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Book of abstracts

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Satellite event:

4th school “CHLORINE-FREE CHEMISTRY OF SILICONES”

(supported by the Russian Science Foundation, project 21-73-30030-П)

Invited lectures

New Horizons of the Silicone Market

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The global silicone industry currently faces a perceived market saturation, largely driven by a conservative reliance on second-generation, dimethyldichlorosilane-based production. This traditional pathway requires an excessive number of technological conversion stages (up to 13–15 for advanced products like extruded rubbers), which limits scalability, increases costs, and stifles innovation. This presentation outlines a strategic paradigm shift toward third-generation, chlorine-free technologies, specifically the direct synthesis of methylalkoxysilanes.

By eliminating chlorine and reducing the production cycle to just 2–3 conversion stages, this approach not only mitigates technogenic risks but also unlocks the potential for entirely new, high-volume market niches. Drawing parallels with the exponential historical growth of PET and polyurethanes through novel applications, we identify massive, underutilized sectors for advanced silicone materials. Key focus areas include: (1) polymethylsilsesquioxane (PMSSO) nanogels as eco-friendly, water-based binders for the wood chipboard industry, replacing toxic phenol-formaldehyde resins; (2) hybrid fillers for green tires; and (3) ladder polyphenylsilsesquioxanes (L-PPSQ) as low-dielectric matrices for advanced microelectronics and high-temperature applications.

Central to this strategy is the "Nesmeyanov Model" of academia-business collaboration, where fundamental science actively drives industrial investment by demonstrating viable, large-scale market opportunities, rather than merely optimizing existing commodity products. The presentation concludes with a roadmap for fostering a robust startup ecosystem around academic centers, projecting a significant expansion of joint Russian-Chinese applied projects to realize these new horizons in silicone chemistry.

This work was supported by Ministry of Science and Higher Education of Russian Federation (FFSM-2024-0001)

Recycling of waste silicone materials

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Silicone polymers and materials, with their unique and excellent properties, have been widely used in a wide variety of fields such as aerospace, electronics & electrical engineering, medical, construction, and so on. Global silicone production is expected to grow at approximately 5% per year. So growing sustainability challenges are posed due to their environmental persistence and the energy-intensive production process. Therefore, the recycling and utilization of siloxane wastes has become a prominent research topic. However, traditional industrial recycling uses concentrated sulfuric acid degradants, causing high pyrolysis cost, severe equipment corrosion, difficult post-treatment, secondary pollution, and narrow waste adaptability. This presentation will present a mild, solvent-free process to transform silicone wastes into valuable precursors by the strategy of “treating wastes with wastes”. This process not only enhances the value of industrial wastes but also reduces energy consumption and raw material losses. By integrating waste reuse with resource-efficient chemistry, this approach demonstrates a new scalable pathway for the silicone industry to achieve circular manufacturing and sustainable development.

This work was supported by National Natural Science Foundation of China (No. 52173102).

Design and properties of bottlebrush polymers based on siloxanes and norbornenes

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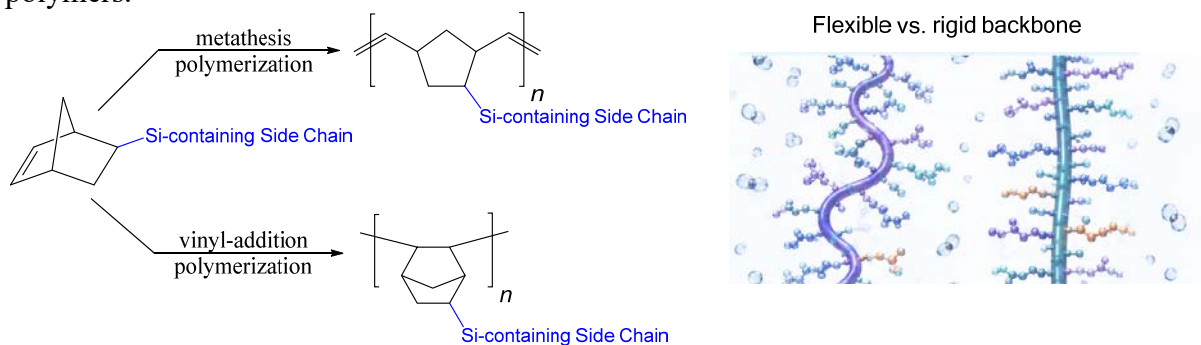
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Bottlebrush polymers are a distinct class of macromolecular materials in which densely grafted side chains suppress intermolecular entanglements, enabling unusual combinations of softness, elasticity, and functionality. Siloxane-containing bottlebrushes are especially attractive because the flexibility, low glass-transition temperature, and high free volume of siloxane fragments complement the advantages of densely grafted architectures. Norbornene provides a versatile platform for constructing such materials. Its rigid bicyclic framework can be combined with flexible Si-containing side chains, while different polymerization mechanisms give fundamentally different backbone structures. ROMP is the dominant route to norbornene-based bottlebrushes and offers excellent architectural control. In contrast, vinyl-addition polymerization preserves the bicyclic unit and produces a rigid, fully saturated backbone with high thermal and chemical stability.

Our results show that Si-containing norbornene monomers can be efficiently polymerized by tailored cationic Pd catalysts, giving high-molecular-weight polymers with tunable structures. Comparison with related ROMP systems suggests that some polymer properties might depend not only on side-chain chemistry and grafting density, but also on backbone nature. Thus, norbornene-siloxane monomers represent a promising platform for combining similar side-chain chemistry with different polymer backbones. Backbone engineering therefore offers an additional tool for tuning the properties of siloxane-containing bottlebrush polymers.



Scheme 1. The synthesis of bottlebrushed polymers based on Si-substituted norbornenes.

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Current Status of the Development of China's Silicon-Based New Materials Industry

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Based on the current status of the development of China's silicon-based materials industry, this report proposes key projects for the development of the silicon-based materials industry. The report focuses on the industrial silicon product tree, chlorosilane product tree, methylchlorosilane product tree, and phenylchlorosilane product tree, and highlights special silicon-based new materials related to applications in industries such as chips, semiconductors, electronics, and new energy, providing industry guidance.

References:

"Dalad Silicon-Based Materials Industry Plan" prepared by Sichuan Fengyong Technology Co., Ltd. This industry plan was funded by the China Association of Fluorine and Silicone Industry.

Silicone Surfactants – Quo Vadis?

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Silicone surfactants, characterized by a siloxane backbone (-Si-O-Si-) with organic side groups, offer exceptionally low surface tension and a distinctive hydrophilic-lipophilic balance, making them highly effective in both aqueous and organic media and widely used across industrial and personal care applications. Nevertheless, current silicone surfactants face critical technical challenges, including limited hydrolysis stability, poor stabilization of oil-in-water (O/W) emulsions, and the presence of low-molecular-weight cyclic siloxanes. To overcome these limitations, we introduce a novel class of high-performance surfactants built on MQ copolymers—densely crosslinked, globular silicone polymers. Our innovative “rigid-flexible” star-shaped architecture employs an MQ copolymer as the hydrophobic core with grafted hydrophilic segments, imparting superior interfacial activity, enhanced thermal and chemical stability, and precise molecular tunability. This work spans molecular design and synthesis, interfacial characterization, and application validation as wetting agents and O/W emulsion stabilizers.

