Information

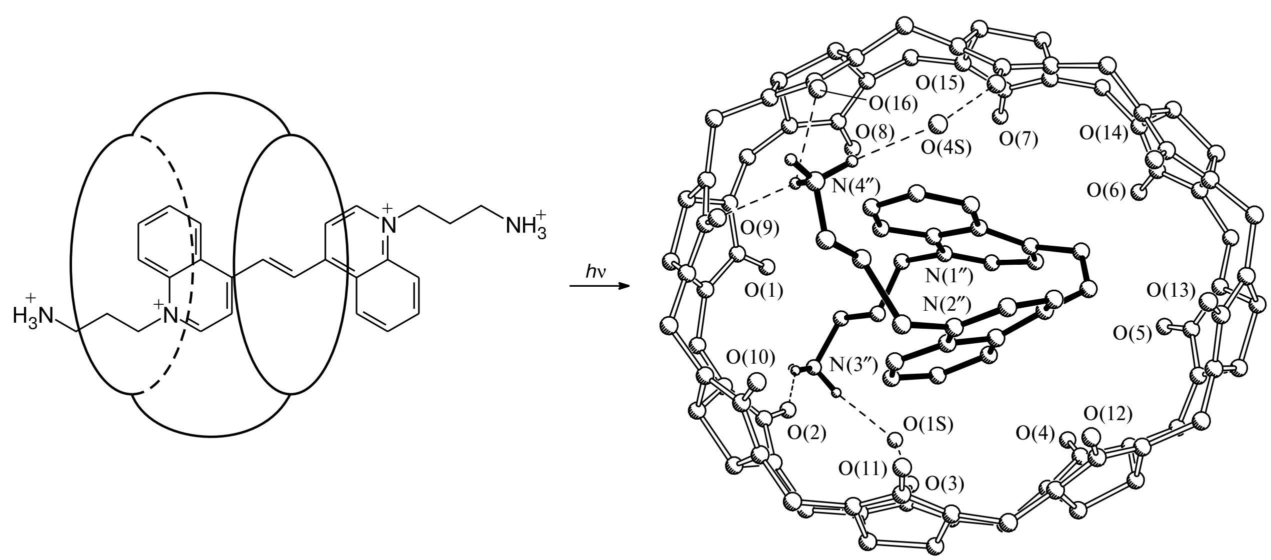
General meeting of the Division of Chemistry and Materials Science of the Russian Academy of Sciences

The annual General meeting of the Division of Chemistry and Materials Science of the Russian Academy of Sciences was held on March 26, 2007, at the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.

The General meeting listened to the reports of Acting Academician Secretary of the Division Academician *V. A. Tartakovsky* and Deputy Academician Secretary of the Division Academician *Yu. A. Zolotov* on the scientific and organizational activity of the Division. The reports by Academician *M. V. Alfimov* "Institutes of the Division of Chemistry and Materials Science of the RAS in the Governmental Programs of the Development of Nanotechnology" and by Corresponding Member of the RAS *S. D. Varfolomeev* "Biofuel and Bioplastics: Chemical Foundations and Technologies" were presented.

The scientific results obtained or completed at the Institutes of the Division in 2006 and presented to the General Meeting of the Division are outlined below.

The self-assembly of photocontrollable molecular machines is studied at the Photochemistry Center. Cucurbiturils form host—guest type complexes with *trans*-iso-



CB[8]·*trans*-**V** CB[8]·*cis*-**V**

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mers of viologen derivatives. On exposure of the complex with *trans*-diquinolylethylene to light, the *cis*-isomer is formed inside the host molecule, thus inducing mechanical motion within the macrocycle cavity.

At the Institute of Structural Macrokinetics and Materials Science Problems, it was found that the predicted and experimentally detected competition in the reaction chain branching and termination plays the decisive role in the appearance and development of explosion and detonation. In 2006, these reactions in mixtures of hydrogen, methane, and syngas with air were completely suppressed by chemical means. It was thus demonstrated that termination of the reaction chains, which was previously neglected, is actually an effective means for energy withdrawal from the chemical reaction zone.

