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ACADEMICIAN CRISTOFOR I. SIMIONESCU – FOUNDER OF THE ROMANIAN SCHOOL OF NATURAL AND SYNTHETIC POLYMERS

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This paper presents the main contributions of academician Cristofor Simionescu to the Romanian education and research in the field of natural and synthetic polymers. There is much evidence that the school created by professor Simionescu remains a sustainable one, with remarkable contributions to the preparation of specialists for research and education domains. The paper provides evidence that the scientific researches coordinated by professor Simionescu were approached at the same level as the ones developed at world level. Many of them are currently being continued and developed by former coworkers, active both in the country and abroad.

Keywords: natural and synthetic polymers, education, research, school founding and development.

One of the main tendencies of the contemporary world is that of forgetting the past, people disregarding the warning expressed by a reputed scholar:

"Man cannot shape future without a keen awareness of one's present condition, and of the limitations of one's past" [Ernst Cassirer (1874–1945), *Eseu despre om* (*Essay about man*, Humanitas, Bucureşti, 1994] – or, in Leibniz's (1646–1716) words: "To leap forward, one has first to step back".

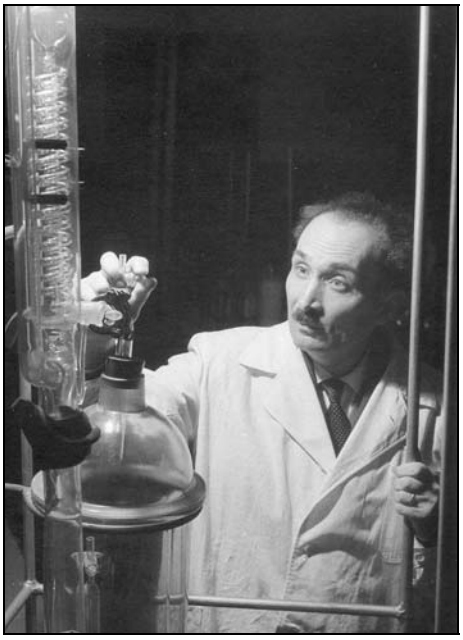
"There is not only one future, but there are many futures – while there is only a past. The future is included in the past and commissioned by it" [Nial Ferguson (1964), *Civilizația:Vestul şi restul* (*Civilization: the West and the rest*), Polirom, Iaşi, 2017].

Not accidentally, the American Chemical Society proposed the creation of a foundation entitled "Chemical Heritage", for capitalizing on cultural heritage in the field of chemical science.

In this context, when we commemorate ten years since Professor Cristofor Simionescu, member of Romanian Academy, passsed away, his scientific contributions remain topical and durable for the creation of the Romanian school of natural and synthetic polymers.

The first aspect I want to evoke concerns the Romanian school of **Natural Polymers – Pulp and Paper**.

The first attempt to set up a department in this field was done in 1948, in Bucharest, but it failed. That is why, academician Cristofor Simionescu, associate professor at that time, received the mission to create, in Iasi, the Department of **Technology of Pulp and Paper**. Together with one of his colleagues, professor Vasile Diaconescu, he succceeds in doing this under the most difficult conditions, inherent to any beginning, and not only. Later on, in 1955, the Department is renamed **The Technology of Pulp, Paper and Rayon Fibers**. Nowadays, as a result of the industrial evolution in Romania, the title of the Department is **Paper Engineering**, as it is meant at providing the necessary high-educated specialists for the Romanian industry [1].



Professor Simionescu in his laboratory, around the 60'ies

In paralell with the organization and development of the educational system, the necessary concern of training specialists for the teaching staff and equally for research activities followed. Thus, having professor Simionescu as PhD supervisor, the first PhD theses were elaborated and defended, such as: *Researches in the field of cellulose fractionation* (Elena Calistru – 1958); *Researches in the field of reed prehydrolysis* (Dorel Feldman); *Researches of applied chemistry in paper technology*

(Emanuel Poppel – 1958); *Studies of carboxymethylcellulose and its applications in paper industry* (Nicolae Asandei – 1959); *Researches in the field of cellulose destruction* (Gheorghe Rozmarin – 1963), their authors becoming in time reputed professors of the department.