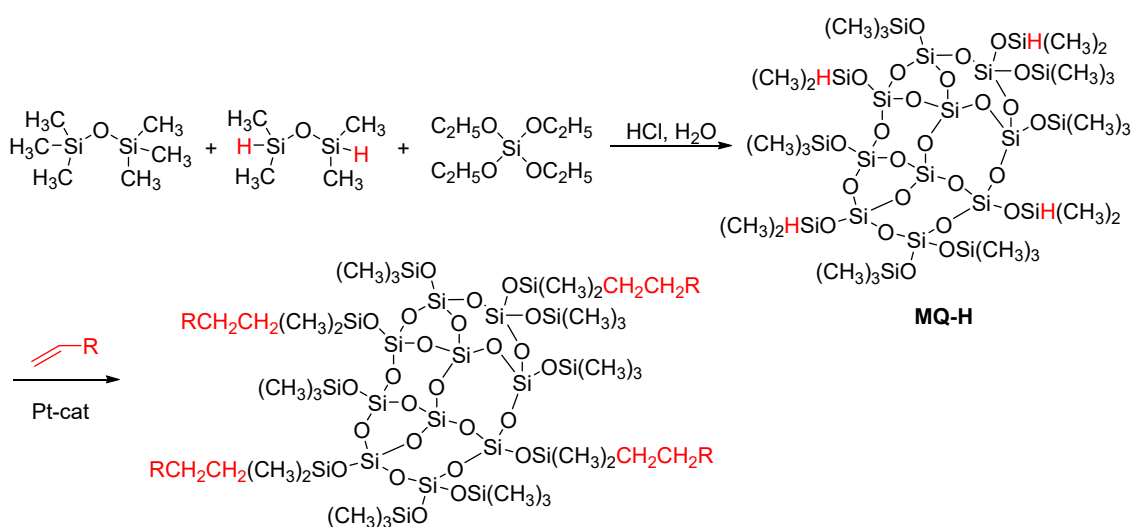


Fig. 1. Synthetic Route to Star-Shaped Amphiphilic MQ Copolymers

The work was carried out with the financial support of Zhejiang Province "Jianbing Lingyan + X" Science and Technology Program International Cooperation Project (2026C04057).

MAGNETOACTIVE POLYMER MATERIALS FOR SOFT ROBOTICS

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Magnetic soft robotics offers transformative potential for untethered, compliant devices, yet its progress is constrained by the poor 3D printability of standard silicone elastomers (PDMS). Traditional mold casting restricts the geometric complexity required for advanced robotic architectures. Here, we present a novel class of 3D-printable magnetoactive polymers utilizing thermoplastic polyurethane-siloxane (TPU-S) matrices [1,2]. We systematically map the interplay between magnetic filler composition, polymer matrix design, and resulting magneto-mechanical actuation. By shifting the material paradigm from castable silicones to highly printable thermoplastics, we demonstrate the fabrication of complex, wirelessly actuated soft robots. This work establishes TPU-S composites as a highly viable, high-resolution alternative for the additive manufacturing of next-generation magnetic soft robotic systems.

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Preparation and Properties of Crystalline Silicon-Containing Polyamides

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Designing and preparing silicon-containing polyamides (Si-PAs) with crystallization properties is a research direction worth exploring. Taking inspiration from natural spider silk, an ultrastrong, lowtemperature-resistant, reusable thermoplastic Si-PA hot-melt adhesive (HMA) has been synthesized by melt polycondensation. Si-PA-TPA, which was synthesized from terephthalic acid and 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, exhibits a crystal structure similar to that of spider silk. The resulting hot-melt adhesive has a reliable bond strength of up to 20.6 MPa at ambient temperature and 9.5 MPa at $-196\text{ }^{\circ}\text{C}$ on stainless steel, notably outperforming comparable polyamide HMAs.

Si-PAs with a certain degree of crystallinity and appropriate melting temperature (T_m) were successfully obtained via solvent-induced crystallization (SINC). The multiple melting behavior was investigated, and it may be attributed to several factors, such as polymorphism, crystal form transitions, and melting recrystallization.

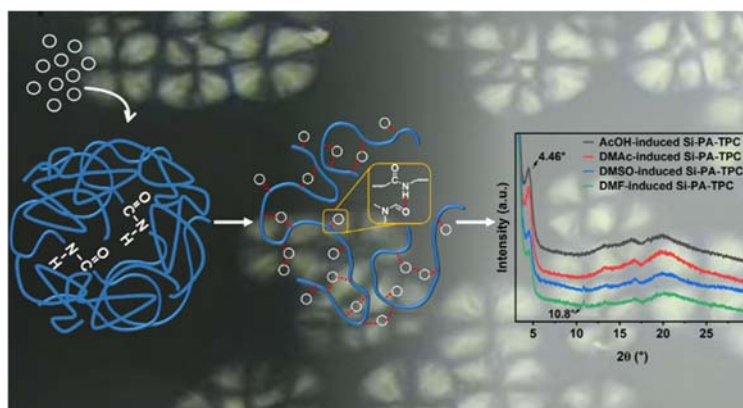


Fig. 1. Schematic illustration of SINC process and XRD patterns of Si-PAs.

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AMMONIA IS A UNIVERSAL MEDIUM FOR THE SYNTHESIS AND PROCESSING OF SILICONES

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The main task solved by modern polymer chemistry is the creation of macromolecular systems with a set of specified useful properties with minimal impact on the environment both at the stage of production and at the stage of operation and disposal. At the same time, the need to improve performance characteristics (mechanical and thermal stability, high hydrophobicity, radiation resistance, etc.) is constantly growing. It is well known that the structure of the macromolecule determines the properties of the polymer. The development of a targeted and simple method for the synthesis of polymers of various molecular structures, in particular silicones, is a relevant area of the chemistry of high-molecular compounds.

The use of ammonia as a reaction medium for the synthesis of organosiloxanes is a unique and promising area of research. This is due to such properties of ammonia as good solubility in it of many organic and inorganic compounds, low viscosity and density, the possibility of removing it from the reaction zone by decompression.

This work will present the results of the synthesis and study of the properties of: narrow-dispersed homo- and heterofunctional polyorganosiloxanes¹, functional star-shaped PDMS, ladder polyphenylsilsesquioxanes^{2,3} obtained in an ammonia environment. Approaches to the processing of siloxane rubbers with various fillers will be considered separately.

This study was financially supported by the Russian Science Foundation (project No. 26-13-00301).