The first compound with the zinc—zinc bond containing a paramagnetic radical anion ligand was synthesized at the G. A. Razuvaev Institute of Organometallic Chemistry. The structure of this compound was established by X-ray diffraction (Fig. 1, *a*). The use of spin-labeled ligand allowed the researchers to prove the existence of the Zn—Zn bond in solution by ESR spectroscopy (Fig. 1, *b*). The density functional theory calculation confirmed the biradical structure of the molecule and showed that the metal—metal bond was mainly formed by s-orbitals (Fig. 1, *c*).

A method of targeted synthesis of star-shaped polymers with a C_{60} fullerene molecule as the branching point was developed at the Institute of High-Molecular Weight Compounds. Conditions for preparing eight- (Fig. 2, reaction (*1*)) and twelve-arm (Fig. 2, reaction (*2*)) polymers from polystyrene and polar poly-2-vinylpyridine were selected. The polymers thus synthesized behave as smart polymers and can be used as micelle-forming agents, nanocontainers, or nanoreactors.

An original approach to the synthesis of water-soluble polymers and hydrophilic/hydrophobic copolymers in reverse miniemulsions was developed at the A. N. Nesmeyanov Institute of Organoelement Compounds. The radical polymerization of acrylamide was initiated by a new redox system comprising a monosaccharide derivative (as the reductant) and cerium(IV) ions (as the oxidant). The reduction was accomplished by a surfactant, which simultaneously stabilized the emulsion. The interaction of the oxidant—reductant pair affords free radicals attached to the inner surface of the monomer drops. The radicals initiate the monomer polymerization. The hydrophobic hydrocarbon fragment of the surfactant becomes incorporated in the polymer chain. Therefore, the chain grows near the interface and the latex particles thus formed have much higher colloidal stability than those obtained by conventional emulsion polymerization. The synthesis

