

## To the 100th Anniversary of Birth of the Doctor of Chemical Sciences, Professor, Merited Scientist of the Russian Federation, Laureate of the State Prize of the USSR Alexander Alexandrovich Zhdanov (1923–2002)

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Alexander Alexandrovich Zhdanov, a world-class scientist and the biggest specialist in the area of organosilicon compounds, actively participated in the advent and development of organosilicon science and industry and made outstanding contributions to establishment of the chemistry of metallosiloxanes and organosilicon-organoelement polymers.

A.A. Zhdanov was born on January 26, 1923 in Moscow and received a comprehensive education in his family. His grandfather, a Moscow architect Georgy Alexandrovich Kaizer, instilled in him love for exact sciences, poetry, and German language, his mother, a physician Anna Georgievna Zhdanova, was a virtuoso pianist, and it was her gift as a set of reagents that discovered little Sasha the magic world of chemical transformations, and his uncle Yury Sergeevich Vasil'ev, a chemist, explained him phenomena occurring in simple chemical experiments. After completing his studies at gymnasium, in 1939 Alexander Alexandrovich entered the Moscow Mendeleev Institute of Chemical Technology and graduated from it in 1944. When completing his graduate work on the synthesis of artificial resins from orthosilicic acid ethyl ester under the guidance of Professor Anatoliy Pavlovich Kreshkov, Zhdanov became acquainted with organosilicon chemistry and forever linked his scientific activity with the synthesis and investigation of novel organoelement compounds and polymers containing not only atoms of silicon and oxygen but also of various metals.

His development as a chemistry scientist happened at the All-Russian Institute of Aviation Materials (VIAM) under the guidance and in close cooperation with the “father” of silicon chemistry Academician K.A. Andrianov. With the active participation of Zhdanov first heat resistant nonmetallic coatings based on aluminum powder-filled polyphenylsiloxane that are capable to withstand heating up to 450°C were prepared. The work was completed as soon as possible—the study of interaction of various hydroxyl-containing compounds of silicon with aluminum that began in 1947 allowed the start of the industrial production of the finished product already by 1950. In the course of these studies, he formulated basic ideas con-

cerning structural features of the ladder (polycyclic) polymers, a new class of organoelement polymeric compounds, metallosiloxanes, and proposed a simple and technological method for the synthesis of polyaluminumorganosiloxanes—the cohydrolysis of organotrichlorosilanes with aluminum halide.

Full-scale fundamental structural studies of poly-metallosiloxanes by various physicochemical analytical techniques were performed by Alexander Alexandrovich already at the Institute of Organoelement Compounds (INEOS) of the USSR Academy of Sciences founded by Academician A.N. Nesmeyanov in 1954. The data collected were summarized as a doctoral thesis entitled “Studies in the Area of Polyelementorganosiloxanes”, which he brilliantly defended in 1967. Since 1954, Zhdanov worked at INEOS for 48 years. In 1971, he headed the Laboratory of Organoelement Elastomers, and, in 1978, after the death of Academician Andrianov, assumed position of the head of the Laboratory of Organosilicon Compounds. Already in 1989, the team engaged in the study of metallosiloxanes was created under his guidance.

The instrument and equipment capabilities of the academic laboratory allowed Zhdanov and coworkers to carry out intense studies and to elaborate effective methods for the synthesis of both monomeric organometallosiloxanes, trialkylsiloxane derivatives of aluminum, titanium, tin, lead, antimony, vanadium, etc., and polymeric organometallosiloxanes containing aluminum, iron, cobalt and nickel. Other polyelementorganosiloxanes containing, along with Si and O atoms, atoms of other elements (B, Al, Ti, Sn, Ge, P, Fe, Co, Ni, etc.) in a chain and polymers with inorganic chains of molecules lacking silicon atoms in the backbone were also synthesized. Further studies resulted in the development of a new, very technological method for the synthesis of metallosiloxanes via the exchange decomposition of sodium silanates with metal halides. This rendered it possible to easily create initially the pilot and later industrial production of aluminum and iron siloxanes serving as efficient catalysts of various chemical processes and thermal stabilizers (polyironsiloxanes).