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Design and Application of Tetraphenylethylene based Organosilicon Materials: From Small Molecules to Polymers

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Since the strategic guidelines of "carbon peaking and carbon neutrality" were proposed to address global climate change and promote green and low-carbon development, further advancement of organosilicon chemistry-as the chemistry of the silicon analog of carbon-has become particularly important. Organosilicon materials have attracted widespread attention and extensive research owing to their excellent cold resistance, heat resistance, weather resistance, hydrophobicity, electrical properties, gas permeability, water-vapor resistance, and ease of processing. On the other hand, compounds exhibiting aggregation-induced emission (AIE) properties achieve enhanced fluorescence in the aggregated state through intramolecular self-adjustment, thereby compensating for the limitations of traditional luminescent materials in this regard, and demonstrating broad application prospects in fields such as fluorescence sensing, electroluminescence, and bioimaging. In this work, the classic aggregation-induced emission luminogen tetraphenylethylene (TPE) was combined with siloxane to synthesize siloxane-modified tetraphenylethylene structures of linear, cyclic, and crosslinked architectures. Their applications were explored in luminescent molecular liquids¹, visual monitoring of Si-O bond hydrolysis², and aggregation-induced emission organosilicon elastomers³, thereby providing insights and references for the preparation of novel luminescent organosilicon materials^{4,5}.

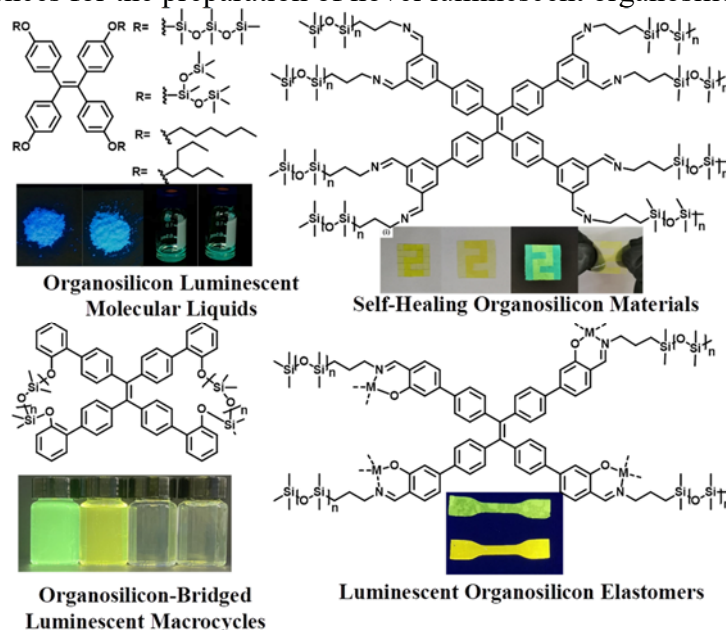


Fig. 1. Tetraphenylethylene-based organosilicon luminescent materials.

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Functionalization of polydimethylsiloxanes: current trends in siloxane ring opening and catalytic rearrangement reactions

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Since their inception and expansion into numerous practical applications, polydimethylsiloxanes (PDMS) remain in demand, strengthening their position both in the production of mass-market products and in highly specialized high-tech areas. This is due to both their unique structure and the wide possibilities for modification with various functional groups, fragments, blocks, etc.

Siloxane ring-opening and catalytic rearrangement reactions applied to functional PDMS are actively developing and remain the primary method for producing PDMS oligomers with a wide range of functional terminations. The literature contains numerous examples of reproducing this method to obtain compounds with specified molecular parameters and types of functional groups¹.

This work demonstrates the introduction of new functional groups into the PDMS structure. Specifically, a method has been developed for introducing azidopropyl terminal and chain-distributed (5-50 mol%) functional groups, as well as the simultaneous introduction of terminal and distributed hydridosilyl and azidopropylsilyl groups within oligomers, and vice versa^{2,3}. In addition, PDMS with terminal alkoxyl groups were synthesized by the method of opening octamethylcyclotetrasiloxane in an alcohol solution in the presence of an initiator. Various process conditions (the influence of concentration and amount of catalyst), the possibility of reusing the reaction system and scaling were studied⁴.

The work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation within the framework of state assignment No. FFSM-2024-0001.

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Straightforward Access to High-Performance Organometallic Catalysts by Fluoride Activation

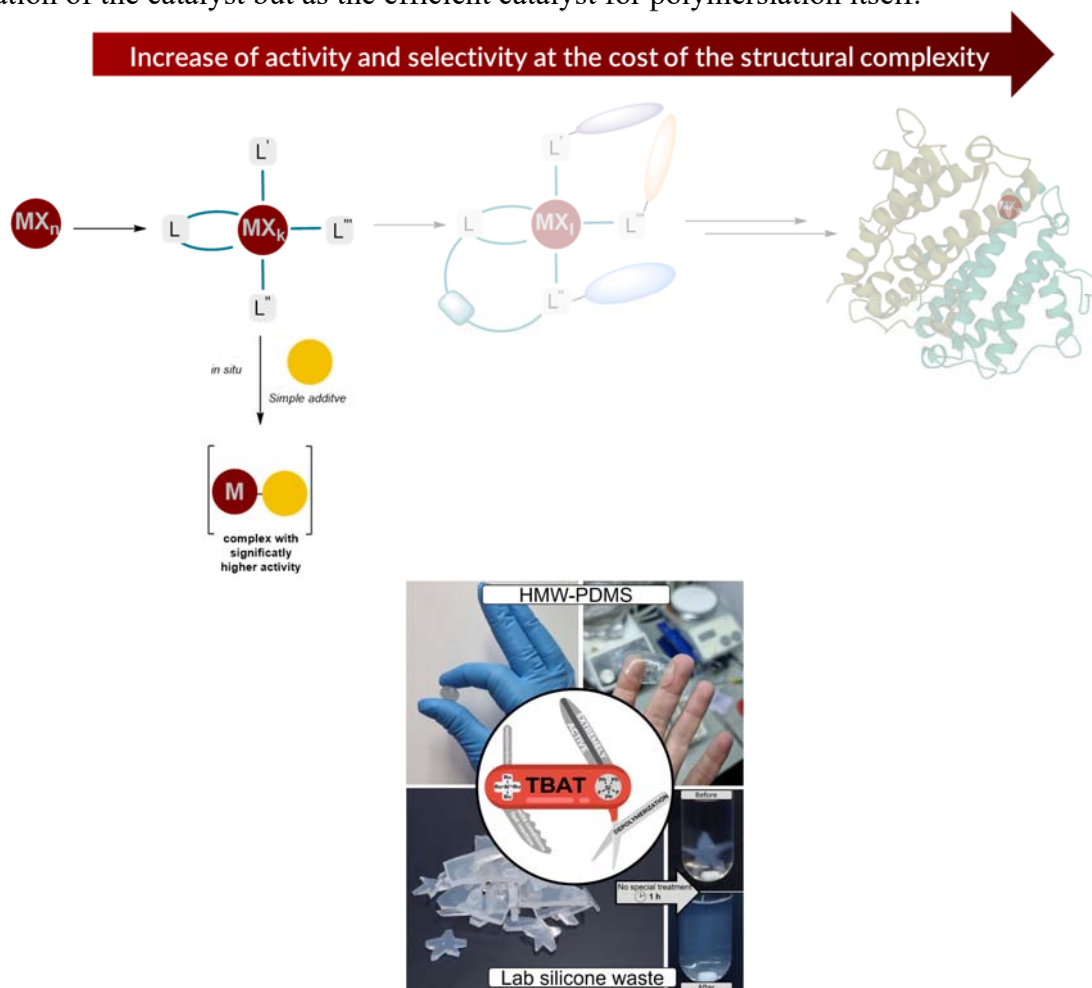
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Catalysis plays a key role in a wide variety of chemical transformations in both academic and industrial settings. The development of active and selective catalytic systems is therefore an important research topic; however, the increasing structural complexity of emerging catalysts, together with the poor stability and difficult isolation of the most active catalytic species, emphasize the need for alternative strategies based on the in situ activation of well-established and relatively simple systems. The addition of active fluoride additive might provide an effective means for improving the performance of some existing catalysts. We demonstrated the effectiveness of this approach on four transformations. Moreover, we showed that TBAT (Tetrabutylammonium Difluorotriphenylsilicate) might be used not only for activation of the catalyst but as the efficient catalyst for polymersiation itself.