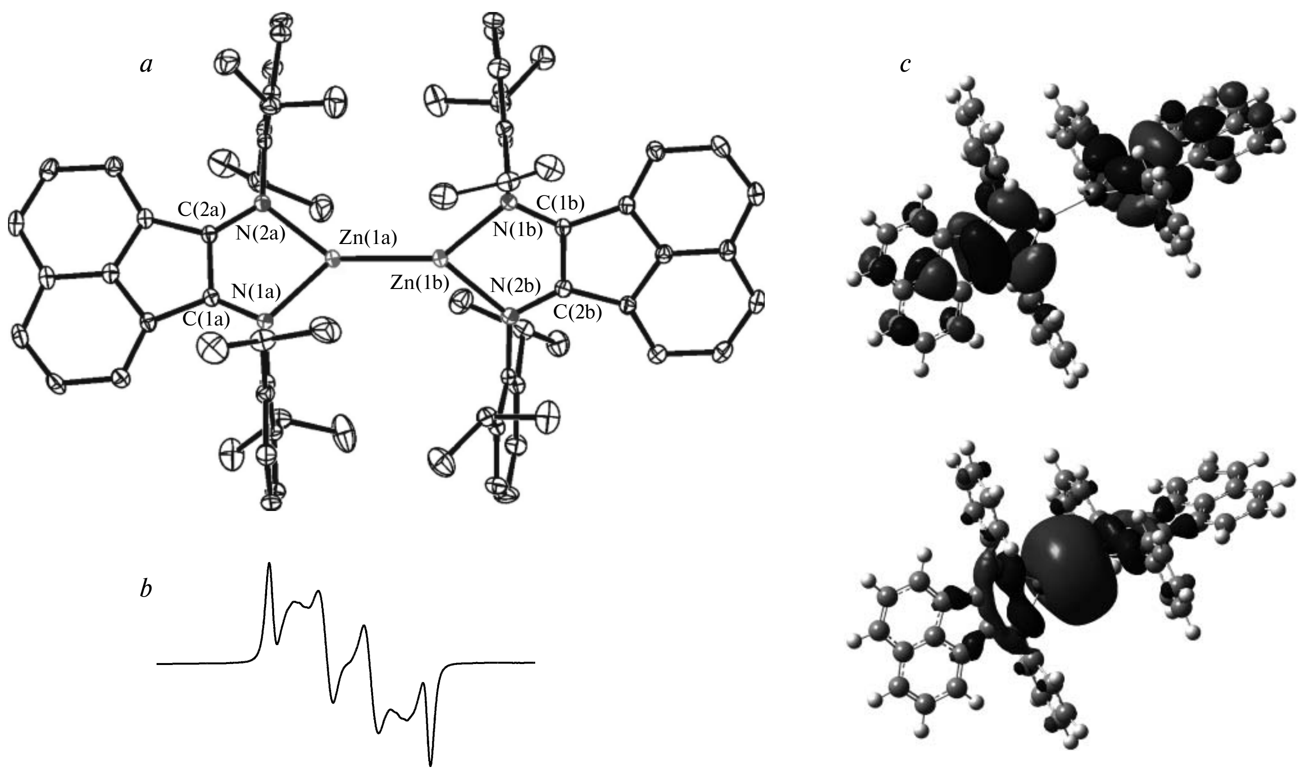


Fig. 1. Stabilization of the direct Zn—Zn bond by the acenaphthene-1,2-diimine radical anion: (*a*) X-ray diffraction data, *d*(Zn—Zn) = 2.3321(2) Å, the ligand rotation angle is 43°; (*b*) ESR data, D = 6.39 mT, the distance between the unpaired electron sites is 7.57 Å; (*c*) DFT calculations.

