for fabrication of soda, the sulfur for powder and sulphuric acid productions, pyrite for sulphuric acid production, etc. The beginning of the exploitation of the crude oil resources in the Ciscarpatian region and the development of the fractional distillation technique for the production of kerosene fractions for lighting pur-

poses by Ignacy Lukaszewicz in the middle of the 19th century initiated the oil refinery upgrading processes in this area, which were later developed by Stanislaw Pilat (1881–1941). At the end of the 19th century and early in the 20th century the sugar industry was rapidly developed, in addition to the paper industry, the tanneries for leather production, and fats and oils processing, etc. The growing sulphuric acid production has often been linked to the manufacture of superphosphate. Numerous gas works produced town gas by the coal degassing process. Coal coking, based on the rich coal reserves, developed rapidly.

Between the two world wars, rapid progress was made in manufacturing paints, lacquers and varnishes, cosmetics, pharmaceuticals and synthetic dyes, etc. The separation and utilization of aromatic and heterocyclic components from coal tar was developing, which was also due to research on coal degassing processes, the physicochemical characteristics of the coal tar, etc. that was carried out by Wojciech Swiętoslawski. However, at that time the chemical industry was not very significant. To change this situation, a government programme of modernization and expansion was announced. Particularly important in this was the role of Ignacy Moscicki, known from his earlier innovations and achievements in Switzerland and Poland concerning the formation and properties of the electric arc, the synthesis of nitrogen oxides and the production of nitric acid and hydrogen cyanide. It was that time that the large Chorzow Works was modernized and new products were added to its output (carbide, calcium cyanamide, nitrogen fertilizers, etc.). A large, completely new chemical factory was built near Tarnów (Moscice) to produce ammonia, nitric acid and ammonium nitrate (by the methods of Tadeusz Hobler, 1899–1975), etc. Both factories were headed by Eugeniusz Kwiatkowski (1888–1974) a talented manager. Altogether, almost 1000 chemical factories existed in Poland in the inter-war period. It is worth mentioning that among them was a unit producing synthetic polybutadiene rubber from ethanol ('KER', Dębica), being among the first in the world. During the Second World War this technology was passed to a US producer by the inventor (W. Szukiewicz).

The last 50 years was a period when the chemical industry, which was largely destroyed during the war, was rebuilt and expanded. At present, the industry employs over 230 000 people and has a stable share of nearly 10% in the sales of all of industry. It produces practically all the basic chemicals and almost all modern sorts of plastics, fibres, surfactants, rubber and fertilizers. It includes two large modern refineries (Plock, Gdansk) and several smaller ones, one large petrochemical centre (Plock—olefins, PE, PP, ethylene oxide, aromatics, etc.), several large companies with

diversified, mainly petrochemical, production (Kedzierzyn-Kozle—ammonia, nitric acid, urea, nitrogen fertilizers, oxo alcohols, phthalates, formaldehyde, etc.; Pulawy—nitrogen compounds and fertilizers, cyclohexanone, caprolactam, etc.; Tarnow—nitrogen compounds and fertilizers, chlorine and derivatives, acetylene, hydrogen cyanide, acrylonitrile, cyclohexanone and caprolactam, PVC, polyacetals and other polymers, etc.; Oswiecim—synthetic rubber, polystyrene, PVC and other polymers, acetaldehyde, acetic acid and esters, chlorine and derivatives, etc.; Wloclawek—nitrogen compounds and fertilizers, PVC, etc.; Police—sulphuric acid, extractive phosphoric acid, nitrogen-phosphorus fertilizers, etc.; Bydgoszcz—polyurethanes, epichlorhydrine, other chlorocompounds, dyes, etc.; Torun, Gorzow and Lodz—respectively, polyester, polyamide and polyacrylonitrile chemical fibers) and many other companies. Some installations are of the highest world standard (licensed oxoalcohols, hydrocracking and many others, as well as own caprolactam, low-energy consuming large ammonia unit based on autothermic catalytic reforming and partial oxidation of natural gas, etc.).

The process of modernization, restructuring, privatisation and development of the chemical industry is now in progress, supported by technological research in about 20 research institutes and centres (among them the oldest institute in Warsaw, created in 1922 by Ignacy Moscicki, presently called the Industrial Chemistry Research Institute), numerous faculties of chemistry at the universities and technical universities (polytechnics), and the scientific institutes of the Polish Academy of Sciences. As a result of their previous R&TD activity, this industry has developed a number of original technologies, some of which are now on the international market (sulfur granulation, sulfuric acid and oleum, cyclohexanone, caprolactam, bisphenol A, trioxane, dioxolane and polyoxymethylene, epichlorhydrine, nonylphenol, and some others). A process developed in Poland for making cyclohexanone from benzene via cyclohexane, known under the trade mark 'CYCLOPOL', has been licensed to many countries and is the basis for a substantial proportion of global cyclohexanone production.