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Organosilicon semiconducting oligomers and polymers for organic electronics

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Silicones are known as good dielectrics, however, their modification with π -conjugated or annulated fragments can lead to appearance of semiconducting properties. Moreover, it can improve the properties of initial organic semiconductors. Thus, 2,7-dialkyl-[1]benzothieno[3,2-b]benzothiophene (BTBT) are known for their high field-effect mobility, but their solution-processed thin films were found to be unstable during long time storage leading to strong degradation of organic field-effect transistors (OFETs) characteristics.¹ However, siloxane dimers of 2,7-dialkyl-BTBT can form not only highly stable thin films, but also self-assembled on the air-water interface monolayer films with good semiconductor properties, which could be used in OFETs, ultrasensitive gas sensors and electronic noses based on them.^{2,3} Similar properties were found for silazane dimers⁴ and organosilicon tetramers⁵ of BTBT. In this work synthesis and properties of siloxane homo- and copolymers with 2,7-dialkyl-BTBT side groups are reported. Dependencies of the content of BTBT-containing side groups and molar weight characteristics of the copolymers⁶ on their physical-chemical properties, phase behaviour and semiconductor characteristics are discussed. The crucial role of siloxane main chain on the semiconductor properties of the comb-shaped polymers is highlighted.⁷ An efficient way for improving field-effect mobility and long-term stability of OFET devices by co-crystallization of organosilicon BTBT-containing comb-shaped copolymers with C8-BTBT is suggested.⁸

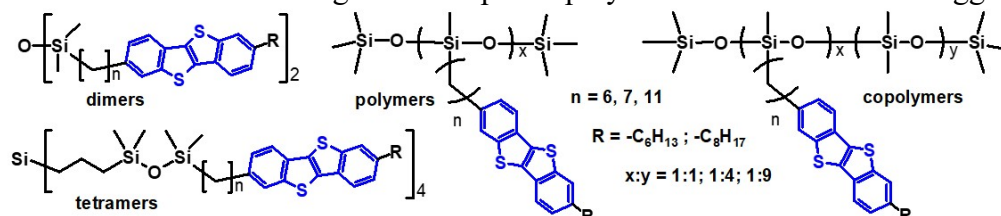


Fig. 1. Chemical structures of the organosilicon semiconducting oligomers and polymers.

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Siloxane-Linked Fluorescent Materials: Synthesis, Properties, and Applications

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Developing new organosilicon materials as viable complements or alternatives to carbon-based counterparts represents a pivotal research frontier in advanced materials science. However, the rapid evolution of this field is currently constrained by a scarcity of versatile synthetic methodologies. To address this, we have devised several novel strategies for synthesizing organosilicon materials, with a particular focus on those exhibiting intriguing fluorescence. Employing the Heck reaction, we have successfully synthesized a series of siloxane-linked fluorescent materials from vinyl-containing organosilicon monomers, including linear disiloxane, cyclosiloxanes, and cage silsesquioxanes, and various halogenated aromatic monomers.¹ This robust and efficient strategy allows for facile tuning of fluorescence by altering the structures of siloxane units and monomer species. Notably, in linear siloxane-linked systems, we discovered that the siloxane linkage functions not merely as a passive spacer, but as an active mediator of efficient through-space conjugation, thereby endowing the polymers with remarkable dual-state emission (Fig. 1).² For example, a spirobifluorene-based polymer achieves photoluminescence quantum yields of 92.7% in solution and 23.4% in the solid state. Furthermore, we elucidate that the pronounced bathochromic shifts observed in these systems originate from a cooperative negative hyperconjugation mechanism: $\pi_{C=C} \rightarrow LP^*(Si)$ delocalization and $n_O \rightarrow \sigma^*_{Si-C}$ electron donation from the bridging oxygen atoms.³ Collectively, these results redefine the role of siloxanes in optoelectronics and open new avenues for rational design of silicon-oxygen-based optoelectronic materials. Leveraging their excellent fluorescence, these materials exhibit promising potential in diverse applications, including chemical sensors, monitoring of food freshness, fingerprint recognition, and UV-shielding components.⁴

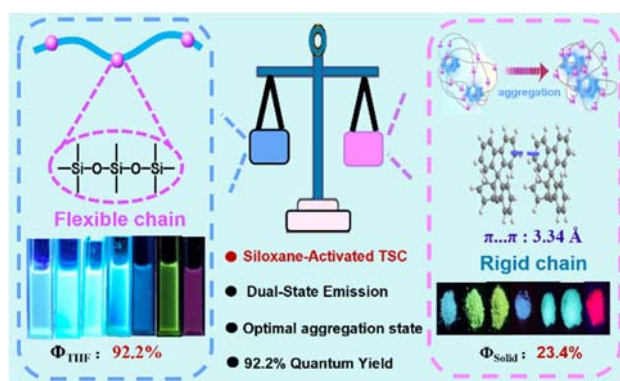


Fig. 1. Schematic presentation of siloxane-activated through-space conjugation for dual-state emission