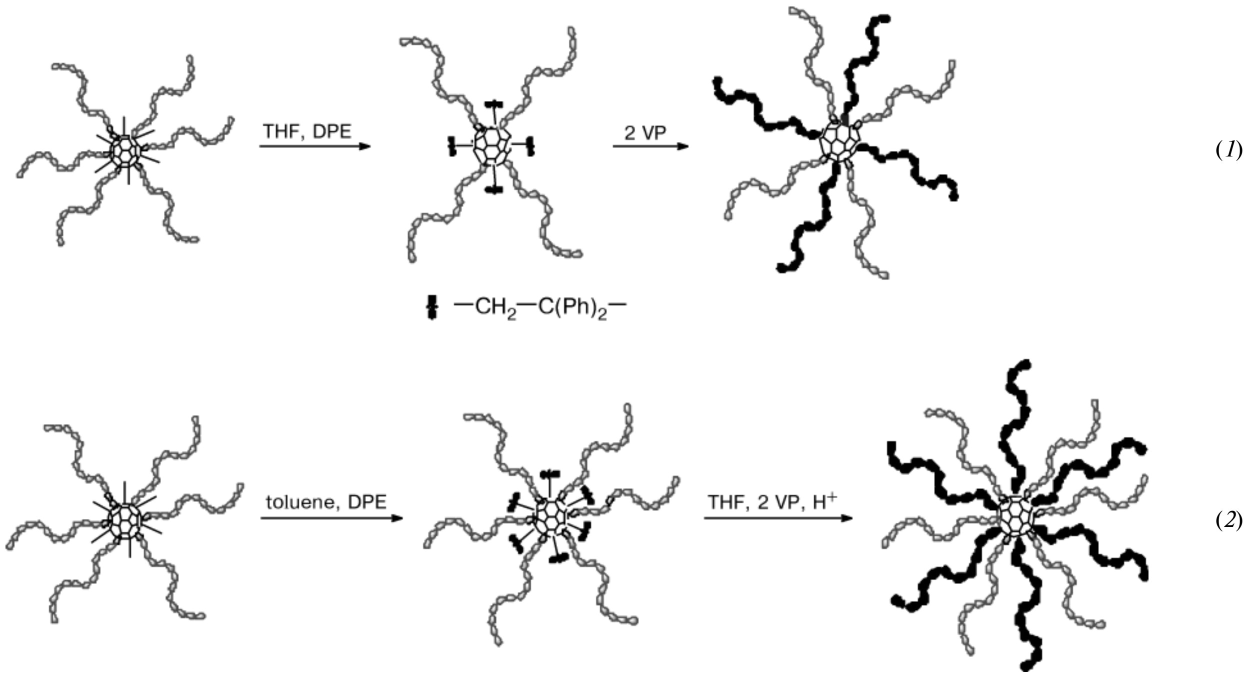


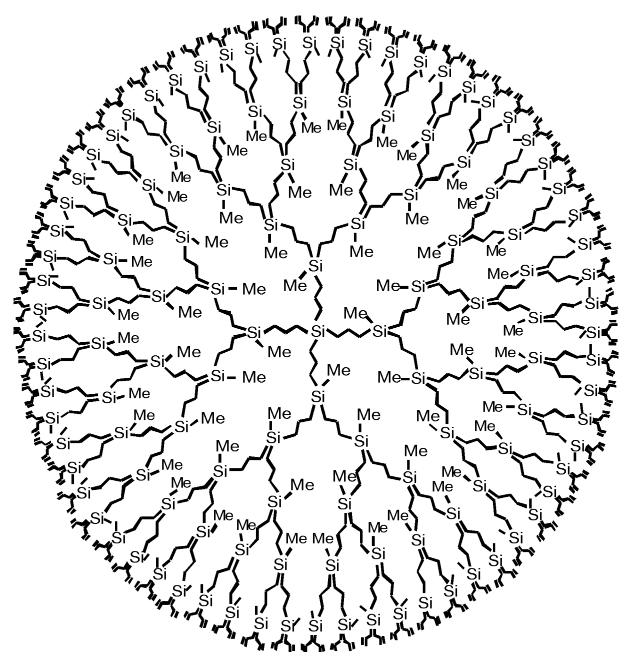
Fig. 2. Targeted synthesis of star-shaped polymers with a C_{60} fullerene molecule as the branching point.

does not require elevated temperatures. The hydrophilic nanoparticles could be used for the design of biomedicinal articles.

A method for the synthesis of nicotinic acid in >80% yield upon treatment of pyridine with methyl hypochlorite generated *in situ* by the reaction of carbon tetrachloride with methanol in the presence of the $Fe(acac)_3$ as a catalyst was developed at the Institute of Petrochemistry and Catalysis. The process involves the intermediate formation of 3-hydroxymethylpyridine, which reacts with an excess of CH_3OCl under the reaction conditions to give nicotinic acid. This method has advantages over the known route to nicotinic acid starting from poorly accessible 3-methylpyridine.

An extensive library of molecular nanoobjects was created at the N. S. Enikopolov Institute of Synthetic Polymeric Materials; the library includes homologous series of siloxane and carboxysilane dendrimers, their hydrophilic and oleophobic derivatives, and a series of hyperbranched polymers with various molecular parameters.

Studies of these systems resulted, in particular, in the development of multicenter initiators for anionic polymerization with a molecular membrane effect and dendrimers with nanocluster metallic structures in the inner sphere.



Ninth-generation organosilicon dendrimer.

The conduction of a well-known conducting polymer, polyaniline, is studied at the A. N. Frumkin Institute of Physical Chemistry and Electrochemistry. Until recently, its conductivity has been ~10^3 S/cm. One of most effective methods for increasing the polyaniline conductivity is interfacial doping. This is done using ~70 nm-thick gold layers on a glass substrate, onto which a layer of the polyaniline and poly(2-acrylamido-2-methylpropanesulfonic acid) interpolymer complex is electrochemically deposited. The film then passes into a highly conducting state with a specific conductivity comparable with that of a gold layer (~10^6 S/cm), which is a result of exchange electronic processes at the polymer—metal interface.