The Humboldtian synergy between educational and research activities has become a characteristic of the school created by Professor Simionescu, actively manifested since its beginnings. Extensive investigations have been devoted to the chemistry of wood and annual plants, performed by interdisciplinary teams from the "Petru Poni" Institute of Macromolecular Chemistry and the teaching staff of the Departament. The studies carried out have enabled an impressive volume of data, included in the following monographs:

• **Cristofor Simionescu**, Margareta Grigoraş, Agata Cernătescu-Asandei, **Chimia lemnului din România [Chemistry of wood in Romania**] (Editura Academiei Române, Bucureşti, 1964 – which received the "Nicolae Teclu" Prize of the Romanian Academy),

• **Cristofor Simionescu**, Margareta Grigoraş, Agata Cernătescu-Asandei, Gheorghe Rozmarin, **Chimia lemnului din România: Plopul şi salcia [Chemistry of wood in Romania: The poplar and the willow]** (Editura Academiei Române, Bucureşti, 1973);

• **Cristofor Simionescu**, Gheorghe Rozmarin, **Chimia stufului [Chemistry of reed]** (Editura Tehnică, Bucureşti, 1966);

• **Cristofor Simionescu**, Viorica Rusan, Valentin Popa, **Chimia algelor marine [Chemistry of seaweeds]** (Editura Academiei Române, Bucureşti, 1974 – which received the "Gheorghe Spacu" Prize of the Romanian Academy).

The importance of these contributions should be outlined from several perspectives, such as: (1) originality of the approached subjects in relation to what was happening at world level; (2) establishment of a data bank permitting to know the potential and biomass reserves, with implications in capitalization; (3) recording of the evolution of forest vegetation in relation to the environment, once known that trees include in their morpho-anatomic structure the influence of the environmental factors over time; (4) study of annual plants and reed has provided data for industrial applications that have been subsequently developed in Romania; (5) mono- and macro-marine algae are currently and hopefully viewed as renewable raw material resources for biofuels and bioproducts.

Another interesting field of research, courageously approached at that time was that of plant tumors, many papers being published between 1956–1968 (analyzing their induction, characterization, inhibition, antioxidants). In this respect, the presence of vegetal tumors was identified in some woody species (such as plum), that were

chemically characterized. The chemical changes observed in the lignin content ascertained the idea that the tumoral process is propagated through radical reactions, as in the biosynthesis of aromatic polymers.

Academician Simionescu at the age of 40 (1960)

Another discovery was that tumors can be induced by the *Agrobacter tumefaciens* bacterium, subsequently used to infect plants, such as tomato and sugar beet. The studies to follow were devoted to the possible inhibition of vegetal tumors growth by using the following antioxidants: **hydroquinone, gallic acid** and its **derivatives (propyl-, ethyl-, octyl- and dodecyl gallate), butylhydroxyanisole, norhydro-guaiaretic acid**, for the *Solanum lycopersicum* plant infected with the crown-gall tumor.

Regarding the originality of these researches, worth mentioning is that, in the same period, **Denham Harman** (1916–2014) forwarded "the theory of free radicals to be applied in the process of human aging", published in 1956 in **Journal of Gerontology, 11(*3*), p. 290–300**. He considered that antioxidants could be a means of prolonging life and that such products can be beneficial in cancer chemotherapy and nutrition. These studies have now been developed in our department, 15 PhD theses being devoted to such topics.

An extensive cycle of papers has been dedicated over the years to the lignin chemistry, materialized, in a first stage, in the establishment of a structural formula for reed lignin (Ioana Anton – PhD thesis elaborated under the scientific supervision of academician Simonescu). Studies in this field continued with investigating the reactions of this polymer, the recognition of the contributions of Romanian researchers being materialized in their inclusion in programs with national and international participation (**Eurolingin** and **Ecobinders**).

The chemical modification reactions of natural polymers have also been an area dealt with in depth, materialized in numerous fundamental and applicative contributions. At present, the grafting reactions of natural hydrophilic polymers have gained a great scientific significance, as they confer hydrophobicity to their processing in blends with synthetic polymers, with the aim of producing composite materials.

In a research program funded during the global oil crisis (1973), the chemical and energetic potential of vegetal biomass was studied as a possible renewable source of raw materials. Based on the studies carried out in that period, a complex model for complex biomass valorization was developed (**Cr. I. Simionescu, V. Rusan and V. I. Popa, Options concerning phytomass valorification, *Cellulose Chemistry and Technology,* 21 (*1*), 3–16, 1987**), used to design and build up a micropilot station at the "Petru Poni" Institute of Macromolecular Chemistry of Iasi. In time, researches have been developed both in Romania and abroad, the concept of complex valorization being defined as **biorefining**, namely at obtaining energy and bioproducts through the fractionation of the vegetal biomass. The term appeared in 1990, in analogy to what was happening in an oil refinery, being defined by the International Energy Agency as a sustainable biomass processing with the possibility of obtaining a wide spectrum of bioproducts (food, chemicals, materials) and bioenergy (biofuels, electric and/or thermal energy).

