

**XIV Andrianov Conference "ORGANOSILICON COMPOUNDS.
SYNTHESIS, PROPERTIES, APPLICATIONS"
June 3-6, 2018, Moscow, Russia**

ОРГАНИЗАТОРЫ:

ФГБУ РОССИЙСКАЯ АКАДЕМИЯ НАУК
ОТДЕЛЕНИЕ ХИМИИ И НАУК О МАТЕРИАЛАХ

НАУЧНЫЙ СОВЕТ РАН
ПО ВЫСОКОМОЛЕКУЛЯРНЫМ
СОЕДИНЕНИЯМ

НАУЧНЫЙ СОВЕТ РАН
ПО ОРГАНИЧЕСКОЙ ХИМИИ

ФГБУН ИНСТИТУТ ЭЛЕМЕНТООРГАНИЧЕСКИХ СОЕДИНЕНИЙ
им. А.Н. Несмеянова РАН

ФГБУН ИНСТИТУТ СИНТЕТИЧЕСКИХ ПОЛИМЕРНЫХ
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АО «ГОСУДАРСТВЕННЫЙ ОРДЕНА ТРУДОВОГО КРАСНОГО
ЗНАМЕНИ НАУЧНО-ИССЛЕДОВАТЕЛЬСКИЙ ИНСТИТУТ ХИМИИ И
ТЕХНОЛОГИИ ЭЛЕМЕНТООРГАНИЧЕСКИХ СОЕДИНЕНИЙ»

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ХИМИЧЕСКИЙ ФАКУЛЬТЕТ

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SCIENTIFIC PROGRAM / НАУЧНАЯ ПРОГРАММА

Sunday, June 3, 2018 / Воскресенье, 3 июня 2018 г.

Time	Lecture #	Title	Speaker
14:00-16:00	<i>Registration / Регистрация</i>		
16:00-16:20	Opening ceremony / Открытие		
Sunday session, 16:20-17:30			
Chairs: Aziz Muzafarov, Mikhail Egorov			
16:20-17:00	PL 1	Light Driven Microgel Objects – Motion Out of Equilibrium	Möller Martin
17:00-17:40	IL 1	Cyclobutadiene Complexes of the s-, p-, and d-Block Elements	Lee Vladimir
18:00-20:00	<i>Welcome party / Фуршет</i>		

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Monday, June 4, 2018 / Понедельник, 4 июня 2018 г. (English language)

Time	Lecture #	Title	Speaker
9:30-16:0	<i>Registration / Регистрация</i>		
Morning session 1, 9:30:00-11:10			
Chairs: Vladimir Papkov, Serguey Chvalun			
10:00-10:40	PL 2	Encoding Tissue Mechanics in Silicone	Sheiko Sergey
10:40-11:10	IL 2	Stereodynamic Behavior of Novel Hypervalent Compounds of 14th Group – Derivatives of Amides, Lactams and Imides	Negrebetsky Vadim
11:10-11:40	IL 3	About a Role of Organosilicon Additives at Spinning of Cellulose Fibers and at Their Thermolysis	Kulichikhin Valery
11:40-12:00	<i>Coffee break</i>		
Morning session 2, 11:30-13:30			
Chairs: Aziz Muzafarov, Sergey Ponomarenko			
12:00-12:40	PL 3	Silicon Chemistry in Outer Space: Past and Future	Avnir David
12:40-13:10	IL 4	Silicon-Based Magnetoactive Elastomers: New Properties and New Applications	Kramarenko Elena
13:10-13:40	IL 5	Nanostructured Silica-Based Materials via Polyethoxysiloxane-Assisted Surfactant-Free Emulsion Technique	Zhu Xiaomin
13:40-14:40	<i>Lunch</i>		
Afternoon session, 14:40-17:10			
Chairs: Vladimir Lee, Feng Shengyu			
14:40-15:10	IL 6	Synthesis of SiCl ₄ from Orthosilicates	Katsoulis Dimitris
15:10-15:40	IL 7	Wagner-Meerwein-Type Rearrangements of Polysilanes	Mueller Thomas
15:40-16:00	O 1	Polyhedral Oligosilsesquioxanes in Polymer	Zhu Qingzeng
16:00-16:20	O 2	Fluorescent Paper Sensor Based on POSS-Containing Porous Polymer for Visual Detection of Nitroaromatic Explosives	Wang Dengxu
16:20 -16:40	O 3	Two Photon Fluorescent Silicon Elastomers	Yujing Zuo
16:40 -18:30	<i>Coffee break & Poster Session 1 (P1-P38)</i>		

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Tuesday, June 5, 2018 / Вторник, 5 июня 2018 г.

Time	Lecture #	Title	Speaker
Morning session 1, 9:30:00-11:10 (English language) Chairs: Xiaomin Zhu, Vadim Negrebetsky			
9:30-10:10	PL 4	Exploration of New Synthesis Methods for Organosilicon Compounds and Polymers	Jie Zhang
10:10-10:50	PL 5	Synthesis of Sulfur-Containing Organosilicon Compounds and Materials	Feng Shengyu
10:50-11:20	IL 8	New Approaches to the Regulation of Gas Separation and Other Properties of Silicon-Substituted Polynorbornenes	Gringolts Mariya
11:20-11:40	<i>Coffee break</i>		
Morning session 2, 11:30-13:20 (English language) Chairs: Maria Gringolts, Zinaida Shifrina			
11.40-12.10	IL 9	Silsesquioxanes - Based Nanoporous Materials for Water Remediation	Hongzhi Liu
12.10-12.40	IL 10	Protatranes and Hydrometallatranes – New Biologically Active Analogues of Silatranes	Kochina Tatiana
12:40-13:00	O 6	Organosilicon Derivative of Benzothienobenzothiophene as Selective and Highly Sensitive Layer for OFET-Based Gas Sensors	Agina Elena
13:00-13:10	O 7	Study of the Intermolecular Interaction of Carbosilane Dendrimers with a Branched Siloxane Shell	Selezneva Elizaveta
13:10-13:20	O 8	Aerobic Oxidation of Hydride Siloxanes: Synthesis of Siloxanols	Goncharova Irina
13:20-14:30	<i>Lunch</i>		
Afternoon session 1, 14:30-16:10 (Официальный язык – русский) Chairs: Olga Shchegolikhina, Elena Kramarenko (Ольга Щеголихина, Елена Крамаренко)			
14:30-14:50	O 9	Polymer Nanoparticles for Biomedical Applications From Hydroxyl-Containing Alkoxysilanes	Ladilina Elena
14:50-15:10	O 10	Self-Organizing Nanocomposites Based on Silicone-Urea Block Copolymers	Komarov Pavel
15:10-15:30	O 11	Preparation of a Hydrophobic Glass-Polymer Material Based on Silica Fabric	Kiryukhin Dmitriy
15:30-15:50	O 12	Boron-Substituted Carboranes as a Platform for Design of Novel Silicon Materials	Anisimov Anton
15:50-16:10	O 13	Ceramic fibers based on polycarbosilane	Zhigalov Dmitriy
16:10-16:30	<i>Coffee break</i>		
Afternoon session 2, 16:30-18:00 (Официальный язык – русский) Chairs: Olga Serenko, Maksim Sherbina (Ольга Серенко, Максим Щербина)			
16:30-16:50	O 14	MQ-Copolymers	Tatarinova Elena

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16:50 -17:10	O 15	Synthesis and Gas Transport Properties of Fe- and Zr-Containing Polydimethylsiloxanes	Belov Nikolay
17:10-17:30	O 16	Deposition of Plasma-Polymerized Hexamethyldisilazane Films onto Polypropylene Track-Etched Membrane Surface	Kravets Lubov'
17.30-17.50	O 17	Tribological Properties of Polyorganosiloxane and Their Mixtures with Basic Oils	Lyadov Anton
17:50-18:00	O 18	Reactions of Silicon Hydrides Catalyzed by Rhodium(III) Sulfoxide Complexes	Novozhilov Vladimir

Wednesday, June 6, 2018 / Среда, 6 июня 2018 г. (русский язык)

Time	Lecture #	Title	Speaker
Morning session: 9:30-11:10 (Официальный язык – русский)			
Chairs: Oleg Borshchev, Elena Agina (Олег Борщев, Елена Агина)			
9:30-10:00	IL 11	Influence of the Silicon Atom on the Properties of Conjugated Oligomers	Borshchev Oleg
10:00-10:20	O 19	Synthesis of New Functional Siloxane Derivatives of Limonene by a Combination of Hydrosilylation and Hydrothiolation Reactions	Drozдов Fedor
10:20-10:40	O 20	Mechanochemical Approach to the Direct Synthesis of Alkoxysilanes	Temnikov Maksim
10:40-10:50	O 21	Low-Melting Silicon Containing Phthalonitrile Monomers for Thermosetting Resins with Improved Processability	Bulgakov Boris
10.50-11.00	O 22	Synthesis of Fluorescent Siloxane Dyes Based on DBMBF2	Belova Anastasiya
11:00-11:10	O 23	Platinum Group Metal Complexes as Catalysts for Polysiloxanehydrosilylation Cross-Linking	Dobrynin Mikhail
11:10-11:20	O 24	Synthesis and Properties of Polynorbornenes Containing Trialkoxysilyl Groups	Alentiev Dmitry
11:20-11:30	O 25	Кремнийорганические Соединения от Немецкого Производителя abcГ GmbH	Danilova Tatyana
11:30-13:10	<i>Coffee break and Poster Session 2(P39-P71)</i>		
13:10-13:30	<i>Closing Ceremony, A. Muzafarov</i>		

14:00 – Круглый стол «Кремнийорганические соединения и полимеры: от теории к практике»

СТЕНДОВЫЕ ДОКЛАДЫ / LIST OF POSTERS

Постерная сессия 1: 4 июня 2018 г. (16:40-18:30)
Poster session 1: June 4, 2018 (16:40-18:30)

- P-1 Synthesis of Polydimethylsiloxane Copolymers Based on N,N'-Ethylenediundeceneamide**
S.N. Ardabevskaia, E.V. Selezneva, S.A. Milenin, A.M. Muzafarov
Enicolopov Institute of Synthetic Polymeric Materials, Moscow Technological University, Moscow, Russia
- P-2 Heat-Conducting Gasket Materials Based on Organosilicon Binders**
P.A. Storozhenko, A.N. Polivanov, T.I. Fedotova, A.V. Levchuk, A.G. Ivanov, A.I. Drachev, M.G. Kuznetsova, V.A. Bardakova, N.V. Tyurikova, N.Yu. Mel'nikova
SSC RF JSC GNIChTEOS, Moscow, Russia
- P-3 Synthesis of Cyclosiloxanes with Different Organic Groups at Silicon Atoms**
Chernov E. V., Kalinina A. A., Talalaeva E. V., Muzafarov A. M.
Enikolopov Institute of Synthetic Polymeric Materials of RAS, A. N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
- P-4 Synthesis and Cross-Linking of Addition Copolymers Based on Silicon-Containing Tricyclononenes**
E.S. Egorova, D.A. Alentiev, M.V. Bermeshev, E.Sh. Finkelshtein
A.V. Topchiev Institute of Petrochemical Synthesis of RAS, Moscow Technological University, Moscow, Russia
- P-5 Silicone Aerogels with Tunable Mechanical Properties Obtained via a Hydrosilylation Approach in Supercritical CO₂**
I.V. Elmanovich, T.A. Pryakhina, D.A. Migulin, M.O. Gallyamov, A.M. Muzafarov
M.V. Lomonosov Moscow State University, A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
- P-6 Buthylene Oxide – Siloxane – Urethane Elastomers: Synthesis and Properties**
Filimonova L.V., Makarova L.I., Buzin M.I., Kononova E.G., Vasil'ev V.G., Afanas'ev E.S., Volkov I.O., Nikiforova G.G., Papkov V.S.
A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
- P-7 Oligoorganometalsilazanes – Precursors of High-Heat-Resistant Multiceramics**
K.N. Gerasimov, O. G. Ryzhova, P. A. Storozhenko, P.A. Timofeev, A.Ya. Yakimova, A.I. Drachev, I.A. Timofeev, A.N. Polivanov, M.G. Kuznetsova.
SSC RF GNIChTEOS, Moscow, Russia
- P-8 Synthesis of Carbosilane Dendrimers with Terminal Carboxyl Groups**
O. Gorbatshevich, A. Muzafarov
N. S. Enikolopov Institute of Synthetic Polymeric Materials of RAS, Moscow, Russia
- P-9 Stereospecific Hydrosilylation of Norbornadiene-2,5 in the Presence of Pd-Catalyst**
Guseva M.A., Chapala P.P., Bermesheva E.V., Bermeshev M.V.
A.V. Topchiev Institute of Petrochemical Synthesis of RAS, Moscow Technological University, Moscow, Russia
- P-10 Synthesis of Epoxysiloxanes by Hydrosilylation in the Presence of Supported Pt(II) Complex**
M. A. Il'ina, D. A. de Vekki and N. K. Skvortsov
St. Petersburg State Institute of Technology, St. Petersburg, Russia

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- P-11 Biologically Active Silicone Polymers**
V. Istratov, T. Krupina, V. Vasnev
A.N. Nesmeyanov Institute of organoelement compounds of RAS, Moscow, Russia
- P-12 New Exocyclic Seven- and Nine-Membered *o*-Carboranyl-methyl-Containing Organosiloxanes. the Effective Method for Synthesis from Bis-(Brommagnesiummethyl)-*o*-Carborane and Chloro(organo)siloxanes**
Izmaylov B.A., Vasnev V.A., Markova G.D.
A.N. Nesmeyanov Institute of organoelement compounds of RAS, Moscow, Russia
- P-13 Comparison of Chlorine-Free Approaches to the Synthesis of Hydride-Containing Siloxanes**
Kalinina A., Pryakhina T., Elmanovich I., Gallyamov M., Muzafarov A.
Enikolopov Institute of Synthetic Polymeric Materials of RAS,
A. N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
- P-14 Carbosilane Dendrimers with a Carboranilic Shell: Synthesis and Properties**
Kapelistaya E.A., Anisimov A.A., Milenin S.A., Zaitsev A.V., Ol'shevskaya V.A., Buzin M.I., Muzafarov A.M.
D. Mendeleev University of Chemical Technology, Moscow, Russia
A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Russia, Moscow
- P-15 A Study of the Impact of the Phenylsilsesquioxane Resin Structure on Properties of Transparent Addition Cure Compositions**
A.G. Kazaeva, I. Yu. Ruskol, E. I. Alekseeva, A. K. Shestakova, A.G. Ivanov
D. Mendeleev University of Chemical Technology, Moscow, Russia
- P-16 Oligoorganosilsesquisilazanes – Preceramic Oligomers of High-Heat-Resistant Ceramic Fibers**
E.N. Khaustov, O.G. Ryzhova, P.A. Storozhenko, P.A. Timofeev, A.N. Polivanov, I.A. Timofeev, A.I. Drachev, M.G. Kuznetsova.
The State Scientific Center of the Russian Federation “State Research Institute for Chemistry and Technology of Organoelement Compounds”, Moscow, Russia
- P-17 Synthesis of Silica Nanogels with an Amphiphilic Surface Layer**
Kholodkov D. N., Kazakova V. V., Muzafarov A. M.
A. N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
- P-18 Radiation Synthesis, Properties and Application of Tetrafluoroethylene Telomers with Silane End Groups**
G. A. Kichigina, P. P. Kushch, and D. P. Kiryukhin
Institute of Problems of Chemical Physics of RAS, Moscow, Russia
- P-19 Synthesis and Structure of Binuclear Complexes of Transition Metals Based on Bis- β -Diketones**
Kim E.E., Kononevich Yu.N., Korlyukov A.A., Volodin A.D., Muzafarov A.M.
D.I. Mendeleev University of Chemical Technology,
A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
- P-20 Curing Peculiarities of Polycarbosilane-Based Polymeric Fibers**
A.P. Korolev, D.V. Zhigalov, G.I. Shcherbakova, M.Kh. Blokhina, A.A. Vorob'ev
State Scientific Center of the Russian Federation “State Research Institute for Chemistry and Technology of Organoelement Compounds”, Moscow, Russia
- P-21 Dicationic Polydimethylsiloxane Ionic Liquids**
V. Krasovskiy, L. Glukhov, E. Chernikova, O. Gorbatshevich, A. Koroteev, L. Kustov a
N. D. Zelinsky Institute of Organic Chemistry of RAS, Moscow, Russia

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- P-22 Synthesis Of Carbofluoroorganochlorosilanes**
Lakhtin V.G., Fedotova T.I., Sokol'skaya I.B., Efimenko D.A., Ushakov N.V., Bykovchenko V.G., Storozhenko P.A.
State Scientific Center of the Russian Federation "State Research Institute for Chemistry and Technology of Organoelement Compounds", Moscow, Russia
- P-23 New Silicon-Containing Ionic Liquid-Based Materials for Gas Separation and Electrochemical Applications**
E.I. Lozinskaya, A.S. Shaplova, D.Yu. Antonov, M.I. Buzin, I.M. Marrucho, Y.S. Vygodskii
A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
- P-24 Synthesis of Titanosiloxanes Containing Functional Alkoxy Groups**
Polshchikova N.V., Meshkov I.B., Tokazova R.U., Buzin M.I., Muzafarov A.M.
Institute of Organoelement Compounds (INEOS RAS), Moscow, Russia
- P-25 Synthesis of Polydimethylsiloxanes with Hydroxyl Groups Distributed on the Chain**
Polyakov G.V., Shchegolikhina O.I., Kalinina A.A., Muzafarov A.M.
Enikolopov Institute of Synthetic Polymeric Materials of RAS, Moscow, Russia
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D. Mendeleev University of Chemical Technology, Moscow, Russia
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Sergienko N.V., Strelkova T.V., Boldyrev K.L., Makarova L.I., Muzafarov A.M.
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- P-29 Polycondensation of Methacryloxypropyltriethoxysilane under Active Medium Conditions**
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Smyshlyayev A.I., Vysochinskaya Yu.S., Anisimov A.A., Shchegolikhina O.I., Muzafarov A.M.
Moscow Technological University, A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Russia, Moscow
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Shugakova E.I., Vysochinskaya Yu.S., Anisimov A.A., Dolgushin F.M., Shchegolikhina O.I., Muzafarov A.M.
Moscow Technological University, A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Russia, Moscow
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Talalaeva E.V., Kalinina A.A., Zenkovskaya D.A., Belova L.O., Demchenko N.V., Muzafarov A.M.
Enikolopov Institute of Synthetic Polymeric Materials of RAS, Moscow, Russia

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P.A. Tikhonov, S.A. Milenin, E.A. Tatarinova, N.V. Demchenko, G.V. Cherkaev, N.G. Vasilenko, D.I. Shragin, A.M. Muzafarov
Institute of Synthetic Polymeric Materials of RAS, Moscow, Russia
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Vysochinskaya Yu.S., Anisimov A.A., Buzin M.I., Vasil'ev V.G., Shchegolikhina O.I., Muzafarov A.M.
N.S. Enikolopov Institute of Synthetic Polymeric Materials of RAS, A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Russia, Moscow
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P.A. Zader, A.A. Anisimov, A.A. Korlyukov, A.M. Muzafarov
D. Mendeleev University of Chemical Technology, Moscow, Russia, A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Russia, Moscow
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A.V. Topchiev Institute of Petrochemical Synthesis of RAS, Moscow, Russia
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S.N. Zimovets, M.N. Temnikov, E.A. Gubkin, E.V. Talalaeva, A.A. Kalinina, A.M. Muzafarov
N.S. Enikolopov Institute of synthetic polymeric materials of RAS, A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
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Zodbinov E.B., Bulgakov B.A., Afanasiev D.V., Babkin A.V.
Lomonosov Moscow State University,
Institute of New Carbon Materials and Technology, Moscow, Russia

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A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Enikolopov Institute of Synthetic Polymeric Materials of RAS, Moscow, Russia
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G.I. Shcherbakova, M.Kh. Blokhina, D.V. Zhigalov, A.P. Korolev, P.A. Storozhenko
SSC RF JSC “State Research Institute for Chemistry and Technology of Organoelement Compounds”, Moscow, Russia
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K. Boldyrev, A. Arzumanyan, S. Milenin, I. Meshkov, E. Tatarinova, A. Muzafarov
INEOS RAS, ISPM RAS, Moscow, Russia
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Kosygin Russian State University, ISPM RAS, INEOS RAS, Moscow, Russia

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E. I. Alekseeva, A. R. Dolotko, I. Yu. Ruskol, E. V. Sokoluk, R. R. Zakirov
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P.A. Storozhenko, A.N. Polivanov, T.I. Fedotova, N.V. Tyurikova, A.I. Drachev, A.V. Levchuk, K.E. Smirnova, V.A. Bardakova
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Institute of Physical and Organic Chemistry, Southern Federal University, Rostov on Don, Russia
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N.A. Golub, M.V. Pletneva, L.O. Belova, A.D. Kirilin
Moscow Technology University, Moscow, Russia
- P-48 Comparison of the Properties of Polydimethylsiloxanes Containing Fragments of Carboxylic Acids of Different Structures**
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A.N. Nesmeyanov Institute of organoelement compounds of RAS, Moscow, Russia
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- P-51 Novel 1,7-Bis-[Chloro(Organo)Siloxanylmethyl]-m-Carboranes. The Effective Method from Bis(Brommagnesiummethyl)-M-Carborane and Chloro(Organo)Siloxanes**
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A.N. Nesmeyanov Institute of organoelement compounds of RAS, Moscow, Russia
- P-52 Novel 1,2-Bis[Chloromethyl](Organo)-Silylmethyl]-O-Carboranes. Effective Method of Synthesis from Exocyclic Seven-Membered o-Carboranylmethyl-Containing Organosiloxanes.**
Izmaylov B.A., Vasnev V.A., Markova G.D.
A.N. Nesmeyanov Institute of organoelement compounds of RAS, Moscow, Russia
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Kalinin S.A., Ivanov P.V., Krylov A.V., Morozova T.A.
Moscow Technological University, Moscow, Russia
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Karpenkov E.I., Mazaeva V.G., Chistyakov E.M., Prokhortsev V.V., Demchenko A.I.
D.Mendeleev University of Chemical Technology, SSC RF "GNIChTEOS", Moscow,

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Khatueva Zh.S., Levento I.Yu., Demchenko A.I., Natsyuk S.N.
State Scientific Center of the Russian Federation "State Research Institute for Chemistry and Technology of Organoelement Compounds", Moscow, Russia
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Kurbatov A.O., Balabaev N. K., Mazo M. A., Kramarenko E. Yu.
Faculty of Physics, Lomonosov Moscow State University, Moscow, Russia
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Lakhtin V.G., Sokol'skaya I.B., Ofitserov E.N., Efimenko D.A., Kalistratova A.V., Ushakov N.V., Storozhenko P.A.
State Scientific Center of the Russian Federation "State Research Institute for Chemistry and Technology of Organoelement Compounds", Moscow, Russia
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Permikin V.V., Vlasova A.V., Lokk E.I., Khonina T.G., Chupakhin O.N.
Postovsky Institute of Organic Synthesis of RAS (Ural Branch), Ekaterinburg, Russia
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K.A. Podolskaya, E.V. Selezneva, S.A. Milenin, A.M. Muzafarov
Enicolopov Institute of Synthetic Polymeric Materials,
Moscow Technological University, Moscow, Russia
- P-60 Investigation of Hydrolytic Polycondensation of Titanium Chemical Complexes with Dyorganodichlorosilanes in the Acetone-Carbamide System**
Polshchikova N.V., Bokova K.V., Trankina E.S., Kononova E.G., Tokazova R.U., Zavin B.G.
Institute of Organoelement Compounds, Moscow, Russia
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E.N. Rodlovskaya, V. A. Vasnev
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G.I. Shcherbakova, A.S. Pokhorenko
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N.S. Enikolopov Institute of synthetic polymeric materials of RAS, Moscow, Russia
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SSC RF JSC GNIChTEOS, Moscow, Russia
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NRC «Kurchatov Institute», ISPM RAS, Moscow, Russia

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SSC RF JSC GNIChTEOS, Moscow, Russia
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Moscow Technological University, Moscow, Russia
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A.Ya.Yakimova, O.G. Ryzhova, P.A. Storozhenko, P.A. Timofeev, A.N. Polivanov, I.A. Timofeev, M.G. Kuznetsova, A.I. Drachev, S.N. Dugin, E.L. Gurkova
SSC RF GNIChTEOS, Moscow, Russia
- P-69 Polyimide-Organosilicone Compositions for Heat-Resistant Coatings and Layered Composite Materials**
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Institute of macromolecular compounds of RAS, Saint-Petersburg, Russia
A. N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
- P-70 New Organosilicon Derivatives of Pyrrolidine-2,5-Dione**
Bolgova Yu., Grebneva E., Trofimova O., Borodina T., Albanov A., Smirnov V.
A.E. Favorsky Irkutsk Institute of Chemistry, SB of RAS, Russia
- P-71 Functionalization of 2-Mercaptobenzothiazole with Iodomethyl Derivatives of Silanes**
Yarosh N.O., Zhilitskaya L.V., Shagun L.G., Dorofeev I.A.
A. E. Favorsky Institute of Chemistry, SB of RAS, Irkutsk, Russia

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PLENARY LECTURES

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Personal details

Martin Möller, Prof. Dr.

Scientific Director of

DWI – Leibniz Institute for Interactive Materials

*Chair of Textile Chemistry and Macromolecular Chemistry
RWTH Aachen University*

Address:

Tel: +49-(0) 241 / 80-233-00

Fax: +49-(0) 241 / 80-233-01

E-mail: moeller@dwi.rwth-aachen.de

Website: <https://www.dwi.rwth-aachen.de/>



Light Driven Microgel Objects – Motion Out of Equilibrium

Qualification of polymer objects to undergo autonomous motion, i.e., driven and directed (i) rotation, (ii) vibration/oscillation or (iii) translation (locomotion), requires the particles to do work. This in turn requires a local energy input. Furthermore, because of the low Reynolds numbers, the actuation must not generate a reciprocating change in the particles conformation or shape. Hence, the most efficient locomotor systems of microorganisms such as flagella or rotational motors rely on complex internal motility, and attempts to mimic flagella synthetically are still in their infancy. Here we report on a rather facile and versatile LCST-hydrogel system where the motion is affected by volume change and bending of the micro object and where it can be precisely controlled by the (i) design of the geometrical shape, (ii) the widely variable material properties and (iii) by the energy intake via infrared irradiation that can be modulated in time and intensity to affect volume changes and bending. The volume change phase transition is not caused by heating of the whole system, but by strictly localized temperature changes generated inside the particles. For this purpose the gels were equipped with 1-4 gold nanorods per μm^3 that absorb light at 780 nm and convert it practically instantaneously to heat. The fact that the critical phase segregation can be switched within milliseconds and that the dynamics and the change in shape can be designed by the geometrical shape and the hydrogel structure provides a means to transform radiation energy to shape and time controlled bending, constriction and whipping. We will report on the motility of microfabricated gel particles with asymmetric and symmetrical mechanical properties that undergo directed rotational and translational motion, and exhibit a characteristic time dependence in the amplitude of the bending as well as characteristic resonance effects.

Biography

In 2002 Martin Möller became professor for Textile Chemistry and Macromolecular Chemistry at RWTH Aachen University, after being professor at the University of Twente (NL) and Ulm University. In 2003 he became scientific director of the DWI. He studied chemistry in Hamburg and Freiburg. He is a member of the "Akademie der Technischen Wissenschaften"/acatech and of the Nordrhein-Westfälische Akademie der Wissenschaften und Künste. In addition, he is active in a large variety of scientific organizations. In 2002 he was decorated with the Körber Award for European Science. In 2012 the Technical University Cluj-Napoca (Romania) honored his work and he was awarded doctor honoris causa (Ro). His field of research is the synthesis of new polymers and self-assembly of polymer systems.

PL 2

Encoding Tissue Mechanics in Silicone

Sergei S. Sheiko

Department of Chemistry, University of North Carolina in Chapel Hill, NC 27599-3290, USA

E-mail: sergei@email.unc.edu

Machines of the Future will synergize biomimetic mechanics with artificial intelligence [ⁱ]. An *ideal actuator* should mimic muscle by being passively elastic while also efficiently converting potential energy into mechanical strokes [ⁱⁱ]. An *ideal body material* should mimic skin by being simultaneously compliant and strong to accommodate actuator motion [ⁱⁱⁱ]. One drawback of biological tissues, however, is that their softness requires water, which is an unreliable engineering material. To overcome this challenge, we have developed a materials design platform that predicts mechanical properties of elastomers by engineering brush-like polymer networks [^{iv}]. Adaptable to any chemistry, the platform harnesses three architectural parameters [n_{sc}, n_g, n_x] (**Figure**) to encode tissue-mimetic softness, strain-stiffening, and extensibility within *single-chemical-component* systems. Applying this platform to archetypal poly(dimethylsiloxane) (PDMS), aka *silicone*, we have designed simultaneously supersoft and extremely strain-stiffening materials without using solvent as a material “softener” [^v].

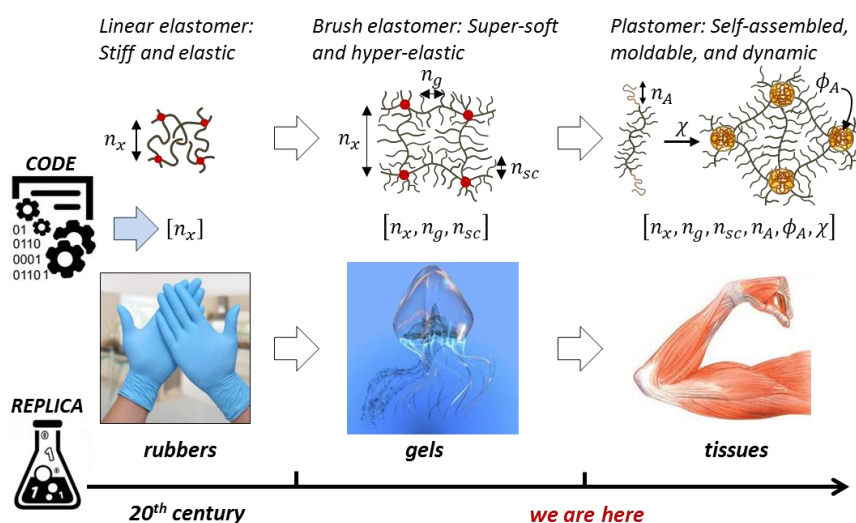


Figure. The evolution from a single-parameter linear chain elastomer to multi-parameter brush architectures towards the programmable replication of tissue mechanical properties.

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- ⁱⁱⁱ S. Wang, et al., *Nature*. **2018**, 555, 83.
- ^{iv} M. Vantankhah-Varnosfaderani, et al., *Nature* **2017**, 549, 497.
- ^v M. Vantankhah-Varnosfaderani, et al. *Science* **2018**, 359, 1509.

PL-3

Silicon Chemistry in Outer Space: Past and Future

David Avnir

Institute of Chemistry, the Hebrew University of Jerusalem, Israel
E-mail: david.avnir@mail.huji.ac.il

A major revolution is taking place in modern astronomy: From the historical count of nine planets of the Sun to the current number of recently discovered exoplanets which is about 4000 and growing every day. This revolution has deep scientific and cultural implications, as there is now strong evidence for planets with Earth-like chemistry and probably also biochemistry, all across the cosmos. It is therefore high time to summarize our knowledge of chemistry in outer space, and evaluate where this knowledge should lead us in future studies of astrochemistry and astro-biochemistry. Of the elements of the periodic table, I will focus from these points of view on one of the most important elements of our universe, silicon.

Topics to be covered in the lecture will include:

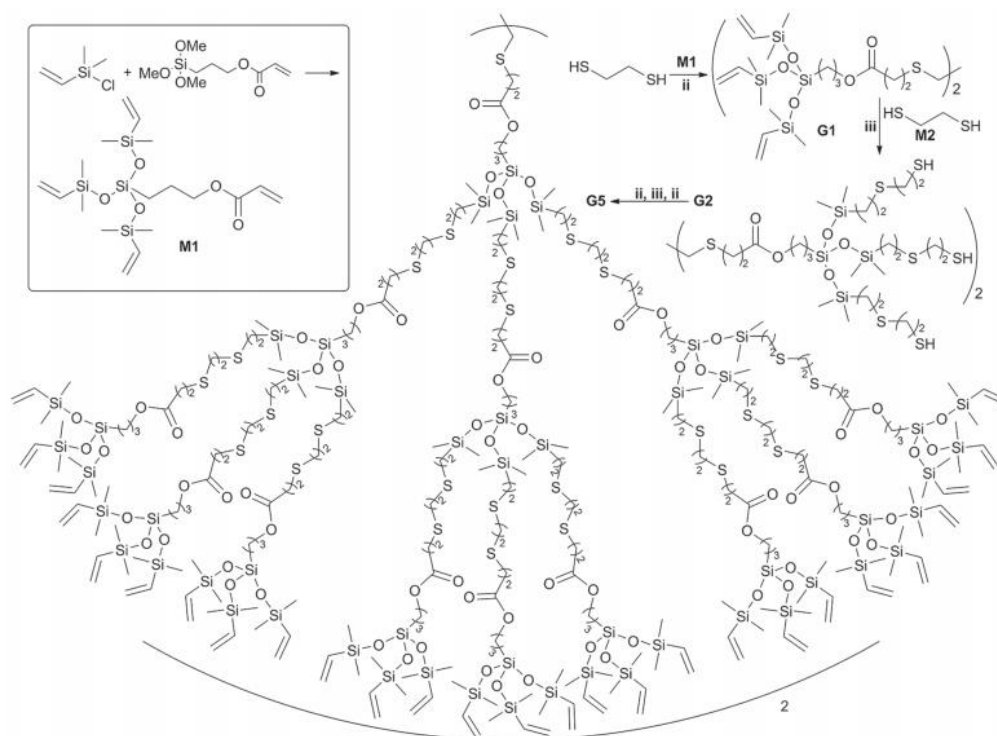
- * The nucleosynthesis of silicon in supernovae and in the core of stars.
- * A survey of silicon compounds in outer space and their synthetic routes, in planets, exoplanets, stars atmospheres, proto-stars, interstellar dust, asteroids, comets and more.
- * Remote analytical methods for detection of astronomical silicon compounds.
- * Hypotheses on the role of silicon in potential extraterrestrial life.
- * Chirality of silicon compounds and its potential use as a biomarker of extraterrestrial life.

PL-4

**Exploration of New Synthesis Methods for Organosilicon Compounds and
Polymers**

Jie Zhang, Shengyu Feng
Shandong University, Jinan, China
jiezhang@sdu.edu.cn

Two efficient reactions, which are thiol-ene and aza-Michael reactions, were applied to synthesize organosilicon compounds, crosslinking systems of silicone rubber, thermoplastic polyurethane, dendrimer and graft polysiloxane. The new synthesis methods including reaction conditions, products and their properties have been explored.



Scheme 1. The overall synthetic strategy of dendrimers.

Entry	Alkene	Product	Time (h)	T (°C)	Yield %
1			4	50	>99
2			24	65	>99
3			4	50	>99
4			8	50	98
5			4	50	99

Figure 1. Functional alkoxy silanes and block soft segment prepared by using aza-Michael reaction.