The development of the scientific grounds for the production of high-purity monoisotopic polycrystalline silicon-28 in a yield of at least 75% was completed at the Institute of the Chemistry of High-Purity Substances. For the international "AVOGADRO" project, a monoisotopic silicon-28 sample weighing more than 5.9 kg and containing more than 99.99382±0.00240% of the major isotope and $3.7 \cdot 10^{15}$ and $6.1 \cdot 10^{15}$ at/cm^3 of carbon and oxygen impurities, respectively, was prepared. A structurally perfect single crystal of high-purity silicon-28 (99.99% isotopic purity) was produced and the possibility of optical recording of the nuclear spin state was established, which is essential for the design of a quantum computer based on monoisotopic silicon.

Reaction-bonded coatings with a glass-like matrix for protection of construction materials subjected to high temperatures up to 1800 °C were synthesized at the I. V. Grebenshchikov Institute of Silicate Chemistry. The glassy matrix is a complex-doped high-silica glass containing zirconium, molybdenum, and boron.

Fundamentally new layered metallic nanocomposites were developed at the A. A. Baikov Institute of Metallurgy and Materials Science. Their strength and ferromagnetic properties are 2—2.5 times superior to the properties of the best foreign analogs, which allows one to increase the lifetime of new instruments and devices for space, sensor and medical technology by an order of magnitude.

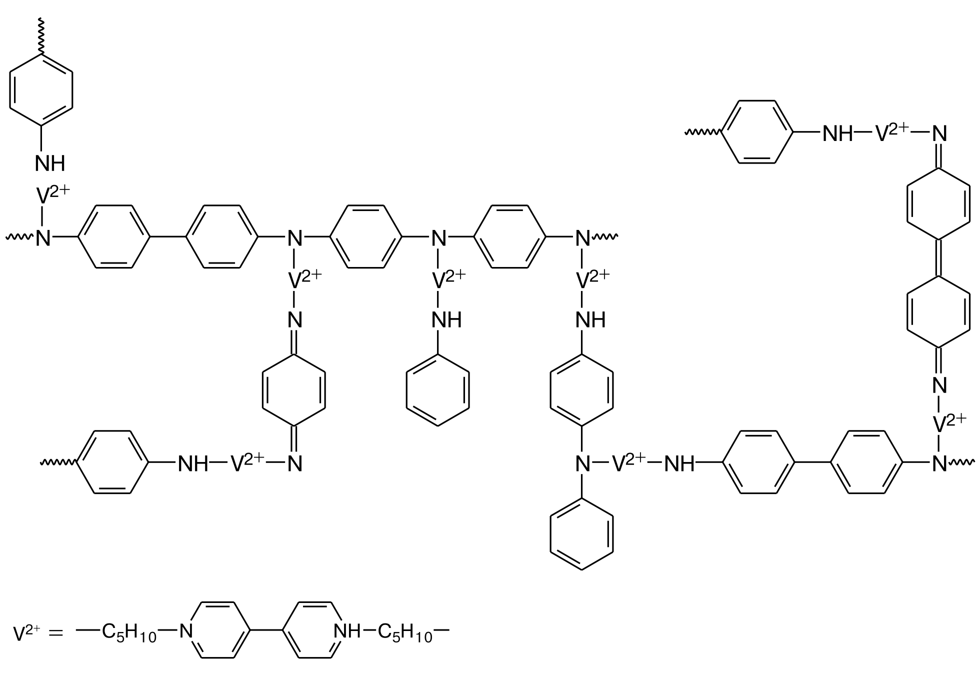
Polymers based on viologen-substituted anilines were synthesized at the A. V. Topchiev Institute of Petrochemical Synthesis.

These polymers may act as mediators for hydrogenase in the bioelectrocatalysis of hydrogen oxidation. They ensure coupling of the enzymatic and electrode reactions, the positively charged viologen groups provide the required enzyme orientation at the electrode, and polyconjugation system provides effective charge transport between the hydrogenase active site and the electrode material. The enzymatic electrode is a graphite cloth coated by a thin layer of viologen-substituted polyaniline with hydogenase immobilized thereon. This electrode modification increases the hydrogen oxidation current to 500 μA cm^{-2}. This is 2.5 times higher than that for conventional graphite electrodes. As a result, the efficiency of bioelectrocatalysis can be increased, which opens up prospects for the design of highly sensitive hydrogen sensors.