Another large-scale program tackled the issue of synthetic papers. In this case, too, rich scientific information has been accumulated in publications, patents and applicative tests, up to industrial level, for some paper grades. Finally, based on the results of the researches, a micropilot plant was designed and built up.

The international recognition of the school of Iasi was confirmed by the 13 International Symposiums on **Cellulose chemistry and technology**, organized under the chairmanship of academician Cristofor Simionescu, starting with the year 1961. At the symposium held in 1965, a group of the scientists of the field entrusted academician Simionescu with the task of setting up the journal **Cellulose Chemistry and Technology** (www.cellulosechemtechnol.ro), issued by the Romanian Academy Publishing House. The journal has been unterruptedly issued for 50 years, even under the most difficult conditions, enjoying the support of the

members of the editorial team everywhere, well-known scientists, not only in the field of chemistry and structure of chemical components of wood, but also in synthetic polymers.

As known, the scientific contributions of academician Cristofor Simionescu have been appreciated both at national and international level. In the field of pulp and paper, worth mentioning is the awarding of the Jubilee Medal of American Chemical Society, which has a Division for cellulose, in 1976, on the occasion of the celebration of the USA bicentenary. The medal was awarded to 20 world-renowned personalities of the field who were invited to contribute with review-papers included in a special volume published on this most special occasion. The medal was handed to Academician Simionescu at the Romania-USA Polymer Seminar, held in Iasi in 1976, a manifestation that can be also considered a recognition of the Romanian school in the field of polymers.

The interest of academician Cristofor Simionescu in synthetic polymers has been described in the conference entitled **Aspects in the field of huge molecules**, presented in The Aula of the Polytechnic Institute of Iaşi, on March 16, 1948. After the reform of education in 1948, the Faculty of Industrial Chemistry of the Polytechnic Institute of Iaşi was organized in two sections: Inorganic Industries and Organic Industries. Later on, starting with the academic years 1952/1953 and 1953/1954, the discipline **Macromolecular chemistry** which, between 1960–1962, became **Macromolecular compounds**, was taught. Study of the **Technology of macromolecular compounds** begins with a separate curriculum, in the academic year 1962/1963, also at the initiative of academician Cristofor Simionescu. In this case, as well, the educational concerns were accompanied by the scientific ones, among which mention should be made of the following:

- Synthesis and polymerization (copolymerization) of new monomers;
- Mecanochemistry of polymers;
- Photo- and semiconductor polymers;
- Plasmo-chemistry;
- Chemistry of multifunctional initiators;
- Electroinitiated polymerization;
- Macromolecular complexes with charge transfer;
- Polymers with very high molecular mass;
- Compatible and bioactive polymers, the origin of life;
- Biostructuration;

scientific areas to which many valuable contributions have been made.

In the field of synthetic polymers, worth mentioning is the elaboration of the four volumes of handbooks on macromolecular compounds:

1. **Cristofor I. Simionescu**, Cleopatra Vasiliu-Oprea, **Tratat de chimia compuşilor macromoleculari, vol. 1 (Handbook of macromolecular chemistry, vol. 1)**, Editura Didactică şi Pedagogică, Bucureşti, 1973, 693 p.

2. **Cristofor I. Simionescu**, Dorel Feldman, **Tratat de chimia compuşilor macromoleculari, vol. 2 (Handbook of macromolecular chemistry, vol. 2)**, Editura Didactică şi Pedagogică, Bucureşti, 1974, 256 p.

3. **Cristofor I. Simionescu**, Victor Bulacovschi, **Tratat de chimia compuşilor macromoleculari, vol. 3 (Handbook of macromolecular chemistry, vol. 3)**, Editura Didactică şi Pedagogică, Bucureşti, 1976, 482 p.

4. **Cristofor I. Simionescu**, Ion Negulescu, **Tratat de chimia compuşilor macromoleculari, vol. 4 (Handbook of macromolecular chemistry, vol. 4)**, Editura Academiei Române, Bucureşti, 1993, 482 p.,

to which one should also add: **Cristofor I. Simionescu**, Cleopatra Vasiliu-Oprea, Victor Bulacovschi, Bogdan C. Simionescu, Claudia Neguleanu, **Chimie macromoleculară (Macromolecular chemistry)**, Editura Didactică şi Pedagogică, Bucureşti, 1985, 460 p. and **Cristofor I. Simionescu,** Constantin Uglea, **Fracţionarea compuşilor macromoleculari (Fractionation of macromolecular compounds)**, Editura Academiei Române, Bucureşti, 1969, 693 p.