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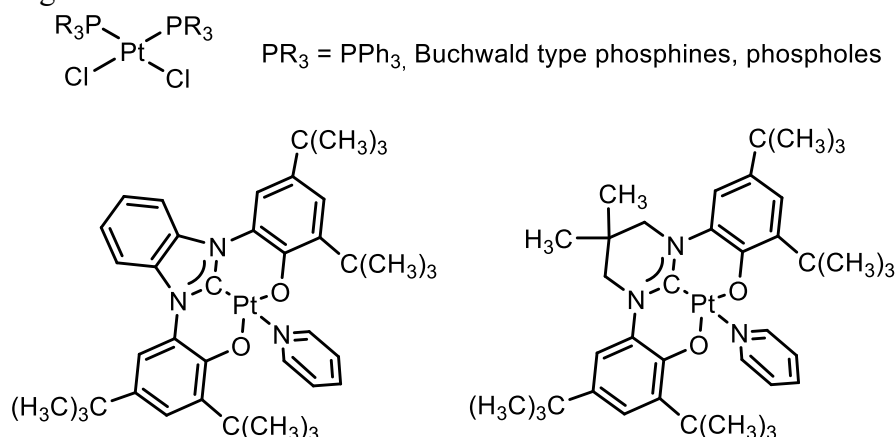
SYNTHESIS OF NOVEL PLATINUM CATALYSTS AND THEIR APPLICATION IN HYDROSILYLATION REACTIONS

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Platinum catalysts, such as the Karstedt's catalyst, are widely used in the hydrosilylation reaction, which enables the production of important industrial silicones such as coatings, adhesives, surfactants, and silicone rubber. However, they have a drawback in the form of colloidal platinum formation, which leads to undesirable side reactions like hydrogenation. Furthermore, excessively high catalytic activity often leads to premature vulcanization, i.e., the reaction commences already upon mixing the components of the reaction medium, which results in multiple defects (cracks, inhomogeneities, bubbles) in the resulting silicone rubber. To address this issue, Karstedt's catalyst is typically employed in combination with inhibitors. Another approach to overcoming this problem involves the incorporation of phosphines or *N*-heterocyclic Carbenes (NHCs) into the platinum complex. The development of new catalysts with controlled or stimuli responsive activity using innovative ligands opens up the prospect of improving the efficiency of industrial synthesis of silicone-containing materials.



The integration of novel ligand designs, such as those involving phenolate-NHC pincer or bulky phosphines PR_3 motifs (Buchwald type, phospholes), presents exciting opportunities for advancing this vital industrial process. Comparing with the Karstedt's catalyst, $(\text{PR}_3)_2\text{PtCl}_2$ complexes exhibit catalytic activity only when heated to 103–105 °C. The ability to switch catalytic activity *via* oxidation of the phenolate-NHC ligand framework opens new avenues for stimuli-responsive catalysis and offers practical advantages for silicone materials manufacturing.

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31 Years in Silicone Industry – GE Silicone, Wacker, Dow Corning and UNICONE*Wayne JIANG*

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This abstract summarizes a 31-year professional experience in the global silicone industry, highlighting the localized development of top international silicone manufacturers and the independent development layout of UNICONE Materials Technology (Shanghai) Co., LTD. From 1993 to 2025, global leading enterprises including GE Silicone, WACKER and Dow Corning completed institutional layout, factory construction, product iteration and continuous capacity expansion in Greater China, realizing the localized production and technical upgrading of high-end silicone products in Shanghai, Zhangjiagang and Nanjing bases.

The author possesses over 30 years of comprehensive industrial experience in silicone sales, marketing, technical services, R&D and overall management, including 16 years of senior management experience in the world's top three silicone enterprises. Starting from 1995, the author successively held core positions at GE Silicone, WACKER and Dow Corning, deeply participating in the localized operation and business development of international silicone giants in China. In 2012, the author founded UNICONE, serving as General Manager and Technical Director. Under his leadership, the company has built the production base and developed a series of innovative micro-nano silicone products with diverse core-shell composite structures, covering pure silicone elastomers, silicone resins and modified composite materials.

Equipped with solid academic backgrounds in polymer materials and business administration, the author has long witnessed and participated in the booming development of China's silicone industry. With profound industrial resources and practical management experience, he has formed in-depth insights into market competition and product application innovation, supporting UNICONE's differentiated competitive advantages and technological breakthroughs in high-end micro-nano silicone material localization.

The Current State of Vinyl Silicone Oil Development

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Vinyl silicone oil serves as a critical reactive polymer platform for addition-cure silicone systems, underpinning major applications ranging from liquid silicone rubber (LSR) and thermal interface materials (TIMs) to electronic encapsulation and advanced adhesives. As the global market shifts from commodity polymers toward customized functional materials, driven by rapid advancements in electric vehicles, AI servers, semiconductor packaging, and high-reliability medical devices, the demand for higher purity and application-specific solutions has intensified.

This presentation provides a comprehensive overview of the current state and future trajectory of vinyl silicone oil development. Historically, industrial focus has centered primarily on optimizing vinyl content. However, this presentation demonstrates that ultimate material performance is fundamentally dictated by molecular architecture. We explore the distinct advantages of different product architectures, including terminal vinyl PDMS for superior processability, side-chain vinyl silicone oils for enhanced network uniformity and mechanical customization, and multi-vinyl systems for specialty applications.

A key focus of the discussion is the application of advanced molecular design to overcome critical formulation challenges, particularly in thermal interface materials. Achieving extremely high inorganic filler loading while maintaining low mixing viscosity, optimal wetting, and post-cure elasticity requires a paradigm shift. Future development must prioritize designing silicone oils specifically for polymer-filler interactions – leveraging chain mobility, branching structures, and hybrid terminal/side-chain systems – rather than focusing solely on curing reactivity.

Furthermore, the presentation addresses current industrial manufacturing challenges, such as stable polymerization control, precise vinyl content management, and the transition of manufacturing methods. Finally, we analyze the global competitive landscape, highlighting the strategic transition of Chinese suppliers from a capacity-driven advantage to technology-driven differentiation against established international leaders. Ultimately, this work outlines a technology roadmap for 2026–2030, emphasizing that the next generation of high-performance silicones will be defined by precise molecular structural engineering.

Research progress of organosilicon materials: recyclable and sustainable

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In nature, no organosilicon compounds have been discovered. Since the 1940s, researches and applications of organosilicon compounds and materials have been greatly carried forward. At present, the science, technologies and industry of organosilicon materials are in an era of vigorous growth. Humankind is paying close attention to global sustainable development. The manufacture of organosilicon raw materials is an energy intensive industry (Fig. 1). This report briefly introduces the backdrop of global sustainable development and relevant research carried out within the organosilicon materials field ^{1,2}.

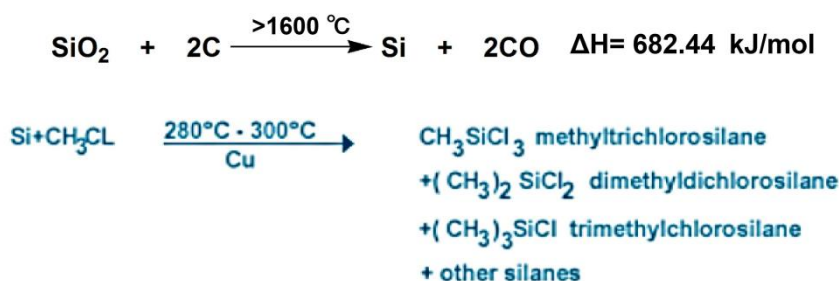


Fig. 1. Organosilicon industrial chemistry

The work was carried out with the financial support of Smart Grid-National Science and Technology Major Project (2025ZD0808802); Taishan Industry Leading Talent Program (tscx202312086).