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PL-5

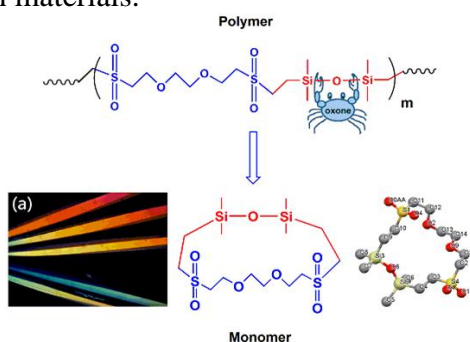
Synthesis of Sulfur-Containing Organosilicon Compounds and Materials

Yujing Zuo, Zhiming Gou, and Shengyu Feng*

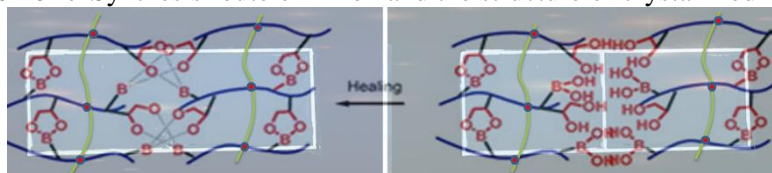
Key Laboratory of Special Functional Aggregated Materials (Shandong University), Ministry of Education; School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P. R. China

E-mail: fsy@sdu.edu.cn

This lecture intends to introduce a series of sulfur containing organosilicon compounds, materials with novel structures synthesized by unique methods. First of all, a range of thioether-bridged siloxanes were synthesized by using thiol-ene "click" reactions, and then sulfone-containing silanes and polysiloxanes were obtained after sulfide oxidation process. Meanwhile, the cleavage and rearrangement of Si-O-Si bonds was deeply discussed during the process of thioether bond oxidation, and a new synthesis method of sulfone-containing polysiloxanes was put forward, which may be widely used in the synthesis of various siloxane polymers. The novel structures of organosilicon polymers obtained will show novel properties and broad applications. Then, we will also introduce polysiloxane-based sulfur containing elastomers obtained through facile thiol-ene "Click" chemistry, and then discuss on the relationship between their structures and performance. This lecture will provide new routes to explore sulfur-containing organosilicon compounds and materials and will enlarge the varieties of organosilicon materials.



Scheme 1. Synthesis route of P1-ox and the structure of crystallized P1-ox



Scheme 2. Illustration of the self-healing process of sulfur contained silicone elastomer

References

- [1] Yujing Zuo, Zhiming Gou, Shengyu Feng*, et al., , *Chem. Eur. J.* 2015, **21**, 10972-10977.
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**ПРИГЛАШЕННЫЕ
ДОКЛАДЫ**

INVITED LECTURES

IL-1

Tetrasilacyclobutadiene Complexes of the *s*-, *p*-, and *d*-Block Elements

Vladimir Ya. LEE

Department of Chemistry, Graduate School of Pure and Applied Sciences,
University of Tsukuba, Tsukuba 305-8571, Japan
E-mail: leevya@chem.tsukuba.ac.jp

Although cyclobutadiene as a 4π -electron species (and thus antiaromatic by Hückel's classification) is highly reactive, it can be successfully stabilized within the coordination sphere of transition metal. This was exemplified by a vast number of the coordination compounds featuring cyclobutadiene as a cyclic polyene ligand. However, if cyclobutadiene complexes of the *d*-block elements are well-known, their analogues of the *s*-block elements (alkali and alkaline earth metals) are still exceptionally rare. Moreover, cyclobutadiene complexes of the *p*-block elements (main group elements), the so-called *pyramidanes*, were unknown prior to our investigations.

In this presentation, we report on our contribution in this field, namely, cyclobutadiene and tetrasilacyclobutadiene complexes of the *s*-, *p*- and *d*-block elements: their synthesis, peculiar structures, bonding properties and reactivity [1],[2],[3]. All reported compounds are isolated and fully characterized by spectroscopic means and X-ray crystallography.

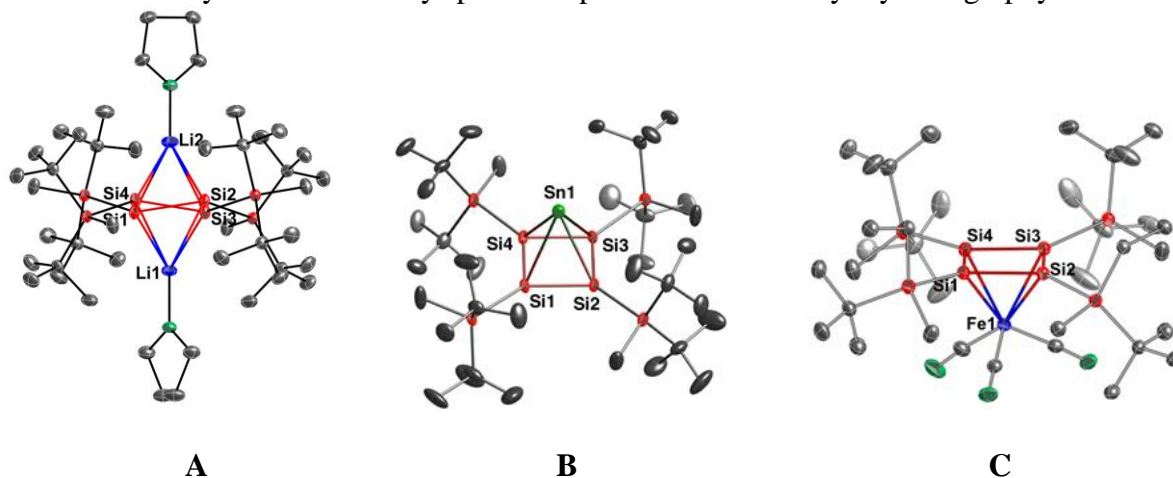


Fig. 1. Tetrasilacyclobutadiene complexes of the *s*-block(A), *p*-block(B) and *d*-block(C) elements.

References:

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IL-2

**Stereodynamic Behavior of Novel Hypervalent Compounds of 14th Group –
Derivatives of Amides, Lactams and Imides**

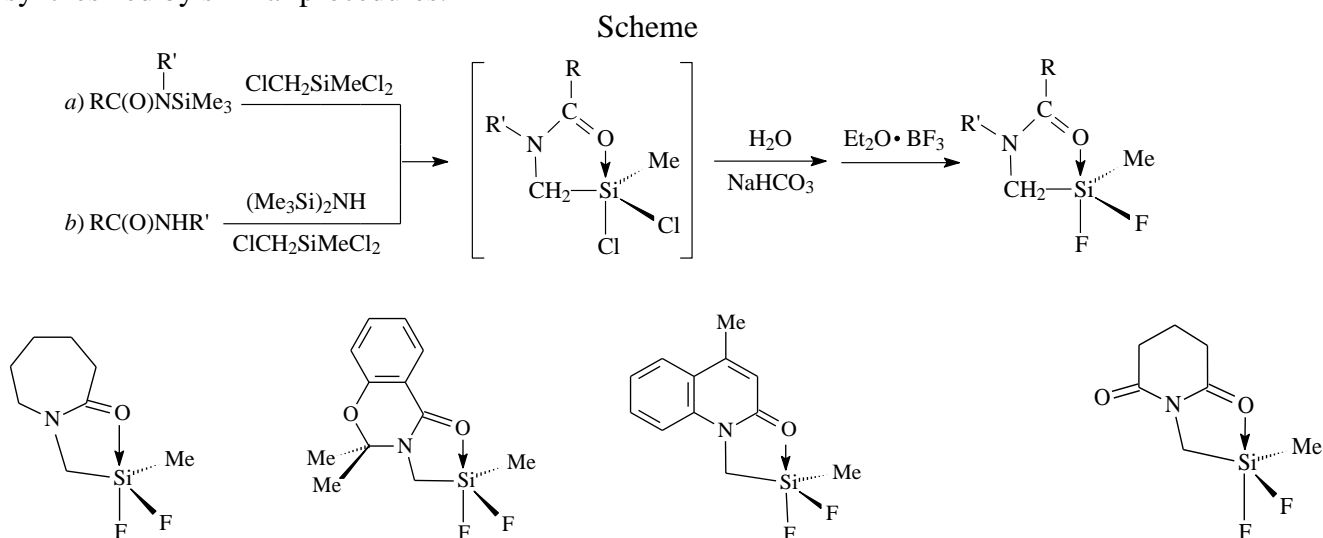
Vadim V. Negrebetsky^a, Yuri I. Baukov^a, Aleksandr A. Korlukov^b

^a Department of Chemistry, N. I. Pirogov Russian National Research Medical University, Ostrovityanov St. 1, Moscow 117997, Russian Federation

^b A. N. Nesmeyanov Institute of Organoelement Compounds, RAS, Vavilova St. 28, 11991 Moscow, Russian Federation

E-mail: negrebetsky1@rsmu.ru

Pentacoordinate mono-(O→Si)-chelate (methyl difluorosilyl)methyl derivatives of amides $RC(O)N(R')CH_2SiMeF_2$ were synthesized according to Scheme. The difluoroderivatives of lactams LCH_2SiMeF_2 and imide $Im^6CH_2SiMeF_2$ (**3**) (Chart) were synthesized by similar procedures.



The possibilities of multinuclear NMR spectroscopy (1H , ^{13}C , ^{15}N , ^{17}O , ^{19}F , ^{29}Si , ^{119}Sn , special one-dimensional (ART, DEPT) and two-dimensional (under superposition of strongly connected spin systems) pulse sequences, NMR ^{13}C , ^{29}Si CP/MAS, as well as DNMR on the nuclei 1H , ^{13}C , ^{19}F and ^{119}Sn for the study of the mechanisms of stereodynamic processes (permutation and diastereomerization) occurring in their coordination node.

The hypervalent state of central atoms in all studied compounds was confirmed by NMR study in solutions and single-crystal X-ray studies. The temperature dependency observed for NMR signals in solution was explained by the ligand exchange in the coordination environment of central atoms and used for determining the activation parameters by DNMR. Quantum-chemical calculations for various isomers of complexes suggested the "turnstile rotation" as the most likely mechanism for the observed stereodynamic processes.

This work was supported by the Russian Foundation for Basic Research (grants No 16-03-00957).

IL-3

**About a Role of Organosilicon Additives at Spinning of Cellulose Fibers
and at Their Thermolysis**

V.G.Kulichikhin^a, L.K.Golova^a, I.S.Makarov^a, M.I.Vinogradov^a, A.K.Berkovich^b,
Ya.V.Golubev^b

^a*A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences*

^b*M.V.Lomonosov Moscow State University, Chemical Department*

E-mail: klch@ips.ac.ru

Blends of carbon and silicon carbide fibers are well known as components of heat isolation constructions. As a rule, the carbon fibers prepared from cellulose precursors are the most popular for this aim because of similar values of the thermal expansion coefficient. The other approach is related with additives of organosilicon compounds into spinning dopes, i.e., introducing them directly to fibers. Three such additives varying from saturated via containing double and, finally, triple bonds (tetraethoxysilane, vinyltriethoxysilane and bis(trimethylsilyl)acetylene) were chosen for this aim. In the case of the cellulose dopes in N-methylmorpholone-N-oxide the additive was introduced via solutions in acetone.

Rheological properties of the concentrated solutions of cellulose do not feel presence of organosilicon additives even at its content of 15-20%. This means that processing of the cellulose containing dopes into fibers by traditional method of the dry-wet jet spinning was performed without any problem. As to mechanical properties of the white fibers, they were on the regular level of the nascent fibers excluding elongation at break for cellulose fibers, which was lower for the additives containing unsaturated bonds. Testing of such composite fibers with IR spectroscopy methods has indicated on cross-links between cellulose molecules formation.

The thermolysis of the composite fibers was performed in accordance with classical schemes inherent for cellulose: pyrolysis and carbonization in the inert atmosphere. The neat and black fibers were analyzed by TEM and SEM methods as well as by X-ray diffraction and mechanical testing. The elementary composition was tested by CHNS/O analyzer "Thermo Scientific Flash 2000". It was shown that at 5% additive of the triethoxivynilsilane the silicon content in the black fiber is equal to 0.4%. The main result consists in observation of the high ordered domains of structural elements with dimensions of 10 nm and interspace of 0.25 nm, corresponding to silicon carbide inclusions of different shape in the carbon matrix. In addition, the carbon residue after carbonization in the case of cellulose fibers was increased on 20-30%. The last fact witnesses about catalytic action of the organosilicon additives on the main stages of carbonization, namely dehydration and depolymerization. The detailed IR spectral data of all stages of carbonization indicate not only participation of silicon-containing additives in chemical transformation of the cellulose, but also on partial polymerization of compounds with unsaturated links and cross-links formation.

This work was supported by the Russian Federal Agency of the Scientific Organizations in frames of the TIPS State Program.

IL-4

Silicone-Based Magnetoactive Elastomers: New Properties and New Applications

E.Yu. Kramarenko^a, G.V. Stepanov^{a,b}, E.G. Kazimirova^a, Yu.A. Alekhina^a,
T.A. Nadzharyan^a, L.A. Makarova^a, N.S. Perov^a

^a Faculty of Physics, Lomonosov Moscow State University, Moscow, Russia

^b State Scientific Res

earch Institute of Chemistry and Technology of Organoelement Compounds, Moscow, Russia

E-mail: kram@poly.phys.msu.ru

Magnetoactive elastomers (MAEs) comprising soft elastomer matrices filled with magnetic microparticles belong to a class of smart materials due to their ability to change a number of physical properties when an external magnetic field is applied. They are receiving a lot of attention nowadays demonstrating a high potential in various industrial and medical applications.

This talk will give an overview of our results on development of highly responsive silicone-based MAEs, the main physical phenomena observed in MAEs [1-6] as well as their dependence on material composition and magnetic field strength. A special attention will be paid to novel applications of MAEs. In particular, we explore the possibility of creating an effective retinal fixator on the basis of MAEs and systems of permanent magnets [7] for treatment of complicated retinal detachments. Furthermore, we investigate the possibility of creating tunable hydrophobic and superhydrophobic coatings based on MAEs whose structure and properties can be controlled by external magnetic fields. Structuring of magnetic filler along magnetic field lines takes place not only within the bulk of MAEs but also on the surface resulting in formation of needle-like “mountains” [8]. Magnetic-field induced roughness defines rather high values of the water contact angles on a MAE surface.

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IL-5

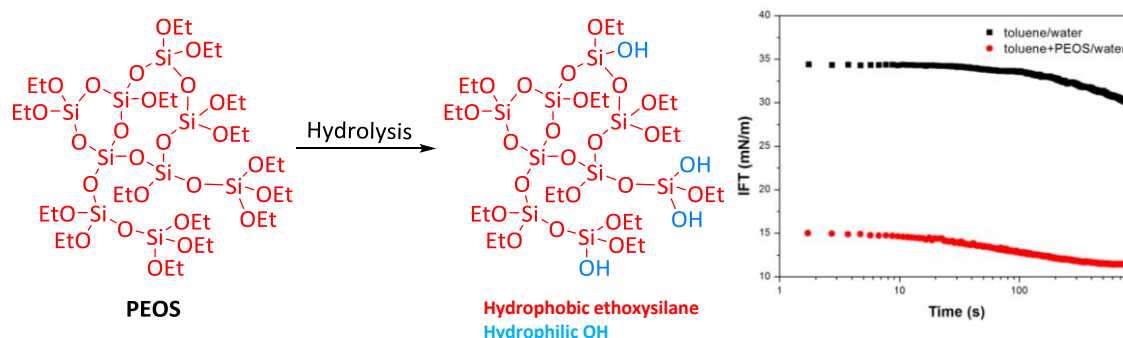
Nanostructured Silica-Based Materials via Polyethoxysiloxane-Assisted
Surfactant-Free Emulsion Technique

Xiaomin Zhu, Yongliang Zhao, Martin Möller

DWI – Leibniz-Institute for Interactive Materials e.V. and Institute for Technical and
Macromolecular Chemistry of RWTH Aachen University, Forckenbeckstrasse 50, Aachen,
52056, Germany

E-mail: zhu@dwil.rwth-aachen.de

Silica-based nanomaterials are of great interest and high demand owing to their chemical inertness, mechanical stability, biocompatibility, and optical transparency. One of the well-established and effective approaches toward design and fabrication of silica nanomaterials is sol-gel technology, where monomeric tetraethoxysilane is mostly used as the silica precursor. In this work we present a unique platform for preparation of silica-based nanostructured materials using a silica precursor polymer, hyperbranched polyethoxysiloxane (PEOS) [1], which is a highly hydrophobic liquid and exhibits pronounced interfacial-activity in oil/water emulsion systems due to hydrolysis-induced amphiphilicity (Scheme 1) [2].



Scheme 1. Interfacial activity of PEOS appears upon hydrolysis at a water/oil interface

A PEOS/oil mixture and water can easily be emulsified in each other without any additional surfactants. In the resulting oil-in-water emulsions the oil phase is enclosed in the silica microcapsules after full conversion of PEOS to silica. By accompanying the conversion of PEOS with radical polymerization of the oil phase, polymer@SiO₂ core-shell nanoparticles are yielded [3]. Double emulsions are obtained by emulsifying a PEOS-stabilized water-in-oil emulsion in water. After polymerization of the oil phase and conversion of PEOS a series of silica-based nanomaterials ranging from nanocapsules and nanorattles to Janus-like nanomushrooms can be synthesized [4]. Summarizing, the use of PEOS offers a facile, low cost, and environmentally friendly approach for mass production of various complex hybrid nanostructures that are amenable to numerous applications.

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IL-6

Synthesis of SiCl₄ from Orthosilicates

Dimitris Katsoulis, John Roberts

The Dow Chemical Co., Midland Michigan 48686 USA

E-mail: dimi.katsoulis@dowcorning.com

A low energy route to silicone tetrachloride is desirable to the polysilicon and silicone industry from both an economic and environmental perspective.

We present here two methods for the synthesis of SiCl₄ from alkyl orthosilicates. The first method involves the chlorination of tetraalkyl orthosilicates in the presence of a catalyst using SOCl₂ as the chloride source / deoxygenating agent. Soluble chloride salts performed better than Lewis base catalysts. The optimized reaction employed a widely used and commercially available soluble chloride salt catalyst (e.g., NBU₄Cl, 0.4 equiv), 16 equiv of SOCl₂ and afforded quantitative yield of SiCl₄ after 3h. As the bulk of the orthosilicate substrate increased the yield of SiCl₄ decreased. [1]

The second method involves the reaction of Si(OMe)₄ with HCl gas at 0 °C in the presence of a catalytic amount of hexamethyl phosphoramide and four equivalents of CH₃CN. Exchange between HCl and alkoxy groups on silicon during the reaction generates methanol. The methanol then reacts with acetonitrile (in the presence of HCl) to form an imidate thus removing it from the reaction mixture. Other Lewis acids and base catalysts were also observed to accelerate the reaction. [2]

Mechanistic considerations for both processes will be discussed.

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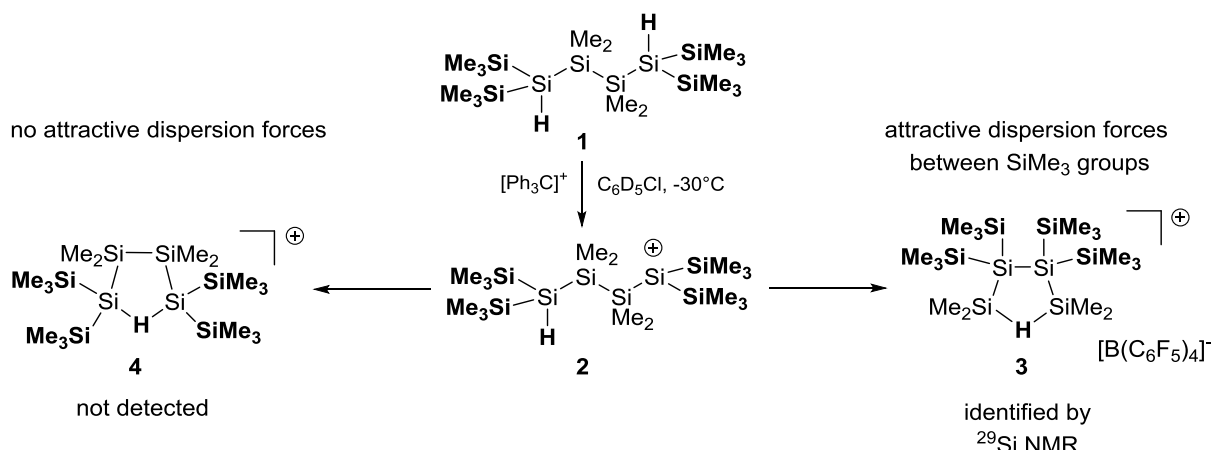
IL-7

Wagner-Meerwein –Type Rearrangements in Oligosilanes

Thomas Müller^a, Lena Albers^a

^a Institute of Chemistry, Carl von Ossietzky University Oldenburg, D-26129 Oldenburg, Carl von Ossietzky-Str. 9- 11, Federal Republic of Germany, European Union
E-mail: thomas.mueller@uni-oldenburg.de

Linear and cyclic, permethylated polysilanes transform in a Lewis acid catalyzed Wagner-Meerwein analogue rearrangement into branched isomers and can be used to build complex oligosilane structures.^[1,2] Our experimental investigations gave astonishing insights into this type of skeletal rearrangement.^[3-5] We used hydrogen-substituted polysilanes to define the position of the initial positively charged atom via a Corey hydride transfer reaction. The rearrangement reaction of the formed cation was followed by ²⁹Si NMR spectroscopy.^[3] Cationic intermediates of these skeletal rearrangements were stabilized and trapped by the formation of Si-H-Si bridges (see Scheme 1 for an example).^[4] Based on the experimental results of our stable silicon cation study, we are able to provide important mechanistic details of the skeletal rearrangement reactions of polysilanes.^[4,5] A computational investigation reveals the importance of attractive dispersion forces for product formation.^[5]



Scheme 1. Cationization of hexasilane **1** and the dispersion energy-driven rearrangement of polysilyl cation **2** to form the bissilylated hydronium ion **3**.^[5]

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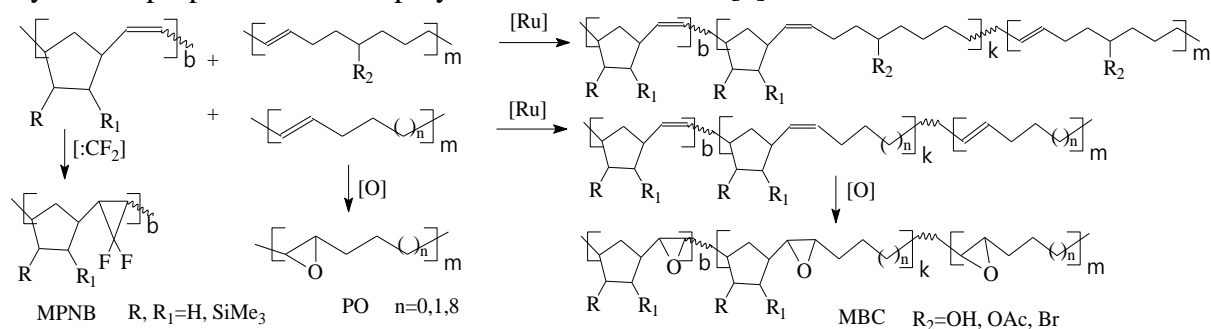
IL-8

**New Approaches to the Regulation of Gas Separation and Other Properties
of Silicon-Substituted Polynorbornenes**

Gringolts M.L., Denisova Yu.I., Morontsev A.A., Roenko A.V., Zhigarev V.A.,
Kudryavtsev Y.V., Finkelshtein E.Sh.

Topchiev Institute of Petrochemical Synthesis RAS, 29 Leninsky Pr., 119991 Moscow, Russia
E-mail: gringol@ips.ac.ru

In this work we developed new approaches to the macromolecular design of silicon-containing metathesis polynorbornenes (MPNB), which are based on the post-polymerization modification of main chain double bonds. One of the transformations includes a new interchain macromolecular reaction, the cross-metathesis between MPNB and a polyolefin (PO) (scheme). In the course of the reaction various macromolecules exchange with their chain fragments via cleavage of double bonds in MPNB and PO. As a result, new norbornene-olefin multiblock copolymers (MBC) that combine the homopolymer properties are formed [1]. The main features of the MPNB cross metathesis with polyolefins C4, C5, C8, C12 mediated by the 1st and 2nd generation Grubbs catalysts were studied, as well as the factors affected the chain structure of the resulting multiblock copolymers. Peculiarities of the process kinetics, including the ¹H NMR monitoring of the reactive Ru-carbene complexes, were studied. The selective insertion of functional substituents into one of the copolymer blocks by the cross-metathesis between the Si-substituted MPNB and PO or MPNB and substituted PO was implemented. A relationship between the chain structure and thermal and crystalline properties of the copolymers was established [1].



The second approach developed in this work is based on the polymer-analogous reactions involving double bonds in MPNB and MBC. The reactions of gem-difluorocyclopropanation (DFC) and epoxidation of homo- and copolymers were studied. The hindered effect of Si-containing substituents (SiMe₃) on the rate and degree of double bond conversion has been revealed. It was shown that shifting the Si-methyl group position away from the main chain accelerated the polymer-analogous reactions. DFC enhanced the gas permeability coefficients for MPNB and epoxidation significantly improved its ideal selectivity. The films of the modified polymers demonstrated high stability during storage at ambient conditions, especially in comparison with pristine MPNB [2].

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This work was supported by the RFBR (Projects 17-03-00596 and 16-33-60213)

IL-9

Silsesquioxanes-Based Nanoporous Materials for Water Remediation

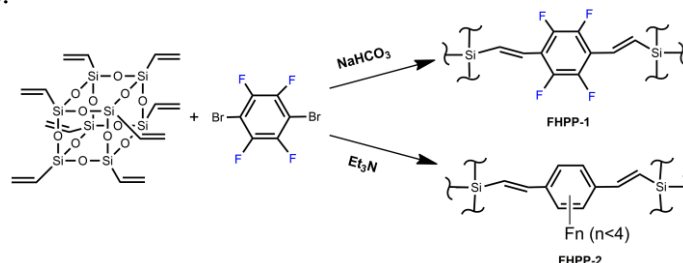
Hongzhi Liu

College of Chemistry and Chemical Engineering, Shandong University, Shanda
nanlu No. 27, Jinan 250100, China.

Email: liuhongzhi@sdu.edu.cn

Water pollution from toxic dyes and heavy metal ions has become a serious issue in recent years due to their potential negative effects on human health and aquatic ecosystems. Among the various potential chemical and physical methods, adsorption has received immense interest because of its high efficiency, low process cost and ease of operation. Porous organic polymers, which could offer advantages such as high surface area, low mass density, structural stability, and easy functionality, have emerged as promising useful adsorbents in water remediation. More importantly, the structures and properties of these porous polymers are easily tuned through rational design, *i.e.* by selecting ideal building blocks and appropriate polymerization methods.

Two different silsesquioxane-based porous polymers (FHPPs), *i.e.* FHPP-1 and FHPP-2 were prepared, respectively, by changing acid scavengers from sodium bicarbonate to triethylamine in the Heck reaction between octavinylsilsesquioxane (OVS) and 1, 4-dibromotetrafluorobenzene. This work opened a new window to prepare and tune fluorine-containing porous polymers based on silsesquioxanes. The desired porous materials were applied to remove dyes and heavy metal in water showing good binding efficiencies.



Keywords: Nanoporous materials, Silsesquioxane, Water remediation

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Hongzhi Liu

2011- Professor, Shandong University, China
2006 - 2009 Postdoctoral Fellow, Gunma University
2009 - 2011 Postdoctoral Fellow, Vienna University of Technology
2002 - 2006 Ph. D. Shanghai Jiaotong University, China
1996 - 1999 M.S. Hefei University of Technology, China
1992 - 1996 B.S. Jinan University, China

Research fields: Silsesquioxane, Porous materials, water remediation

IL-10

**Protatranes and Hydrometallatranes – New Biologically Active Analogues
of Silatranes**

T. A. Kochina, Yu. A. Kondratenko

*Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences,
nab. Makarova 2, 199034 St. Petersburg, Russia.*

E-mail: t-kochina@mail.ru

Atranés are organic and organometallic derivatives of triethanolamine $N(C_2H_4OH)_3$ (TEA). The beginning of research in this area was laid by academician M. G. Voronkov. The most outstanding representatives of atranes are silatranes possessing specific biological activity. A comprehensive study of silatranes led to the discovery of new representatives of atranes, among which a special place is occupied by the atranes of ionic structure: Tris(2-hydroxyethyl)ammonium salts of protic acids (protatranes) and coordination compounds of TEA with salts of transition metals (hydrometallatranes). In order to obtain potentially biologically active atranes, triethanolammonium salts of biologically active carboxylic acids, $[NH(C_2H_4OH)_3]NX$ **1-14** were firstly synthesized with high yields by the interaction of TEA with the appropriate carboxylic acid in methanol, X= $C_9H_7O_2$ (**1**), $C_7H_5O_2$ (**2**); $C_7H_5O_3$ (**3**); C_2O_4 (**4**); C_2HO_4 (**5**); $C_3H_2O_4$ (**6**); $C_3H_3O_4$ (**7**); $C_4H_4O_4$ (**8**); $C_4H_5O_4$ (**9**); $C_4H_4O_5$ (**10**); $C_4H_5O_5$ (**11**); $C_6H_5O_7$ (**12**), $C_6H_6O_7$ (**13**) and $C_6H_7O_7$ (**14**); n=1 for **1-3**, **5**, **7**, **9**, **11** and **14**; n=2 for **4**, **6**, **8**, **10** and **13**; n=3 for **12**. The conformation of tris(2-hydroxyethyl)ammonium cation and cation-anion interactions in the synthesized protatranes were studied by the X-ray diffraction and IR spectroscopy. The peculiarity of the structure of tris(2-hydroxyethyl)ammonium cations $[(OHCH_2CH_2)_3NH]^+$ is that they are in the endo-conformation: three oxygen atoms of hydroxyethyl groups surround the ammonium hydrogen atom H_N with the formation of three intramolecular hydrogen bonds. Tris(2-hydroxyethyl)ammonium cations and anions are linked each other by intermolecular hydrogen bonds involving oxygen atoms of the OH groups of protatrane cation and COO groups of the anion. The structure of the protatrane of succinic acid (**8**) is markedly different from the structure of other protatranes. In the cation **8**, two hydroxyethyl branches, as in the endo-conformation, surround the ammonium hydrogen atom, but the third branch is inverted in the opposite direction from the hydrogen atom of N^+H group. Thus, in cation **8**, the trifurcated hydrogen bond passes into bifurcated one, and endo-exo-conformation, which is extremely rare for tris(2-hydroxyethyl)ammonium salts, is realized.

Interaction of TEA with Co(II), Cu(II), Zn(II) salts of carboxylic acids (benzoic, cinnamic, salicylic, succinic) was investigated. The binuclear complex $[Zn_2(TEA)(C_6H_5COO)_3]$ was obtained by the interaction of TEA with zinc benzoate in methanol. Zinc-containing complexes with the composition $[Zn(TEA)(H_2O)_2](SO_4)(H_2O)$, $\{Zn(TEA)(Cin)_x\}$, the $\{Zn(TEA)_2(Cin)_x\}$ were also synthesized. A number of cationic mononuclear complexes $[Co(TEA)_2](Sal)_2$, $[Co(TEA)_2](Cin)_2$, $[Co(TEA)_2](Suc)$ consisting of $[Co(TEA)]^{2+}$ cations and anions of the corresponding acids were obtained by the interaction of TEA with cobalt salts. TEA complexes with copper (II) salts were also synthesized: $[Cu(TEA)_2][C_4H_4O_4]$, $[Cu_2(TEA)_2(C_6H_4(OH)CO_2)_2](H_2O)$ and $[Cu_2(TEA)_2(C_6H_5CHCHCO_2)_2](H_2O)$.

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IL-11

Influence of the Silicon Atom on the Properties of Conjugated Oligomers

O.V. Borshchev^{a,b,*}, M.S. Skorotetcky^{a,b}, N.M. Surin^{a,b}, S.A. Ponomarenko^{a,c}

^a *Enikolopov Institute of Synthetic Polymer Materials of Russian Academy of Sciences, Moscow, Russia;*

^b *Luminescent Innovation Technologies LLC, Moscow, Russia;*

^c *Moscow State University, Chemistry Department, Moscow Russia;*

E-mail: borshchev@isp.m.ru

Various conjugated oligomers are widely used in science and technology. In our work, we synthesize and study conjugated molecules containing a silicon atom, of various architectural organizations. In the case of linear conjugated oligomers, we have shown that the introduction of a silicon atom significantly increases the solubility, the molar extinction coefficient and the quantum yield of the luminescence of oligomers, and a small shift in the maxima of the absorption and luminescence spectra to the red region is observed [1], [2], [3].

Recently we have developed a new class of highly efficient luminescent materials with unique properties - nanostructured organosilicon luminophores (NOLs) [4], [5], [6]. These are branched molecules, where two types of organic chromophores are connected to each other via silicon atoms, which brake the conjugation between them and fix them specifically in the space at 1-2 nm distance necessary for efficient Förster energy transfer. It was recently shown that silicon atoms break the conjugation as well as increase the luminescence efficiency in bithiophenesilane dendrimers [7], [8]. The new NOLs used in various devices of organic photonics and electronics, such as spectral shifting fibers [9], organic light-emitting diodes (OLEDs) [10], CIGS photovoltaic devices [11]. NOLs are commercialized by a startup Limited Liability Company "Luminescent Innovative Technologies" (LumInnoTech LLC). All the details can be found on www.luminnotech.com

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УСТНЫЕ ДОКЛАДЫ

ORAL LECTURES

O-1

Polyhedral Oligosilsesquioxanes in Polymers

Zhu Qingzeng, Bei Yiling, Zhao Bingjie, Zhu Hongxia, Cui Jinhua, Cheng Lin

Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250199, China,
E-mail: qzzhu@sdu.edu.cn

The novel polybenzimidazole (PBI) bearing a polyhedral oligosilsesquioxanes (POSS) pendant moiety copolymers were prepared by an N-substituted reaction. The POSS containing phenyl groups dispersed well in the copolymer matrix. The grafted POSS pendant moieties can break the PBI intermolecular hydrogen bonding and face-to-face packing. As a result, POSS-g-PBIs showed better solubility than the pure polybenzimidazole because of less tight molecular chain packings. This type of copolymer also exhibited good comprehensive properties, such as thermal stability and mechanical properties. The approach and mechanism described in this work can contribute to the improvement of the solubility and processability of polymers that have a rigid backbone and strong molecular interactions including hydrogen bonding.

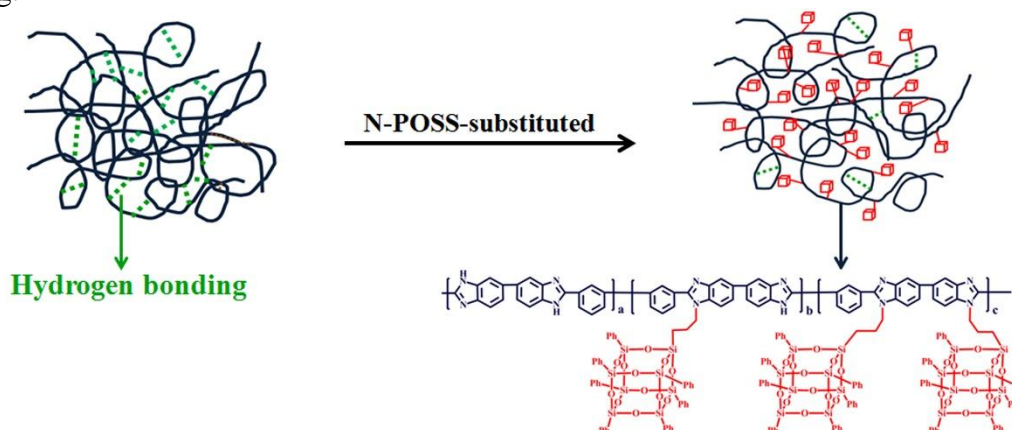


Fig. 1. Schematic illustration of POSS-g-PBI.