The role and importance of Zhdanov in the development of silicone chemistry in INEOS and the country in general can hardly be overestimated. He became the link or, as they said, the “drive belt” that joined together the flight of scientific thought of Academician Andrianov and the staff of the laboratory and institute and in collaboration with commissions, councils, and other various bodies. Zhdanov took upon himself all immense daily routine without regard to his own personal interests trying to free Andrianov from the scientific bureaucracy. Together they organized the Scientific Council on Synthetic Materials at the Presidium of the USSR Academy of Sciences that subsequently became a separate institution, the Institute of Synthetic Polymeric Materials (ISPM), in which Zhdanov, during the establishing period, was a deputy director. Largely thanks to his authority, the chemistry of silicone polymers became among the major research areas in ISPM.

Despite the perfect qualities and talent of Alexander Alexandrovich this own carrier had developed only after the death of Andrianov, when he was fully able to manifest himself as a completely independent scientist and talented experimentalist. Zhdanov brilliantly completed a long metallosiloxane epoch by the synthesis of single-crystal polyphenyl(cobalt)siloxane. Structure elucidation of this polymer set the vector for the whole area of metallosiloxane polyhedrons. Along with carboranes and ferrocene derivatives, polyhedral metallosiloxanes became a peculiar visiting card of INEOS. Zhdanov's studies laid the foundation not only for a huge variety of compounds of this type but also for stereoregular organocyclosiloxanes that until now have no analogs in silicone chemistry. Perhaps, these discoveries became a kind of gift of fate for that huge scientific and administrative work he performed holding various posts.

Zhdanov was a genuine flesh and blood of Andrianov's school—initially a pupil, then an associate, and, eventually, a follower of Academician Andrianov. He actively participated in the creation and development of organosilicon science and industry in the country and made an outstanding contribution to the advent of the chemistry of metallosiloxanes and organosilicon-organoelement polymers. The achievements of his half a century research were reflected in more than 500 articles; he owned about 200 USSR certificates of authorship and patents. For scientific achievements Zhdanov was awarded the government awards: the “Order of International Friendship” and medals “In Commemoration of the 100th Anniversary of the Birth of Vladimir Ilyich Lenin”, “For Labor Valor”, and “For Labor Distinction”.

Zhdanov spent a lot of time training young scientific personal. More than 40 candidates of sciences (Ph.D.) and several doctors of sciences (Dr. Sci) theses were defended under his supervision. The works of Zhdanov and his pupils created fundamentals of the

industrial technology for the manufacture of many organoelement materials (coatings, plastics, synthetic oils, and resins) demanded by modern technics. At the same time, he was an easy to talk to person, open in communication, brightly represented Andrianov's school abroad, and enjoyed a great authority of colleagues. Superbly erudite, witty, with a good sense of humor Alexander Alexandrovich will always be for us the model of the true scientist of that time, the time of great changes, great hope, optimism, and demand for science.

In this special issue of the journal, we have managed to collect articles of both Zhdanov's pupils and followers working in the field of organoelement oligomers and polymers in Russian Federation and abroad.

The article by V.V. Kireev et al. (Mendeleev University of Chemical Technology of Russia, Topchiev Institute of Petrochemical Synthesis, RAS) “Functional Oligoaryloxycyclotriphosphazenes and Noncombustible Binders Based on Them” describes the use of carboxyl-containing aryloxycyclotriphosphazene for curing the ED-20 epoxy resin or phosphazene-containing epoxy oligomer and the properties of the cured self-extinguishing or noncombustible compositions.

In article “Non-Isocyanate Poly(siloxane-urethanes) Based on Oligodimethylsiloxanes Containing Aminopropyl and Ethoxy Substituents” E.S. Trankina et al. (INEOS RAS, ISPM RAS) present the environmentally friendly method for the synthesis of cross-linked poly(siloxane-urethanes) avoiding the use of toxic isocyanates.

B.A. Zachernyuk et al. (Moscow Automobile and Road Construction State Technical University, Mendeleev University of Chemical Technology of Russia, INEOS RAS, Russian Biotechnological University) in review “Practical Application of Selected Functional Organosilicone Polymers” generalize information about the preparation and properties of modifying siloxane coatings on the surface of fibrous materials and a number of functional organosilicone polymers used for the hydrophobization of fibers, textile, leather, building materials and the creation of adhesive compositions and other practically valuable organosilicone products.