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SILICONE BASED COMPOSITES. PERFORMANCE AND STRUCTURE*Chvalun S.N.*ISPM RAS
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The development of modern technologies requires the creation of a wide range of polymer and composite materials with various morphologies and adjustable physical-mechanical characteristics. The priority of technological policy is to achieve technological sovereignty – the presence of critical cross-cutting technologies of its own development in the direction of "new materials and substances technologies, their modeling, and development." Solving the assigned tasks in modern conditions is an extremely complex challenge and requires the identification of key priorities, which will be discussed during the talk.

The new approach to the design of elastomeric materials based on MQ copolymers. This technology exploits the dualistic properties of these objects that have both properties of macromolecules and colloid particles. MQ copolymers exhibit their molecular nature as homogeneous linking agents in the presented composites. They are also very efficient as active fillers. These fillers significantly enhance the mechanical indicators of vulcanized rubber: they are not inferior to aerosils but do not require a heterophase mixing of ingredients. MQ copolymers are indeed homogeneous linking agents in developed composites and are very efficient as active fillers. These fillers significantly enhance the mechanical properties of vulcanized rubber: they are not inferior to aerosils but do not require a heterophase mixing of ingredients. Variation of rubber type, MQ filler concentration and mechanical stress affected strongly the SAXS scattering. This permanent deformation completely disappears after heat treatment in the sample based on PDMS-A and is significantly reduced (up to about 15%) in the material based on PDMS-E. It also completely changes the shape of the deformation curve in the unloading, which acquires a pronounced "S" shape, with a sharp (instead of smooth) decrease in stress in the sample at the last (less than 50% deformation) stage of unloading. This behavior probably indicates a two-level structural organization in this composite material, associated both with the distribution of particles (or aggregates) of the MQ resin in the polymer matrix, and with the specific interaction of this active filler with silicone rubbers. The reported data clearly show that these additives affect the properties of vulcanized rubber to some extent. This implies that the reasonable control of its molecular parameters and optimization of concentrations also deserve detailed studies.

Gas separation membranes based on polycycloolefins with organoelement substituents: advances over the past 10 years

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The development of gas separation membranes is one of the most important directions of the application of organoelement polymers. Owing to valuable gas transport characteristics, membranes based on polysiloxanes have been applied in industry for over 40 years. At the present time they are still being studied. A number of classes of rigid-chain highly permeable glassy polymers have been developed on the basis of carbon-chain backbone polymers (such as polyolefins, polyacetylenes, polynorbornenes) bearing side trithethylsilyl groups.¹

Thanks to wide opportunities of macromolecular design, polycycloolefins represent a convenient class of polymers for both the investigations into fundamental structure-property relationships and the development of novel functional materials for various technological purposes. The simplicity of monomer synthesis, opportunity of polymerizations by different pathways, and universality of synthetic approaches to polymer post-modification characteristic of this class of polymers made it possible for the researchers to synthesize a wide range of polymeric structures with useful applied properties, including gas transport, sorption, dielectric, adhesion properties etc.^{2,3}

Polycycloolefins with organoelement side substituents combine high gas transport characteristics of organoelement polymers and outstanding synthetic opportunities of polycycloolefins. Over the last decade, a great amount of polynorbornenes bearing organosilicon and organogermanium substituents with promising gas transport characteristics has been synthesized. Among these characteristics, there are: high separation selectivity for CO₂/N₂, CO₂/CH₄, and H₂S/CH₄ gas pairs, high gas permeability, time stability of gas transport characteristics. The most interesting combination of properties is observed for the polymers bearing substituents with Si–O–C moieties,^{4,5} as well as the polymers with trialkylgermyl substituents.⁶

In the planned review lecture, the actual approaches to the synthesis of such polymers and initial monomers for them will be presented, the comparative analysis of gas transport characteristics for the membranes based on these polymers will be conducted, and the prospects of their application will be highlighted.

This work was carried out within the State Program of TIPS RAS.

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Direct Synthesis of Organoalkoxysilanes: A Cornerstone of Green Chemistry for Silicones

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The practical application of silicones has spanned over 80 years. Nowadays, it is pointless to list the fields of practical activity in which silicones are used. They cover such areas as aircraft and spacecraft engineering, medicine and pharmacology, construction of buildings and roads, and the production of textiles and paper.¹⁻³ It would be easier to name the areas where silicones are not used, but even searching for those would require considerable effort.

Like many other fields of technology, silicone production can be represented in terms of generations according to its technological paradigms⁴ (Fig. 1):

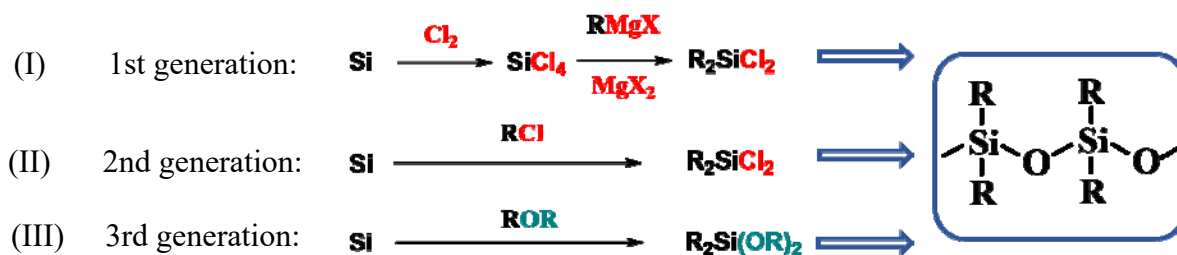


Fig. 1: Scheme of generations of silicone production.

The first generation is the synthesis of silicon tetrachloride and the subsequent organomagnesium synthesis of organochlorosilanes (Fig. 1, I). The second generation is the direct synthesis of organochlorosilanes. The transition to it was revolutionary, instantaneous on our timescale. This second technological paradigm (Fig. 1, II) became dominant at all production facilities in a multitude of variations. Nevertheless, the second generation of silicone production is already exhausting itself. This is due to the environmental and economic limitations of the process. These drawbacks are absent in the third generation of silicone production – the direct synthesis of alkoxysilanes (Fig. 1, III).

The presentation analyzes the current state of the field of direct synthesis of alkoxysilanes. The main approaches, problems and prospects of this process are highlighted. The proposed reaction mechanism is considered, as well as the factors that have a significant influence on the course of the process. Among such factors are: temperature, type and content of catalyst, promoting additives, method of conducting the process, etc. Emphasis is placed on the possibility of producing organoalkoxysilanes by the direct synthesis method.

This work was carried out with financial support from the Russian Science Foundation (RSF) (project No. 22-13-00279).