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Fluorescent Paper Sensor Based on POSS-Containing Porous Polymer for Visual Detection of Nitroaromatic Explosives

Ruixue Sun^{a,b}, Xiaojuan Huo^{a,b}, Hang Lu^b, Shengyu Feng^{a,b}, Dengxu Wang^{a,b,*}, Hongzhi Liu^b
^a National Engineering Technology Research Center for Colloidal Materials, Shandong University, Jinan 250100, P. R. China

^b Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P. R. China
E-mail: dxwang@sdu.edu.cn

Development of rapid, sensitive, and visual detection of nitroaromatic explosives is of great importance for homeland security and human safety. Herein, three novel POSS-containing porous polymers, HPP-1~HPP-3, were prepared by Heck reactions of octavynilsilsesquioxane with ethene derivatives containing bis-, tri-, or tetrakis- bromophenyl groups. Based on highly sensitive detection of explosives, including *p*-nitrotoluene (NT), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), 4-nitrophenol (NP), 2,4-dinitrophenol (DNP) and picric acid (PA), and high selectivity for detecting TNT and PA, by HPP-2 dispersion in ethanol, a fluorescent paper sensor was developed by a new fabrication process, *i.e.*, vacuum filtrating of HPP-2 dispersion in ethanol, followed by washing and natural drying. The resultant paper sensor was found to be sensitive to solution, solid and vapor phase of explosives with rapid response time of < 10 s by visually observing the fluorescence quenching phenomenon (Fig. 1 left). Moreover, this paper sensor is recyclable with desirable fluorescence resuming ratio, which is higher than 75% after 10 times recycle detection (Fig. 1 right). This developed paper sensor is promisingly applied for rapid, on-site and visual sensing of explosive residuals. The remarkable fluorescence and reusability of this sensor could be expanded to other fluorescence detection of residuals.

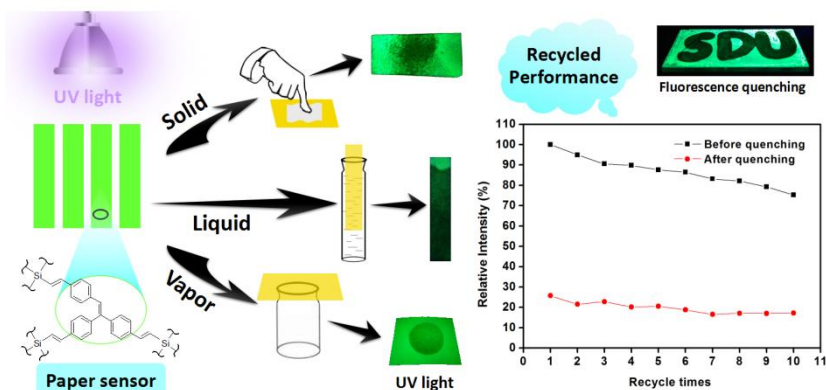


Fig. 1. (left) The detection of nitroaromatic explosives with paper sensor in solution, solid, and vapor phases; (right) the recycled performance of paper sensor.

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O-3

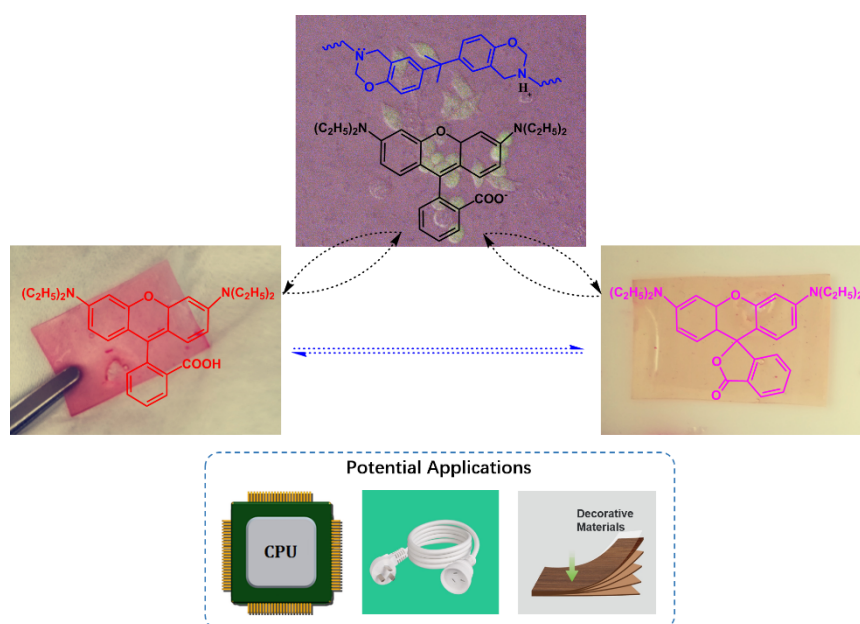
Two Photon Fluorescent Silicon Elastomers

Yuqing Zuo

Institute of Fluorescent Probes for Biological Imaging, School of Chemistry and Chemical Engineering, School of Materials Science and Engineering, University of Jinan, Jinan 250100, P. R. China

E-mail: zuoyuqing0888@163.com

Two-photon fluorescence has been applied in luminescent imaging techniques due to its unique advantages, including low photodamage to the samples, weak background fluorescence, and high spatial resolution. To the best of our knowledge, two-photon fluorescent polysiloxane-based elastomers have not been reported to date. This lecture intends to introduce a series of polysiloxane-based elastomers with strong two photon fluorescence. Two photon luminescence of elastomers was detected. More interestingly, the fluorescence intensity of elastomers exhibited thermally responsive properties, which could be observed by the naked eye. Furthermore, elastomers were applied in devices by monitoring the CPU surface temperature in situ. In addition, HeLa cells were cultured on the surfaces of the elastomers to investigate their cytocompatibility and to explore their potential applications in biomedical fields.



Scheme 1. Illustration of the thermal responsive process and the application of the elastomers

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O-4

Organosilicon Derivative of Benzothienobenzothiophene as Selective and Highly Sensitive Layer for OFET-Based Gas Sensors

E.V. Agina^a, A.S. Sizov^a, A.A. Trul^a, V.P. Chekusova^a, O.V. Borshchev^a, A.A. Vasiliev^b,
S.A. Ponomarenko^a

^a ISPM RAS, Profsoyuznaya st. 70, Moscow 117393, Russia

^b NRC Kurchatov Institute, Akademika Kurchatova pl. 1, 123182, Moscow, Russia

E-mail: agina@printeltech.com

We report a self-assembled Langmuir-Schaefer monolayer field-effect transistor (Fig.1a) with semiconducting layer of organosilicon dimer of [1]benzothieno[3,2-b][1]-benzothiophene (BTBT) (Fig.1b) as a basis for the highly sensitive air stable multiparametric sensor for selective real-time detection of toxic chemical gases such as H₂S and NH₃. For this purpose the semiconducting monolayer has been deposited using a Langmuir-Schaefer technique, which enables formation of a 2D-crystalline monolayer film with high device yield and excellent reproducibility and could be easily scaled up to industrial applications without losing the device performance.[1] Chemically inert nature of the organosilicon semiconducting material enables OFETs manufacturing under ambient conditions including air and water vapors. The devices fabricated are able to operate in dry air and allows ultrafast selective detection of two different analytes (H₂S and NH₃) at low concentrations down to 10 ppb (Fig.1c). The LS OFET sensor is reusable and can be utilized in real-time air monitoring systems. Mechanisms of the analytes interactions with the OFET semiconducting layer and influence of the toxic gas on the OFET key electric parameters are discussed.

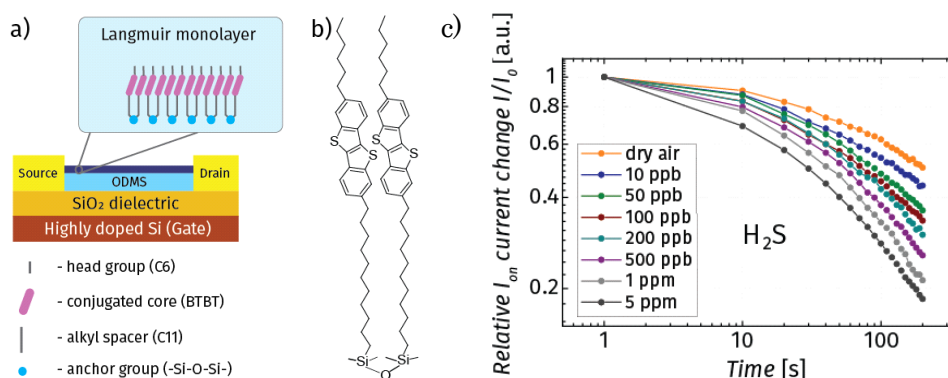


Fig. 1. LS OFET device architecture (a), chemical structure of semiconducting organosilicon dimer (b), dependence of the relative mobility change μ/μ_0 as a function of time upon exposure to different concentrations of hydrogen sulfide: (c).

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This work was supported by RFBR (grant 17-03-00222) and leading science school NSh-5698.2018.3.

O-5

**Study of the Intermolecular Interaction of Carbosilane Dendrimers with a
Branched Siloxane Shell**

Selezneva E. V.^{1,2}, Tikhonov P. A.², Tatarinova E. A.², Goncharova I. K.³, Arzumanyan A. V.³,
Boldyrev K. L.³, Malakhova Yu. N.⁴, Buzin A. I.², Milenin S.A.², Muzafarov A.M.³.

¹ *Moscow Technological University (Fine Chemical Technologies Institute), Vernadsky Avenue, 119454 Moscow, Russia*

² *Institute of Synthetic Polymeric Materials, a foundation of the Russian Academy of Sciences (ISPM RAS), Moscow, Russia*

³ *A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), Moscow, Russia*

⁴ *National Research Center Kurchatov Institute, Moscow, Russia*

E-mail: sellisaveta@gmail.com

Carbosilane dendrimers with a silicon branch point in an exclusively carbon-silicone skeleton are non-polar, inert, neutral, thermally and hydrolytically stable compounds. The main objective of the present study is to create prerequisites for the synthesis and systematic study of carbosilane dendrimers with a siloxane shell, which is characterized by the absence of specific interactions such as hydrogen bonds and other polar interactions. It will allow to obtain new data both from the mutual influence of silicone branched structure in the dendrimer shell on the intermolecular interaction, and on the behavior of the molecules separately.

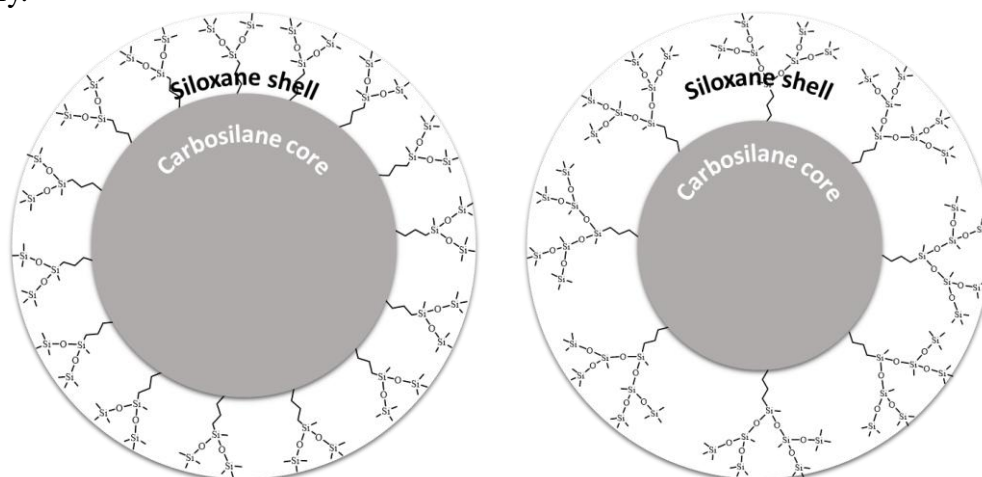


Fig. 1. Structures of the dendrimers obtained

In this work, a homologous series of carbosilane-siloxane dendrimers from 4 to 7 generations which include carbosilane dendrimers in the core with siloxane branched dendrones of 1 and 2 generations in the shell of macromolecules will be obtained.

We will represent the synthesis and exploration of these dendrimers by NMR, GPC, Langmuir–Blodgett. Also the jump in viscosity was observed on the flow curve between the 4 th and 6 th generation of the carbosilane-siloxane dendrimers. This data confirms the general pattern of the formation of a network of entanglement in high- generation carbosilane dendrimers.

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O-6

Aerobic Oxidation of Hydride Siloxanes: Synthesis of Siloxanols

Goncharova I.K.,^a Arzumanyan A.V.,^a Novikov R.A.,^b Milenin S.A.,^c Boldyrev K.L.,^c
Solyev P.N.,^b Volodin A.D.,^a Smol'yakov A.F.,^a Korlyukov A.A.,^a Muzafarov A.M.^{a,c}

^a Nesmeyanov Institute of Organoelement Compounds, 28 Vavilova St., Moscow, Russian Federation.

^b Engelhardt Institute of Molecular Biology, 32 Vavilova St., Moscow, Russian Federation

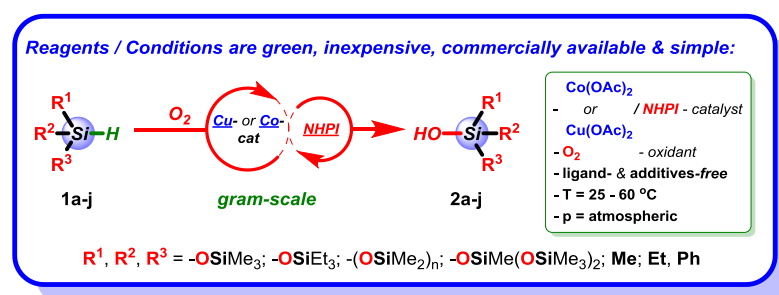
^c Enikolopov Institute of Synthetic Polymeric Materials, 70 Profsoyuznaya St., Moscow, Russian Federation

E-mail: ikgoncharova@mail.ru

Siloxanols are a very practically important class of compounds due to their applicability as building blocks for polymers and silicone materials. However, to date, studies on the preparation of siloxanols are represented by only a few examples, which are highly limited for the selective synthesis of siloxanols of different structures in gram-scale.

At the first stage of our research we showed a limited applicability of hydride siloxanes oxidation for the synthesis of siloxanols in the presence of [M]/BuOOH–oxidizing system [1-2]. This limitation was due to harsh reaction conditions.

So at the second stage a highly efficient preparative method for the synthesis of siloxanols based on aerobic Co(OAc)₂ or Cu(OAc)₂/NHPI–catalyzed oxidation of hydride siloxanes in gram-scale using “green”, commercially available, simple inexpensive reagents and mild reaction conditions has been proposed (scheme 1). This is a general reaction for the synthesis of mono-, oligo and polymeric siloxanols with various structures (linear, branched and cyclic).



Scheme 1.

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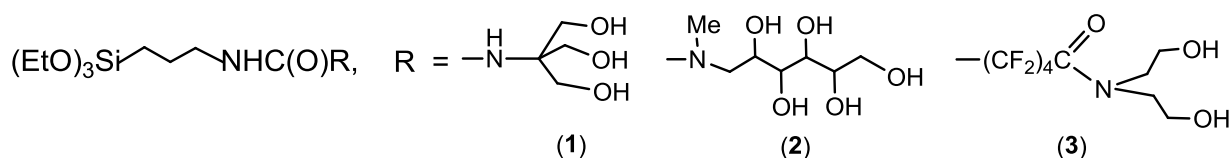
This work was supported by the grant of the Russian Science Foundation (RSF grant No. 14-23-00231).

O-7

Polymer Nanoparticles for Biomedical Applications from Hydroxyl-Containing Alkoxysilanes

Ladilina E.Yu.^a, Lermontova S.A.^{a,b}, Zakharycheva N.S.^b, Lyubova T.S.^a, Klapshina L.G.^a.
^a *Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Russia*
^b *Lobachevsky Nizhegorodsky State University, Russia*
E-mail: eladilina@gmail.com

Water-soluble hyperbranched polysiloxane functionalized with amide and hydroxide groups have been obtained using hydrolysis of sol-gel monomers **1-3** containing at least two hydroxyl groups at the silicon non-hydrolyzable substituent [1, 2]:



Polysiloxanes form nanoparticles of different sizes (1.3, 91 and 115 nm for polymers based on **1**, **2** and **3**, respectively) in aqueous solutions, and form a small number of aggregates. Such the nanoparticles can be used as the solubilizers for the preparation of stable aqueous suspensions based on insoluble (or slightly soluble) metal complexes and/or fluorescent organic dyes (diketonates and porphyrazines of rare earth metals, porphyrazines). Investigations of the luminescent properties of siloxane-based particles doped porphyrazine showed a strong red fluorescence enhancement in an aqueous solution. This effect depends on the nature and position of the substituent in the benzene ring of tetraaryltetracyanoporphyrazine. Nanoparticles containing both porphyrazine and tetrakis (hexafluoroacetylacetonate)gadolinium, due to a combination of fluorescent and paramagnetic properties, can be promising as new nanostructured agents for noninvasive tumor diagnostics: in fluorescent and magnetic resonance bioimaging. They are potentially good T₂ contrasters. Doped siloxane nanoparticles are capable of interacting with biological fluids - blood serum and serum albumin. The fluorine-containing polymer shows a greater propensity to bind to lipids than to proteins. Despite the absence of covalent binding to complexes or dye, as well as protein molecules, such the nanoparticles can be used for biomedical applications, in particular, for bioimaging.

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O-8

SELF-ORGANIZING NANOCOMPOSITES BASED ON SILICONE-UREA BLOCK COPOLYMERS

P.V. Komarov^{ab}, D.V. Guseva^c, P.G. Khalatur^{ab}

^a *Institute of Organoelement Compounds of RAS, Moscow 119991, Russia*

^b *Tver State University, Tver 170002, Russia*

^c *Moscow State University, 119991, Moscow, Russia*

E-mail: pv_komarov@mail.ru

Over the past few decades, a large variety of multiphase polymer materials has attracted much attention due to their remarkable variability. In particular, supramolecular aggregates can be formed in so-called "smart" nanomaterials resulting in self-assembly initiated by functional groups, which in turn can be arranged into various spatial nanostructures. These systems include thermoplastic silicone-urea (TPSU) block copolymers containing two blocks based on nonpolar polydimethylsiloxane and polar urea groups. Due to the chemical nature of these blocks, TPSUs possess a number of unique properties, including very low glass transition temperature, high oxidation resistance, thermal stability, hydrophobicity, physiological inertness and increased permeability. Although these polymers are studied for a long time, their internal structure still is not reliably known.

We discuss the results of atomistic molecular dynamics simulations of both unfilled and nanosilica filled silicone-urea copolymers consisting of soft poly(dimethylsiloxane), and hard bis(4-isocyanatocyclohexyl) methane segments (HS and SS, respectively). The simulations show that due to hydrogen bonding between the urea groups, the polymer segments tend to microphase separate into soft and hard domains that can be pictured as an intertwined sponge-like network where two effectively infinite HS-rich and SS-rich domains are present simultaneously. The HS-rich regions act as physical (reversible) crosslinks, functionally similar to those in chemically crosslinked elastomers, and at the same time as a pseudo-reinforcing filler of the rubbery soft segment matrix. Thus, the microphase segregated copolymer itself can be regarded as a spontaneously occurring nanocomposite with hard inclusions embedded in a soft (elastically compliant) phase. The incorporation of silica nanoparticles results in slight improvement of the thermophysical and mechanical properties of the copolymer.

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Preparation of a Hydrophobic Glass-Polymer Material Based on Silica Fabric

D. P. Kiryukhin, G. A. Kichigina, P. P. Kushch, V.G. Dorohov, V.V. Barelko

*Institute of Problems of Chemical Physics RAS,
Chernogolovka, Moscow oblast, 142432 Russia
E-mail: kir@icp.ac.ru*

Glass-fiber and highly porous ceramic materials are widely in demand as heat-insulating, electro-insulating and heat-shielding materials. Special requirements are imposed to such materials used in constructions, [javascript::](#) designs, transport and rescue equipment intended for work in the Arctic under extreme conditions. One of the main disadvantages of these materials is their high hydrophilicity, which levels their performance at extremely low temperatures and can lead to the destruction of constructions and equipment. In the production of hydrophobic fluoroplastic lacquer fabrics, fiberglass is used as a base, and a suspension of fluoroplastic powders is used as the impregnating medium. The content of fluoroplastic in such tissues is about 60-80% by weight. In works [1,2] for receiving hydrophobic fluorinated fiber glass fabrics it is offered to use as the impregnating environment radiation-synthesized tetrafluoroethylene (TFE) telomeres solutions in a [javascript::](#)various telogenes, and as a basis – aluminum-borosilicate fiber glass fabric.

In this work, silica-based fabric SF-11-13, having other chemical composition (SiO_2 96%, Al_2O_3 3.5 – 4.0%, impurity $\leq 1.0\%$), characterized by high resistance to elevated temperatures, and exposure to chemical aggressive liquids is used as the basis. Radiation-synthesized telomers of TFE in acetone and pentafluorochlorobenzene (PFCB) were used as the impregnating medium. For removal of the technical lubricant, in addition to the heat treatment used earlier [1,2], some other ways have been proposed and an analysis of their effectiveness has been made. It was shown that samples of hydrophobic silica fabrics were obtained using of TFE telomeres solutions radiation-synthesized in acetone and PFCB. The content of fluoroplastic in such samples is less 10% by weight. The best and easiest way to remove the technical lubricant is preliminary thermal treatment of the tissue at 600°C. The presence of a fluoropolymer coating providing hydrophobicity of silica tissue is indicated by IR absorption spectra. Comparison of the properties of materials obtained on the basis of industrial aluminoborosilicate and silica fabrics suggests that for the hydrophobization of SF-11-13 the required quantity of telomers is higher, which is due to the density of weaving used tissue.

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O-10

Boron-substituted carboranes as a platform for design of novel silicon materials

Anisimov A.A.^a, Vysochinskaya Yu.S.^{a,b}, Kapelistaya E.A.^a, Zaitsev A.V.^a, Buzin M.I.^a,
Ol'shevskaya V.A.^a, Shchegolikhina O.I.^a, Muzafarov A.M.^{a,b}

^aA.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation

^bN.S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 117393 Moscow, Russian Federation

E-mail: anisimov@ineos.ac.ru

Among the numerous types of polymeric compounds organosilicon polymers (polysiloxanes) with carborane structural fragments are of special interest due to the ability of carboranes to induce thermal and chemical stability in materials [1]. In this connection the developing of new methodologies for functionalization of the linear polycarboranylsiloxanes with the aim of increasing their thermal stability is the essential step in preparation of new polymers. Herein, we report on recent advances in the synthesis and properties of new series of carborane-substituted silicon compounds [2,3]. Some of them are presented in Figure 1.

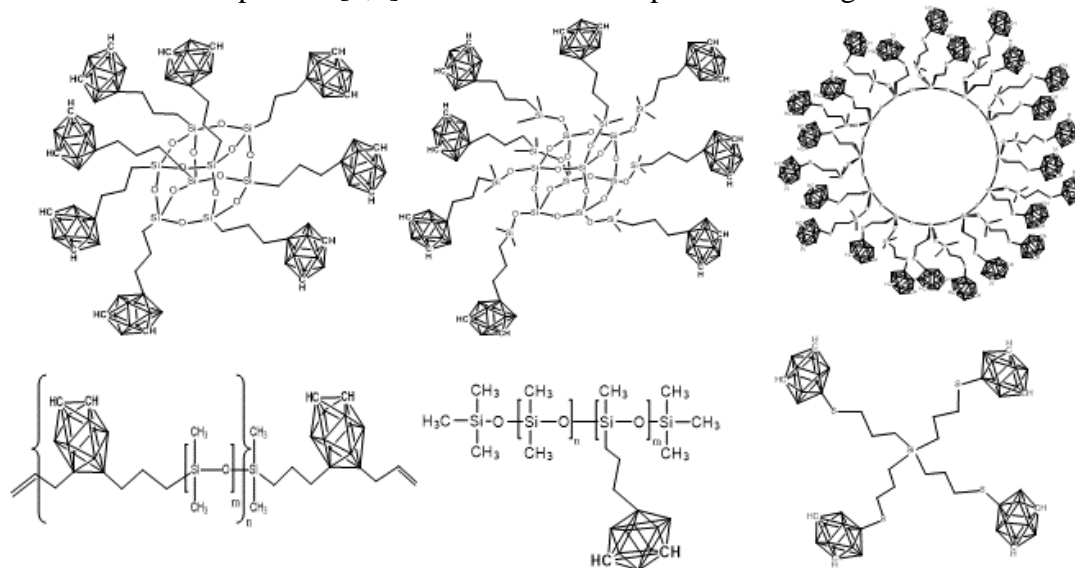


Figure 1.

Synthetic chemistry of these compounds, as well as evaluation of their physico-chemical properties will be presented.

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O-11

Ceramic fibers based on polycarbosilane

D.V. Zhigalov, G.I. Shcherbakova, A.P. Korolev, M.Kh. Blokhina, A.A Vorob'ev.

SSC RF JSC "State Research Institute for Chemistry and Technology of Organoelement
E-mail: Zhigalov@eos.su

Polycarbosilanes (PCS) are well known preceramic organosilicon poly(oligo)mers, used for obtaining silicon carbide components of composite materials like SiC fibers, matrixes, binders, powders and coatings to create components of high-temperature (up to 1200°C or more) oxidizing resistant ceramic composite materials for structural purposes, which are used for the manufacture of critical parts, components and products of aviation, aerospace, power-engineering and other industries.

Researches of GNIChTEOS have developed PCS synthesis technology [1]. To produce PCS we use available raw material and standard chemical processing equipment. There are no processes that are performed under the pressure above 0.5 MPa and temperature above 430 °C. The synthesized PCS were defined by Синтезированные ПКС были охарактеризованы physicochemical methods: IR, ¹H, ¹³C, ²⁹Si NMR, TEM, SEM, TGA, GPC, elemental analysis.

PCS was melt spun into polymeric fibers, and then they were thermally stabilized in air at a temperature up to 300°C. Ceramic fibers comprising an amorphous SiCO phase and β-SiC were prepared by the following pyrolysis in vacuum or argon at a temperature up to 1100-1300°C. Coreless SiC fibers were analyzed by SEM and X-ray phase analysis. Tensile strength of the fibers amounted to 2,100 MPa, fiber diameter was in the range of 8-25 μm.

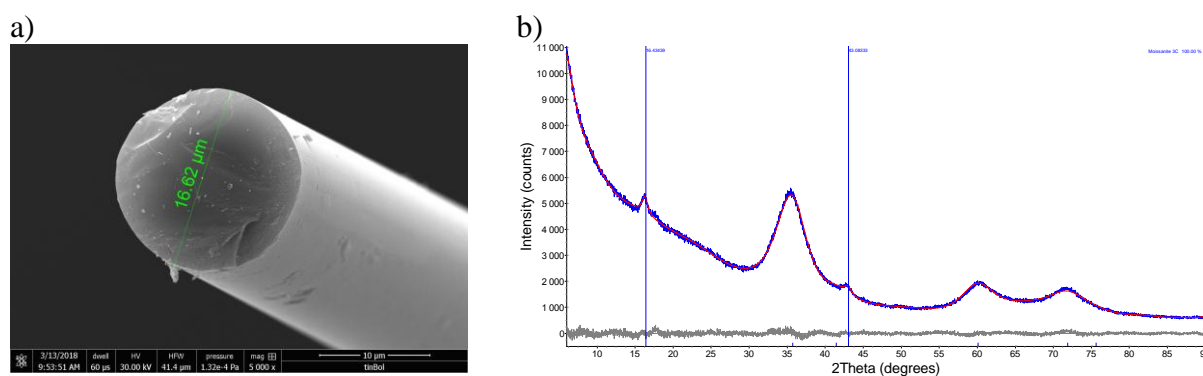


Fig. 1. Coreless SiC fiber. a – microphotography SEM; b – X-ray diffraction

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O-12

MQ-copolymers

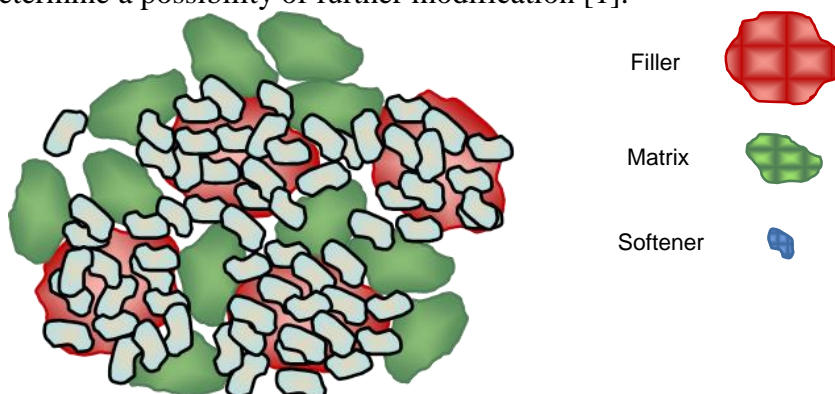
Elena Tatarinova^a, Ivan Meshkov^a, Aziz Muzafarov^{a,b}

^aEnicolopov Institute of Synthetic Polymeric Materials Russia Academy of Sciences, Profsoyuznaya st.70, 117393 Moscow, Russia

^bA.N. Nesmeyanov Institute of Organoelement Compounds of Russia Academy of Sciences, Vavilova st.28, 119991 Moscow, Russia

E-mail: tatarinova@ispm.ru

MQ copolymers, often called MQ resins, consisting of mono- (M) and tetra- (Q) functional siloxane units occupy an important place among organosiloxane polymers. The peculiarity of the macromolecules structure is the presence of an inorganic component $\text{SiO}_{4/2}$ and an organic component in the $\text{R}_3\text{SiO}_{1/2}$ unit, and this allows to classify these compounds as hybrid nanosized organo-inorganic materials. At the present time, the interest in such objects is increasing due to the expanding needs for high quality composite materials. A possibility of introducing various organic alkyl and aryl substituents into the triorganosiloxane unit extends the range of possible structure, including latent functional groups (vinyl, silanol, hydridsilyl), which determine a possibility of further modification [1].



Scheme 1. Schematic model of the MQ-copolymer structure.

The report will present the results of studies on the methods of syntheses of MQ copolymers with different ratios of units. Moreover, data for obtaining of MQ structures with various radicals at the silicon atoms will be listed.

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O-13

Synthesis and gas transport properties of Fe- and Zr-containing polydimethylsiloxanes

N.A. Belov^a, A.N. Tarasenkov^b, N.A. Tebeneva^b, N.G. Vasilenko^b, G.A. Shandryuk^a,
Yu.P. Yampolskii^a, A.M. Muzafarov^{b,c}

^a A.V. Topchiev Institute of Petrochemical Synthesis of RAS

^b N.S. Enikolopov Institute of Synthetic Polymeric Materials of RAS

^c A.N. Nesmeyanov Institute of Organoelement Compounds of RAS

E-mail: belov@ips.ac.ru

Organopolysiloxanes have found widespread use as materials for gas separation membranes with high gas permeability [1–3]. Such membranes became promising ones in purification of natural gas and biogas [4–6].

Current work is devoted to investigation of gas permeation properties of membranes being three-dimensional polydimethylsiloxane networks with non-aggregated metal atoms. The materials are synthesized on the basis of industrial siloxane rubbers SKTN-D ($M \sim 9 \cdot 10^4$), SKTN-E ($M \sim 12 \cdot 10^4$) and polyfunctional metasiloxanes as cross-linking agents (Fe[OSi(Me)(OEt)₂]₃ and Zr[OSi(Me)(OEt)₂]₄). The content of Fe-siloxane in composition with SKTN-D is equal to 25, 33, 40 and 50 w.%, respectively. While in the case of Zr-siloxane, a single composition with SKTN-E (75 w.%) is prepared. Introduction of polyfunctional metasiloxane both facilitates uniform distribution of dispersed metal in the polymeric compositions and significantly improves their mechanical properties. So, tensile strength of the compositions increases as content of the metasiloxane increases. Analysis of DSC-curves show that glass transition and melting temperatures of the compositions equal app. -120 and -45 °C respectively that is in agreement with corresponding temperatures for linear PDMS. Heats of melting are in general proportional to content of SKTN rubber in composition and slightly decrease while content of the metasiloxane increases.

Permeability (P) and diffusion (D) coefficients of gases He, H₂, N₂, O₂, CO₂, hydrocarbons C₁-C₄ were measured on barometric setup "Barotron" by means Daynes-Barrer technique. Permeability coefficients of the most gases are similar to P values determined previously for linear PDMS while diffusion coefficients of the gases are systematically lower than D values of corresponding gases. Surprisingly, $P(n\text{-C}_4\text{H}_{10})$ and C₄-C₁ selectivities appear noticeable higher than parameters having been determined previously. The differences of the parameters are shown to be resulted from higher solubility coefficients of gases in compositions prepared.

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O-14

**Deposition of Plasma-Polymerized Hexamethyldisilazane Films onto
Polypropylene Track-Etched Membrane Surface**

L. Kravets^a, V. Altynov^a, N. Lizunov^a, V. Satulu^b, B. Mitu^b, G. Dinescu^b

^a *Joint Institute for Nuclear Research, Flerov Laboratory of Nuclear Reactions,
Joliot-Curie Str. 6, 141980 Dubna, Russia*

^b *National Institute for Laser, Plasma and Radiation Physics, Atomistilor Str. 409,
077125 Magurele, Bucharest, Romania*

E-mail: kravets@jinr.ru

The synthesis and characterization of the polymer bilayer composite membranes prepared by deposition of thin films onto one side of a porous substrate using a plasma polymerization method were studied. Polypropylene track-etched membrane (PP TM) with thickness of 10.0 μm and pore diameter of 300 nm (pore density of 10^8 cm^{-2}) was used as porous substrate. To produce the membrane, PP-foil 'Torayfan' T2372 (Toray Co., Japan) was irradiated by xenon ions accelerated at the cyclotron and then subjected to physicochemical treatment using the method described in [1]. The deposition of the polymer films onto the membrane surface was conducted by RF-discharge (13.56 MHz, 100 W) generated at a working pressure of 0.7 Pa established by a mixture of argon, used as feed gas, with hexamethyldisilazane (HMDSN) vapors used as precursor. The deposition time was varied. The schematic diagram of the setup and the processing procedure are described in detail in [2].

The investigation of the surface morphology of the composite membrane was carried out by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface properties were characterized by measuring the water contact angles. The chemical structure was investigated by X-ray photoelectron spectroscopy (XPS) and Fourier-transformed infrared spectroscopy (FTIR) in attenuated total reflectance (ATR) mode. The measurements of the current-voltage characteristics of the membranes were carried out with a direct current regime in the voltage range of -1 to $+1$ V using a PC-controlled potentiostat 'Elins P-8S' (Russia) with a scan rate of 50 mV/s. A two-chambered cell with Ag/AgCl electrodes, containing a water solution of potassium chloride of identical concentration on both sides of the membrane was used for this purpose.

It has been shown that deposition of the plasma-polymerized HMDSN films onto the surface of PP TM results in bilayer composite membranes with both the layers having hydrophobic properties. The developed bilayer membranes present the 'diode-like' properties, namely the ion transport in electrolyte solutions depends on the current direction through the pores. This effect is caused by decreasing the pore diameter in the deposited polymer films that results in changing the pore geometry as well as existence in the pores of an interface between two layers of different nature. The membranes of this kind can be used for directional ion transport.

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This work was supported by the bilateral project (No 4648-17/21) with JINR, FLNR (Dubna) and NILPRP (Bucharest) and the grant (No 17-08-00812) from Russian Foundation for Basic Research.

O-15

Tribological properties of polyorganosiloxane and their mixtures with basic oils

Anton Lyadov, Yuliya Maksimovs, Angelica Shahmatova, Oleg Parenago
A.V.Topchiev Institute of Petrochemical Synthesis, RAS
E-mail: lyadov@ips.ac.ru

One of the ways of creating lubricants with an extended range of serviceability, including those used in arctic conditions at extremely low temperatures, is the use of polyorganosiloxanes. They are characterized by low pour point temperatures (up to -110°C), high heat resistance (up to 350°C), low saturated vapor pressure ($0.133 \div 133 \mu\text{Pa}$), low volatility, low viscosity, high hydrophobicity and lyophilicity. In addition, silicon fluids are characterized by high radiation resistance, thermal and chemical stability. The disadvantage of most polyorganosiloxanes is the poor compatibility with hydrocarbons and low lubricity, especially in sliding friction. To improve the anti-wear and anti-friction properties of silicone fluids, different basic oils can be added to them.