Many of the research fields initated by academician Simionescu have evolved either under his leadership or they have been creatively taken over by his coworkers. Some of these are to be highlighted. Thus, the researches in the field of mechanochemistry of polymers are remarkable, some of them being reviewed in the book: **Cristofor I. Simionescu** and Cleopatra Vasiliu-Oprea, **Mecanochimia compuşilor macromoleculari** (**Mechanochemistry of macromolecular compounds**), Editura Academiei, 1967, 344 p., translated into Russian and highly appreciated abroad.

Mention should be also made of the contributions in the field of photo- and semiconductor polymers, [**Cristofor I. Simionescu**, Mircea Grigoraş, **Poliacetilene (Polyacetylenes)**, Editura Tehnică, Bucureşti, 1987, 288 p.], a field of special actuality, materialized in the synthesis of some polymers used in the construction of computers and solar energy reception systems.

The reactions of modification of natural polymers, and especially those of obtaining cellulose drivatives, have opened the way to the creation of supports for the immobilization of enzymes and drugs. In this respect, different initiators and monomers were studied, to achieve controlled realease systems for drugs [2]. Such investigations were approached in the years ’70, when researchers such as **Robert Langer (1948)** from MIT began to develop systems based on modified polymers to be used as drug delivery systems for medical applications. Important aspects of the field of biocompatible and bioactive polymers were systematized in the monograph

entitled **Polimeri biocompatibili şi biologic activi [Biocompatible and biologically bioactive polymers]**, authored by **Cristofor I. Simionescu** and Valeria Gorduza, Editura Academiei Române, Bucureşti, 1980, 480 p.

One of the most dear fields of investigation initiated and coordinated by academiciam Cristofor Simionescu referred to the origin of life [(**Cristofor I. Simionescu**, Ferencz Denes, **Originea vieţii (Origin of life)**, Editura Academiei Române, Bucureşti, 1983, 110 p.], a domain approached at that time in important schools of scientific research worldwide [*e.g.*, **Sidney Walter Fox** (1912–1998), USA].

The team led by Professor Simionescu proposed a model which involved the synthesis of some precursors of the living matter from the possible constituents of the primary atmosphere of the earth under the conditions of cold plasma discharge. In these studies, such compounds have been evidenced and subsequently confirmed by the current researches, leading to the identification of the living matter precursors in the universe [3].

Recently, two astrophysician teams have identified prebiotic molecules in the vicinity of protostars similar to our Sun, in the early stages of evolution. Thus, the presence of **methyl isocyanate** involved in the synthesis of amino-acids and peptides was observed (Niels Ligterink-Leiden, Netherlands and Rafael Martin-Domench, Institute of Astrobiology, Madrid, 2017). Supernova SN 1987 ended violently in 1987 and, in the area where explosion occured, the formyl ion (HCO^+) and sulfur monoxide were identified (2017). The presence of some of the mentioned intermediates was also found in the products resulted from the decomposition – in cold plasma – of the mixtures of methane, ammonia and water, considered as model for the primary atmosphere of the earth [3].

All these constitute examples illustrating that the education and research projects founded by academician Cristofor Simionescu have never been conjuctural, instead they demonstrate his most clear and all-embracing vision over the whole domains of natural and synthetic polymers, so that the results attained appear as basic elements of a long-lasting, sustainable structure now substantiating important areas of common investigation, towards which renewed interest is being manifested in the scientific communities all over the world. Many of the reserach fields dealt with by Professor Simionescu have been taken over and are being successfully continued by his coworkers.

Attached to the school up to the sacrifice of his personal life, academician Simionescu firmly belived in its values and hoped it will live regardless of political interests, which made him to say:

“Ministers come and go, the laws of education are changing over shorter or longer intervals, the last one being always the most praiseworthy. Teachers come and go,

like all humans. But the school, in its most profound substance, must remain the fundamental institution of the state, withstanding circumstances." **(Cr. I. Simionescu, Gânduri V,/Thoughts V, 1993)**.

Laudatio for Professor Ştefan Procopiu, *Doctor Honoris Causa*
of the Polytechnic Institute of Iaşi – 1967

In the sustainable construction of the School of Natural and Synthetic Polymers, academician Cristofor Simionescu was supported by many of his coworkers who had joined him, both in moments of success and of difficulties; however, above all, the unconditioned support of his family should not be forgotten – especially that of the most distinguished lady, his wife – Natalia Simionescu.

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