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Tuning the Dielectric and Mechanical Properties of PDMS/MQ Composites for Advanced Soft Actuators

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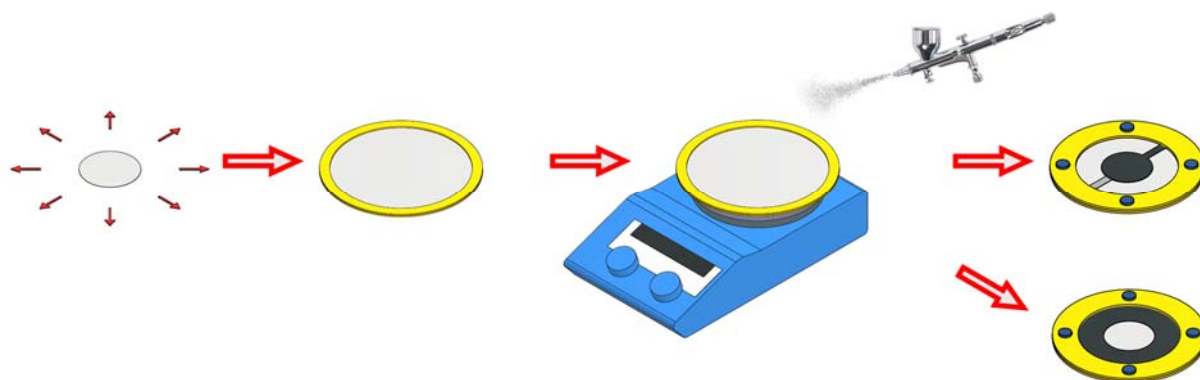
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Artificial muscles are soft actuators that respond to external stimuli—such as electric fields, temperature, or pH—by producing force and shape changes.¹ However, many existing soft actuators generate insufficient force and strain for practical applications. Among emerging technologies, dielectric elastomer actuators (DEAs) show exceptional promise due to their ability to closely mimic natural muscle behavior. DEAs function as soft capacitors, deforming under an applied voltage and returning to their original shape upon discharge. Despite their potential, current DEAs require impractically high operating voltages, posing safety concerns.

According to Pelrine's model two key strategies to achieve large deformations at reduced voltages: (1) optimizing the ratio of the dielectric constant (ϵ) to Young's modulus (Y), and (2) minimizing the elastomer thickness (z).²

This work explores PDMS/MQ composites and approaches to enhance ϵ/Y for improved performance.³ We demonstrate a circular DEA (cDEA) fabricated via equibiaxial stretching and electrode deposition, capable of reversible expansion under an electric field. Additionally, we present a load-bearing cDEA design that displaces weights upon actuation. Preliminary results will be discussed, highlighting progress toward low-voltage, high-performance artificial muscles.



This work was supported by RSF (project № 26-63-00052)

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Oral talks

The use of polyhydroxyl methylsilsesquioxanes and superbranched polymethylsiloxanes as surfactants for polymerization of methyl methacrylate

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The fields of use of polymer suspensions cover the production of paints, textile impregnation, as well as the creation of films and clothing. Monodisperse polymethylmethacrylate (PMMA) microspheres, characterized by excellent transparency, biocompatibility and low price, are the most in demand among acrylic dispersions [1]. Technologically, the synthesis of such microspheres is realized by various methods of radical polymerization [2], but the industry is dominated by the heterophase method, which is environmentally friendly, allows achieving high molecular weight and uses water as a reaction medium [1]. Despite the advanced technology, the current challenges remain increasing the concentration of the target polymer and the stability of the dispersions, minimizing the residual monomer and eliminating toxic surfactants [3]. Basically, the possibility of using organosilicon surfactants is being actively studied for this purpose. In this context, polydimethylsiloxanes modified with hydrophilic groups (terminal or distributed along the main chain) are most often considered [4].

This work is devoted to the use of superbranched polymethylethoxysiloxanes modified with polyethylene glycol (PMEOS-PEG, fig.1a), capable of chemical transformations during polymerization processes, and polyhydroxyl polymethylsilsesquioxanes (PMSSO, fig.1b) as surfactants for the heterophase polymerization of methyl methacrylate.

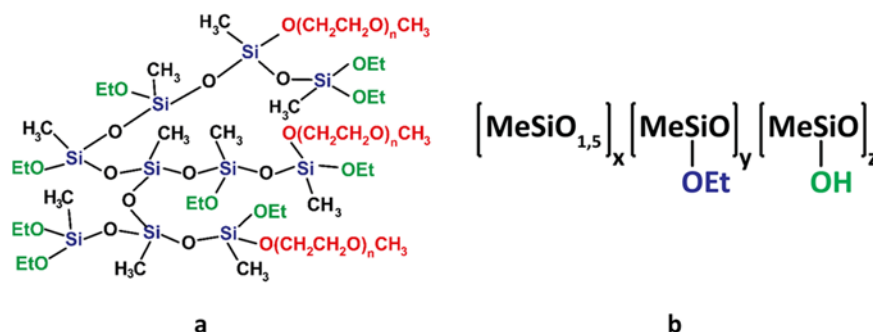


Fig. 1. General chemical structure of PMEOS-PEG(a) and PMSSO(b)

The report will show the results of a study of the effect of the composition of synthesized superbranched PMEOS-PEG and polyhydroxyl silsesquioxanes on the characteristics of polymer suspensions obtained by heterophase polymerization of methyl methacrylate. The particle size, the dispersion of the polymer suspension, and the electrokinetic potential ξ were determined using a ZetasizerNano ZS Malvern particle analyzer (Great Britain).

The work was carried out with the financial support of the Russian Science Foundation (project No. 21-73-30030_P).

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Composite material based on cobaltocenium-containing polysiloxane and carbon nanotubes for electrocatalysis

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The rising global demand for electrical energy calls for alternative energy carriers. Molecular hydrogen is particularly favorable due to its superior gravimetric energy density relative to conventional fuels and the fact that its combustion generates only water as a byproduct. These attributes position hydrogen as a highly effective energy vector with significant potential for real-world application. A viable route for generating green hydrogen is the electrochemical reduction of water, facilitated by the hydrogen evolution reaction (HER) via catalysis [1].

An emerging strategy for developing heterogeneous HER catalysts involves modification of carbon nanotubes (CNT) with polymer-metal complexes [1]. These complexes offer well-defined structures and enhance the grafting density of catalytic active sites onto the solid support. Of the various polymer ligands used in polymer-metal complexes, polysiloxanes are the most promising. They combine flexibility, thermo- and UV-stability, broad operating temperature range, and low surface energy. Uniquely, polysiloxanes also show CH- π interactions with CNT and are readily functionalizable with organometallic compounds, paving the way toward tunable and versatile catalytic systems [2,3]. As metal centers, cobaltocenium molecules are reported for hydrogen production [4].

In this study, we developed heterogeneous HER catalyst based on CNT modified with cobaltocenium-containing polysiloxanes (Cc-PMHS/SWCNT). Cc-PMHS was earlier synthesized in our scientific group [5]. In HER catalysis, the overpotential of Cc-PMHS/SWCNT is 590 and 220 mV for 0.1M and 0.5M H₂SO₄, respectively. The Faradaic efficiency of Cc-PMHS/SWCNT reaches 98%. Cc-PMHS/SWCNT demonstrate catalytic performance for at least 24 h [1].