Physical, chemical and tribological properties of mixtures of polyorganosiloxanes and basic oils were studied. It was found that the addition of about 10 wt. % hydrocarbon oil to polyorganosiloxane leads to a noticeable increase in the diameter of the wear scar, which, with further increase in the hydrocarbon oil content in the mixture, sharply decreases and at its concentration ~ 30 wt. % has a value lower than for the pure hydrocarbon component (fig. 1). A similar but less pronounced dependence is also observed for extreme pressure properties. The values of the density and viscosity of mixtures in the same range are determined. Based on the data of elemental, IR and X-ray fluorescence analysis, the assumptions about the nature of the effect found are made.

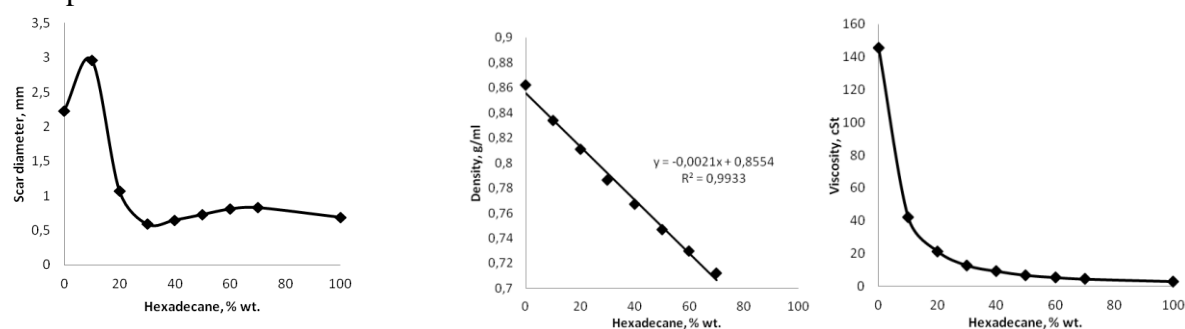


Fig. 1. Influence of hydrocarbon content in the mixture with polydiethylsiloxane on: A – antiwear parameter, B – density and C – viscosity.

This work was done as part of TIPS RAS State Plan

O-16

Reactions of Silicon Hydrides Catalyzed by Rhodium(III) Sulfoxide Complexes

V.V. Novozhilov, A.A. Eliseeva and N.K. Skvortsov

St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 190013 Russia

E-mail: novozhilow@gmail.com

We have shown that rhodium(III) sulfoxide complexes $[\text{RhCl}(\text{R}_2\text{SO})]$, in spite of coordination saturation, are effective catalysts for different reactions of silicon hydrides, being no worse than the traditional Wilkinson's catalyst $[\text{RhCl}_3(\text{Ph}_3\text{P})_3]$ and sometimes surpassing it in activity and selectivity.

Influence of solvents and an electron-donating additives (triphenylphosphine, phenanthroline, dibenzylsulphid) in the reaction of diphenylsilane with methanol catalyzed by planar complexes of rhodium(I) – $[(\text{Ph}_3\text{P})_3\text{RhCl}]$, platinum(II) – $[\text{Pt}(\text{Et}_2\text{SO})_2\text{Cl}_2]$ and octahedral complexes of rhodium(III) – $[\text{Rh}(\text{Et}_2\text{SO})_3\text{Cl}_3]$ has been studied.[1]. The substantial influence of these parameters on the rate of reaction was found and the «scales» of the solvents activities were obtained, is different for different catalysts.[1].

The hydrosilylation reaction of styrene with methyldichlorosilane catalyzed by complexes of rhodium, platinum, palladium and nickel has been studied. It was for the first time shown that an efficient catalyst is the coordinatively saturated octahedral complex of rhodium(III) – $[\text{Rh}(\text{DMSO})_3\text{Cl}_3]$. In the presence of this catalyst, the reaction proceeds with preferred formation of α -adduct.[2]

In dehydrocondensation reaction silicon hydrides reacts with the absence of a second substrate and form compounds containing siloxane bonds. Thus, as a result of the reaction of diphenylsilane catalyzed by the complex of mer-, cis- $[\text{RhCl}_3(\text{Me}_2\text{SO})_3]$, 1,1,3,3,5,5,7,7-octaphenylcyclotetrasiloxane is formed in high yield [3]. The complex $[\text{RhCl}_3(\text{Me}_2\text{SO})_3]$ also catalyzes the reaction of 1,1,3,3-tetramethyldisiloxane with the formation of a mixture of cyclic and linear oligomeric siloxanes.

As a result of the dehydrocondensation of polymethylhydrosiloxane catalyzed by $[\text{RhCl}_3(\text{Me}_2\text{SO})_3]$, a cross-linked siloxane polymer is formed with inclusions of the rhodium(III) complex, which exhibits activity in the methanolysis and hydrosilylation reaction of phenylacetylene.

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O-17

Synthesis of new functional siloxane derivatives of limonene by a combination of hydrosilylation and hydrothiolation reactions

F.V. Drozdov^a, V.V. Velikorodnaya^c, G.V. Cherkaev^a, N.V. Demchenko^a, M.I. Buzin^b,
A.M. Muzafarov^{a,b}

^a N.S. Enikolopov Institute of synthetic polymeric materials, Russian Academy of Science, Profsoyuznaya st. 70, 117393, Moscow, Russia

^b A.N. Nesmeyanov Institute of Organoelement, Russian Academy of Science, Vavilova st. 28, 119991, Moscow, Russia

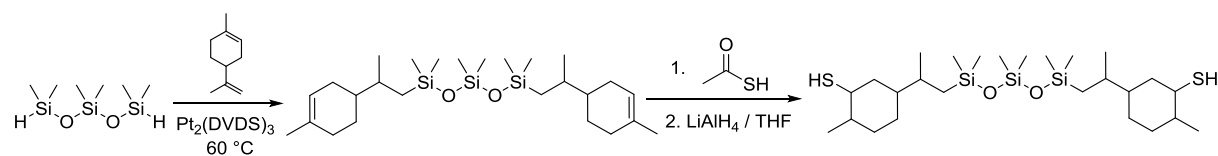
^c Moscow Technological University (Fine Chemical Technologies Institute), Vernadsky Avenue, 119454 Moscow, Russia

E-mail: drozdov@ispm.ru

Nowadays, the scientific community is challenged with the possibility of obtaining environmentally friendly polymers based on renewable sources, such as plant raw materials, and in particular terpenes. Terpenes are natural hydrocarbons both cyclic and acyclic structure, which are widely obtained from essential oils of plants, fruits and resin of coniferous trees. The most common among terpenes are pinene and limonene, the world production of which exceeds 70,000 and 300,000 tons annually. Due to the steric hindrance of the double bond in the limonene cycle (4-isoprenyl-1-methylcyclohexene), it was possible to obtain only low-molecular homopolymers by different polymerization methods. A significant advance in polymer chemistry was done with development of the thiol-ene reaction, which was also used in the chemistry of terpenes for the preparation of both functional monomers and for the synthesis of polymers by polyaddition to thiol-ene. Despite significant progress in the functionalization of terpenes, an analysis of literature data shows that there are only a few references to the hydrosilylation of terpenes [1].

Therefore, the aim of this paper was, firstly, to demonstrate the possibility of carrying out the hydrosilylation reaction limonene's double bond with hydride-containing siloxane compounds; second, by combination of hydrosilylation and thiol-ene reactions, obtain various functional derivatives and use them as a monomeric base for the synthesis of siloxane-based copolymers based on limonene.

It has been shown that hydrosilylation carried out regioselectively on isoprene double bond of limonene, while cyclohexene double bond remained unaffected.



Nevertheless, cyclohexene double bond reacts readily with different thiols by the hydrothiolation reaction. This selectivity of both reactions opens the possibility of obtaining various limonene derivatives and use them as a monomeric base for the synthesis of siloxane polymers based on limonene.

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Mechanochemical approach to the direct synthesis of alkoxy silanes

Temnikov M.N.^a, Anisimov A.A.^a, Zhemchugov P.V.^a, Kholodkov D.N.^a, Naumkin A.V.^a,
Goloveshkin A.S.^a, Chistovalov S.M.^a, Muzafarov A.M.^{a,b}

^a A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences
(INEOS RAS)

Moscow, Russian Federation

^b N.S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences
(ISPM RAS)

Moscow, Russian Federation.

E-mail: temnikov88@ineos.ac.ru

The discovery of direct synthesis of organochlorosilanes by E. Rochow in the 1940s made it possible to raise the chemistry and production of silicone materials to a completely new level [1]. As a result, organosilicon compounds found applications in nearly every area of human activity and in everyday life.

However, the situation concerning the ecological and economic components of production and further application of organochlorosilanes, which satisfied the demands of people in the XX century, no longer meets the requirements of green chemistry principles. This is primarily due to the emission of hydrogen chloride-containing waste in the production of silicone polymers from the corresponding chlorine-containing organosilicon monomers.

Alkoxy silanes might have become an alternative to chlorosilanes.

In this work, we present a mechanochemical approach to the direct synthesis of alkoxy silanes. This method allows a considerable simplification of the traditional multistage process by eliminating three stages that include silicon and catalyst preparation, and adapts it to the green chemistry requirements (Fig. 1.). Vibration milling, removed the oxide film, and mechanoactivation of the large silicon fraction (1000-2000 μm) occur in the reactor working space. Abrasion from the reactor walls and grinding bodies made of brass result in a developed catalytic surface on silicon, as it has been proven by a set of physical analytical methods.

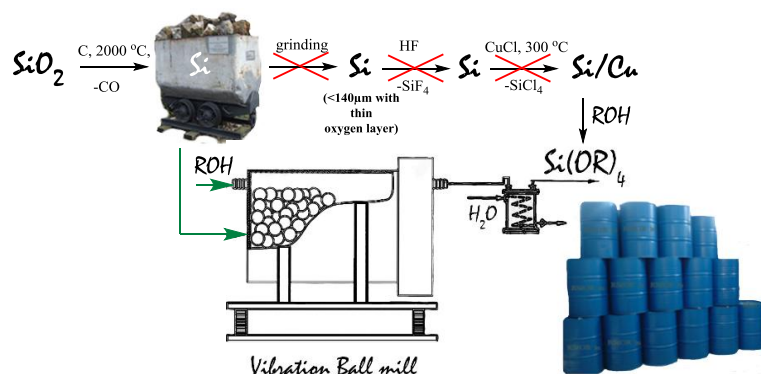


Fig. 1. Direct synthesis of alkoxy silanes by mechanochemical approach

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O-19

Low-melting silicon containing phthalonitrile monomers for thermosetting resins with improved processability

Bulgakov B.A.^{1,2}, Babkin A.V.^{1,2}, Morozov O.S.², Kepman A.V.^{1,2}

¹*Lomonosov Moscow State University, Moscow, Russia*

²*Institute of New Carbon Materials and Technology, Moscow, Russia*

E-mail: bbulgakov@inunit.ru

Polymer matrices developed from bis-phthalonitrile (PN) demonstrate the highest heat resistant properties among the known thermosets. Since the beginning the main disadvantage of that type of resins was narrow processing window caused by high melting points of the PN monomers. Melting points of the first generation of PN monomers were 175–200 °C while fast polymerization occurred above 200°C.

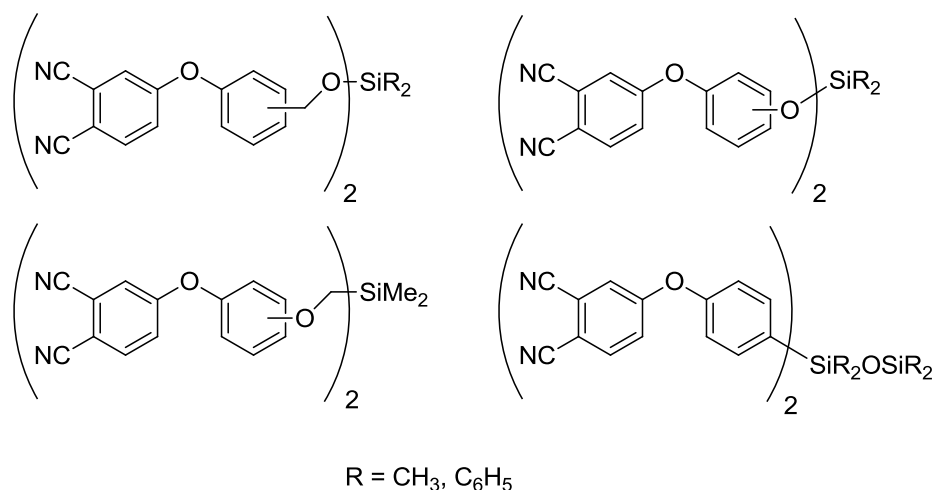


Fig. 1. Organosilicon-linked bis-phthalonitrile monomers .

The scope of low-melting phthalonitriles bridged with various flexible organosilicon linkers was synthesized (Fig. 1). Glass transition temperatures of the amorphous PNs were in a range of (-4)–27 °C [1–4]. Thermosets obtained after curing of these monomers in the presence of aromatic diamines demonstrated thermal properties featured to PN matrices such as heat deflection temperature (>420 °C), high decomposition temperature ($T_{5\%} > 530$ °C in Ar) and a char yield ($Y_c > 80\%$). The use of these monomers for the first time provided fabrication of composite materials by cost-effective vacuum infusion and RTM techniques.

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O-20

Synthesis of fluorescent siloxane dyes based on DBMBF₂

Belova A.S.^a, Kononevich Yu.N.^a, Anisimov A.A.^a, Sazhnikov V.A.^b, Surin N.M.^c,
Svidchenko E.A.^c, Shchegolikhina O.I.^a, Muzafarov A.M.^{a,c}

^aA. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation

^bPhotochemistry Center, Russian Academy of Sciences, 119421 Moscow, Russian Federation

^cN. S. Enkolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 117393 Moscow, Russian Federation

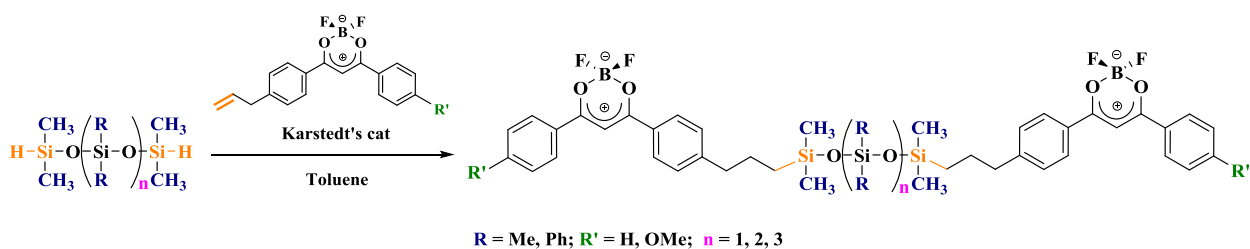
E-mail: belova.asya@gmail.com

Fluorescent dyes based on boron difluoride complexes (DBMBF₂, BODIPY) are perspective objects for creating fluorescent materials of various purposes on their basis. A significant interest in the study of these compounds is due to the fact that they possess a number of valuable photophysical and photochemical properties, such as intense fluorescence with high quantum yield, high extinction coefficient and high photostability. Thus, a current task at present is to study new dibenzoylmethane derivatives of boron difluoride (DBMBF₂) with unique fluorescent properties.

It is known that DBMBF₂ derivatives aggregate in solutions and form excimers in the excited state. Such excimers are of special interest for materials science, in particular for organic electronics, where they can be used as sensors and organic light-emitting diodes (OLED).

The approach to obtain excimers is the fixation of fluorophores in one molecule at a close distance with the possibility of intramolecular interfluorophore π - π interaction. Linear and stereoregular cyclic siloxanes are convenient matrices for fixing of fluorophores, such structures allow several fluorophores to be located in one plane, promoting interfluorophore π - π interaction and the formation of excimers in the excited state.

In this work we obtained a number of multichromophore siloxane dyes of linear and cyclic structure, containing various derivatives of DBMBF₂ (Scheme 1).



Scheme 1. Synthesis of linear siloxane derivatives DBMBF₂

The structure of the obtained compounds were confirmed by the ¹H, ¹³C, ¹⁹F, ²⁹Si NMR spectroscopy, IR spectroscopy, mass spectrometry (ESI), and their photophysical properties were studied.

Platinum group metal complexes as catalysts for polysiloxane hydrosilylation cross-linking

Dobrynin M.V.^a, Islamova R.M.^a

^a Saint Petersburg State University, Saint Petersburg, Russia
E-mail: mdobrynin42@yandex.ru

Polysiloxanes as materials are often used in form of cured silicone rubbers and hydrosilylation is one of reactions that are suitable for this task. This approach considers mixing vinyl- and hydride-containing polysiloxanes and addition of hydrosilylation catalyst that is usually coordination complex of platinum group metal. [1]

In our work nitrile platinum(II), cyclometalated iridium(III) and acetylacetonate rhodium(I) complexes (**Figure 1**) were employed for hydrosilylation curing of vinyl-terminated polydimethylsiloxane and poly(dimethylsiloxane-co-methylhydrosiloxane). Compared to industrially used Karstedt's catalyst [2], all of them improve properties of silicone rubbers and allow curing at certain conditions without additional reagents. Platinum(II) nitrile complexes allowed to cure silicone rubbers both at RT and at heating (20–80 °C) without inhibitors and improve their thermal stability (by ca. 30 °C) and elongation at break (by ca. 60%). [3] Cyclometalated iridium(III) complexes are active only at temperatures above 80 °C; resulting rubbers possess luminescent properties and higher thermal stability (by 80–120 °C). [4] Acetylacetonate rhodium(I) complexes allow to cure polysiloxanes at room temperature and to improve their elastic properties (elongation at break increased by 90–100%).

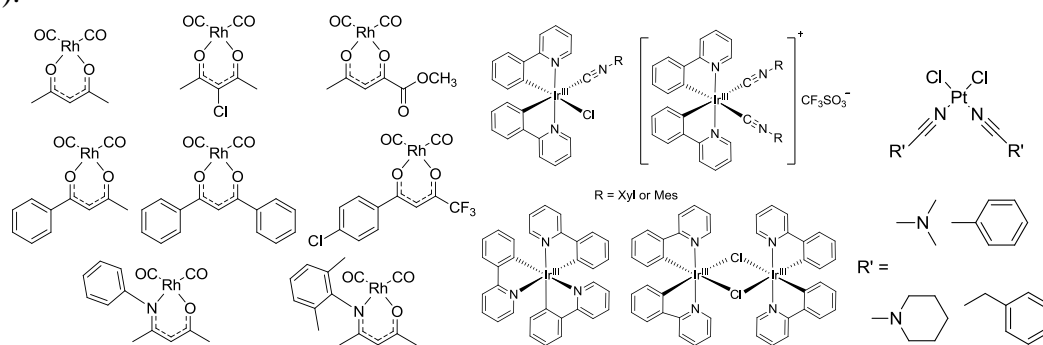


Fig. 1. Platinum group complexes used for hydrosilylation cross-linking

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This work was supported by Russian Foundation for Basic Research (RFBR) grant mol_a 18-33-00769. Physicochemical measurements were performed at Center for Magnetic Resonance, Center of Thermal Analysis and Calorimetry, Chemical Analysis and Materials Research Centre of Saint Petersburg State University.

O-22

Synthesis and properties of polynorbornenes containing trialkoxysilyl groups

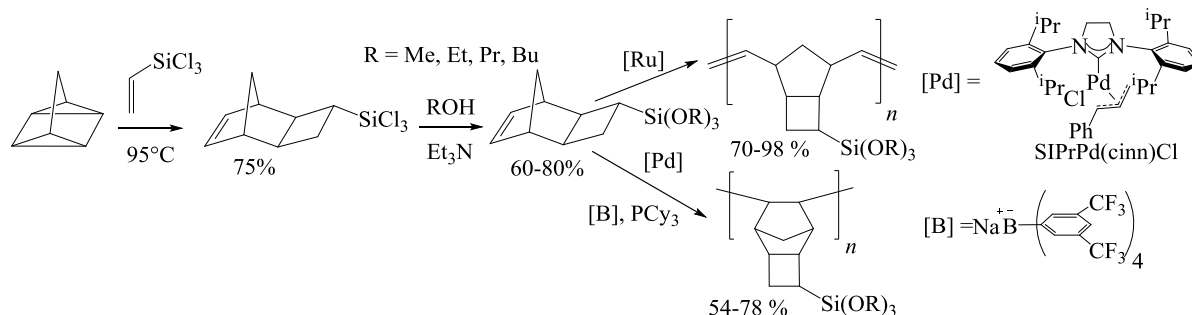
Dmitry A. Alentiev^a, Maxim V. Bermeshev^{a,b}, Lyudmila E. Starannikova^a,
Andrey F. Asachenko^a, Maxim A. Topchiy^a, Pavel S. Griбанov^a, Mikhail S. Nechaev^{a,c},
Yuri P. Yampolskii^a, Eugene Sh. Finkelshtein^a

^a A.V. Topchiev Institute of Petrochemical Synthesis RAS, 29 Leninsky prospekt, 119991 Moscow, Russia

^b D.I. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya sq., 125047 Moscow, Russia

^c M.V. Lomonosov MSU, Chemistry Department, 1-3 Leninskiye gory, 119991 Moscow, Russia; E-mail: d.alentiev@ips.ac.ru

Polynorbornenes containing side Si-O-groups are promising materials for membrane gas separation of hydrocarbon mixtures. Earlier it was shown that polynorbornenes containing Si-O-Si-groups had high C₄/C₁ selectivity controlled by solubility [1]. At the same time, polynorbornenes containing Si-O-C-groups are interesting objects because of the presence of long alkyl fragments which could significantly increase the solubility of heavy hydrocarbons. In this work new ROMP and addition polynorbornenes containing trialkoxysilyl groups of different length were synthesized and their gas transport properties were investigated. The monomers were obtained by cycloaddition reaction of trichlorovinylsilane to quadricyclane followed by nucleophilic substitution of Cl atoms by alkoxy groups. The metathesis polymerization was carried out in the presence of the 1st generation Grubbs catalyst. The addition polymerization was conducted using three-component catalytic system based on N-heterocyclic carbene Pd-complex (SIPrPd(cinn)Cl) (Scheme 1).



Scheme 1. Synthesis and polymerization of norbornenes containing trialkoxysilyl groups.

The obtained polymers turned out to be amorphous and high molecular weight. ROMP polymers were glassy or rubbery depending on the alkoxy-group length. All addition polymers were glassy. Gas transport properties of the obtained polymers depended on alkoxy-group length: the permeability of addition polymers decreased with the growth of substituent length. The selectivity of hydrocarbon separation turned out to be solubility controlled: the values of C₄/C₁ selectivity were determined to be as high as 48. We obtained a surprising result: certain ROMP polymers possessed higher permeability than their addition isomers.

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O-23

**Кремнийорганические Соединения от Немецкого Производителя
abcr GmbH**

Tatyana Danilova

**СТЕНДОВЫЕ
ДОКЛАДЫ**

**POSTER
PRESENTATIONS**

P-1

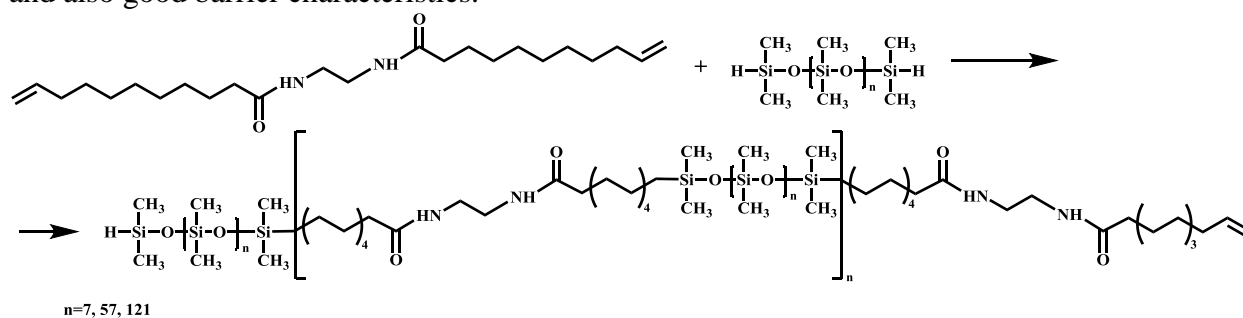
Synthesis of polydimethylsiloxane copolymers based on N,N'-ethylenediundeceneamide

Sofia N. Ardabevskaia^{a, b}, Elizaveta V. Selezneva^{a, b}, Sergey A. Milenin^a, Aziz M. Muzafarov^a
^a *Enicolopov Institute of Synthetic Polymeric Materials, Profsoyuznaya street, 117393 Moscow, Russia*

^b *Moscow Technological University (Fine Chemical Technologies Institute), Vernadsky Avenue, 119454 Moscow, Russia*

E-mail: sofi-agatova@rambler.ru

Polydimethylsiloxane (PDMS) and polyamides are used in many areas of the modern industry. PDMS has high chemical and physical stability, good biocompatibility, optical transparency, hydrophobicity and flexibility. Polyamides have good mechanical properties including high flexibility, good resilience and high impact strength. Previously copolymers based on PDMS and other polymers, such as polyurethane, polyester and polyamides was obtained [1, 2]. However, the physicochemical properties of copolymers based on polyamides have not been studied in detail yet. We believe that using PDMS and PA as units of copolymer, the properties are typical for each polymer individually be combined in a single molecule. This will provide new polymer materials with high chemical and physical stability, and also good barrier characteristics.



Scheme 1. Synthetic scheme of polydimethylsiloxane copolymers based on N,N'-ethylenediundeceneamide

We have developed and implemented synthetic scheme of such copolymers with different nature of constituent units, which involves two reactions - the interaction of acids with amines, and hydrosilylation reaction of PDMS and obtained N,N'-ethylenediundeceneamide in the presence of Karstedt catalyst. A number of copolymers with different siloxane chain length (n=7, 57, 121) was synthesized. The structures of the products obtained were confirmed by ¹H NMR spectroscopy and gel-permeation chromatography. In this work we explored the properties of these polymers by DSC, TGA and other physical-chemical methods, and also investigate their solubility.

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P-2

Heat-Conducting Gasket Materials Based on Organosilicon Binders

P.A. Storozhenko, A.N. Polivanov, T.I. Fedotova, A.V. Levchuk, A.G. Ivanov,
A.I. Drachev, M.G. Kuznetsova, V.A. Bardakova* N.V. Tyurikova, N.Yu. Mel'nikova

SSC RF JSC GNIChTEOS

*e-mail: fedotova@eos.su

Advanced materials designed to remove heat from the heating elements of electronic devices must have good thermal conductivity, high dielectric properties, be elastic, easy to handle and cut, have, if required by operating conditions, an adhesive layer on one or both sides, be environmentally friendly and not to emit harmful substances when heated, and have small overall dimensions.

At present researchers of GNIChTEOS are engaged in the development of processes for thin-film glass fiber reinforced self-extinguishing heat-conductive processible gasket materials possessing the required thermal conductivity, dielectric parameters and operability in a fairly wide temperature range. The gasket materials are based on extended organosilicon low molecular elastomers.

In the framework of this study, experimental samples of two types of heat-conducting gaskets were produced, whose photographs are given below: a thin single-layer heat-conducting material reinforced with fiberglass, and two-layer heat-conducting material, one layer of which is reinforced with glass fiber and the other one is an outside sticky adhesive layer. The experimental samples were tested, and test results are presented in the tables 1 and 2.

Table 1 Thin single-layer heat-conducting material

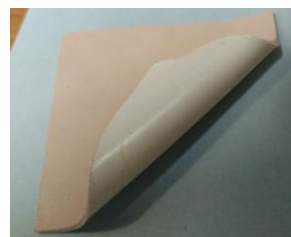
No	Parameter	Value
1	Thickness, mm	0.16 ÷ 0.3
2	Hardness (Shore A)	85.0
3	Thermal conductivity, W/m · K	0.9

Table 2 Two-layer heat-conductive material

No	Parameter	Value
1	Thickness, mm	0.508 ÷ 6.35
2	Hardness (Shore 00)	5.0
3	Thermal conductivity, W/m · K	1.0



Thin single-layer heat-conductive material



Two-layer heat-conductive material

P-3

Synthesis of cyclosiloxanes with different organic groups at silicon atoms

Chernov E. V.^a, Kalinina A. A.^{a, b}, Talalaeva E. V.^a, Muzafarov A. M.^{a, b}

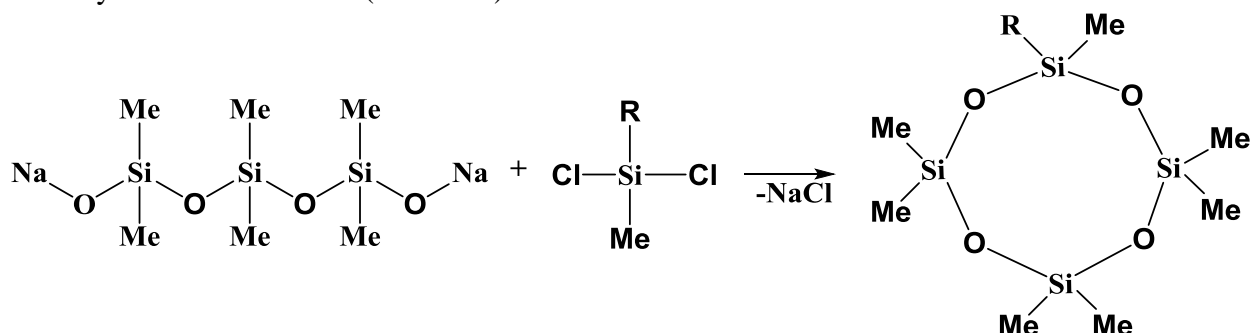
^a*Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, Moscow, Russian Federation*

^b*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russian Federation*

ak4erniy@gmail.com

Synthesis of cyclosiloxanes with different organic groups at silicon atoms is an actual problem in view of the possibilities of their use for the production of functional copolymers with a given set of properties. Nowadays, the synthesis of cyclosiloxanes with different organic groups at silicon atoms is carried out either by hydrolysis of the corresponding diorganochlorosilanes and hetero-functional condensation of hydroxy- and chlorine-containing precursors [1]. These approaches are characterized by low selectivity and yields and in the second case also by the complexity of monitoring the reaction conditions. In this connection, the previously developed method of directed synthesis of sodium dimethyltrisiloxanediolates opens new prospects for solving the synthesis problem [2].

The aim of this work is the synthesis of mixed cycles of a given structure from sodium dimethyltrisiloxanediolates (scheme 1).



The results of the investigation of the solvent's influence (THF, MTBE) and the ratio of the initial reagents to the yield of the desired product will be present and optimal conditions for the synthesis of D_4^R , with $R=\text{Vin-}, \text{Me-}, \text{H-}$ will be found. The obtained products are characterized by a combination of physical and chemical analysis methods: gas-liquid and gel permeation chromatography, IR and ^1H NMR spectroscopy.

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This work was supported by the grant of the RFBR 18-03-00867. A.

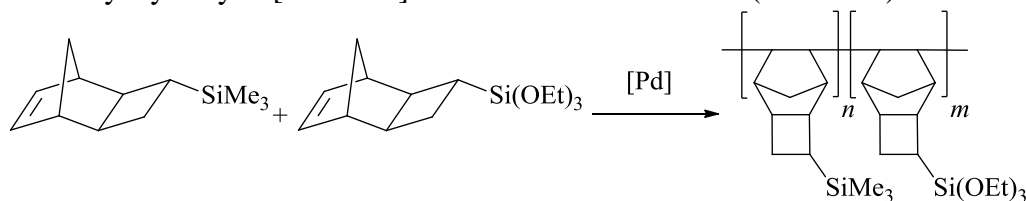
P-4

Synthesis and cross-linking of addition copolymers based on silicon-containing tricyclononenes

Elena S. Egorova^{a,b}, Dmitry A. Alentiev^a, Maxim V. Bermeshev^{a,c}, Eugene Sh. Finkelshtein^a
^a A.V. Topchiev Institute of Petrochemical Synthesis RAS, 29 Leninsky prospekt, 119991 Moscow, Russia
^b Moscow Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies), 86 Vernadskogo prospekt, 119571 Moscow, Russia
^c D.I. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya sq., 125047 Moscow, Russia, E-mail: d.alentiev@ips.ac.ru

Addition polymerization of norbornenes containing trimethylsilyl groups results in the formation of rigid-chain saturated polymers. In comparison with isomeric metathesis polymers, they possess higher free volume, chemical and thermal stability, which open prospects of their application for membrane gas separation. However, they possess some significant disadvantages, such as moderate mechanical properties and inertness to chemical modifications (for example, cross-linking). One of the ways removing these disadvantages is the introduction of reactive side groups into these polymers, which could be performed by copolymerization with co-monomers containing reactive substituents.

Earlier we attempted to cross-link addition copolymer based on 5-trimethylsilylnorbornene containing 5-10 mol.% of 5-ethylidenenorbornene units, but the attempt proved to be unsuccessful [1]. In this work, in order to study the possibility of cross-linking of silicon-containing polynorbornenes, we synthesized new addition copolymers bearing reactive Si(OEt)₃ groups, which can form interchain siloxane bonds upon hydrolysis. For this, addition copolymerization of 3-trimethylsilyltricyclo[4.2.1.0^{2,5}]non-7-ene with 3-triethoxysilyltricyclo[4.2.1.0^{2,5}]non-7-ene was carried out (Scheme 1).



Scheme 1. Addition copolymerization of tricyclononenes SiMe₃- and Si(OEt)₃-groups.

The capability to cross-link the obtained polymers in the presence of Sn-catalyst was shown. The cross-linking was performed by the hydrolysis of Si(OEt)₃-groups followed by the formation of interchain siloxane bridges. Depending on the initial polymer molecular weight, insoluble polymer was formed or an increase of molecular weight was observed as a result of cross-linking. The degree of cross-linking proved to depend on both the amount of catalyst and the copolymer composition. This gives two independent ways to control the cross-linking. The cross-linking of Si-containing polynorbornenes could be applied for their modification: the cross-linked polymers are more resistant to organic solvents and vapors and possess better film-forming properties.

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This work was done as part of TIPS RAS (No. 79) State Plan (theme No. 3).

P-5

Silicone aerogels with tunable mechanical properties obtained via a hydrosilylation approach in supercritical CO₂

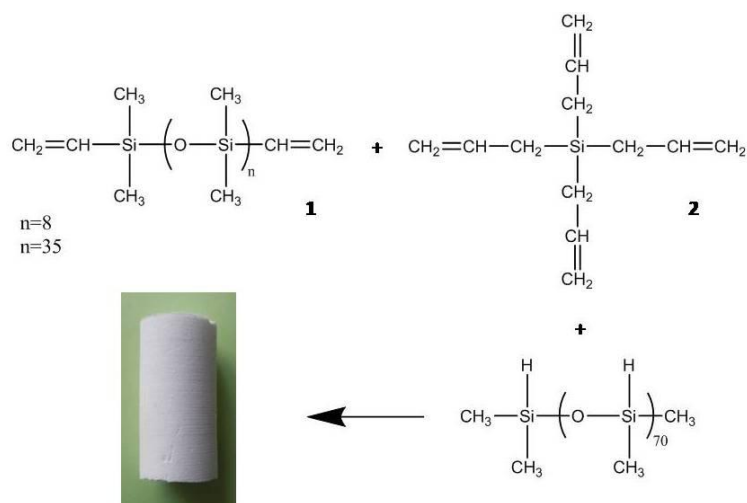
Igor V. Elmanovich^{a,b}, Tatyana A. Pryakhina^b, Dmitry A. Migulin^b, Marat O. Gallyamov^{a,b},
Aziz M. Muzafarov^b

^aM.V. Lomonosov Moscow State University, Faculty of Physics

^bA.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences

E-mail: elmanovich@polly.phys.msu.ru

This study explores a hydrosilylation approach to monolithic silicone aerogels synthesis directly in supercritical CO₂[1]. The as-formed aerogels show substantial improvement in mechanical stability as compared to pure inorganic silica-aerogels and can withstand axial deformation of about 75%. Aerogels formed in this one-pot one-step process have a low density of 0.1–0.17 g/cm³, a superhydrophobic surface with water contact angles up to 150° and a thermal conductivity of about 0.05 Wm⁻¹K⁻¹ [2].