The X-ray photoelectron diffraction technique was implemented at the Institute of Solid-State Chemistry of the Ural Branch of the RAS. This technique was used to study quasi-ordered structures like NbO_x. Two nonequivalent states of oxygen were detected on the niobium surface, above and below the Nb(110) single crystal face. The low-dimension NbO_x structures can be valuable for the development of functional elements of superconducting detectors for infrared photons, which are 1000 times as sensitive and fast responding than semiconductor detectors.

Rare-metal nanomaterials and instruments based on them for high-precision quick testing of foodstuffs with an order of magnitude higher sensitivity compared with the best foreign analogs were designed at the A. A. Baikov Institute of Metallurgy and Materials Science (a trial series of the instruments was manufactured and tested).

An electroanalytical kit for rapid detection of narcotic drugs was elaborated at the A. N. Frumkin Institute of Physical Chemistry and Electrochemistry. A multisensor



test system was used as a solution containing a set of metal ions capable of forming compounds with narcotic drugs. Different narcotic agents affect the electrochemical behavior of the test system in different ways. The response of the test system to various drugs is represented as a multidimensional image. The database composed using these images allows identification of substances with visualization of the result.

An original procedure of thermal vacuum deposition of thin-film amorphous materials based on chalcogenide glass-like semiconductors modified by lanthanides was developed at the N. S. Kurnakov Institute of General and Inorganic Chemistry. The chemical modification changes the nanostructure parameters, electric and optical characteristics, and crystallization kinetics, which is crucial for the phase transformation rates.

Highly efficient supported catalysts for the production of a new polymeric material, ultrahigh-molecular-weight polyethylene were developed at the A. V. Shubnikov Institute of Crystallography. This material is designed for operation under drastic conditions. Using these catalysts the manufacturing process for different polyethylene brands, in particular, a high-strength fiber used for modern armored protection means, were tested.

At the Institute of Solution Chemistry, a number of electrorheological fluids, which execute reversible transitions from the plastic to a solid state (on the millisecond time scale) under the action of electric field, were composed. Hybrid organic/inorganic nanocomposites and nanomaterials constructed according to the core—shell principle were used as components of the disperse phase. Samples of the electrorheological fluids have high electrorheological response parameters and are promising for the design of devices in automotive engineering, robotics, space engineering, medicine, and other fields.

A new process for production of 1,4-*trans*-polyisoprene or synthetic gutta-percha was developed at the A. V. Topchiev Institute of Petrochemical Synthesis and implemented at the pilot unit of the plant Tolyattikauchuk. Synthetic gutta-percha is a large-scale polymer produced by foreign companies for tire, footwear, and cable industries and medicine but not produced in Russia. The developed process is characterized by a high activity of the catalyst system, which is 10—12 times as high as the activity of foreign analogs, which allows the process to be made environmentally safe and low-cost.

An environmentally safe process for the manufacture of high-quality diatomite with low impurity content needed for the production of a wide range of materials was developed at the N. S. Kurnakov Institute of General and Inorganic Chemistry. On the basis of the process flow scheme developed for the xonotlite and wollastonite production and using wastes from the JSC Voskresensk Mineral Fertilizers, a pilot plant with a 800—1000 tpy capacity was constructed.

The scientific grounds for the selective catalytic processes for production of individual isomeric C_4, C_6, C_8, C_{10}, C_{12}, and C_{14} olefins were elaborated at the Institute of Problems of Chemical Physics.

The Institute of Solution Chemistry developed resource-saving technologies for extensive processing of flax, which ensures 100% use of the raw material in the manufacture of a series of new products, in particular, flaxseed cellulose for the production of cannon propellants, surgical cotton, and biologically active dressing materials.