The study was supported by the Russian Science Foundation (project 24-13-00038). The physicochemical measurements were performed at the Research Park of St. Petersburg State University (Centre for Optical and Laser Materials Research, Centre for Physical Methods of Surface Investigation, Interdisciplinary Resource Centre for Nanotechnology, Centre for Innovative Technologies of Composite Nanomaterials).

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TBAT as “Multitool” catalyst for polysiloxanes synthesis, modification and recycling

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A convenient, stable, and non-toxic substance, tetrabutylammonium difluorotriphenylsilicate (TBAT), was proposed as an efficient organocatalyst for all stages of polymer lifetime – synthesis, modification, and recycling.¹ The fluorine-containing initiator showed high activity in the polymerization of siloxanes compared to classic organocatalytic systems such as tetramethylammonium hydroxide. At the same time, TBAT stands out favorably among state-of-the-art catalytic systems (*e.g.*, hydroxides, alkoxides, or silanates of amidines, guanidines, proazaphosphatranes, and phosphazenes) for its low price and high availability, while exhibiting the same level of activity. By kinetically controlled ROP, a high-molecular-weight PDMS was prepared at room temperature using ppm-level loadings of TBAT. The system also proves suitable for ring-opening polymerization of other cyclic siloxanes containing methyl(vinyl), methyl(3,3,3-trifluoropropyl), and methylphenyl substituents. Variation of reaction conditions enables the depolymerization of synthesized, commercial, and post-consumer samples. Thus, TBAT is a suitable catalyst for the full cycle of processing and reuse of PDMS, as well as for its modification (Fig. 1).

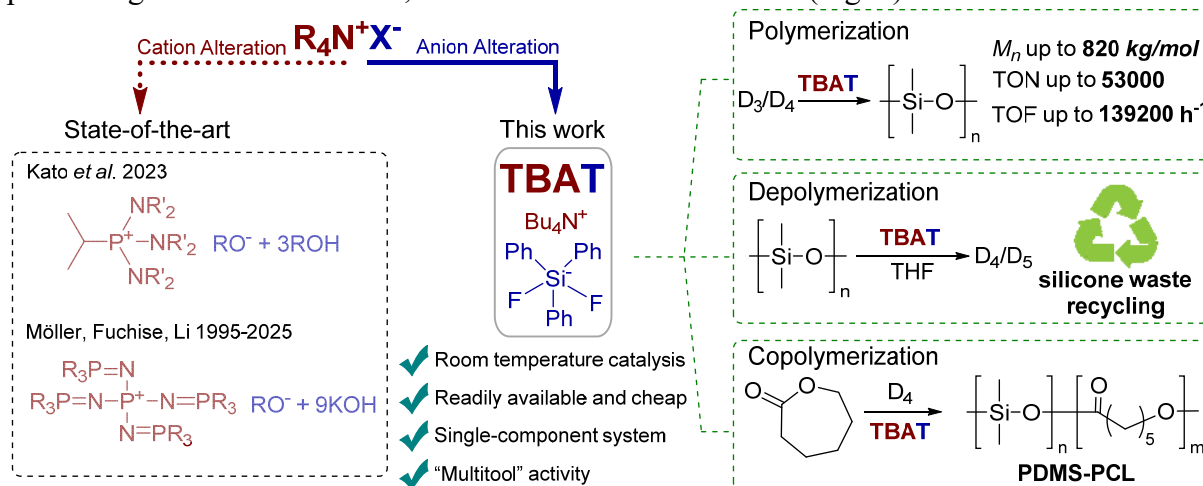


Fig. 1. Application of TBAT for polymerization, copolymerization and recycling of PDMS.

This work was supported by the Russian Science Foundation (Grant No. 24-43-00096) and NSFC (Grant No. 22361132535).

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Synthesis of amphiphilic compounds based on stereoregular macrocyclic silsesquioxanes

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Organosilicon cyclic structures are widely spread in industry and being used for obtaining different polymer structures. Cyclosiloxanes are intensively applied in industry for synthesis of high-molecular weight siloxanes with different ratios of units and properties. Besides the most popular in industry cyclosiloxanes like D₃, D₄, D₅ etc., there is a type of stereoregular macrocyclic silsesquioxanes, which performs an interest with the fundamental point of view.

Stereoregular macrocyclic silsesquioxanes were firstly discovered in the A.N. Nesmeyanov Institute of organoelement compounds (INEOS). At certain conditions with the addition of alkali oligocyclization with the formation of metallosiloxane occurs. Metal ions work as templates and fix surrounding organosilicon fragments in a specific way, therefore self-organized structures appear¹ (Fig. 1). Via changing template, we can vary the macrocycle size, and adding different ligands can affect the architecture of the macrocycle².

By treating metallosiloxanes with chlorosilanes of different functionality allows to obtain stereoregular macrocyclic silsesquioxanes, which appears to be perfect substrates for further chemical modification.

In our work we used stereoregular macrocycles with vinyl and hydride groups for further modification by sequential hydrothiolation-hydrosilylation reactions³. To synthesize amphiphilic structures, we decided to use dodecyl chains as hydrophobic substituents, and polyethylene oxide chains with polymerization ratio 7, 12 and 25 as hydrophilic substituents respectively. All the obtained silsesquioxanes were analyzed using physico-chemical methods of analysis including ¹H, ²⁹Si, ¹³C NMR spectroscopy, GPC and differential-scanning calorimetry and mass-spectrometry MALDI-ToF. Moreover, the resulting amphiphilic structures were studied with spinning drop tensiometer, and isotherms of interfacial tension were built. The CMC were calculated using tangent method.

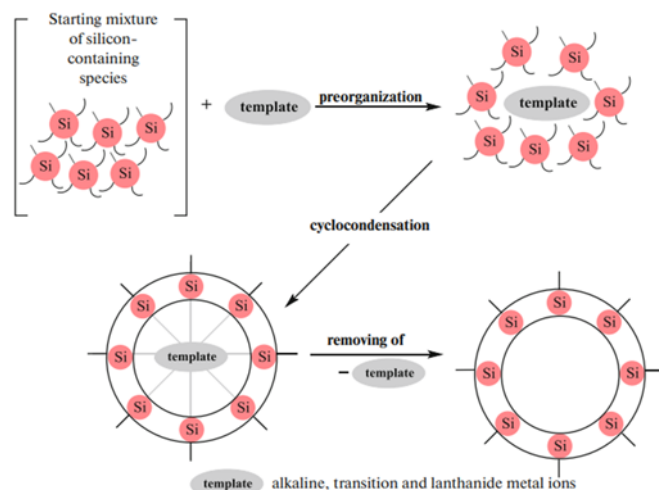


Figure 1. Schematic representation of stereoregular macrocyclic silsesquioxanes formation

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