Scheme 1. Reaction scheme of aerosilicagel synthesis via hydrosilylation in sc CO₂

Further, it is shown that using a three-component system consisting of a divinyl siloxane, tetraallylsilane and a polyhydrid siloxane (Scheme 1) it is possible to obtain aerogels with tunable flexibility and Young's moduli. By varying the **1:2** ratio, one can obtain monolithic aerogels with Young's moduli from 40 to 130 kPa. The development of such a simple tool to control mechanical properties of aerogels is an important result of the presented work that can be used in thermal insulation engineering for buildings, vehicles and aerospace applications.

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P-6

**Buthylene oxide – Siloxane – Urethane Elastomers:
Synthesis and Properties.**

Filimonova L.V., Makarova L.I., Buzin M.I., Kononova E.G., Vasil'ev V.G., Afanas'ev E.S.,
Volkov I.O., Nikiforova G.G., Papkov V.S.
A.N. Nesmeyanov Institute of Organoelement Compounds RAS.
28, Vavilov str., Moscow, 119991, Russia
E-mail: lufilia@inbox.ru

Poly (siloxane urethanes) are copolymers, as a rule, of a polyblock structure, in which special properties characteristic for each of the components are combined: mechanical strength and wear resistance of polyurethanes with thermo-, frost and hydrolytic resistance of polysiloxanes. In the work, poly (buthylene oxide siloxane urethanes) (**PBOSU**) based on oligo (buthylene oxides) and oligo (dimethyl siloxane diols) with $-\text{CH}_2\text{O}(\text{CH}_2)_2\text{OH}$ end groups have been synthesized. Synthesis of the copolymers was carried out in solution and in bulk. In both methods, prepolymers with terminal $-\text{NCO}$ groups, 2,4-toluene diisocyanate, and aromatic diamines as cross-linking agents were used.

When synthesized in solution (MEK), the reaction proceeds at room temperature, without a catalyst and a chain extender and follows by heating the film at 100 °C to complete the crosslinking process.

All PBOSUs have high deformation-strength characteristics: the tensile strength-at-break reaches 58 MPa, and the elongation at break of individual samples is 1000%. It should be noted, the strength of the films decreases with increasing MM and the mass content of the siloxane blocks. There is also a decrease in the modulus of elasticity G' due to a decrease in the concentration of hydrogen bonds. It agrees well with the data of IR spectroscopy. The glass transition temperature of PBOSUs depends on MM of oligo (siloxane diols) and the component ratio.

If the threshold temperature of the decomposition does not depend on the content of siloxane blocks for the samples obtained by one-step synthesis in solution developed by us, then for the PBOSU samples obtained without solvent the introduction of the siloxane blocks induces a slight increase in the thermal stability [1].

A preliminary assessment of the hemocompatibility of the organic polyurethane and PBOSUs of various compositions at the A.N. Bakulev National Medical Research Center for Cardiovascular Surgery has shown that these polymers are promising materials for further *in vitro* and *in vivo* studies. They might be applied in the development of artificial heart lobe valves, as well as in balloons for counterpulsation. It is important to note, the synthesis of copolymers takes place without catalysts (usually, organic tin compounds), which is essential for using materials that come in contact with blood.

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Oligoorganometalsilazanes – Precursors of High-Heat-Resistant Multiceramics.

K.N. Gerasimov^a, O. G. Ryzhova^a, P. A. Storozhenko^a, P.A. Timofeev^b, A.Ya. Yakimova^a,
A.I. Drachev^a, I.A. Timofeev^b, A.N. Polivanov^a, M.Ga. Kuznetsova^a.
^aSSC RF GNIChTEOS, Moscow, ^bJSC "Kompozit» Moscow region, Korolev city
E-mail: djiolta@mail.ru

Organosilicon oligomers and polymers of the silazane class are the starting components in the development of ceramic matrix composites (CMCs) that are serviceable in oxidizing environment under extreme thermal and mechanical stresses. An efficient method of increasing the thermal stability of CMC is the modification of pre-ceramic oligomers refractory metals with the formation of fragments Si-N-M where M = Ti, Zr, Hf, Y, Ta. The resulting oligoorganometalsilazanes (OOMSs) at pyrolysis provide the formation of ceramic matrices, including self-reinforced fibrous nanostructured generations (FNSG) of new compositions: silicon oxycarbide and silicon nitride.

The analysis of thermal stability of OOMS by TGA and DTA showed that the introduction of Si-N-M fragments leads to an increase in the inorganic residue yield (IRY) at each stage of pyrolysis. At the same time, the higher the content of M, the higher the thermal stability.

IRY after pyrolysis in argon depending on the nature of the metal of the Si-N-M fragment in the OOMS decreases in the series: Zr > Hf > Ta > Ti. When studying the thermal-oxidative stability, a pronounced dependence was not found. For all studied OOMS samples IRY after pyrolysis in air were 5-8% higher than in argon.

In the process of pyrolysis of the obtained OOMS followed by heat treatment in the argon atmosphere in the temperature range (850-1350)°C, FNSG were obtained both on the surface and in the volume of amorphous high-temperature multiceramics of the Si-N-M composition with uniform distribution of all elements. Studies of the morphology and composition of multi-ceramics by SEM and X-ray microanalysis showed that the nature of the metal has a significant effect on the type, composition, size of the FNSG and the temperature of thermal transformations of OOMS, leading to their formation. Thus, the formation of FNSG (figure 1) for titanium-containing ceramics is observed at 850°C, and for ceramics modified Zr, Hf and Ta at 1350°C. Moreover, in the latter case, nanoscale FNSGs are formed. The formation of FNSGs occurs with the participation of spherical ceramic particles containing metals that play the role of catalysts and determine the diameter of FNSG.

Modification of oligomethylhydridesilazanes (OMGS) with yttrium was carried with yttrium (yttrium (III) tris(hexamethyldisilazide)). The features of the introduction of yttrium both in OMHS and Ta-OOMS are investigated. It is shown that multi-ceramics based on yttrium-containing OMHS have high oxidation resistance.

Oligoorganometalsilazanes were studied by elemental analysis; ¹H, ²⁹Si NMR spectroscopy; IR spectroscopy; and the morphology and composition of ceramics, were investigated by SEM and X-ray diffraction microanalysis, respectively.



Fig. 1. Micrographs FNSG: a) Ti- OOMS at 850°C; b) Zr - OOMS at 1350°C ; c) Hf - OOMS at 1350°C ; d) Ta- OOMS at 1350°C .

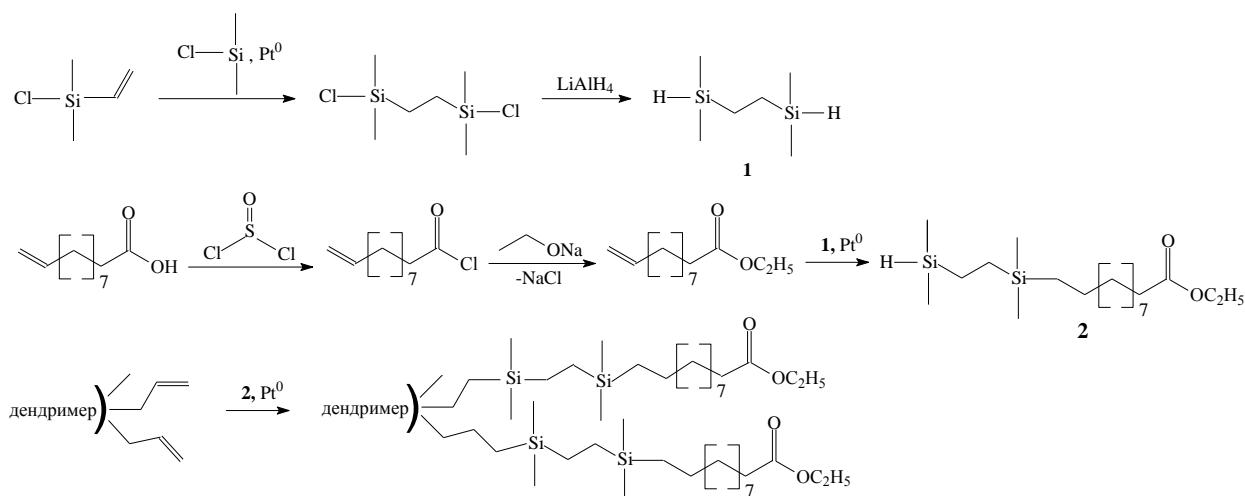
P-8

Synthesis of carbosilane dendrimers with terminal carboxyl groups

O. Gorbatshevich, A. Muzafarov

*N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences,
117393 Moscow, 70 Profsoyuznaya St., Russia*

The applications of dendrimers in science and technology conditioned by their nano-size, topologically unique structure and universal physico-chemical properties. Carbosilane dendrimers characterized by high kinetic and thermodynamic stability due to low polarity and high strength (306 kJ / mol) of Si-C bond are widely used in nanotechnology and catalysis. Carbosilane dendrimers play a special part in drug chemistry. Drugs based on them against human immunodeficiency virus (HIV-1), herpes simplex virus (HSV-2), Dengue virus, hepatitis C (HCV) and others are being tested. Nanosize globular form, functional groups on the periphery, hydrophobic or hydrophilic internal cavities, monodispersity and low toxicity determine the role of carbosilane dendrimers in pharmaceutical preparations as carriers of drugs and delivery agents to the focus of a disease. The most effective is usage of anionic carbosilane dendrimers with carboxyl, phosphate and sulfate peripheral groups (inhibitory ability to viruses above 70%). Synthesis of carbosilane dendrimers with terminal carboxyl groups is still a major problem. The report presents a new scheme for the synthesis of carbosilane dendrimers with peripheral carboxylic groups:



The known procedure was used to prepare the carbosilane dendrimer [1]. The hydrophilizing modifier was synthesized from undecenic acid, by functionalization with a hydride group. The structure of the modifier and dendrimer with carboxyl groups was studied by IR and NMR spectroscopy. Monodispersity is confirmed by gel permeation chromatography.

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P-9

Stereospecific hydrosilylation of norbornadiene-2,5 in the presence of Pd-catalyst

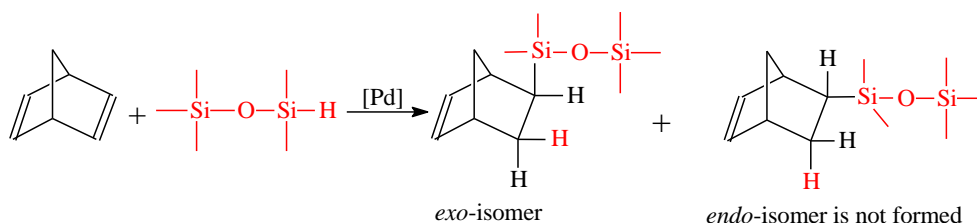
Guseva M.A.,^{a,b} Chapala P.P.,^b Bermesheva E.V.,^b Bermeshev M.V.^a

^a A.V. Topchiev Institute of Petrochemical Synthesis of RAS, 29 Leninsky prospekt, 119991 Moscow, Russia;

^b Moscow Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies), 86 Vernadskogo prospekt, 119571 Moscow, Russia,

E-mail: m.guseva@ips.ac.ru

Silicon-containing norbornenes are promising monomers for the targeted synthesis of polymer membrane materials. Recently we have shown that the presence of flexible substituents containing Si-O-Si or Si-O-C fragments in polymers provides high permeability of gaseous hydrocarbons and selectivities [1]. Especially attractive properties have been found for addition polynorbornenes. Unfortunately, addition polymerization is very sensitive to the presence of substituents in a norbornene derivative and substituted norbornenes are less reactive in polymerization than norbornene. At the same time, norbornenes obtaining by Diels-Alder reaction are the mixture of *exo*- and *endo*-isomer. Usually the reactivity of *exo*-isomer is greater than that of *endo*-one. Therefore, the use of pure *exo*-isomer for polymerization can reduce the undesirable influence of a substituent on the monomer reactivity. In this work we have developed a convenient and simple approach to the synthesis of Si-substituted norbornenes (Scheme 1). This approach gives only *exo*-isomer of a norbornene derivative. It is based on the direct hydrosilylation reaction of norbornadiene-2,5 with an appropriate silane. So it is no need to use Grignard or other metalorganic reagents for the synthesis of such kind monomers. The approach is one step method in contrast to the earlier developed three step method of Si-substituted *exo*-norbornenes synthesis [1].



Scheme 1.

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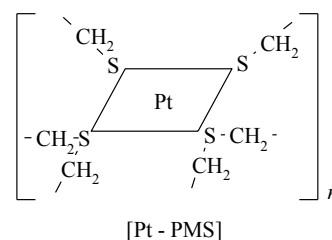
P-10

Synthesis of Epoxysiloxanes by Hydrosilylation in the Presence of Supported Pt(II) Complex

M. A. Il'ina, D. A. de Vekki and N. K. Skvortsov

St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 190013 Russia
E-mail: Ilina_Masha@list.ru

Catalytic hydrosilylation of olefins is significant reaction for the production of industrially important organosilicon materials and is dominated by the selectivity, activity and stability of hydrosilylation catalysts. Furthermore, the high and volatile price of platinum as the industrially most considerable catalytic metal is a strong motivation for the reduction of precious metal consumption, such as catalyst recycling. Supported transition metal complexes catalysts are used more and more widely because they can combine the advantages of easy catalyst recovery, characteristic for a heterogeneous catalyst, with the high activity and selectivity of homogeneous complexes. A number of supported platinum and rhodium complexes have been proved to be efficient catalysts for the hydrosilylation of olefins [1, 2], but the hydrosilylation of olefins catalyzed by sulfur containing supported complexes has received less attention. As alternative sulfur-containing catalysts, we synthesized platinum(II) complexes on a polymeric supporter - polymethylene sulfide [Pt-PMS]. Analysis of the catalytic activity was carried out in one of the important industrial reactions - hydrosilylation of allyl glycidyl ether by monomeric and oligomeric hydrosiloxanes with different amounts of terminal or internal silicon hydride groups of linear or cyclic structure.



Hydrosilylation of allyl glycidyl ether by hydrosiloxanes proceeds mainly with the formation of an antimarkovnikovsky addition product. The temperature regime of operation [Pt-PMS] is not less than 100-120°C, the kinetic curves of hydrosilylation are characterized by the presence of an induction period and have a pronounced S-shaped character. The magnitude of the induction period depends on the temperature, the concentration of platinum and the structure of hydrosiloxane. The induction period is absent when the complex is pretreated with hydrosiloxane before the addition of ether. The reactivity of hydrosiloxanes depends on the electronic characteristics of the substituents at the silicon atom and the steric factor (hydrosiloxanes with internal silicon hydride groups have a lower reactivity than with the terminal ones). During hydrosilylation of allyl glycidyl ether, [Pt-PMS] can withstand at least 10 cycles, in order to maintain a high conversion of the ether after the third cycle, it is necessary to increase the contact time of the catalyst with the reaction mixture.

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P-11

Biologically active silicone polymers

Vladislav Istratov, Tatiana Krupina, Valerii Vasnev

A.N. Nesmeyanov Institute of organoelement compounds

Vavilov Str.28, Moscow 119991, Russia

E-mail: slav@ineos.ac.ru

Silatranes are low molecular compounds known due to their unique biological properties. To date, a great number of researches concerning silatranes of various structures has been carried out, and the main parameters influencing the physiological activity of these compounds have been established. Unfortunately, at present there are practically no publications devoted to silatran-containing polymers; It seemed to us important to estimate the influence of polymer backbone structure bearing silatran groups on its biological activity. To this goal, we synthesized a number of copolymers with introduced silatran fragments. The specific content of silatran fragments in the polymer was varied by comonomers ratio used for the synthesis. The structure of copolymers was confirmed by elemental analysis, IR, NMR spectroscopy and GPC. For copolymers, the hydrophobicity of the surface of poly-dimensional films formed by polymers of different structures was estimated from the value of the contact angle of wetting. The dependence of the properties of copolymers on the amount of silatran fragments contained in them was established. By the method of radial growth of the fungal colonies, an investigation was made of the antifungal action of polymers and low molecular weight silatranes of relative structure with respect to the fungi *Verticillium dahliae* and *Aspergillus niger*. It was found that there is an effect of inhibiting the growth of fungi, especially noticeable at later stages. Depending on the molecular weight and the structure of the comonomers, the inhibition was 10-70% compared to the corresponding control.

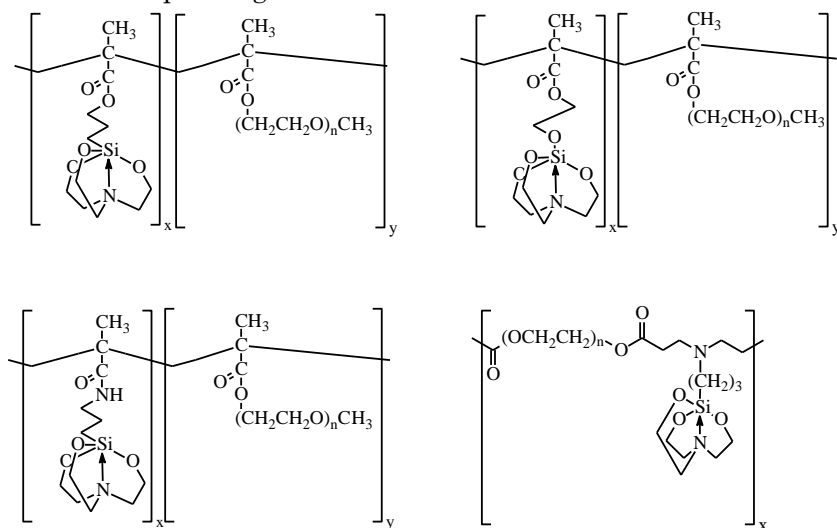


Fig. 1. Common structures of examined polymers

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P-12

New exocyclic seven- and nine-membered *o*-carboranymethyl-containing organosiloxanes. The effective method for synthesis from bis (brommagnesiummethyl)-*o*-carborane and chloro(organo)siloxanes

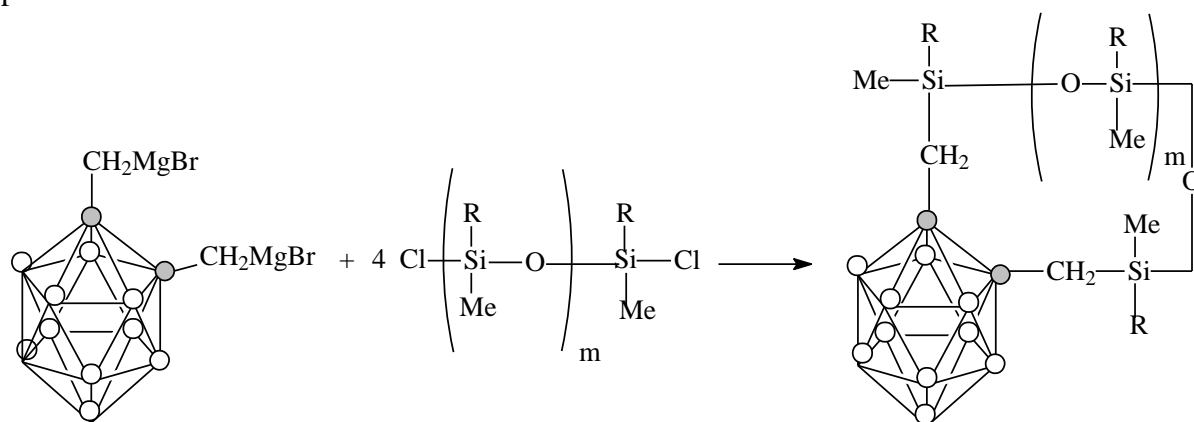
Izmaylov B.A., Vasnev V.A., Markova G.D.

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., Moscow, 119991, Russia

E-mail address: mgaly@yandex.ru

The efficient method for synthesizing of organosiloxanes from 1,2-bis (brommagnesiummethyl)-*o*-carborane with four fold molar excesses of 1,3-dichloro-tetramethyl-disiloxane and 1,7-dichloro-hexamethyl-trisiloxane has been developed. 1,2- (*o*-Carborano) -4,6-bis (dimethylsila)-5-oxa-cycloheptane (**I**) and 1,2- (*o*-carborano)-4,6,8-tris(dimethylsila)- 5,7-dioxa-cyclononane (**IX**) in 78% yields.

The use in the reaction of other chloro(organo)siloxanes with various radicals at silicon atoms made it possible to obtain 1,2- (*o*-carborano)-4,6-bis [(methyl organosila]-5-oxa-cycloheptanes (**II-VIII**) and 1,2- (*o*-carborano)-4,6,8-tris [(methyl organosila]-5,7-dioxa-cyclononanes (**IX-XVI**) with yields up to 78% and to expand the range of new promising products.



where $m = 1, n = 0$, $\text{R} = \text{M}$ (**I**), Ph (**II**), $-\text{CH}_2\text{Ph}$ (**III**), $\text{C}_4\text{H}_9\text{S}$ (**IV**), $-\text{CH}_2\text{CH}_2\text{CN}$ (**V**), $-\text{CH}_2\text{CH}_2\text{CF}_3$ (**VI**),
Vin. (**VII**), ALL (**VIII**)
 $m = 2, n = 0$, $\text{R} = \text{Me}$ (**IX**), Ph (**X**), $-\text{CH}_2\text{Ph}$ (**XI**), $\text{C}_4\text{H}_9\text{S}$ (**XIII**), $-\text{CH}_2\text{CH}_2\text{CN}$ (**XIII**),
 $-\text{CH}_2\text{CH}_2\text{CF}_3$ (**XIV**), Vin (**XV**), All (**XVI**)

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P-13

Comparison of chlorine-free approaches to the synthesis of hydride-containing siloxanes

Kalinina A.^{a, b}, Pryakhina T.^b, Elmanovich I.^{b, c}, Gallyamov M.^{b, c}, Muzafarov A.^{a, b}

^a*Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, Moscow, Russian Federation.*

^b*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russian Federation.*

^c*Faculty of Physics, M.V.Lomonosov Moscow State University, Moscow, Russian Federation.*

bychkova@ispm.ru

Polyorganosiloxanes containing hydride groups at the silicon atoms in the main chain are valuable precursors for preparation of a given structure polymers [1]. The presence of Si-H bonds in polyhydrosiloxanes determines the variety of approaches to their further modification using polymer analogous transformations: this is the hydrosilylation of various reagents with unsaturated groups, and alcoholysis in the presence of metals, and the dehydrocondensation of the Si-H groups to form of a Si-Si bond and of Si-O-Si bond in the presence of silanols. The main objective in these cases is to obtain a polyorganosiloxanes polymer matrix of a given architecture with a high and controlled content of hydride groups and a minimum content of defective units. The solution of this problem is a difficult problem due to the lability of Si-H bond. Solving this problem is a difficult problem due to the lability of the Si - H bond in both acidic and alkaline conditions, which are usually present in systems for the preparation of an organosiloxane polymer chain.

The aim of this work is to study the hydrolytic polycondensation of methyldiethoxysilane in an active medium [2] and under pressure [3], comparing the efficiencies of these approaches for the preparation of oligomethylsiloxanes with a controlled content of hydride groups. The paper will present the results of a study of the influence of various conditions on the composition of the products formed and the conversion of hydrosilyl groups. The products of hydrolytic polycondensation are distinguished and characterized by a combination of physicochemical methods of investigation (GLC, GPC, IR- and NMR spectroscopy).

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P-14

Carbosilane dendrimers with a carboranilic shell: synthesis and properties

Kapelistaya E.A.^a, Anisimov A.A.^b, Milenin S.A.^c, Zaitsev A.V.^b, Ol'shevskaya V.A.^b,
Buzin M.I.^b, Muzafarov A.M.^{b,c}

^a D. Mendeleev University of Chemical Technology of Russia

^b A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences

^c N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences

E-mail: eakapelistaya@gmail.com

Dendrimers are hyperbranched and mono-dispersed macromolecules, which emanate from a central core and are obtained by divergent, convergent or combined divergent/convergent methods. Their well-defined size, molecular weight, internal connectivity, and specific number of end groups give access to dendritic macromolecules having special properties and a variety of functions. [1]

Modification of dendrimers outer layer is a promising way to give them new properties. For example, there is a range of works, where carbosilane dendrimers with a carboranilic shell and their transformations were studied. The authors believe that these compounds are convenient, functional matrices for obtaining new molecular systems and materials.[1],[2] Nevertheless, only low generations of dendrimers were synthesized and their properties were not investigated

In this study, we have developed a new method of various carbosilane dendrimers (G0, G1, G3, G5) with boron-substituted carborane polyhedra at the periphery. In this purpose hydrothiolation of allylic groups was used. This type of carborane was chosen due to free CH groups left in its structure after conjugation with dendrimer. That is why further molecule modification became possible.

The synthesis of the target molecules, as well as data on the study of their physicochemical properties and the establishment of the structure-property relationship, will be presented in the report.

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P-15

A study of the impact of the phenylsilsesquioxane resin structure on properties of transparent addition cure compositions

A.G. Kazaeva^a, I. Yu. Ruskol^{a,b}, E. I. Alekseeva^b, A. K. Shestakova^b, A.G. Ivanov^b

^a *D. Mendeleev University of Chemical Technology of Russia, Moscow, Russia*

^b *The State Scientific Center of the Russian Federation «State Research Institute for Chemistry and Technology of Organoelement Compounds», Moscow, Russia*

E-mail: alinakazaeva@mail.ru

At the moment curing silicone compositions for light-emitting diode protection are actively competing with epoxy-based encapsulants due to better long-term behavior. The hydrosilylation reaction is preferable curing method for the light-emitting diode silicone encapsulant. One of the main components of addition cure compositions with high refractive index is phenylsilsesquioxane resin. Effect of resin's structure on physical, chemical and physical mechanical properties of transparent cross-linked compositions was investigated. Phenylsilsesquioxane resins of the formula **I** were synthesized by acidolysis of phenyltrimethoxysilane in the presence of divinyltetramethyldisiloxane [1]. Phenylsilsesquioxane resins are solid transparent substances with a refractive index of $1.54 \div 1.55$ soluble in organic solvents.

$[\text{PhSiO}_{1.5}]_a[\text{PhSiOX}]_b[\text{ViMe}_2\text{SiO}_{0.5}]$, where X = -OH and (or) -OCH₃, $a = 2 \div 5$, $b = 0 \div 1$ (**I**)

A significant number of hydroxyl groups in phenylsilsesquioxane resin leads to incompatibility with the linear oligomers of addition cure composition. The hydroxyl groups were substituted with trimethylsiloxy groups, and phenylsilsesquioxane resins of the formula **II** were obtained.

$[\text{PhSiO}_{1.5}]_a[\text{PhSiO}(\text{OMe})]_b[\text{Me}_3\text{SiO}_{0.5}]_c[\text{ViMe}_2\text{SiO}_{0.5}]$, where $a = 2 \div 5$, $b = 0 \div 1$, $c = 0 \div 1$ (**II**)

The structure of synthesized phenylsilsesquioxane resins is confirmed by IR and NMR spectroscopy, refractometry and chemical analysis.

The increase in the content of phenylsilsesquioxane units in the resin results in an increase of the refractive index and the glass transition temperature of both the resin and addition cure composition. Products of partial acidolysis with residual methoxy groups have lower glass transition temperature and refractive index than resins with the fully substituted groups.

Phenylsilsesquioxane resins of the formula **II** have lower refractive index and glass transition temperature than the resins of formula **I**, with the same content of phenylsilsesquioxane units.

When the coefficient a in formulas **I** and **II** increases from 2 to 5, Shore A hardness of the cross-linked composite based on phenylsilsesquioxane resins decreases from 50 to 20, the tensile strength decreases from 2 to 1 MPa, and the elongation at break increases from 80 to 160%.

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P-16

Oligoorganosilsesquisilazanes – Preceramic Oligomers of High-Heat-Resistant Ceramic Fibers.

E.N. Khaustov^a, O.G. Ryzhova^a, P.A. Storozhenko^a, P.A. Timofeev^b, A.N. Polivanov^a,
I.A. Timofeev^b, A.I. Drachev^a, M.G. Kuznetsova^a.

^a *The Stare Scientific Center of the Russian Federation State Research Institute for Chemistry and Technology of Organoelement Compounds, Moscow*

^b *JSC "Kompozit» Moscow region, Korolev city*

E-mail: djiolta@mail.ru

Oligoorganosilsesquisilazanes are of great interest as unique pre-ceramic fiber-forming oligomers.

The fragmentary composition of the main unit of oligoorganosilsesquisilazane (OOSS) modified with difunctional structural fragments, without terminal fragments, can be presented as follows:

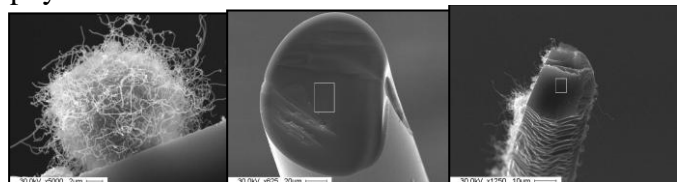


Physical-chemical properties of the OOSS was investigated in regard of the nature of the substituents at silicon, the composition and functionality of the structural fragments. The investigations were performed by NMR spectroscopy, IR spectroscopy, TGA, DTA, MMD, viscometry. The microstructure of the surface of the ceramic fibers, their composition and the thermal stability were studied by SEM and TGA methods. The obtained OOSS are characterized by high thermal and thermo-oxidative stability. The yield of the inorganic residue in air and in argon is 80 wt % and 60 wt % respectively. Molecular mass is in the range of 1400-2000. Dynamic viscosity is in the range of 5000-10000 mPa*s.

The fibers were melt spun with the following curing and pyrolysis. It is shown that during the curing process at temperatures above 180 °C condensation processes occur with the participation of terminal fragments, accompanied by an increase in the molecular weight. In the IR spectra of OOSS, a decrease in the absorption band with a frequency of 1170 cm⁻¹ attributed to the Si-NH₂ bond of the terminal fragments is observed.

The peculiarity of the pyrolysis of OOSS is to obtain depending on the composition of OOSS ceramic fibers, on the surface of which (sample 2) is the formation of nanotubes of SiO_x composition at a temperature of 850 °C in a nitrogen atmosphere. Micrographs and compositions of ceramic fibers are shown in Figure 1

On the basis of the obtained data, the prospects of using OOSS as pre-ceramic oligomers for obtaining high-heat-resistant ceramic fibers are considered, the use of such fibers in the development of composite materials provides thermal stabilization and enhancement of physical and mechanical characteristics.



A-SiC_{1,1} O_{0,6} B-SiC_{0,9} O_{1,1} C- SiO₂

Fig. 1. Microphotograph and composition of the produced fibers: A- volume (sample 1); B - the composition and morphology of the volume of fibers with the surface modified nanotubes (sample 2); C- morphology and composition of the SiO_x nanotubes.

P-17

SYNTHESIS OF SILICA NANOGELS WITH AN AMPHIPHILIC SURFACE LAYER

Kholodkov D. N.², Kazakova V. V.¹, Muzafarov A. M.^{1,2}

¹N. S. Enicolopov Institute of synthetic polymeric materials RAS, Moscow, Russia

²A. N. Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia

dima_holodkov@mail.ru

Hybrid nanoparticles, nucleus of which consists of inorganic or metallic particles and shell consisting of organic polymers, has unique properties – their ability to recycle and compatibility with environment [1]. Organic shells that consist of two different homopolymer chains, which is grafted chaotically or alternatively, is studied intensively in last years, since their unique phase behavior and potential application in encapsulation, «smart-materials» and etc. At the present time investigation of colloidal system, that has self-organized nanometer scale particles on a phase boundary, is under great attention. This material was named «colloidosomes» and has an irreversible self-assembly, which is the reason of its low extension in practical application. There are also difficulties in colloidosome synthesis and regulation of their properties switching from micro- to nanoscale-particles.

This work shows a synthesis strategy of a silica nanogels with an amphiphilic surface layer.

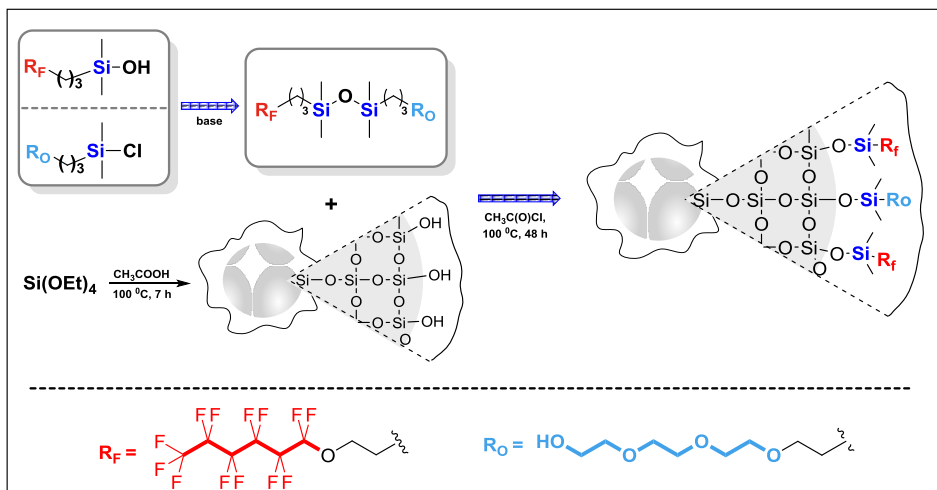


Fig. 1 – General scheme of synthesis

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P-18

Radiation synthesis, properties and application of tetrafluoroethylene telomers with silane end groups.

G. A. Kichigina, P. P. Kushch, and D. P. Kiryukhin

*Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow oblast, 142432
Russia*

E-mail: kga@icp.ac.ru

Fluorinated organosilicon compounds are widely used to create hydrophobic and superhydrophobic coatings on various materials. One of the ways to obtain compounds of this type is the telomerization of tetrafluoroethylene (TFE) in silanes under the influence of UV-radiation. The compounds with the general formula $R(C_2F_4)_nX$ are formed. The radiation-initiated telomerization of TFE was observed in chemically different solvents. By varying the synthesis parameters (telogen, TFE concentration, radiation dose), telomers with a chain length of a few units to hundreds of units can be obtained.

In this work the kinetics of radiation-initiated telomerization of tetrafluoroethylene in dichlorodimethylsilane (DCDMS) and chlorotrimethylsilane (CTMS) have been studied and telomers with the general formula $R(TFE)_nX$, where the most likely end groups R and X are Cl, $(CH_3)_2Cl_2Si$, and $(CH_3)_3ClSi$ are obtained. The telomerization proceeds much more efficiently in DCDMS, it can be associated with its reactivity. The telomers synthesized in these telogens are translucent colloidal solutions. Their viscosity is determined by the initial concentration of TFE. The molecular structure of TFE telomers in chlorosilanes was studied by IR spectroscopy. Examination of the spectra gives information not only about the structure of the telomers, but also allows conclusions about the chain length of the product. The absorption bands of the stretching vibrations of the C-F (1208 and 1152 cm^{-1}) tetrafluoroethylene chains, as well as the absorption bands of the methyl end groups (700 - 1300 and 3000 cm^{-1}) of silanes and the stretching vibrations of C-Cl bonds ($\sim 810\text{ cm}^{-1}$). The telomere samples obtained in chlorosilanes with different initial TFE concentrations were subjected to elemental analysis for chlorine. The mean length of the telomere chain is determined by the content of chlorine, which depends on the initial concentration of TFE. The length of the chain of telomers obtained in DCDMS is ~ 35 and 70 , and in CTMS ~ 20 and 30 units of TFE at TFE concentrations of 0.2 and 1.0 mol/l .

Previously, it was shown that solutions of telomeres of TFE are applicable for the production of fluorine-containing hydrophobic material (lacquer) based on aluminoborosilicate fiberglass [1]. TFE telomeres obtained in CTMS having a chain length ($n \sim 20$ TFE units) were used to modify the glass fabric. The application of solutions of telomeres was carried out by the method of multiple impregnation of the tissue. As a result, a hydrophobic glass-polymer material containing 3-5% fluoropolymer was obtained, in contrast to industrial samples of lacquers, where the amount of fluoropolymer introduced reaches 60-70%. The measured wetting angles are $105^\circ - 115^\circ$, which indicates the hydrophobicity of the resulting material.