The development of individual technologies was possible, due, amongst other factors, to the progress in theory and research concerning unit operations and processes. Fundamental and applied chemical engineering research initiated in Poland by Tadeusz Hobler were developed successfully by Janusz Ciborowski (1918–1986), Stanislaw Bretsznajder (1907–1967) and others, at several technical universities and at the institute of the Polish Academy of Sciences.

The carefully selected and now gradually introduced model of the ecology-oriented strategy of sustainable

development of the chemical industry is based in this country, similarly as in other countries, on programmes such as Clean Technologies, Responsible Care philosophy and obligations, Product Stewardship practice, 'cradle-to-grave' policy, etc. As the chemical industry is a particularly science-dependent and technology-based kind of industry, it has become clear, that chemical technology is a fundamental tool for the realization of an environmentally-friendly strategy. Bearing this in mind, The Chemical Technology Congress held in Wroclaw in 1997 named the main priorities in technological research areas concerning Process and Product Research and Technological Development. Among them are: all possible routes to increase selectivity (catalysts, optimization of parameters, recycling of by-products, etc.), to limit energy consumption (heat-exchange and utilization of heat, exothermic processes replacing endothermic, integration of the processes and operations, such as combinations of reactions via separation or heat transfer, a gradual replacement of distillation and cryogenic techniques in the separation of mixtures by adsorption and membranes, etc.), to limit, utilize and neutralize wastes, emissions and discharges (zero-waste and low-waste technologies, closed cycles, recycling and re-utilization, safe waste processing and disposal, etc.), to limit feedstock consumption and materials consumption in auxiliary operations (water treatment, steam production, etc.), to develop processes based on alternative hydrocarbon and non-hydrocarbon raw materials, some refinery processes (hydrotreatment of every kind,  $C_5$ - $C_6$  isomerization, alkylation on solid acids, etc.), some petrochemical processes (olefins production, chemistry and technology of  $C_1$ , methods of direct transformation of low alkanes, selective oxidation, hydrogenation and isomerization, polymerization on single-site catalysts, etc.), zeolite chemistry, biotechnology, the enrichment of poor mineral raw materials, among others. Priorities in more fundamental studies include kinetics, macrokinetics, mechanisms of reactions and of processes, dynamics of the system reagent-catalyst-reactor, multifunctional reactors, organization of processes, nonstationary conditions, new methods in modelling and process design, etc. The accepted priority programme also contains the main fields of research to develop advanced products and materials of various molecular and supramolecular structure and functionality (superengineering polymers, thermostable, nonflammable, biocompatible, biodegradable, composites, superabsorbents, materials for optoelectronics, adhesives, carriers for drugs, medicines or fertilizers, chemical fibres, special ceramics, catalysts, carriers, adsorbents, indicators, sensors and many others).

In all research areas, the ultimate aim is to improve existing or to develop new more advanced technolo-

gies, operations, equipment and products, environment-friendly, with low energy and feedstock consumption.

Various research centres are carrying out multidirectional investigations on chemical methods, catalysts, technology and engineering for environmental protection, on water treatment and waste processing, recycling and reutilization of by-products, waste and post-consumer products, on various syntheses of fine chemicals (specialities) and intermediates, biologically active compounds, on industrial analytical methods, on integrated computer-assisted control systems, and many other subjects.

## Organization of chemistry research and education in Poland

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There are 22 chemistry departments at 11 universities and 11 technical universities. Chemistry research is often present at Higher Schools of Agriculture, Medicine and Economy (altogether 24 chairs or institutes). There are eight institutes of the Polish Academy of Sciences which are involved in research in various aspects of chemistry. Apart from these institutions, there are 12 institutes working for industry which carry out research in chemistry—mostly applied chemistry.

Within the Polish Academy of Sciences there are two committees which collect members of the chemical community—Committee of Chemistry with the chairman Prof. Bogdan Marciniak, and Committee of Analytical Chemistry with the chairman Prof. Adam Hulanicki.

The Polish Chemical Society (founded in 1919) has more than 3000 members and every year it organises annual congresses with over 1000 participants presenting the results of research from all branches of chemistry and also many specialized symposia.

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