The mechanochemical synthesis of organoelement polymers is covered by V.V. Libanov et al. (Institute of High Technologies and Advanced Materials, Far Eastern Federal University) in article “Mechanochemical Interaction of Phenylboronic Acid with Polyphenylsilsesquioxane and a Hydroxy(phenyl)siloxane Oligomer”. It has been first shown that phenylboronic acid can be successfully used as a starting material for the production of polyboronphenylsiloxanes under conditions of mechanochemical activation.

N.S. Bredov et al. (Mendeleev University of Chemical Technology of Russia, State Research Insti-

tute of Chemistry and Technology of Organoelement Compounds) proposed a review article “Modern Approaches to Obtaining Organofunctional Silsesquioxanes”, in which using particular examples demonstrated relationships between the composition and structure of oligomeric organosilsesquioxanes and conditions for their formation during the hydrolytic and acidhydrolytic polycondensation of organotrialkoxysilanes containing various functional groups in organic radicals bonded to silicon atoms.

The one-step synthesis of monosilicon-substituted norbornenes with siloxane and aryl fragments and their polymerization are described by D.A. Alentiev et al. (Topchiev Institute of Petrochemical Synthesis, RAS). This one-step hydrosilylation of 2,5-norbornadiene allows the synthesis of monomers with a higher content of polymerization-reactive exo-isomer in products compared with similar adducts formed via the Diels–Alder reaction. The synthesized monomers show high reactivity in both metathesis polymerization and addition polymerization more sensitive to the substituent volume.

The review by Hanqi Qian and Bo Jiang (Harbin Institute of Technology, China) addresses the application of silicone resins for heat resistant coatings. The challenges and future opportunities of heat resistant coatings based on silicone resins are considered. The influence of main and side chain modification of the silicone resin on its heat resistance is discussed, and the physical and chemical properties of inorganic fillers combined with silicone resins are summarized for the aim of ceramization and further improving the degree of heat-resistance of the material.

A new approach to the synthesis of bithiophenesilane dendrimers with efficient intramolecular energy transfer which is based on the use of chlorosilanes bearing a hydride group and the Stille reaction is considered by M.S. Skorotetskii et al. (ISPM RAS; Department of Chemistry, Moscow State University). The synthesized dendrimers containing 16 and 18 of bithiophenesilane donor units and one central acceptor fragment possess a high molar extinction coefficient and a high quantum yield of luminescence with a short fluorescence lifetime.

M.N. Temnikov et al. (Tula State Lev Tolstoy Pedagogical University, INEOS RAS) proposed review “Silicones in Cosmetics” (will be published in Series B, Issue 5) which focuses on main organosilicon derivatives used in the cosmetic industry, their properties, and action mechanisms. Silicones are compared with compounds based on natural components, and their

safety and application prospects in cosmetics are discussed.

The evolution of organometallosiloxanes is reviewed by O.I. Shchegolikhina et al. (INEOS RAS, Tula State Lev Tolstoy Pedagogical University, Moscow Institute of Physics and Technology). The review illustrates the development of organometallosiloxane chemistry from the first polymer systems to individual organometallosiloxanes and functional oligomeric compounds and evaluates critically the state of the art of the chemistry of organometallosiloxanes and their further evolution.

The review by O.A. Serenko (INEOS RAS) “Poly-metalorganosiloxanes as a Reflection of Milestones in the Development of Advanced Technologies in the Chemistry of Silicones” is devoted to the analysis of areas of the practical application of oligomeric and polymeric organometallosiloxanes as reduced fire risk coatings, antifriction and heat-resistant coatings, materials with high refractive index, and protective coatings for space equipment.

New fluorescent materials based on polysiloxanes and boron bis( $\beta$ -diketonates are described by Yu.N. Kononevich et al. (INEOS RAS, Mendeleev University of Chemical Technology of Russia, Photochemistry Center, Federal National Research Center “Crystallography and Photonics, RAS, ISPM RAS). It is shown that the polymers under study feature the elastic behavior, possess high thermal and thermo-oxidative stability, and exhibit an intense fluorescence in a wide wavelength range typical for excimers of boron complexes formed from aggregates in the excited state.

Obviously, the papers collected in the present special issue do not cover and indeed could not cover the whole range of various organosilicon and organoelement polymers, their synthesis methods, and diverse properties and applications—areas that were established and elaborated due to the invaluable contribution made by A.A. Zhdanov. However, they illustrate main trends in the current development of this area and prospects for its further advancement.

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