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P-19

**Synthesis and structure of binuclear complexes of transition metals
based on bis- β -diketones**

Kim E.E.^{a,b}, Kononevich Yu.N.^b, Korlyukov A.A.^b, Volodin A.D.^b, Muzafarov A.M.^b

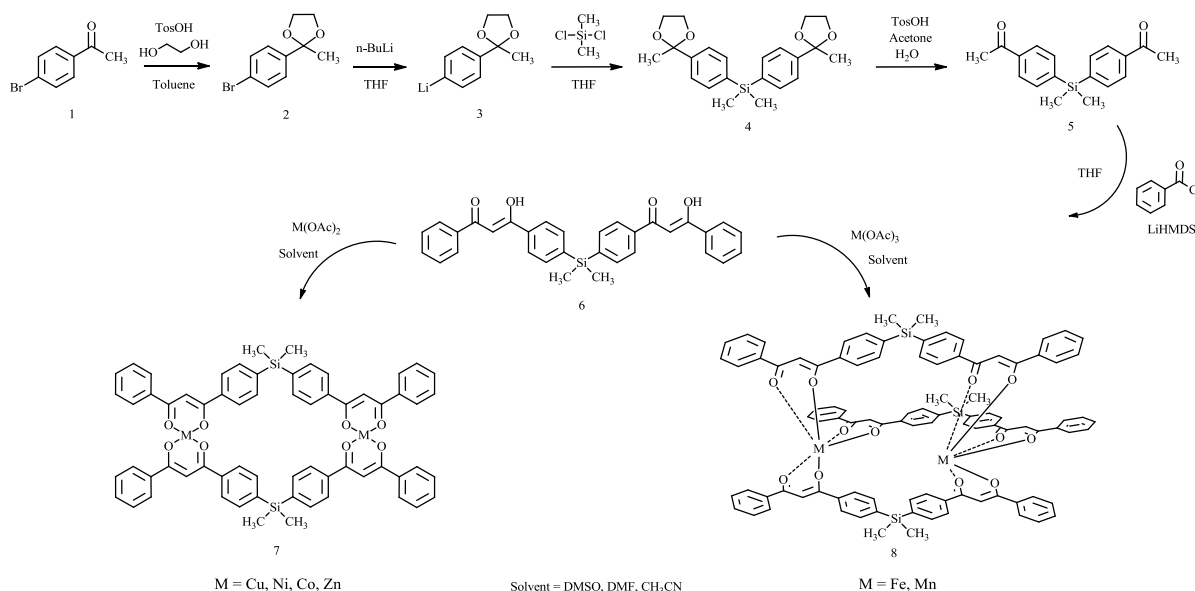
^a D.I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation

^b A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, 119991 Moscow, Russian Federation

E-mail: ela-kim@mail.ru

The design and synthesis of complicated multidentate ligands for the creation of polynuclear complexes with predetermined functions or structures occupy an increasingly prominent place in coordination chemistry. This approach has become common practice in such wide contexts as bioinorganic modelling, photochemistry, or molecular devices. Various ligands with distinct geometries and coordination modes have been designed and the bis- β -diketones have been proven to be qualified to construct the new supramolecular architectures. The opportunity to control the shape, flexibility and functionality allows bis- β -diketones to be excellent building units for the creation of cyclic structures as well as multiple-stranded helicates, MOF's, linear molecular platforms and metallamacrocycles. Metallo-supramolecules have generated a great deal of interest due to their various interesting properties, among which the catalytic, magnetic and optical activity must be mentioned.

In this work, new bis- β -diketone ligands based on organosilicon derivatives of dibenzoylmethane were synthesized and their interaction with transition metal ions was studied (Scheme 1).



Scheme 1. Synthesis of bis- β -diketone ligand and complex compounds.

The structure of the obtained compounds was confirmed by ¹H, ¹³C, ²⁹Si NMR spectroscopy, IR spectroscopy, mass spectrometry (ESI), elemental analysis and X-ray diffraction analysis.

P-20

Curing peculiarities of polycarbosilane-based polymeric fibers

A.P. Koroley, D.V. Zhigalov, G.I. Shcherbakova, M.Kh. Blokhina, A.A.Vorob'ev
*Stare Scientific Center of the Russian Federation "State Research Institute for Chemistry and
Technology of Organoelement Compounds" (SSC RF "GNIChTEOS")*
E-mail: alex193@list.ru

It is known that coreless silicon carbide fibers are produced in the result of curing (cross-linking) and carbidization of polymeric fibers based on polycarbosilane. We have studied molding and thermal treatment conditions (curing and carbidization) of polymeric fibers based on polycarbosilane..

The polymeric fibers were molded at a standard single-screw extruder (L/D=25) from polymer melt through a spinneret, continuous thin filament was formed therewith.

The spun fiber prepared from a single polycarbosilane batch was cured at different temperatures in oxidizing environment.

Temperature range 175 ÷ 300°C was selected for oxidizing. An increase of fiber weight versus oxidizing temperature is shown in Fig.1

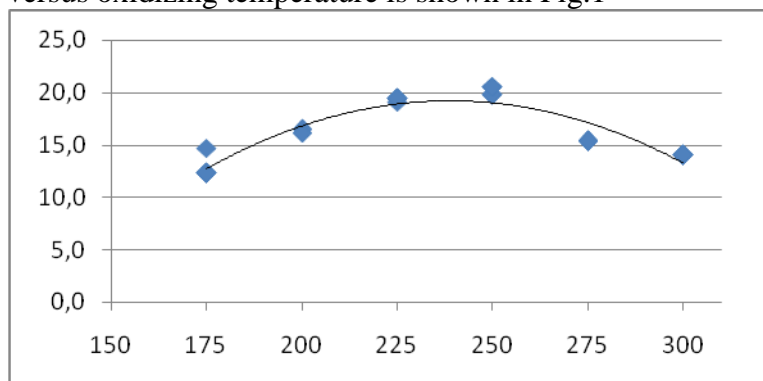


Fig. 1. An increase of sample weight (wt %) depending on oxidizing temperature.

Fiber curing (its shift to the infusible and insoluble state) is one of the most important and complicated stages of silicon carbide fiber production. In the process of oxidation curing polymer molecules cross-linking occurs due to Si-H and Si-CH₃ groups oxidation and new Si-O-Si and Si-O-C bonds forming, and their weight increases by 8 – 20 wt % therewith.

Then carbidization was carried out at 1000-1400°C under an inert atmosphere which resulted in coreless silicon carbide fibers analyzed by SEM with EDS.

According to the results of SEM with EDS correlation dependence between fiber weight increase and oxygen amount in fiber structure was found, moreover optimum conditions of polycarbosilane-based fiber curing were determined.

P-22

Synthesis of Carbofluoro organochlorosilanes

Lakhtin V.G.^a, Fedotova T.I.^a, Sokol'skaya I.B.^a, Efimenko D.A.^a,

Ushakov N.V.^b, Bykovchenko V.G.^a, Storozhenko P.A.^a

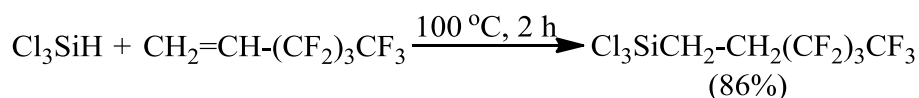
^a State Scientific Center of the Russian Federation "State Research Institute for Chemistry and Technology of Organoelement Compounds" (SSC RF "GNIChTEOS")

E-mail: vlakhtin@rambler.ru

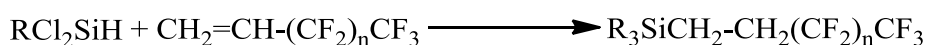
^bA.V.Topchiev Institute of Petrochemical Synthesis of RAS, Moscow E-mail: ushakov@ips.ac.ru

C-fluorinated organosilanes are valuable in terms of application monomers, which can be used for water-repellency treatment of various materials. We have studied the hydrosilylation reactions of fluoro-olefins of linear structure 6,6,6,5,5,4,4,3,3-nonafluorohexene-1 (C₆-F), 8,8,8,7,7,6,6,5,5,4,4,3,3-tridecafluorooctene -1 (C₈-F) and 10,10,10,9,9,8,8,7,7,6,6,5,5,4,4,3,3-heptadecafluorodecene -1 (C₁₀-F) by various hydrosilanes in the presence of Speier catalyst.

Hydrosilylation of C₆-F by trichlorosilane was performed in an autoclave, because under standard conditions this reaction does not proceed, apparently due to the low boiling point of the initial olefin (T_b= 60°C):



Starting with C₈-F fluoro-olefin, it is possible to carry out the process under standard conditions:



where n = 5,7; R = Cl, Me, Et, Ph

Table 1 presents the obtained results on C₈-F and C₁₀-F hydrosilylation under optimum conditions.

Table 1. C₈-F and C₁₀-F hydrosilylation by various hydrosilanes under optimum conditions (hydrosilane: fluoro-olefin ratio = 1.2 : 1)

No	Initial reagents	Temp. °C	Reaction time, h	Desired products	Yield of the desired product, % theor.
1	Cl ₃ SiH + C ₈ -F	80-90	4	Cl ₃ SiCH ₂ CH ₂ (CF ₂) ₅ CF ₃	74.6
2	Cl ₃ SiH + C ₁₀ -F	100	1.5	Cl ₃ SiCH ₂ CH ₂ (CF ₂) ₇ CF ₃	78,5
3	MeCl ₂ SiH + C ₁₀ -F	100	1.5	MeCl ₂ SiCH ₂ CH ₂ (CF ₂) ₇ CF ₃	91.4
4	EtCl ₂ SiH + C ₁₀ -F	100	1	EtCl ₂ SiCH ₂ CH ₂ (CF ₂) ₇ CF ₃	90.5
5	PhCl ₂ SiH + C ₁₀ -F	80	1	PhCl ₂ SiCH ₂ CH ₂ (CF ₂) ₇ CF ₃	88.0
6	PhCl ₂ SiH + C ₁₀ -F	20-25	1	PhCl ₂ SiCH ₂ CH ₂ (CF ₂) ₇ CF ₃	29.3

The table shows that organodichlorosilanes are more reactive in such reactions. In all cases a minimum temperature of ~80°C is required to ensure complete reaction. Phenyl dichlorosilane is an exception; it reacts with C₁₀-F at room temperature already, giving the notable yield of the desired product (Table 1, No 6). In all the reactions studied, the addition of hydrosilane to fluoro-olefin proceeded according to Farmer's rule. All synthesized compounds were identified by ¹H NMR spectroscopy and chromatography-mass spectrometry.

P-23

**New silicon-containing ionic liquid-based materials
for gas separation and electrochemical applications**

E.I. Lozinskaya^a, A.S. Shaplov^{a,b}, D.Yu. Antonov^a, M.I. Buzin^a, I.M. Marrucho^c,
Y.S. Vygodskii^a

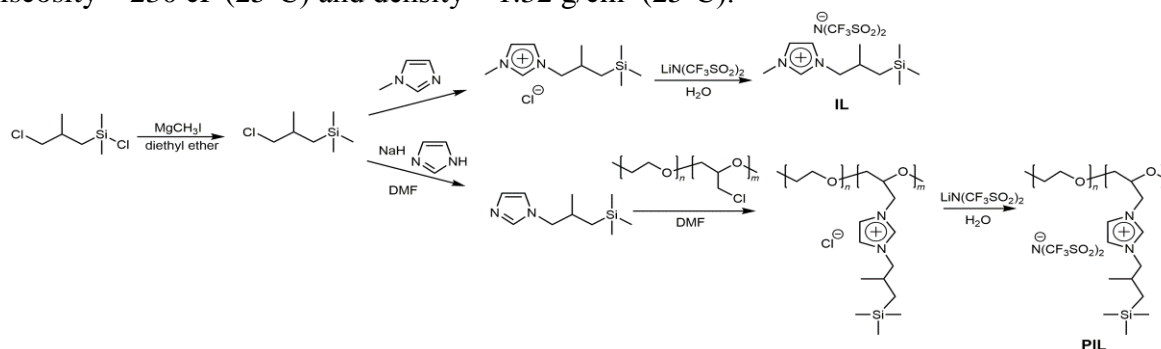
^a A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS), Vavilov St., 28, 119991, Moscow, Russia.

^b Luxembourg Institute of Science and Technology (LIST), 5 Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg

^c Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal.

E-mail: helloz@ineos.ac.ru

By present moment ionic liquids (ILs) and their polymeric analogues (PILs) demonstrate great potential for practical use as the materials for capacitors, batteries and gas separation membranes [1-3]. Their physicochemical properties can be tailored to satisfy specific practical tasks by careful selection of anions, cations and functional groups. For instance, the introduction of an organosilicon substituent instead of an aliphatic one in the cation can bring unique physical characteristics, namely, low glass transition temperature and melting point, high heat capacity and hydrophobicity. The first part of this work is devoted to the synthesis of new filler for supported ionic liquid membranes for gas separation (SILM). It was shown previously [4] that SILMs containing siloxane functionalized imidazolium ILs exhibit higher gas permeability in comparison with membranes based on ILs having alkyl side chains. Thus, the synthetic route for the preparation of novel IL with silyl-functionalized imidazolium cation (1-methyl-3-trimethylsilylisobutylimidazolium bis(trifluoromethylsulfonyl)imide) has been developed. The salt represents yellowish liquid with dynamic viscosity – 230 cP (25°C) and density – 1.32 g/cm³ (25°C).



The 2nd direction of the research is dedicated to the synthesis of Si-containing cationic polyelectrolyte by the modification of a neutral poly(epichlorohydrin-co-ethylene oxide). The flexible nature of oligo(ethylene oxide) chain, high degree of charge delocalization in bis(trifluoromethylsulfonyl)imide-anion and bulky Si-substituent are expected to enhance the mobility of ions and the ionic conductivity of PIL, respectively.

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P-24

SYNTHESIS OF TITANOSILOXANES CONTAINING FUNCTIONAL ALKOXY GROUPS

Polshchikova N.V.^{a*}, Meshkov I.B.^b, Tokazova R.U.^a, Buzin M.I.^a, Muzafarov A.M.^a

^a *FGBUN Institute of Organoelement Compounds (INEOS RAS), Moscow, Russia*

^b *FGBUN Institute of Synthetic Polymeric Materials (ISPM), Moscow, Russia*

e-mail: cherkun4ik@gmail.com

Titanosiloxanes, representatives of metallasiloxanes, due to their unique properties, are widely used as protective coatings possess high thermostability and mechanical strength, electro - and moisture-insulating properties; as catalysts for condensation of carbamide -, phenol-formaldehyde resins, epoxidation of alkenes, agents of "cold vulcanization" of siloxane elastomers [1]. Of particular interest are functional titanosiloxanes forming hybrid metal-siloxane structures during the curing, characterized by high thermostability of metal-oxide framework and elastic organosiloxane fragments evenly distributed in the oxide matrix [2, 3]. Such systems can be used as multipurpose thermostable binding agents.

In the present work was carried out the synthesis of some monomeric and oligomeric functional titanosiloxanes, by exchange interaction silanolate precursors of different type chlor(triisopropoxide)titanium (Fig. 1)

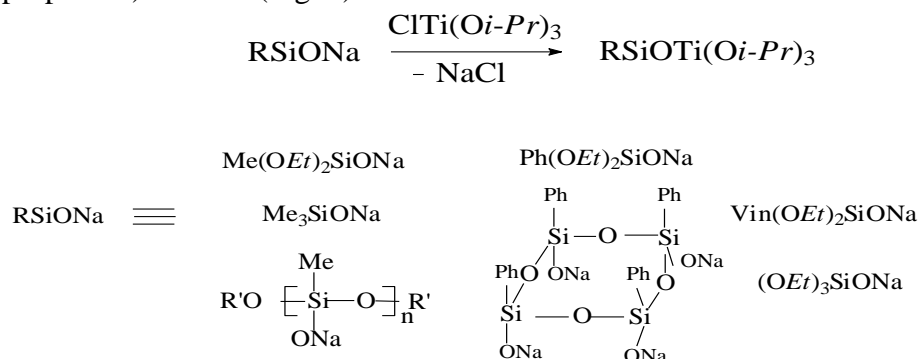


Fig.1 Scheme of synthesis of functional titanosiloxanes

This method made it possible to obtain alkoxy-titanosiloxanes of various architectures with a high yield (85-97%) under mild conditions. All compounds are characterized by ¹H-NMR spectroscopy and elemental analysis.

The resulting titanosiloxanes were applied from the solution to a glass surface and cured under various temperature conditions (25°C, 200°C and 600 °C) in the air. In all cases powders were obtained, which were investigated by elemental analysis and TGA.

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P-25

Synthesis of Polydimethylsiloxanes with Hydroxyl Groups Distributed on the Chain

Polyakov G.V.^a, Shchegolikhina O.I.^b, Kalinina A.A.^a, Muzafarov A.M.^{a,b}

^a *Enikolopov Institute of Synthetic Polymeric Materials of Russian Academy of Sciences (ISPM RAS)*

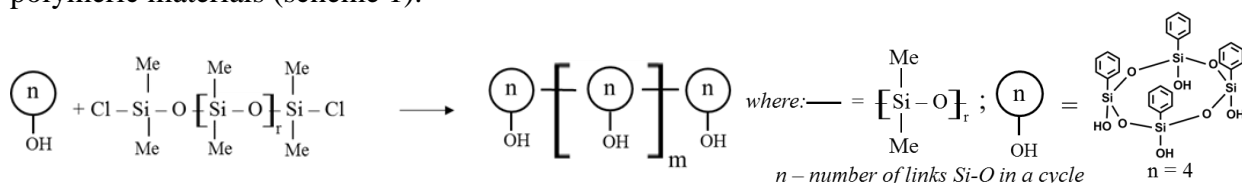
^b *A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS)*

E-mail: glebpolyakov93@yandex.ru

Control of the polymer structure at the stage of synthesis is one of the main goals of modern macromolecular chemistry. The choice of the synthesis method, precursors and reaction conditions is achieved by controlling the location and strength of intermolecular interactions in the supramolecular architecture, which makes it possible to achieve the required properties of the final polymeric materials. Among intermolecular interactions, hydrogen bonds are a unique tool with a wide range of interaction forces, which makes it possible to vary the properties of the material through self-organization processes.

In this respect, organocyclosiloxane polyols are unique model compounds and can serve as building blocks for the targeted molecular design of organosilicon polymers, namely polyorganosilsesquioxanes, with specified properties [1].

The aim of this work is to investigate the reaction of stereoregular oligophenylcyclosiloxane polyols with α, ω - dichloropolydimethylsiloxane and the properties of the resulting polymeric materials (scheme 1).



Scheme 1

The report will present data on the synthesis of new polydimethylsiloxanes with hydroxyl groups distributed on the chain based on the heterofunctional polycondensation reaction of *cis*-tetraphenylcyclotetrasiloxantetrol with α, ω - dichloropolydimethylsiloxane.

The structure of new compounds synthesized is confirmed by physicochemical methods of analysis: NMR, IR spectroscopy and GPC.

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P-26

New organosilicon derivatives of sydnones.

Sazonova N.V.^a, Trankina E.S.^b, Frolova N.G.^b, Cherepanov I.A.^b.

^aD.Mendeleev University of Chemical Technology of Russia

Russia, 125047, Moscow, Miusskaya Sc.9

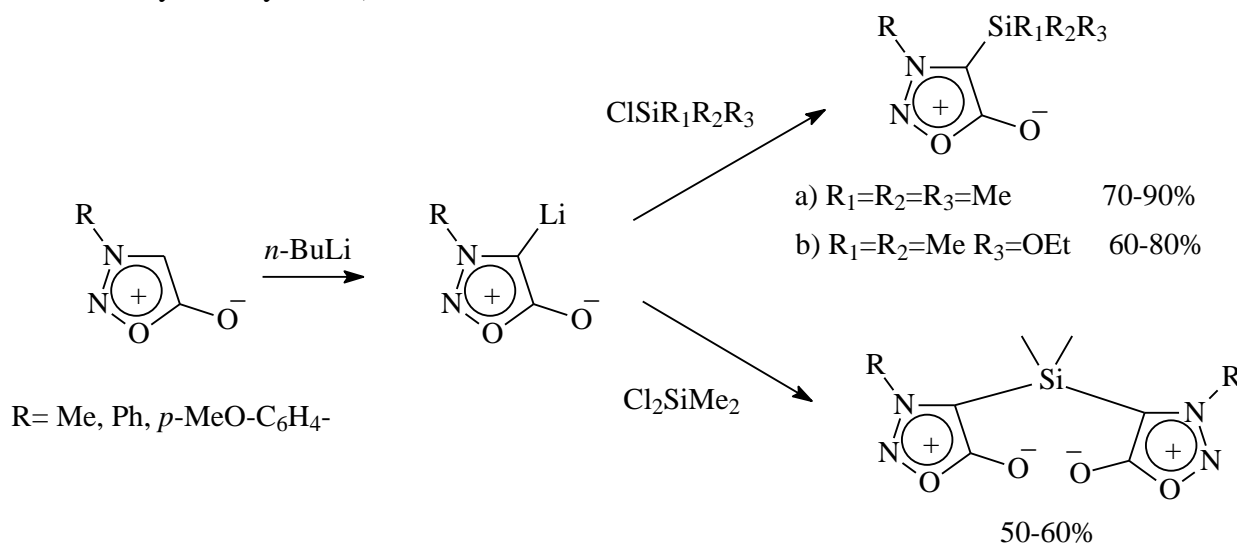
^bA.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences

Russia, 119991, GSP-1, Moscow, V-334, Vavilova St. 28, INEOS

E-mail: trankina@ineos.ac.ru

Sydnones are representatives of an important class of mesoionic heterocyclic compounds. They possess a unique structure and unusual physical and chemical properties (e. g. high dipole moment, unusual electronic structure, high extinction in UV range, etc.). At present, only a few silicone derivatives of sydnones are known [1,2]. Synthesis of new organosilicon compounds, containing of mesoionic heterocyclic fragments in its structure allow to use them for creation of new organosilicon materials with improved physico-mechanic properties.

We have been investigate the reaction of 4-lithium derivatives of sydnones with the various mono- and difunctionalmethylsilanes (chlorotrimethylsilane, dichlorodimethylsilane, chloroethoxydimethylsilane) Scheme 1.



Scheme 1

The structure of the obtained compounds is confirmed by NMR-spectroscopy (¹H, ¹³C, ²⁹Si) and X-ray.

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P-27

Aerobic oxidation of p-tolylsiloxanes: synthesis of p-carboxyphenylsiloxanes

K.P. Silaeva^{a,b}, I.K. Goncharova^b, A.V. Arzumanyan^b, A.M. Muzafarov^{b,c}

^aD.Mendeleev University of Chemical Technology of Russia, Moscow, Russia

^bNesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia

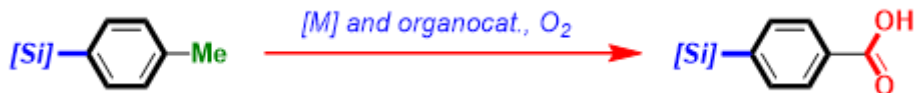
^cEnikolopov Institute of Synthetic Polymeric Materials, Moscow, Russia

E-mail: ksusha_silaeva@mail.ru

Siloxanes and materials, which based on them, have different valuable properties: hydrophobicity, heat and frost resistance, biocompatibility. However, low mechanical strength and poor compatibility with organic polymers are their main disadvantages. There is a way to improve mechanical properties of siloxane materials, which bases on an introduction of "polar" groups (e.g. $-C(O)OH$, $-C(O)NH_2$, $-OH$, $-NH_2$) into an organic substituents. These groups will lead to an increase in intermolecular interaction and thus increasing the strength of material. So high strength and valuable properties of siloxane materials can expand the sphere of their application.

The common ways to the synthesis of organosilicon compounds are not functional-group tolerant and cannot provide monomers with "polar" organic substituents. Also the post-modification functionalization is a pretty difficult issue. The most of present in organic chemistry methods requires destructive for organosilicon substrates conditions: usage of acids and bases, oxidants and reductants, protonic solvents. So these approaches usually lead to complex mixtures of side products.

One of the most attractive methods for synthesizing organosilicon compounds containing "polar" groups involves the oxidation of *p*-tolylsilyl derivatives to the corresponding *p*-carboxyphenylsilyl derivatives [1]. In turn, the methods of aerobic oxidation of organic and organometallic compounds are the most rapidly developing direction in modern chemistry [2]. A special place among the processes of aerobic oxidation is occupied by methods in which the combination of [M] and organocatalyst is used as the catalytic system. Such systems allow selective oxidation of C-H- and Si-H- bonds under mild reaction conditions [3]. Thus, a method for the synthesis of *p*-carboxyphenylsiloxanes based on aerobic [M]/organocat. – catalyzed oxidation of *p*-tolylsilylsiloxanes has been proposed (scheme 1).



Scheme 1.

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P-28

MQ-resin with (β -oxyethoxymethyl)dimethylsiloxane groups.

Sergienko N.V., Strelkova T.V., Boldyrev K.L., Makarova L.I., Muzafarov A.M.

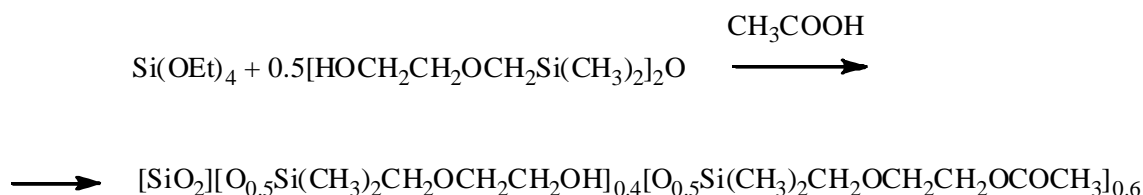
*A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences,
Russia, 119991, GSP-1, Moscow, V-334, Vavilova St. 28, INEOS*

E-mail: natotenija@rambler.ru

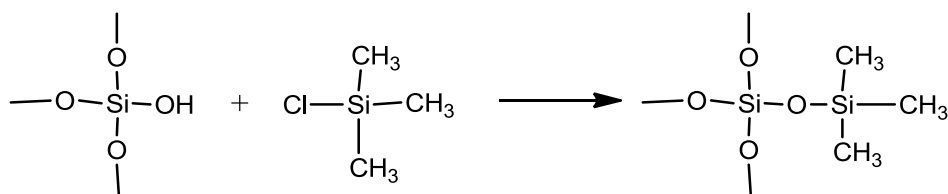
MQ-resin with hydroxyl groups in the organic radical are of interest as potential precursors for producing organic-inorganic polyurethanes.

A method of synthesizing such compounds by condensation of the products of hydrolysis of tetraethoxysilane with triethylsilylpropyl ether of triethylene glycol was described [1].

In the present work, the possibility of obtaining MQ-resin with hydroxyl groups in an organic radical by the interaction of bis-(β -oxyethoxymethyl)tetramethyldisiloxane with tetraethoxysilane in an active medium has been studied. It was found that up to 60% of the alcohol groups during the reaction are acetylated



A quantitative evaluation of the residual silanol groups was carried out, as well as their blocking according to the following schem



Methanolysis of these oligomers leads to the formation of MQ-resin with (β -oxyethoxymethyl)dimethylsiloxane groups.

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P-29

Polycondensation of methacryloxypropyltriethoxysilane under active medium conditions

Shikhovtseva I. S.^a, Kalinina A. A.^{b,c}, Demchenko N. V.^b, Muzafarov A. M.^b

^a *Moscow Technological University (MIREA), Moscow, Russia;*

^b *N.S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences, Moscow, Russia;*

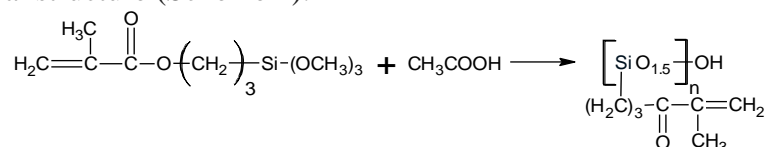
^c *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia*

vershininai@mail.ru

At present, the production of functional silicone polymers of a given architecture remains relevant. Particular attention is paid to the functional polyhedric force sesquioxanes because of the wide range of possibilities for their application. Synthesis of such structures is complicated and characterized by a long duration of the process and low selectivity, and as a consequence, the defectiveness of the synthesized structures [1].

One of the promising methods for the synthesis of siloxanes of various structures, characterized by a high level of control over the course of the process and the composition of the products formed, is the polycondensation of alkoxy silanes in the active medium [2][3]. Earlier, the prospects of using this method for the synthesis of silsesquioxanes of a polycyclic structure, so-called nano-gels similar in composition to polyhedral silsesquioxanes, but representing a rigid chaotically looped macromolecule, were previously shown.

The aim of this work is to investigate the polycondensation of methacryloxypropyltriethoxysilane in excess acetic acid and to search for conditions that allow the preparation of methacryloxy-containing silsesquioxanes of a branched, nano-gel or polyhedral structure (Scheme 1).



Scheme 1.

The report will assess the influence and order of taking the monomer, the temperature of the process, the rate of formation of water on the composition and structure of the polymethacryloxypropyl silsesquioxanes formed, the identification of the structures being carried out by gel permeation chromatography, ¹H NMR spectroscopy, and IR spectroscopy.

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P-30

**Amphiphilic "Janus"- structures based on stereoregular
cyclotetrasiloxanes: synthesis and properties.**

Smyshlyayev A.I.^{a,b}, Vysochinskaya Yu. S.^{b,c}, Anisimov A.A.^b, Shchegolikhina O.I.^b,
Muzafarov A.M.^{b,c}

^a *Moscow Technological University, Lomonosov Moscow State University of Fine Chemical Technologies, Moscow, Russia*

^b *A. N. Nesmeyanov Institute of Organoelement compounds of RAS, Moscow, Russia.*

^c *N. S. Enkolopov Institute of Synthetic Polymeric Materials of RAS, Moscow, Russia.*

E-mail: andrew.smyshlyayev@gmail.com

Supramolecular systems are of great interest for modern chemistry. Since these objects allow us to consider a common position all kinds of molecular associates, from the smallest possible (dimer) to the largest (organized phases). Recent advances in this field are related with the research of the processes of self-assembly and self-organization. As such systems are amphiphilic compounds, which contain two types of groups, which, depending on external conditions, may correspond to a certain self-organization. However, their flaw is the non-availability of a strictly defined geometry of the macromolecule.

Amphiphilic "Janus" structures with a well-defined architecture largely attracted our attention at creating nanostructured systems with a variety of shapes and a unique number of properties. As a feature of the geometry of the core determines the unique possibility to self-organize. In this work, as precursors for the preparation of new "Janus"-structures were chosen such polyfunctional compounds as stereoregular organosilsesquioxane synthesized with high yield. Consequently, we synthesized new "Janus" structures based on *cis*-tetra[(dimethylsiloxy) phenyl]cyclotetrasiloxane and *cis*-tetra[(dimethylsiloxy) vinyl]cyclotetrasiloxane[1] with various hydrophilic fragments.

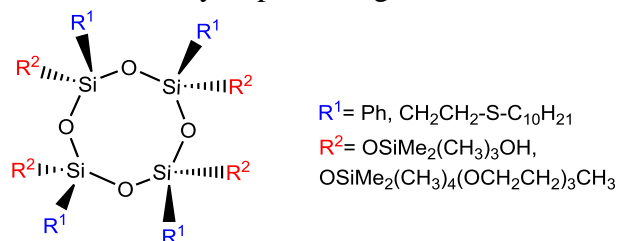


Fig. 1. Amphiphilic stereoregular cyclotetrasiloxanes

All the obtained compounds were fully analyzed by a complex of modern methods of physical and chemical analysis: IR-, NMR-spectroscopy, HRMS, elemental analysis, TGA and DSC.

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P-31

**Polyhedral vinylmetallasiloxanes: synthesis, structure, use for the
production of hybrid materials.**

Shugakova E.I.^{a,b}, Vysochinskaya Yu.S.^{b,c}, Anisimov A.A.^b, Dolgushin F.M.^b,
Shchegolikhina O.I.^b, Muzafarov A.M.^{b,c}

^a *Moscow Technological University, Lomonosov Moscow State University of Fine Chemical
Technologie, Moscow, Russia*

^b *A. N. Nesmeyanov Institute of Organoelement compounds of RAS, Moscow, Russia.*

^c *N. S. Enikolopov Institute of Synthetic Polymeric Materials of RAS, Moscow, Russia.*

E-mail: shuga-kova@mail.ru

Polymer gels with various functional and interesting properties are well-known class of materials, which have found application in various fields of science and technology.

Their properties depend not only on the chemical structure of the network but also on the physical structure, including crosslinking points, polymer chains or network compositions.

It can be assumed, that the design of the cross-linked polymer at the macromolecular level should lead to exponential development in functional polymer gels and, therefore, in the whole field of high molecular weight compounds (HMWCs).

Recently, the trend towards the use of metal-organic frameworks (MOF) as a new molecular matrix for the synthesis of polymer networks has become more and more evident. This is due to a complex of new physico-chemical properties that are not characteristic of classical gels.

The aim of our study is the synthesis of various polyhedral vinylmetallasiloxanes and the preparation of polymer gels on their basis. Organometallasiloxanes are a unique class of organosilicon compounds containing Si-O-M chain, where M is a metal ion. These compounds combine properties of organic and inorganic components. Vinyl containing metallasiloxanes are the only functional representatives of the class. Vinyl group attached at the silicon atom makes it possible to use these complexes for production of hybrid polymer gels. Aspects of the synthesis and structure of vinylmetallasiloxanes will be presented as well as a possibility of preparation of new hybrid materials based on them will be demonstrated by the hydrolytation reaction.

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P-32

Synthesis of sodium diorganosiloxanediolates

Talalaeva E. V.^a, Kalinina A. A.^{a, b}, Zenkovskaya D. A.^a, Belova L. O.^c, Demchenko N. V.^a,
Muzafarov A. M.^{a, b}

^a*Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, Moscow, Russian Federation.*

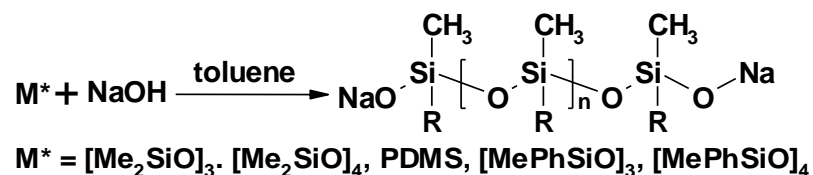
^b*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russian Federation.*

^c*Moscow Technological University (MIREA), Moscow, Russian Federation.*

talalaeva@ispm.ru

One of the most important tasks of modern polymer chemistry is the development of methods for obtaining synthones with a given architecture. Promising precursors for directed polymer synthesis is sodium diorganosiloxanediolates. However, up to the present time the literature has described the only way of synthesis of sodium diorganodisiloxanediolates, the so-called Hyde salts [1]. The disadvantage of this method is the formation of salt in the form of aqueous crystalline hydrate, which excludes the possibility of its use as catalysts and makes it difficult to use as a precursor for the directed synthesis of polyorganosiloxanes. At the same time, the ability to synthesize different sodium salts of is an urgent task.

Thus, the goal of this work is the synthesis of sodium diorganosiloxanediolates of various lengths (Scheme 1) by the interaction of cyclic and linear siloxanes and alkali.



Scheme 1.

In this paper will present the results of a study of the effect of the monomer/alkali ratio, the boiling time, the type of monomer on the composition and structure of salt products. The products obtained are characterized by a combination of physical and chemical analysis methods: gas-liquid and gel-permeation chromatography, IR and ¹H NMR spectroscopy.

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P-33

Synthesis and properties of star-shaped polydimethylsiloxanes with carbosilane dendrimers as cores.

P.A. Tikhonov^{a*}, S.A. Milenin^a, E.A. Tatarinova^a, N.V. Demchenko^a, G.V. Cherkaev^a,
N.G. Vasilenko^a, D.I. Shragin^a, A.M. Muzafarov^{a,b}.