The Institute of Chemistry of the Far Eastern Division of the RAS developed the foundations for the hydrothermal destruction of cobalt complexes with ethylenediaminetetraacetic acid under flow-type hydrothermal oxidation conditions. This process underlies the method developed for treatment of nuclear power plant still bottoms for removal of long-lived radionuclides. The obtained still bottom decontamination factors (more than 10000) and the ratio of the treated solution volume to radioactive solid precipitate volume (more than 1000) are much higher than these characteristics obtained by other methods used in world practice.

At the N. D. Zelinsky Institute of Organic Chemistry, ionic liquids were used as solvents and catalysts for practically valuable reactions of nitro compounds. These were used, for example, to develop an explosion-safe method for the synthesis of high-energy trinitroethyl carboxylates used as plasticizers of energy intensive compositions. The developed methods are distinguished by high rates and selectivities; they do not require organic solvents, allow repeated use of ionic liquids and the catalyst.

A high oxygen conductivity in vacancy-ordered oxide compounds was found at the Institute of Solid-State Chemistry of the Ural Branch of the RAS. The mechanism of ion-electron transport was interpreted. Owing to the discovered effect in combination with high thermodynamic stability, these materials can be used as ceramic membranes for new natural gas processing and hydrogen production processes and for direct conversion of chemical energy to power.

A number of laboratory models of electrocatalytic reactors for partial oxidation of natural gas were designed. Ferrite-based materials elaborated at the Institute were used as membranes. By this method, syngas was produced from natural gas. High efficiency of the process characterized by the ratio $H_2/CO \approx 2$ and conversion and selectivity parameters at about 93—97% was demonstrated.

New multicomponent catalysts for fuel cells with operation temperature of 50—200 °C were developed at the A. N. Frumkin Institute of Physical Chemistry and Electrochemistry. Using these catalysts, membrane—-electrode blocks for fuel cells with polybenzimidazole-based membranes and operating temperature of 150—200 °C were designed. The use of the synthesized catalysts reduced twice the platinum consumption compared that for known catalysts.

The Institute of Physicochemical Problems of Ceramic Materials developed a suspension procedure of highly porous coating deposition based on CeO_2—γ-Al_2O_3 (with CeO_2 content increased to 50% w/w) supported on cellular and honeycomb metallic and ceramic block supports. The block supports thus obtained ensure a high activity of supported Pt-catalysts in the range of 100—130 °C in CO oxidation with oxygen.

The Institute of Chemistry and Technology of Rare Elements and Mineral Resources developed electrochemical procedures for the synthesis of a molybdenum carbide—molybdenum catalyst system for a fuel processor placed directly on board a vehicle.

The synthesis of carbohydrate cancer markers was accomplished at the N. D. Zelinsky Institute of Organic Chemistry. The works on the creation of a cancer vaccine using synthetic oligosaccharides were started.

At the N. D. Zelinsky Institute of Organic Chemistry and at the A. N. Nesmeyanov Institute of Organoelement Compounds, new data on the antiviral activities of some 1-boraadamantane derivatives with respect to the H5N1 bird flu virus were obtained; this opens up the way for creation of effective drugs for treating this serious disease.

The search for neuroprotecting agents and cognitive stimulants for treating neurodegenerative diseases (for example, Alzheimer´s disease) has been started at the Institute of Physiologically Active Compounds. The drug Dimebon has successfully passed the second-stage clinical trials in 16 Russian clinics and proved to be much superior to every other known drug for the therapy of Alzheimer´s disease.

At the same Institute, a biosensor for determination of the activity of neurotoxic esterase in blood was devised. The sensor opens up the possibility of early detection of delayed neurotoxicity caused by organophosphorus compounds. The use of these sensors allows fast evaluation of the impact of neuropatic organophosphorus compounds on humans. This is important, in particular, for minimization of the consequences of chemical terrorist attacks and chemical plant accidents.