^a *Institute of Synthetic Polymeric Materials of Russian Academy of Sciences (ISPM RAS),
Moscow, Russia*

^b *A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences
(INEOS RAS), Moscow, Russia*

*e-mail: tikhonpavel@yandex.ru

Star-shaped polymers have a number of unique properties, such as a high relaxation time of polymer arms and a low viscosity compared to linear polymers of the same molecular weight. These properties find applications in medicine [1], catalysis [2] and in creation of composites with tunable rheology [3,4].

The main goal of this work is the synthesis of a series of polymer stars with carbosilane dendrimers 2,4,6,8 generations as core and polydimethylsiloxane arms with different lengths, divided by bidodecylmethylsilyl groups as well as the study of their properties, in particular, rheological characteristics and investigation of the nature of crystalline mezophase, previously observed in 128-arm systems [5].

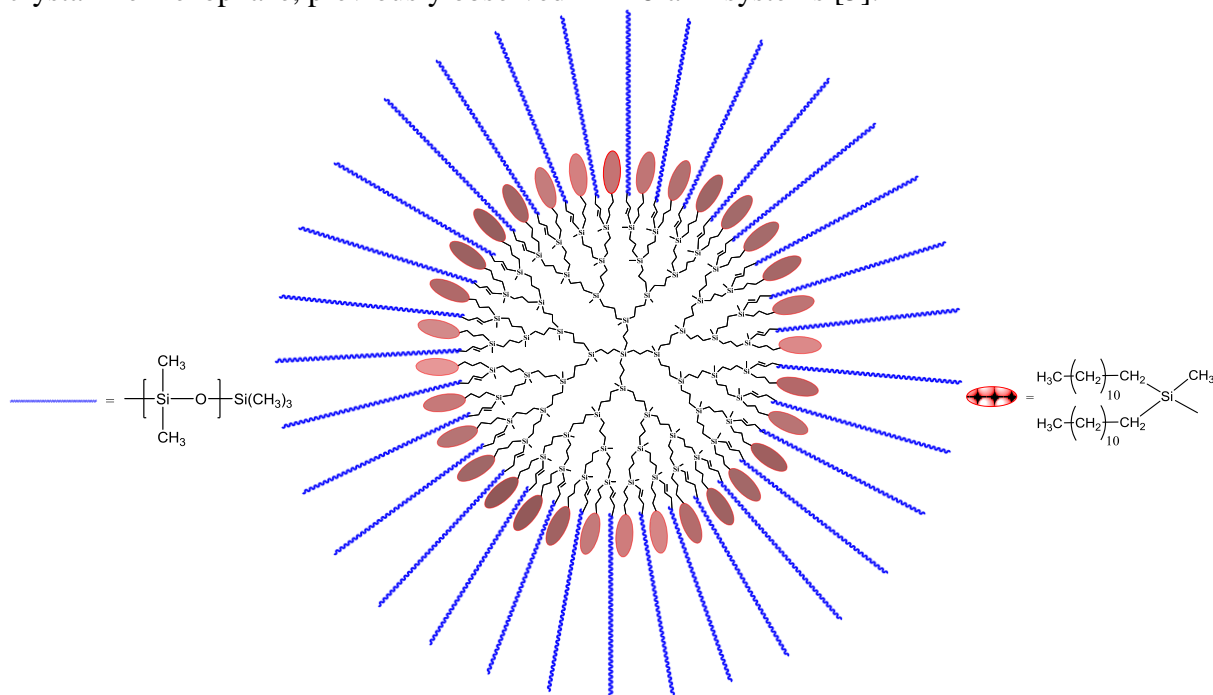


Fig. 1. Star-shaped PDMS with carbosilane dendrimer 4-th generation as core.

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P-34

**New star-shaped polydimethylsiloxanes with cyclosilsesquioxane cores:
synthesis, structure and properties**

Vysochinskaya Yu.S.^{a,b}, Anisimov A.A.^a, Buzin M.I.^b, Vasil'ev V.G.^b, Shchegolikhina O.I.^b,
Muzafarov A.M.^{a,b}

^a *N.S. Enikolopov Institute of Synthetic Polymeric Materials, a foundation of the Russian
Academy of Sciences, Russia, Moscow*

^b *A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of
Sciences, Russia, Moscow*

E-mail: vysochinskaja@yandex.ru

Star-shaped polymers are an example of branched structures which are characterized by existence of the branching-out center which is called "a core", and the linear fragments - "beams" coming from the center of branching. Such polymers owing to their unique structure have many valuable properties, doing them very interesting to use in various fields of the industry. Star-shaped polymers have already proved as lubricants and surfactants, additives to oils and fuel materials, viscosity modifiers as well as for transportation of medicinal substances and oth. [1].

In spite of the fact that there is rather large number of publications devoted to the synthesis and studies of such polymers there is only a few articles devoted to the synthesis and properties of star-shaped polymers of completely siloxane nature. Such interest to siloxane systems is caused by a complex of their properties: high thermostability and low-temperature resistance, water repellency, bioinertness and small changes of physical characteristics in the wide range of temperatures. Therefore preparation and investigation of star-shaped polyorganosiloxane is the attractive and perspective direction in polymer chemistry.

The unique method for the preparation of functional stereoregular cyclic organosilsesquioxanes has been developed in our laboratory [2]. The cycles of various sizes can serve as a core for the synthesis of star-shaped polymers. Their structure allows not only to control functionality of a core, but also a structure of a target product. In this work the synthesis of new star-shaped polydimethylsiloxanes with various size and type of a core (4-, 5-, 6-, 8-, 12- SiO-units and silsesquioxanes cube) will be presented. All compounds obtained have been characterized by NMR- and IR - spectroscopy and GPC. The data obtained by DSC TGA methods, rheology both in the block and solution data have allowed us to establish "structure - properties" the relationship.

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POSS with *p*-tolyl substituents at the silicon atom: synthesis and structure

P.A. Zader^a, A.A. Anisimov^b, A.A. Korlyukov^b, A.M. Muzafarov^{b,c}

^a D. Mendeleev University of Chemical Technology of Russia, Moscow, Russia.

^b A. N. Nesmeyanov Institute of Organoelement compounds of RAS, Moscow, Russia.

^c N. S. Enkolopov Institute of Synthetic Polymeric Materials of RAS, Moscow, Russia.

E-mail: paul.zadyor@gmail.com

Polyhedral oligomeric silsesquioxanes (POSS) are the unique class of silicone compounds. These compounds are of a great interest because of its special structure and the complex of physical and chemical properties. Thus, the silsesquioxane cubes found application as matrixes for obtaining of organo-inorganic supramolecular systems and nanometer fillers for the production of composite materials of new generation.

Functional POSS are of a great interest because the further modification is becoming available. It is important to solve of very different problems. Thus, the development of approaches to obtain of functional POSS is an actual task [1].

During the work two POSS with *p*-tolyl substituents at the silicon atom have been synthesized. Obtained compounds are interesting, because the *p*-tolyl groups can be modified to *p*-carboxyphenyl groups by the oxidation reaction.

The obtained POSS were completely characterized by a set of methods of physical and chemical analysis: NMR-, IR- spectroscopy, HRMS and element analysis. Also, molecular and crystal structures were established using the X-ray diffraction analysis. This method hasn't been used for these compounds (fig. 1) before.

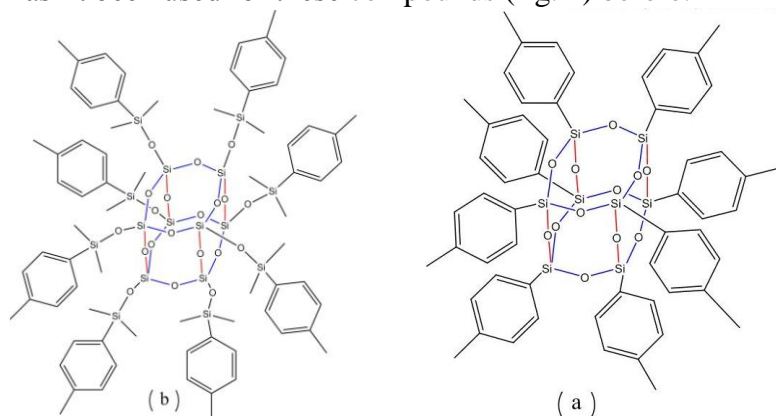


Fig. 1. (a) octa-*p*-tolyloctasilsesquioxane, (b) octa-(*p*-tolyldimethylsiloxy)octasilsesquioxane.

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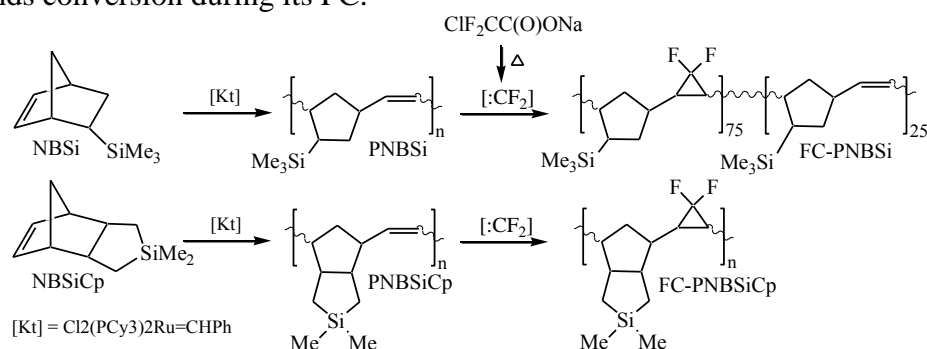
This work was supported by the Russian Science Foundation (grant no. 14-23-00231).

P-36

Effect of backbone double bonds gem-difluorocyclopropanation on gas-separation properties of metathesis Si-substituted polynorbornenes

V. A. Zhigarev, A. A. Morontsev, N. A. Belov, R. Yu. Nikiforov, M. L. Gringolts
A. V. Topchiev Institute of Petrochemical Synthesis, RAS, 29 Leninskii pr., Moscow, Russia
E-mail: zhigarev@ips.ac.ru

It is known that silicon-substituted polynorbornenes possess high gas permeation properties [1]. Olefin metathesis derived polynorbornenes (MPNB) contain double bonds in their backbone which leads to chemical instability but opens opportunity to polymer modification. Recently we have started to study the influence of polynorbornene double bonds modification on polymer gas-separation properties. The epoxidation (EP) of double bonds in MPNB has reduced polymer gas-permeability; however their selectivity has extremely increased [2]. In this work, we studied the gem-difluorocyclopropanation (FC) of MPNB double bonds. Initial MPNB were synthesized by ring-opening metathesis polymerization of corresponding Si-containing norbornenes in the presence of 1st generation Grubbs' catalyst, $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}$. The FC of polymers was carried out by the action of difluorocarbene formed during sodium chlorodifluoroacetate thermolysis in methyl benzoate media at elevated temperature (Scheme 1). The conditions supplying highest conversion of double bonds in FC were found and high molecular weight polymers with good film-forming properties were synthesized. It was shown that the presence of bulky SiMe_3 substituents in the side chain of MPNB prevents complete double bonds conversion during FC. After FC, the poly(5-trimethylsilylnorbornene) (PNBSi) contained 20-25% unchanged double bonds [3]. We synthesized poly(4,4-dimethylbicyclo[5.2.1.0^{2,6}]-4-siladecene-8) (PNBSiCp) in which Si-methyl group shifted one carbon atom further from MPNB backbone and observed exhausted double bonds conversion during its FC.



Obtained polymers were characterized by ^1H , ^{13}C , ^{19}F , ^{29}Si – NMR, IR spectroscopy, GPC and DSC methods. It was shown that introduction of difluorocyclopropane fragment in MPNB considerably influenced gas-separation properties: gas permeability coefficients (P) of He, H_2 , O_2 , N_2 , CO_2 , CH_4 gases increased in 3- 2,5 times for FC-PNB, 1.2-1.4 for FC-PNBSi and 4-4.5 for FC-PNBSiCp.

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P-37

Preparation of silicone resins based on a copolymer of regular structure.

S. N. Zimovets^{1,2}, M. N. Temnikov², E. A. Gubkin³, E.V. Talalaeva^{1,3}, A. A. Kalinina¹,
Muzafarov A. M.^{1,2}

¹ N. S. Enicolopov Institute of synthetic polymeric materials RAS, Moscow, Russia

² A. N. Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia

³ Moscow Technological University

sofi_zimovets@mail.ru

Silicone resins have found wide application in various spheres of human activity: high thermo- and thermo-oxidative stability, resistance to UV radiation, a wide range of operating temperatures, bioinertness, processability, etc. Traditional methods for obtaining such drawbacks: composite heterogeneity, difficulty in controlling material properties and poor reproducibility. A solution to these problems can be a copolymer with a regular arrangement of functional and non-functional blocks. The functional block is responsible for the formation of a three-dimensional polymer containing residual functional groups [1], and the non-functional block provides the desired product with the necessary set of physico-chemical properties.

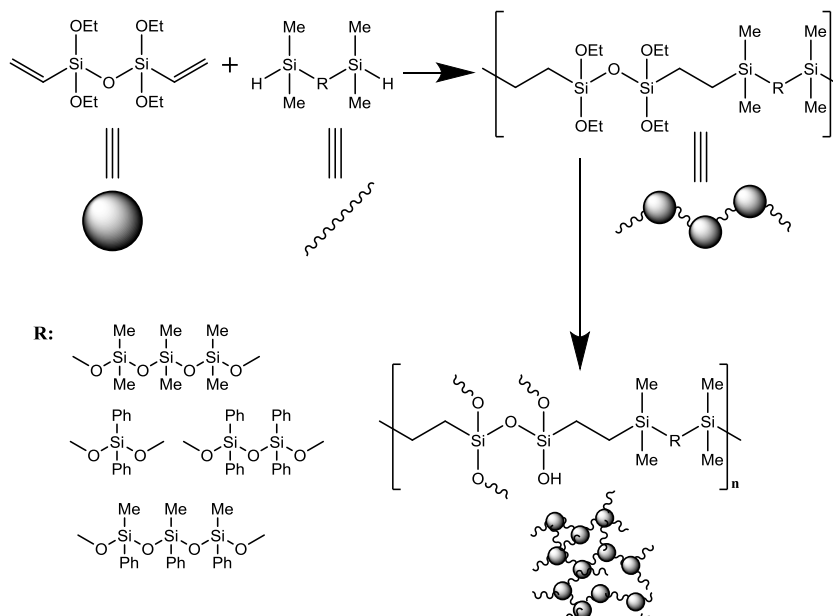


Fig. 1 – General scheme of synthesis

This work was supported by Foundation RFBR (№ [18-33-00909](#))

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P-38

Flame-retardant silicon-containing phthalonitrile matrix reinforced with unidirectional carbon fibers.

Zodbinov E.B.^{1,2}, Bulgakov B.A.^{1,2}, Afanasiev D.V.³, Babkin A.V.^{1,2}

¹Lomonosov Moscow State University, Moscow, Russia

²Institute of New Carbon Materials and Technology, Moscow, Russia

³P. I. Baranov Central Institute of Aviation Motor Development, Moscow, Russia

E-mail: elvewka@gmail.com

Polymer matrices developed from bis-phthalonitrile (PN) demonstrate the highest heat resistant properties among the known thermosets. Since the beginning the main disadvantage of that type of resins was narrow processing window caused by high melting points of the PN monomers. The synthesis of silicon- and phosphorus-containing PN (Fig. 1, [1]) monomers allowed to develop resin compositions suitable for cost-effective injection techniques of composite manufacturing. Here carbon fiber reinforced phthalonitrile matrices obtained by resin transfer molding (RTM) are reported and discussed. The composites retain mechanical properties at temperatures up to 300°C and demonstrate incredible flame-retardant properties (LOI > 80%, [2]).

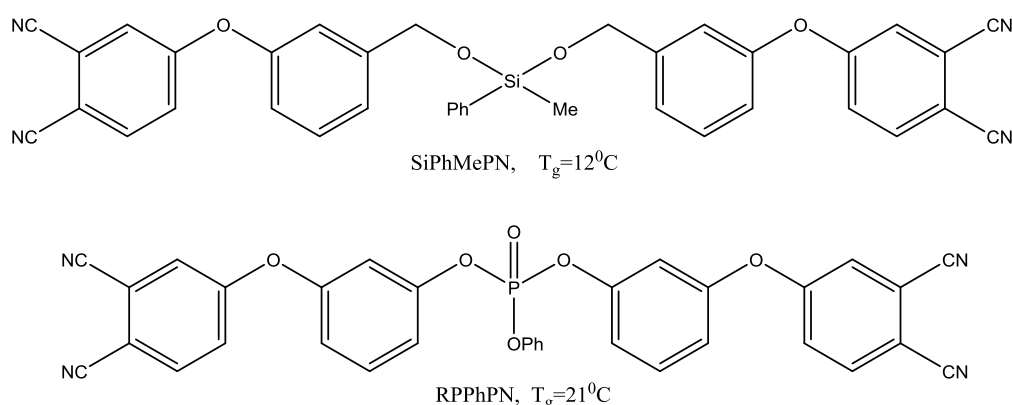


Fig. 1. The key PN monomers used in the resin composition

The impregnation was performed at 150°C in a metal mold assisted with vacuum and pressure implementation. Composites demonstrated in-plane shear strengths of 72±7 MPa at 25°C and 61±5 MPa at 300°C.

Overall mechanical properties retention of the composites with PH matrices at 300°C was up to 85%, and thus such a materials could be considered for applications for jet engine blades or skin parts of supersonic aircrafts, spacecraft heat-shields, exhaust pipes or engine covers in automotive or interior parts of submarines.

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P-39

**Metalloalkoxysiloxanes - a new precursors for nanocomposites preparation
by sol-gel method**

Andropova U.S.^{a,b}, Tebeneva N.A.^b, Tarasenkov A.N.^b, Serenko O.A.^a, Muzafarov A.M.^a
^a*A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science,
119991, GSP-1, Russia, Moscow, Vavilova St. 28*

Fax: +7(499)135-50-85

^b*Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Science, 117393,
Russia, Moscow, Profsoyuznaya St. 70*

Fax: +7(495)718-34-04

E-mail: hrh_uly@mail.ru

Sol-gel method is a common method for polymeric nanocomposites obtaining. One of its variants is in situ nanoparticles formation within the polymer matrix. This method allows to obtain filled systems from the polymer solution (or melt) by premixing it with the inorganic phase precursor. Composite materials obtained using of tetraethoxysilane, methyltriethoxysilane, methyltrimethoxysilane etc. as precursors are well known. However, the hydrolytic processes of these alkoxy derivatives are needed the moisture and catalyst to be presented, which inhibits the application of this filling method in industry. One of the solutions to this problem is the search and use of new, more reactive precursors of the composite dispersed phase.

Metalloalkoxysiloxanes are multifunctional sol-gel agents for the preparation of organo-inorganic polymer systems during in situ polymer filling. Their use as precursors allows us to exclude water and catalyst adding into the reaction mixture [1]. Aim of this work is to study the structure and properties of polymer nanocomposites in which various metalloalkoxysiloxanes act as precursors of the dispersed phase, namely tris-(methyldiethoxysiloxy)iron, tetrakis-(methyldiethoxysiloxy)zirconium, tetrakis-(methyldiethoxysiloxy)hafnium. Polyaryleneetherketones and polyimides of various chemical structures were used as the matrix polymer. It is shown that the inorganic phase of nanocomposites can be varied from dispersed particles to a continuous grid by changing the central metal atom type in the metalloalkoxysiloxanes with same silicone framing. At the same time, the structure of the metalloalkoxysiloxane precursor alkyl group determines its reactivity in gelling reactions and compatibility with the polymer matrix. The chemical structure of the matrix polymer has an effect on its ability to stabilize the growth of nanoparticles.

Thus, metalloalkoxysiloxanes are promising precursors for the preparation of polymer nanocomposites by the in situ filling method. Their application allows us to develop a new universal approach to the hybrid organo-inorganic polymer nanocomposites production in which well-controlled chemical processes will be used.

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This work was financially supported by the Russian Foundation for Basic Research (Project № 18-03-00514 and Project № 18-33-00096 mol_a)

P-40

**Synthesis of Metallocarbosilanes Simultaneously Containing Nanoparticles
of Zr and Ta or Hf and Ta**

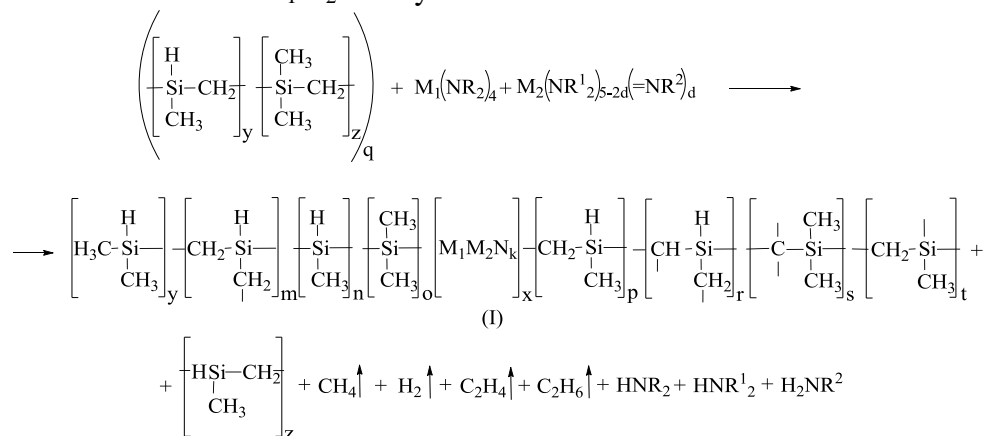
G.I. Shcherbakova, M.Kh. Blokhina, D.V. Zhigalov, A.P. Korolev, P.A. Storozhenko
SSC RF JSC "State Research Institute for Chemistry and Technology of Organoelement
Compounds", 105118 Moscow, Russian Federation
E-mail: mariya_blokhina@mail.ru

Zirconium and hafnium carbides are known to form an infinite series of solid solutions with tantalum monocarbide [1], the melting points of mixed carbides being higher than those of individual compounds. Melting point of Ta₄ZrC₅ is 3810-3840°C, and Ta₄HfC₅ – 3970-4010°C [2], therefore, the use of mixed carbides ZrC-TaC and HfC-TaC as modifiers of SiC ceramics should significantly increase its thermal stability.

The synthesis of ceramic-forming metallopolycarbosilanes (M₁M₂PCS) having fiber-forming properties and a given molar ratio of Ta:Zr (Ta:Hf) [3], metal atoms is realized at GNIICHTEOS, which allows after pyrolysis of M₁M₂PCS to produce SiC ceramics modified by mixed carbides of refractory metals with a maximum melting point.

Metallopolycarbosilanes (M₁M₂PCS) are prepared through the interaction of raw polycarbosilane (raw PCS) with alkyl amide compounds of zirconium and tantalum or hafnium and tantalum of formula M₁(NR₂)₄, where M₁ – Zr, Hf, R – CH₃, C₂H₅ and formula M₂(NR¹₂)_{5-2d}(=NR²)_d, where M₂ – Ta; R¹ – CH₃, C₂H₅, R² – t-C₄H₉, d = 0, 1.

General scheme of M₁M₂PCS synthesis:



The physicochemical properties of the synthesized M₁M₂PCS and ceramics samples based on them were studied by NMR, IR, TGA, X-ray phase analysis, SEM, elemental analysis.

The polymers obtained can be used as precursors for the preparation of components of high-temperature resistant ceramic composites based on silicon carbide modified with mixed carbides of refractory metals (Zr and Ta, Hf and Ta).

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P-41

Methylsilsequioxane Dendrimers. Synthesis and properties

Konstantin Boldyrev^{a,b}, Ashot Arzumanyan^a, Sergey Milenin^b, Ivan Meshkov^{a,b},
Elena Tatarinova^b and Aziz Muzafarov

^aA.N. Nesmeyanov Institute of Organoelement Compounds of Russia Academy of Sciences,
Vavilova st.28, 119991 Moscow, Russia

^bEnicolopov Institute of Synthetic Polymeric Materials Russia Academy of Sciences,
Profsoyuznaya st.70, 117393 Moscow, Russia

E-mail: boldyrevkl@ispm.ru

The comparison between the physical properties of dendrimers and polymers shows the specific structure and behavior of dendrimers [1].

Methylsilsequioxane dendrimers are of fundamental interest, since they are analogous to such siloxane structures - namely polydimethylsiloxanes, comb-shaped polymers [2], hyperbranched polysilsesquioxanes [3], to provide the same elemental composition but different molecular structure. Therefore, the study and comparison of the properties of these structures afford us to establish a ratio structure - properties.

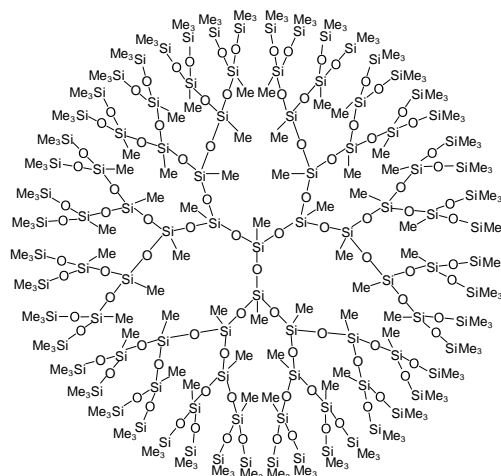


Fig. 1. Methylsilsequioxane Dendrimers of 4th generation with non-functional periphery. The dendrimers synthesized were characterized by ¹H, ¹³C, ²⁹Si NMR spectroscopy, GPC and DSC analysis.

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P-42

Preparation of microcapsules with a polydimethylsiloxane core

Borisov K.M.,^{a,b} Bokova E.S.,^a Kalinina A.A.,^b Muzafarov A.M.^c

Kosygin Russian State University.

Enikolopov Institute of Synthetic Polymeric Materials RAS

Nesmeyanov Institute of Organoelement Compounds RAS

bora.91@mail.ru

Encapsulation of various agents is an actual topic of modern research. Such filled particles can have a wide range of applications. Known examples of obtaining so-called "dry water" or "dry oil" are able to overturn modern principles of delivery, both at the macrolevel (transport of petroleum products) and at the micro and nano levels (transport of drugs in the physiological environment). Principles of encapsulation are the basis for the creation of self-healing materials, antifriction and anticorrosive coatings, etc.

In the literature, much attention is paid to colloidosomes (microcapsules), the shell of which is a polysiloxane structure [1,2]. One of the options for forming microcapsules is the approach in which hyperbranched polyethoxysiloxane forms a shell of microcapsules during the condensation process at the interface.

The aim of this work is to encapsulate the functional and non-functional PDMS in microcapsules with a shell of SiO₂ composition, as well as the functionalization of such microcapsules.

The report will present the results of the study of the obtained microcapsules with PDMS core.

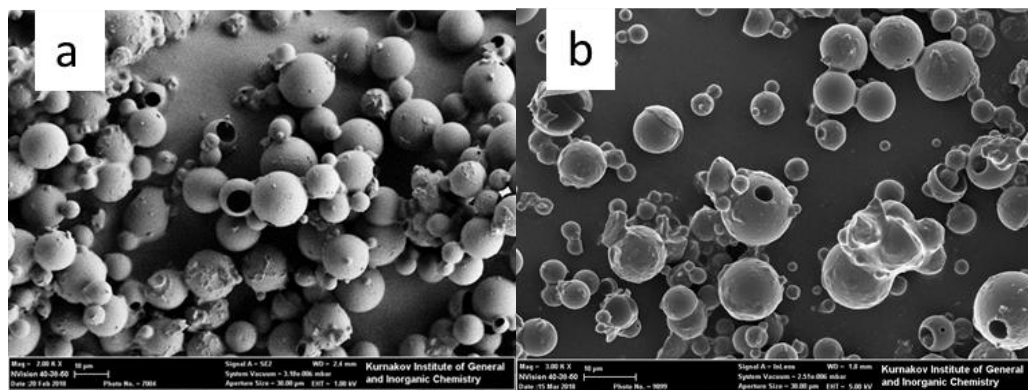


Fig.1. A photograph of microcapsules filled with PMS 50 (a) and SCTN-A (b)

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P-43

**Polyaddition silicone polymeric materials.
Traditional and new aspects of application in medicine.**

E. I. Alekseeva^a, A. R. Dolotko^a, I. Yu Ruskol^a, E.V. Sokoluk^a, R. R. Zakirov^b

^a JSC "GNIChTEOS", Moscow, Russia

^b SIC "Silicone", St.-Petersburg, Russia

E-mail: alexelena3@yandex.ru

Polyaddition silicone materials are widely used in medicine all over the world due to unique combination of properties. Vulcanization of such compositions, usually consisting of a mixture of vinyl and hydride oligoorganosiloxanes, occurs in the presence of platinum complex catalysts. The peculiarity of this process is no release of by-products [1], which makes it possible to cure the polymer composition, both in open and in closed volumes.

A special technology for producing highly pure compounds has been developed, which permits to obtain vulcanizates with a minimum level of toxic and coloring impurities. In total these properties turned out to be a crucial for creating medical accessories. Influence of the type and ratio of initial components, conditions of vulcanization and other factors on the properties of vulcanizates is investigated. On the basis of the studied regularities, a wide range of products was created: from gel-like and elastomeric to solid materials. All of them are widely used in medical practice: 1) Low-modulus gel-like compositions (with Young's modulus of 0.05 – 10.0 kPa) are used in the manufacture of breast implants, coatings for the treatment and prevention of hypertrophic and keloid scars. The most important characteristic of these coatings is the period of preservation of the so-called "stickiness", at least 2 months at a temperature of 30±10°C. 2) The elastomeric implants of complex configuration belong to a separate group. These materials are capable of vulcanization in a layer of any thickness and have resistance to bending, which determines their use for the correction of soft tissues: facial surgery, etc. A series of elastomers with step-by-step Shore A hardness has been developed. To predict the behavior of implants obtained, the process of their thermal aging was studied; it was shown that they have stable physical mechanical and other characteristics at a certainly higher temperature than the body temperature (80°C). 3) Silicone compositions for intraocular lenses (IOL) have a variable refractive index (from 1.39 to 1.51). The use of IOL with a high refractive index (≥ 1.46) made it possible to reduce the thickness of the lenses and increase their shelf life. 4) Dental silicone impression materials includes 3 main composition ("line"): base layer - two component system with a very thick consistency and Shore A hardness ≥ 60 ; correcting layer 1 - two component system with a fluid texture and Shore A hardness ≥ 45 ; the corrective layer 2 - two - component system with intermediate consistency and Shore A ≥ 45 . 5) LIM/LSR materials are suitable for various gaskets, inserts, shaped products, including orthopedic, etc. 6) High-purity, biologically inert materials are designed for protective coatings of cardiac devices. 7) Silicone coating materials for fiber cables and lasers used in medicine for diagnosis in gastroenterology, proctology, etc. It should be noted that the development of a cluster of silicone polymer materials is of great social importance and contributes to solving the problem of import substitution.

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P-44

Study of the possibility of using robotics to produce an abrasion-resistant silicone coating of sheet monolithic polycarbonate

P.A. Storozhenko, A.N. Polivanov, T.I. Fedotova*, N.V. Tyurikova, A.I. Drachev,
A.V. Levchuk, K.E. Smirnova, V.A. Bardakova
SSC RF JSC GNIChTEOS
*e-mail: fedotova@eos.su

Organosilicon composition, which is a product of hydrolytic copolycondensation of alkoxysilanes in low molecular weight alcohols, has been synthesized by sol gel method. The composition was used to study abrasion resistant coating based on alkoxo technology. Polymethylmethacrylate solution was prepared as a sublayer.

The composition was applied in a painting chamber of $20 \pm 5^\circ \text{C}$ equipped with air purification filters of F5 class, intake and exhaust ventilation, a climate control system, "Yantar E5" bipolar ionizer, using air blow gun - VMG1 and drying box CM 50/250-3000 IIC at ambient temperature and relative humidity of 50-55%.

The composition was applied by spraying with "Fanuc" robot (Japan), equipped with K-20 HVLP spray gun in a few modes in order to determine the thickness of the layer required to achieve a specified (not less than 4H) hardness of the coating. The sublayer was a sheet polycarbonate with the size of 2.0 * 1.0 m, 6 mm thick, and 1.4 * 1.5 m, 6 mm thick.

The obtained experimental data are presented in the table.

Table

	The operating mode of the robot and the spray gun	Adhesion	Hardness	Coating thickness
Sub layer	Movement of the robot arm V=370mm/s, step 55mm, height to the sublayer – 115mm., material feed - 4 clicks	+	not measured	3 microns
	Movement of the robot arm V=400mm/s, step 55mm, height to the sublayer 115mm, material feed - 7 clicks	+	not measured	2 microns
Top coating	Movement of the robot arm: V=370mm/s, step 55mm, height to the sublayer 115mm, material feed - 4 clicks	+	4H	2-3 microns
	Movement of the robot arm: V=300 mm/s, step 55 mm, height to the sublayer 115mm, material feed - 4 clicks	+	4H	4 microns

P-45

Investigation of cyclic products of hydrolytic co-condensation of dimethyldichlorosilane and methyltrichlorosilane by chromatography-mass spectrometry and ²⁹Si-NMR

Filippov A.M.^a, Ruskol I.Yu.^{a,b}, Shestakova A.K.^a, Shulyatieva T.I.^a, Belutina V.V.^b

^aThe Stare Scientific Center of the Russian Federation «State Research Institute for Chemistry and Technology of Organoelement Compounds», Moscow, Russia

^bD. Mendeleev University of Chemical Technology of Russia, Moscow, Russia

E-mail: amphil@yandex.ru

Hydrolytic condensation of dimethyldichlorosilane and methyltrichlorosilane leads to the formation of branched siloxanes and cyclic products. This work is devoted to the study of the composition and structure of cyclic products of hydrolytic co-condensation of dimethyldichlorosilane and methyltrichlorosilane.

Hydrolysis is carried out at a molar ratio $(\text{CH}_3)_2\text{SiCl}_2 : \text{CH}_3\text{SiCl}_3 = 2,5 : 1$ with a large excess of water in the presence of toluene. Cyclic products separated by distillation at reduced pressure were divided into two fractions. The composition of each fraction was determined by GC (chromatograf «Cristall» with FID). The obtained compounds were identified by ²⁹Si NMR spectra ("Bruker AM 360" spectrometer (71.6MHz) in a CDCl₃ solution with Cr(AcAc)₃) and mass spectra (Agilent spectrometer 240 Ion Trap GC/MS). Characteristics of the obtained compounds are given in table 1.

Table 1. Cyclic products of hydrolytic co-condensation of dimethyldichlorosilane and methyltrichlorosilane

№	t _{ret} , min	Compound*	M, Da	m/z, (I, % rel.)	δ _{Si} , ppm
1	3,513	D ₄	296	281(100) 265(12) 193(10)	-19,42
2	4,571	D ^{OH} D ₃	298	283(20) 281(15) 267(100) 251(14)	-18,89; -19,07; -55,21
3	4,815	T ₂ D ₃	356	341(100) 325(36) 73(28)	-14,84; -58,47
4	4,929	T ₂ D ₃	356	341(100) 325(41) 73(29)	-7,32; -18,43; -54,03
5	5,012	D ₅	370	355(98) 267(100) 73(70)	-21,85
6	5,914	T ₂ D ₄	430	415 (6) 399(10) 327(100) 73(50)	-10,99; -19,05; -19,21; -19,48; -63,88; -64,69
		D ^{OH} D ₄	372	357(1.9) 341(100) 325(60) 73(80)	-21,01; -21,36; -56,45
7	6,215	T ₂ D ₄	430	415(90) 327(100) 73(46)	-19,21; -62,95
8	6,281	T ₂ D ₄	430	415(76) 327(100) 73(46)	-
9	6,649	D ₆	444	429(60) 341(100) 325(35) 73(80)	-22,53

*D – (CH₃)₂SiO; D^{OH} – (CH₃)(HO)SiO; T – (CH₃)SiO_{1,5}

Correctness of interpretation of signals of ²⁹Si NMR spectra is confirmed by a good coincidence of the quantitative composition of the studied mixtures calculated from NMR spectra and data of the GC method.