A new class of bioactive compounds, hybrid macromolecular antioxidants (HMAO) based on hydrophilic polymers (dextran, starch, polyvinyl alcohol, poly(ethylene glycol)) with sterically hindered phenol fragments chemically grafted to the macromolecular chain was created at the N. M. Emanuel´ Institute of Biochemical Physics. The HMAO antiradical activity in water is hundreds of times higher than the activity of blends composed of sterically hindered phenols (SHP) and the polymer. The mechanism of this phenomenon has been studied by structural physical methods. An important structural factor is the size of the spacer separating the SHP core from the polymer chain. The antioxidant activity of HMAO was demonstrated using biological models.

A substantial group of compounds capable of spontaneous resolution into enantiomers was found in the series of aromatic ethers of C_3 alcohols at the A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Scientific Center. Studies of uniformly varied series of compounds within this group allowed the researchers to reveal the parameters affecting crystallization, to deliberately design aggregate-forming substances, and to develop preparation procedures for chiral medical drugs.

Generally, the Institutes of the Division were involved in 12 fundamental research programs held by the Presidium of the Russian Academy of Sciences, 13 fundamental research programs of the Division, and 75 international projects. The total number of subject matters developed was 558. The Division was in active cooperation with commercial companies (12 projects), nonprofit associations (477 contracts with Russian customers were concluded), higher educational institutions (33 basic chairs and 22 scientific and educational centers continued to work at the Institutes). The research results were published in Russian (about 3000 papers) and foreign (about 1400 papers) journals and as 110 published books and 130 granted patents.

G. N. Konnova

General meeting of the Russian Academy of Sciences

The annual General meeting of the Russian Academy of Sciences was held on March 27 and 28, 2007, in the Great Hall of the Presidium of the RAS in Moscow.

In his opening speech, President of the RAS Academician *Yu. S. Osipov* listed prominent achievements in science as presented by Divisions of the Academy.

The report on the activity of the Russian Academy of Sciences in 2006 was delivered by the Chief Academic Secretary of the Presidium of the RAS Academician *V. V. Kostyuk*. The General meeting approved the report and adopted the relevant resolution.

The presentation of the M. V. Lomonosov Big Gold Medals of the RAS took place at the Meeting. The M. V. Lomonosov Big Gold Medals of 2006 were awarded to Academician *N. P. Laverov* for the outstanding contribution to the solution of mineral resource problems in Russia, in particular, for the development of scientific grounds for exploration of uranium deposits, and to Professor *Charles Rodney Ewing* (USA) for the outstanding achievements in the studies of radiation impacts on minerals, the design of conserving matrices for burial of highly radioactive elements in deep geologic formations.

The winners delivered scientific reports.

Presentation of other Gold Metals named after outstanding scientists of 2006 also took place at the Meeting.

The N. N. Semenov Gold Medal was presented to Academician *Yu. N. Molin* for great contribution to the studies of elementary chemical reactions, development of fundamentally new methods based on quantum spin coherence for kinetic and mechanistic studies of fast reactions.

The A. M. Butlerov Prize was presented to *S. P. Gromov* for the series of works "Molecular design of photosensitive supramolecular systems with specified properties based on crown-containing unsaturated compounds," the I. V. Grebenshchikov Prize was presented to Academician *V. Ya. Shevchenko* for the work "Structural Chemistry of Nanoworld," the V. N. Ipat´ev Prize was presented to *Yu. M. Milekhin* for the series of works "Development of the scientific grounds and practical implementation of new processes for the manufacture of energetic condensed systems for advanced military rockets and competitive civil products," the A. N. Nesmeyanov Prize was presented to Academician *Yu. N. Bubnov* and *M. E. Gurskii* for a series of works "Allylboranes. Reactivity principles and applications in organic synthesis," and the L. A. Chugaev Prize was presented to Academician *N. T. Kuznetsov*, *K. Yu. Zhizhin*, and *E. A. Malinina* for a series of works "Coordination compounds of boron cluster anions."

The General Meeting heard and approved the report of the Chairman of the RAS Charter Commission Academician Yu. A. Osip´yan. The charter presented by the Commission was approved by the members of the General Meeting with one abstained.

G. N. Konnova