It was found that molecules D^{OH}D₃ and D^{OH}D₄ with the entry into the zone of electronic ionization (EI) lose methyl group and then molecule of methane, which leads to the formation of cations with two T-units. The same cations are formed in the conditions EI from the molecules T₂D₂ (not published) and T₂D₃ (table 1).

P-46

Group 13 element silicon pyramidanones

Olga A. Gapurenko^a, Vladimir Ya. Lee^b, Ruslan M. Minyaev^a, Vladamir I. Minkin^a

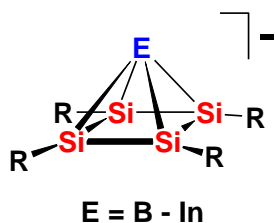
^a Institute of Physical and Organic Chemistry, Southern Federal University, Rostov on Don 344090, Russian Federation;

^b Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan.

E-mail: gapur@ipoc.sfedu.ru

More than thirty years a nonclassical structure of pyramidane C[C₄H₄] remains hypothetical and studied only on theoretical level. However several of its derivatives E[C₄R₄] (E = Ge, Sn, Pb; R = SiMe₃) are experimentally realized and characterized very recently [1], [2]. Other group 14 element pyramidanones are also synthesized and studied by DFT approach, i. e. E[E'R₄] (E = Ge, Sn, Pb; E' = Si, Ge; R = Si^tBu₂Me) [2], [3]. Moreover, some group 15 element pyramidanones (E[E'₄R₄]⁺; E = P, Sb; E' = C, Si, Ge; R = SiMe₃, Si^tBu₂Me) and related compounds are studied experimentally and theoretically [4], [5], [6].

In this work we present DFT calculations of the pyramidal structures with group 13 element on the apex and Si₄ basal rings (Scheme 1).



Scheme 1. Group 13 element pyramidanones.

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This work was supported by the Russian Ministry of Science and Education (Project Part, Project 4.844.2017/4.6).

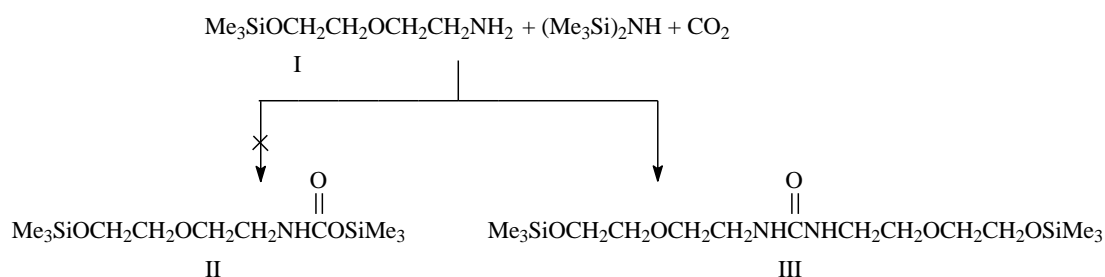
P-47

Chemical transformations of siliconcontaining derivatives of 2-(2-aminoethoxy)ethanol

N.A. Golub, M.V. Pletneva, L.O. Belova, A.D. Kirilin
Moscow Technology University, Moscow, Russia,
e-mail: golub-n.a@mail.ru

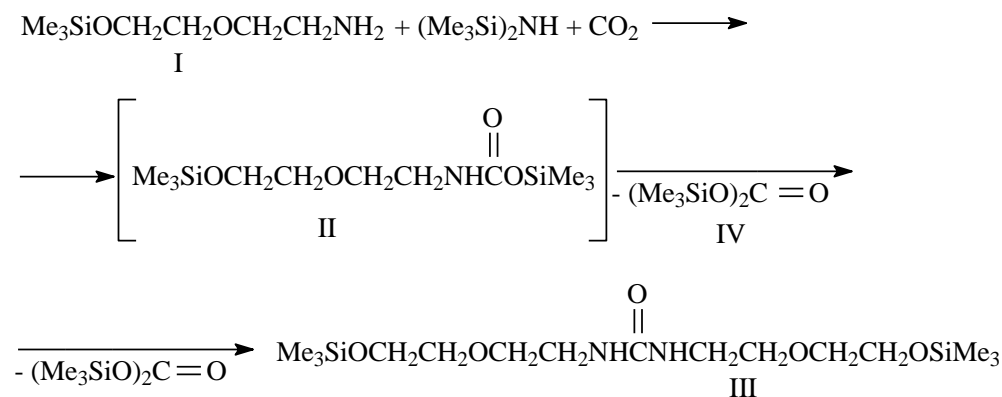
The behavior of 2-(2-[(trimethylsilyl)oxy]ethoxy)ethylamine (I) in the N-siloxy-carbonylation reaction was studied for the first time.

We have found that the use of hexamethyldisilazane/carbon dioxide as the N-siloxycarbonylation system does not lead to the expected production of O-silylurethane (II), but to the formation of a previously unknown siliconcontaining urea, N,N'-bis(2-(2-[(trimethylsilyl)oxy]ethoxy)ethyl)urea (III). (Scheme 1)



Scheme 1.

The nature of the initial reagents and obtained results are indicate that the N-siloxycarbonylation reaction of 2-(2-[(trimethylsilyl)oxy]ethoxy)ethylamine (I) passes through the formation of O-silylurethane - trimethylsilyl-2-(2-[(trimethylsilyl)oxy]ethoxy)ethyl carbamate (II), which turned out to be a thermally unstable compound. Thus O-silylurethane (II) under the conditions of fractional distillation during the isolation stage is symmetrized to urea (III), as that this reaction is accompanied by exudation siliconcontaining carbonate also (IV). (Scheme 2)



Scheme 2.

P-48

**Comparison of the properties of polydimethylsiloxanes containing
fragments of carboxylic acids of different structures**

Gorodov.v.^a, Tikhonov P.A.^a, Milenin S.A.^a, Buzin M.I.^{b,c}, Vasil'ev V.G.^b, Bakirov A.V.^{a,d},
Shragin D.I.^{a,b}, Muzafarov A.M.^{a,b}

^a *N.S. Enikolopov Institute of Synthetic Polymeric Materials of Russian Academy of Sciences (ISPM RAS)*

^b *A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS)*

^c *Moscow Pedagogical State University named after V.I. Lenin*

^d *National Research Center Kurchatov Institute*

E-mail: gorodovvv@ispm.ru

Earlier we reported [1],[2] on synthesis, the thermal and rheological properties of polydimethylsiloxanes (PDMS) containing fragments of undecenoic and benzoic acids (Fig.1). In this report, we will talk about the synthesis and properties of the telechelic PDMS with the carboxypyrrolidone fragment (Fig.2) and compare their properties with those previously obtained.

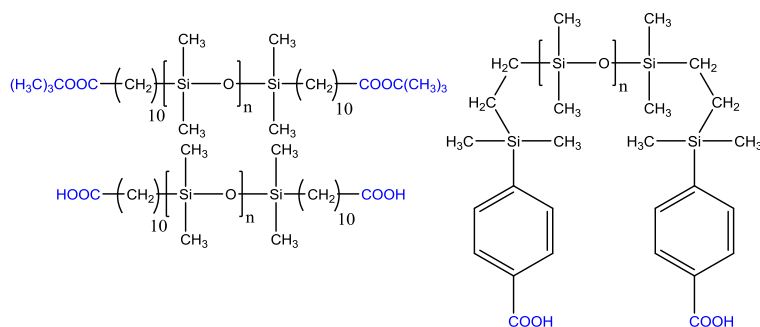


Fig. 1. Telechelic polydimethylsiloxanes containing fragment of undecenoic acid and benzoic acid

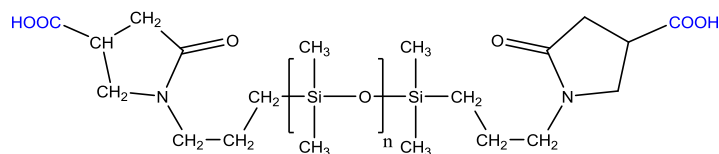


Fig. 2. Telechelic polydimethylsiloxanes containing fragment of carboxypyrrolidone

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P-49

Polyglycerols bearing silatrane moieties

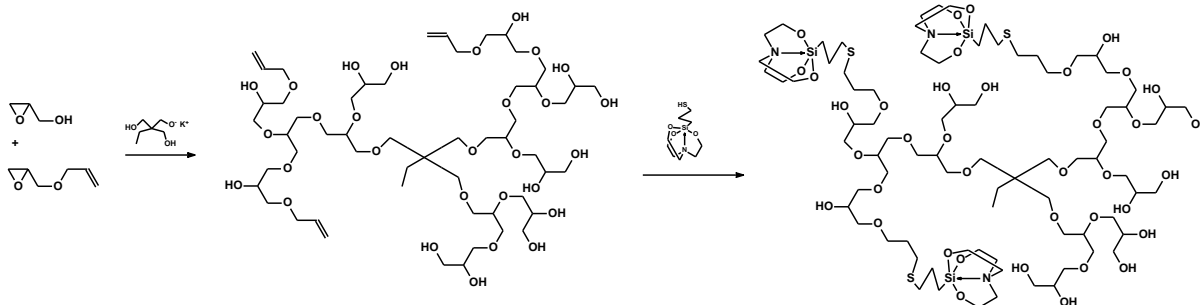
Vladislav Istratov, Raisa Dvorikova, Valerii Vasnev

A.N. Nesmeyanov Institute of organoelement compounds

Vavilov Str.28, Moscow 119991, Russia

E-mail: slav@ineos.ac.ru

Functional hyperbranched polyglycerols (PGs) have recently garnered considerable interest due to their potential in biomedical applications. Here, we present a synthesis of amphiphilic hyperbranched PGs possessing silatrane functionalities. Allyl glycidyl ether monomer was polymerized with glycidol through anionic ring-opening multibranching copolymerization to yield a series of hyperbranched polymers with controlled molecular weights (1000-4000 g/mol), relatively low molecular weight distributions (1.3-1.6) and incorporation of an adjustable fraction of allyl moieties (typically, 5-25% monomer ratio). The free allyl groups within the hyperbranched PG copolymers were further efficiently S-alkylated with previously obtained by common route thiopropyl-functionalized silatranes (Scheme 1). Furthermore, the biological activity of the prepared polymers towards *Aspergillus niger* and *Fusarium solani* was demonstrated via microbiological culture growth experiments, performing close to low molecular silatrane antifungal activity. Taken together, the high biological activity and polymer backbone providing prolonged life time holds the prospect of usage for biological and biomedical applications.



Scheme 1.

This work was supported by Russian Foundation for Basic Research (grant Nr 17-03-01089)

P-50

Novel organosilicone polymers

Vladislav Istratov, Oleg Baranov, Valerii Vasnev

A.N. Nesmeyanov Institute of organoelement compounds

Vavilov Str.28, Moscow 119991, Russia

E-mail: slav@ineos.ac.ru

Silatrane are intracomplex organosilicon ethers of tris (2-hydroxyalkyl) amines have attracted steady attention of researchers in recent years. These low-molecular compounds are known due to their unique biological properties [1]. By now, a large experience has been accumulated for the production of silatrans of various structures, and the main parameters influencing their physiological activity have been established [2]. Unfortunately, the overwhelming majority of publications are devoted to low-molecular-weight silatrans, and studies of silane-containing polymers are practically absent. In this work, polymethacrylates containing silatrane structures in the side chains, with varied hydrolytic stability of the polymer-silatrane bond were synthesized and studied. The structure of copolymers was confirmed by a complex of physical methods: elemental analysis, IR, NMR spectroscopy and GPC. It was established that the solubility of polymers in water depended on the content of silatrane fragments in macromolecules; Depending on this parameter, both insoluble and water-soluble polymers were obtained. For copolymers was evaluated hydrolytic stability and kinetic curves of polymers hydrolysis associated with the release of low-molecular silatrans were obtained.

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This work was supported by Russian Foundation for Basic Research (grant Nr 17-03-01089)

P-51

**Novel 1,7-bis [chloro(organo)siloxanylmethyl]-*m*-carboranes.
The effective method from bis(brommagnesiummethyl)-*m*-carborane and
chloro(organo) siloxanes**

Izmaylov B.A., Vasnev V.A., Markova G.D.

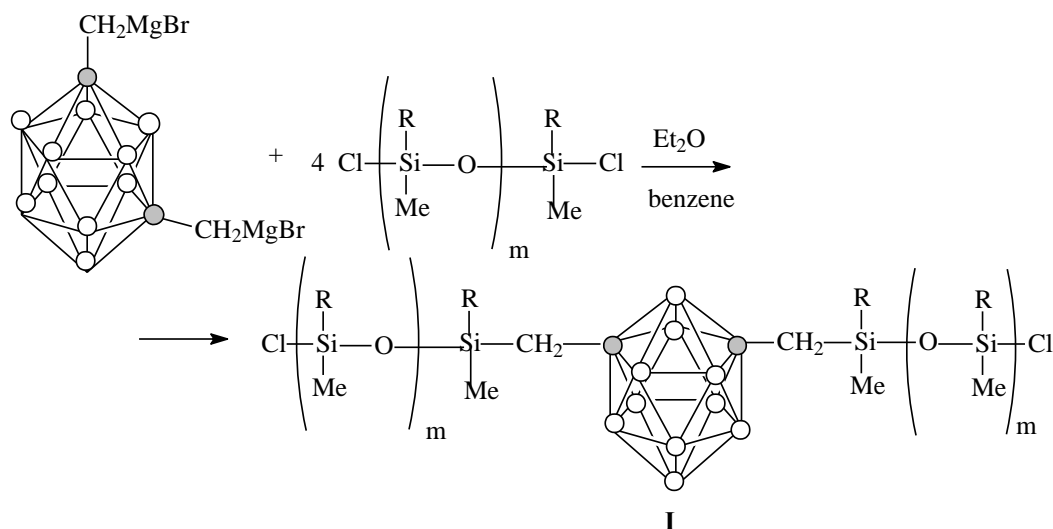
A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., Moscow, 119991, Russia

E-mail address: mgaly@yandex.ru

In the present work, the effective method for the synthesis of new 1,7-bis[chloro(organo)siloxanylmethyl]-*m*-carboranes from bis(brommagnesium methyl)-*m*-carborane and chloro(organo)siloxanes: 1,7-bis[chloro-1,1,3,3-tetramethyl-disiloxanylmethyl]-*m*-carborane (**I**), 1,7-bis[chloro-1,1,3,3,5,5-hexamethyl-trisiloxanylmethyl]-*m*-carborane (**VII**) and 1,7-bis[chloro-1,1,3,3,5,5,7,7-octamethyltetrasiloxanylmethyl]-*m*-carborane (**XIII**) with yields up to 85% was developed.

The use in the reaction of other (organo)siloxanes with different radicals at silicon atoms allowed to obtain the corresponding chloro(organo)siloxanes:

1,7-bis[chlorotetraorgano-disiloxanylmethyl]-*m*-carboranes (**II-VI**), 1,7-bis[chlorohexaorgano-trisiloxanylmethyl]-*m*-carboranes (**VIII-XII**) and 1,7-bis[chlorooctaorgano-tetrasiloxanylmethyl]-*m*-carboranes (**XIV-XVIII**) with yields up to 85% and expand the range of new promising products that are well soluble in organic solvents.



where $m = 1$, $R = \text{Me}$ (**I**), Ph (**II**), $-\text{CH}_2\text{Ph}$ (**III**), $\text{C}_4\text{H}_3\text{S}$ (**IV**), $-\text{CH}_2\text{CH}_2\text{CN}$ (**V**), $-\text{CH}_2\text{CH}_2\text{CF}_3$ (**VI**)

$m = 2$, $R = \text{Me}$ (**VII**), Ph (**VIII**), $-\text{CH}_2\text{Ph}$ (**IX**), $\text{C}_4\text{H}_3\text{S}$ (**X**), $-\text{CH}_2\text{CH}_2\text{CN}$ (**XI**), $-\text{CH}_2\text{CH}_2\text{CF}_3$ (**XII**)

$m = 3$, $R = \text{Me}$ (**XIII**), Ph (**XIV**), $-\text{CH}_2\text{Ph}$ (**XV**), $\text{C}_4\text{H}_3\text{S}$ (**XVI**), $-\text{CH}_2\text{CH}_2\text{CN}$ (**XVII**), $-\text{CH}_2\text{CH}_2\text{CF}_3$ (**XVIII**)

This research did not receive any specific grant from funding agencies in the public, commercial or not-for-profit sectors.

P-52

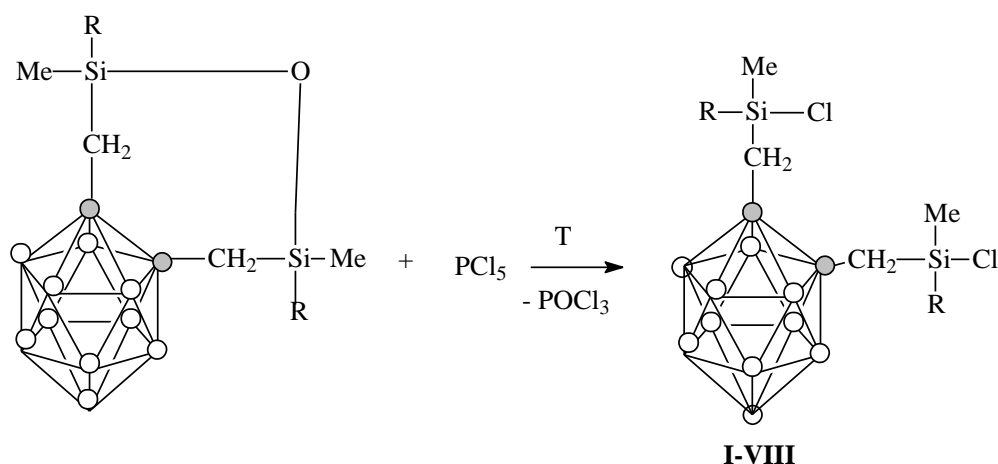
**Novel 1,2-bis[chloromethyl](organo)-silylmethyl]-*o*-carboranes.
Effective method of synthesis from exocyclic seven-membered
o-carboranymethyl-containing organosiloxanes.**

Izmaylov B.A., Vasnev V.A., Markova G.D.

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., Moscow, 119991, Russia

E-mail address: mgaly@yandex.ru

One of the main monomers used for the preparation of high thermostable carboranymethyl-containing oligomers and polymers of organosiloxane- and organosilazane structure is 1,2-bis[chloro-dimethylsilylmethyl]-*o*-carborane, which we obtained earlier with a yield up to 60% [1,2]. Presently we have developed a new, original and more efficient method for the preparation of 1,2-bis[chloro(dimethyl)silylmethyl]-*o*-carborane (**I**), as well as other, no less interesting and promising 1,2-bis[chloro(methyl)(organo) -silylmethyl]-*o*-carboranes (**II-VIII**) with phenyl, benzyl, tienyl, β -cyanethyl, γ -trifluoropropyl, vinyl and allyl radicals at silicon atom by the reaction of 1,2- (*o*-carborano)-4,6-bis[(methyl (organo) -silyl]-5-oxa-cycloheptanes with phosphorus trichloride with a yield up to 93%.



where R = Me(**I**), Ph (**II**), —CH₂Ph (**III**), —C₄H₃S (**IV**), —CH₂CH₂CF₃ (**VI**), —CH₂CH₂CN (**V**),
Vin. (**VII**), All (**VIII**)

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This research did not receive any specific grant from funding agencies in the public, commercial or not-for-profit sectors.

P-53

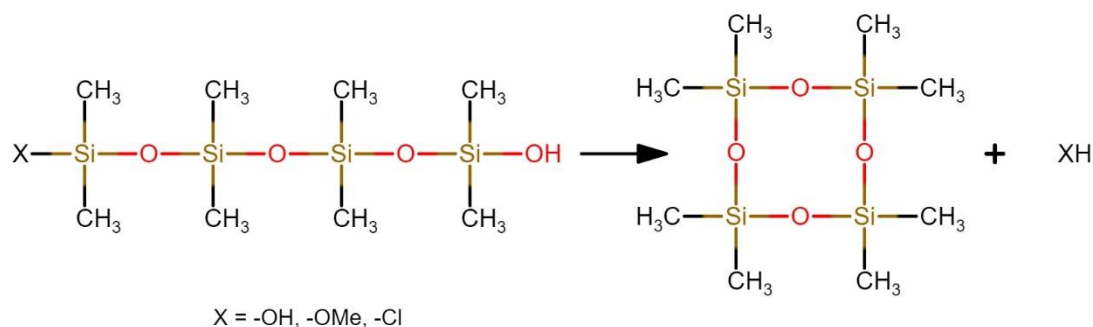
Quantum chemical modeling of oligosiloxane cyclisation

Kalinin S.A.^a, Ivanov P.V.^a, Krylov A.V.^a, Morozova T.A.^a

^a *Moscow technological university, Moscow, Russia*

E-mail: kalinin.xyma@gmail.com

In paper mechanism of intramolecular condensation of siloxanes, such as 1,7-dihydroxy-1,1,3,3,5,5,7,7-octamethyltetrasiloxane, 1-hydroxy-1,1,3,3,5,5,7,7-methoxytetrasiloxane and 1-hydroxy-1,1,3,3,5,5,7,7-octamethyl-7-chlorotetrasiloxane, are investigated. Authors have choose the approximation method, have determined the oligosiloxanes structures and have investigated effect of leaving group nature and solvent molecule on reaction mechanism.



Scheme 1. Scheme of reaction

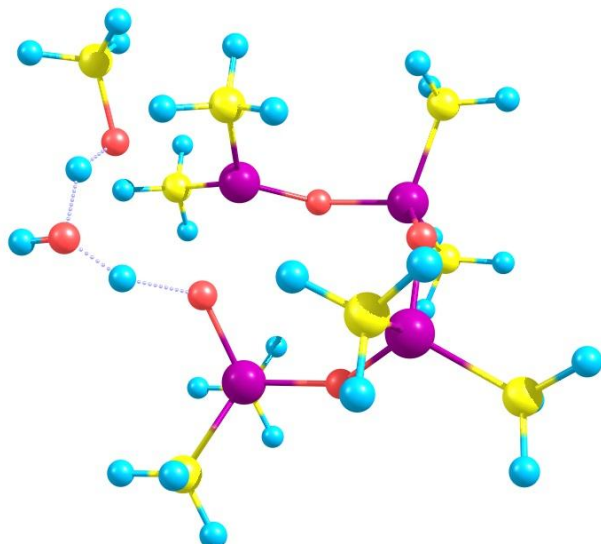


Fig. 1. Transition state structure

P-54

Comparative Analysis of Oligoorganohydrosiloxane Production Methods

Karpenkov E.I.^{a,b}, Mazaeva V.G.^b, Chistyakov E.M.^a, Prokhortsev V.V.^b, Demchenko A.I.^b
^a *D.Mendeleev University of Chemical Technology of Russia*
^b ¹ *State Scientific Center of the Russian Federation "State Research Institute for Chemistry and Technology of Organoelement Compounds", Moscow*
E-mail: fragraund@yandex.ru

Oligoorganohydrosiloxanes have found wide application in many branches of the national economy. For example, in the textile industry, they are used as waterproofing finishing agents [1], in composite materials they often act as cross-linking agents [2]. Hydrosiloxane are most widely used as precursors for the production of various carbofunctional compounds [3].

One of the challenges in the synthesis of this subclass of substances is the lability of hydridesilyl bond to acids and bases used as catalytic systems. Therefore, the search for optimal methods and development of new ones for the preparation of oligoorganohydrosiloxanes are still relevant objectives.

We have compared such methods as equilibrium cation copolymerization, hydrolysis of chlorosilanes and acidohydrolytic co-condensation of ethoxysilanes in our study. The target value of the active hydrogen in the co-oligomer was 0.8 wt %. The data obtained during the study are presented in the table 1.

Table 1. Comparative characteristics of the methods.

Method	SiH [*] losses, %	D ^H units content, %	Active hydrogen **, wt %	Yield, %
Equilibrium cation copolymerization	0.42	51.9	0.83	88
Hydrolysis of chlorosilanes	0.39	56.9	0.88	61
Acidohydrolytic co-condensation of ethoxysilanes	10 ^{***}	46.7	–	30

* – is determined by ²⁹Si NMR spectrum

** – is determined by Chugaev-Zerevitinov method

*** – is calculated without taking into account the produced gel.

The highest yield of the product and the content of active hydrogen closest to the target value is due to the equilibrium cationic copolymerization. So, this method for obtaining hydride-containing oligomers with a given value of hydro-silyl units and their statistical distribution along the main chain of the macromolecule can be rightfully considered one of the best.

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Synergism of Lubricating Properties of Oligoorganosiloxane Solutions in Organic Media

Khatueva Zh.S., Levento I.Yu., Demchenko A.I., Natsyuk S.N.

State Scientific Center of the Russian Federation "State Research Institute for Chemistry and Technology of Organoelement Compounds", Moscow

E-mail: zhamyana@mail.ru

Extensive use of oligoorganosiloxanes is based on the properties of these fluids, namely: a wide range of operating temperatures (-130 °C to 350 °C), low dependence of viscosity versus temperature, low saturated vapor pressure, low surface tension, chemical inertness, low toxicity, poor flammability, high compressibility.

Despite the obvious advantages oligoorganosiloxanes have limitations in their application due to low lubricity in sliding friction. The solution to this problem is the introduction of long-chain alkyl substituents at silicon, resulting in the increase of the lubricating capacity of oligoorganosiloxanes, such fluids have satisfactory temperature indexes and good compatibility with mineral and synthetic media [1].

While studying the lubricating properties of oligoorganosiloxane solutions with the addition of organic liquids in concentrations of 10 to 90 wt %, a synergism of lubricating properties was noted (fig. 1, 2).

This effect is to improve the lubricating properties of the mixture as compared to pure components. It is noted that when 10 wt % of dioctyl sebacate (DOS)/petroleum oil I-20 are added, the lubricating properties deteriorate sharply, and with a further increase in concentration, the diameter of the wear spot decreases.

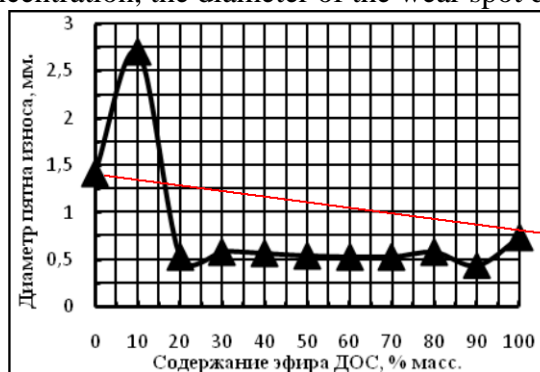


Fig. 1. Dependence of wear spot diameter of oligomethyloctylsiloxane fluid – DOS ether composition on DOS concentration.

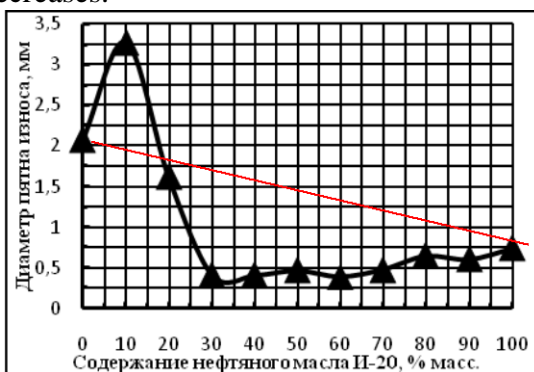


Fig. 2. Dependence of wear spot diameter of oligodiethylsiloxane fluid (132-24) – industrial oil И-20 composition on И-20 oil concentration.

The phenomenon of synergism of the lubricating properties of oligoorganosiloxanes with organic media can be explained by the formation as a result of thermomechanical decomposition, of a surface layer saturated with silicon with increased hardness and covered with a soft oxide layer or a layer of compounds of a different composition, which reduces friction and improves lubricity.

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P-56

Molecular dynamics simulations of single siloxane dendrimers: Molecular structure and intramolecular mobility

Kurbatov A.O.^a, Balabaev N. K.^b, Mazo M. A.^c, Kramarenko E. Yu.^a

^aFaculty of Physics, Lomonosov Moscow State University, Moscow 119991, Russia

^bInstitute of Mathematical Problems of Biology, Keldysh Institute of Applied Mathematics RAS, Pushchino, Moscow Region 142290, Russia

^cSemenov Institute of Chemical Physics RAS, Moscow 119991, Russia

E-mail: kurbatov@polly.phys.msu.ru

Molecular dynamics simulations of two types of isolated siloxane dendrimers of various generations (from the 2nd to the 8th) have been performed for temperatures ranging from 150 K to 600 K. The first type of dendrimer molecules has short spacers consisting of a single oxygen atom (Fig.1 (a)). In the dendrimers of the second type, spacers are longer and comprised of two oxygen atoms separated by a single silicon atom (Fig.1 (b)).

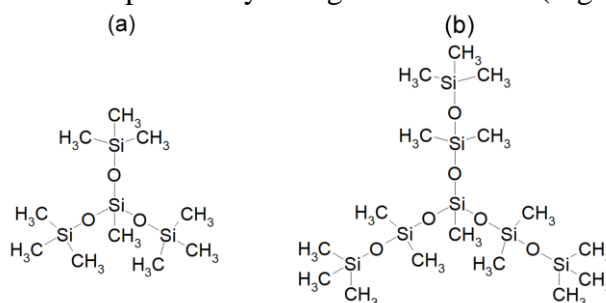


Fig. 1. Molecular structure of the first generation siloxane dendrimers with short (a) and longer (b) spacers.

A comparative analysis of molecular macroscopic parameters such as the gyration radius and the shape factor as well as atom distributions within dendrimer interior has been performed for varying generation number, temperature, and spacer length. It has been found that the short-spacer dendrimers of the 7th and 8th generations have a stressed central part with elongated bonds and deformed valence angles. Investigation of the time evolution of radial displacements of the terminal Si atoms has shown that a fraction of the Si groups have a reduced mobility. Therefore, rather longtime trajectories (of the order of tens of nanoseconds) for two temperatures (300 K and 600 K) are required for dendrimers from the 4th to the 7th generations to study dendrimer intramolecular dynamics. The radial and angular motion of Si atoms inside each dendron was studied. The distributions of the characteristic relaxation times, obtained from the autocorrelation functions of each type of motion for each Si atom, were constructed. The boundaries of each type of mobility were estimated. It was shown that dendrons are stretched and tapered with increasing generation.

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P-57

Hydrosilylation of Squalene

Lakhtin V.G.^a, Sokol'skaya I.B.^a, Ofitserov E.N.^b, Efimenko D.A.^a,
Kalistratova A.V.^b, Ushakov N.V.^c, Storozhenko P.A.^a

^a State Scientific Center of the Russian Federation "State Research Institute for Chemistry and Technology of Organoelement Compounds", Moscow

E-mail: vlakhtin@rambler.ru

^b D.Mendeleev University of Chemical Technology of Russia, Moscow

E-mail: ofitser@mail.ru

^c A.V.Topchiev Institute of Petrochemical Synthesis of RAS, Moscow

E-mail: ushakov@ips.ac.ru

Squalene as a natural alicyclic triterpene is a biologically active compound with a variety of useful therapeutic and cosmetic properties. The presence of squalene in human skin distinguishes it from all mammals. One of the key functions of squalene in the body of mammals, plants, bacteria and fungi is its participation as a key precursor in the biosynthesis of steroid compounds. In this regard, squalene derivatives are promising in terms of developing new medications to control the level of cholesterol, or for the treatment of bacterial and fungal infections.

We have made an attempt to synthesize new potentially biologically active derivatives of this compound - squalene epoxidase inhibitors. With this purpose, hydrosilylation of squalene by a number of organochlorohydrosilanes R_3SiH ($R_3 = Cl_3, MeCl_2, Me_2Ph$) and a mixture of α - and β -isomers of adducts resulting from vinyltrimethoxysilane (VTMoS) addition to tetramethyldisiloxane (TMDS): $HSi(Me_2)O(Me_2)Si-C(Me)-Si(OMe)_3$ and $HSi(Me_2)O(Me_2)Si-(CH_2)_2-Si(OMe)_3$ was performed.

It is found that hydrosilanes with chlorine atoms at silicon are not active in this reaction, and Me_2PhSiH is added to squalene with a low yield. The most active reagent in this reaction is a mixture of α - and β -isomers of $HSi(Me_2)O(Me_2)Si-C(Me)-Si(OMe)_3$ and $HSi(Me_2)O(Me_2)Si-(CH_2)_2-Si(OMe)_3$ adducts. The spectral characteristics of the adducts of the reaction of VTMoS with TMDS ($\alpha + \beta$ product) were specified. For the first time NMR signals on the 1H , ^{13}C , ^{29}Si nuclei of the mixture of $\alpha + \beta$ -isomers were completely identified.

The obtained results allowed drawing the following conclusions:

- The size of substituents at silicon in the addition reactions with respect to multiple bonds of squalene is not a determining factor in the reactions under study.
- ~70% of the adducts of the α - and β -isomers mixture enter into the addition reaction to squalene.
- The portion of the attached β -isomers proved to be primary - three times as much as the α -isomers, although in the pre-reaction mixture this ratio was 2: 1, which apparently means that they have less stereochemical hindrance in this reaction.
- Addition to squalene proceeds both according to Markovnikov's rule and against it, almost equally.

P-58

**NEW PHARMACOLOGICALLY ACTIVE GLYCEROHYDROGELS
BASED ON BIOGENIC ELEMENT GLYCEROLATES,
BIOCOMPATIBLE PRECURSORS IN SOL-GEL PROCESSING**

Permikin V.V.^a, Vlasova A.V.^b, Lokk E.I.^b, Khonina T.G.^a, Chupakhin O.N.^{a,b}

^a *Postovsky Institute of Organic Synthesis of Russian Academy of Sciences (Ural Branch), Ekaterinburg, Russia*

^b *Institute of Chemical Engineering, Ural Federal University, Ekaterinburg, Russia*

E-mail: vasilij_permikin@mail.ru

Earlier we developed methodological approaches to the synthesis of biologically active hydrogels for medical purposes. The approaches consist in using biogenic elements (mainly silicon) polyolates as precursors in sol-gel processing in the solution of the corresponding polyol approved for medical use, in using combined element containing polyolates to achieve synergistic pharmacological action and/or of methyl substituted silicon polyolates to increase the pharmacological activity, as well as in using bioactive additives or drugs as templates and modifiers of formed hydrogel properties.

In this work these approaches received further theoretical and experimental development, namely:

- variation of the synthesis conditions (pH, the molar ratio of precursor / polyol / water, and the use of gellating additives) will provide hydrogels with the controlled structure (colloidal or polymeric) and the optimal concentration of active components, element-containing glycerol derivatives in bio accessible form.
- pharmacologically active gels can be used to deliver the drugs to the affected tissues, including both immediate and sustained delivery as well as controlled release and targeted delivery

Based on the approaches developed, a number of novel pharmacologically active element-containing hydrogels based on silicon, titanium, zinc, boron, and iron glycerolates promising for the creation of medicinal agents for topical application in soft, liquid, and solid dosage forms was synthesized [1–4].

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P-59

The synthesis of new organosilicon monomers and polymers with several types of functional groups in the molecule

Kseniya A. Podolskaya^{a,b}, Elizaveta V. Selezneva^{a,b}, Sergey A. Milenin^a, Aziz M. Muzafarov^a
a Enicolopov Institute of Synthetic Polymeric Materials, Profsoyuznaya street, 117393 Moscow, Russia

b Moscow Technological University (Fine Chemical Technologies Institute), Vernadsky Avenue, 119454 Moscow, Russia

Recently, rapid development of high-tech nanobiomedicine and biotechnology, as well as surface engineering, membrane technologies and environmentally friendly production was observed. That's why it is very interesting to obtain various polyfunctional polymer materials, in particular based on polydimethylsiloxanes, which have unique properties, such as: wide temperature range of application, resistance to atmospheric and ozone impact, resistance to aging, good electrical insulation properties and biocompatibility, and also the ability to easy functionalization, which not only determines their properties, but also extends the scope of their application [1-3].

In this work, it is planned to develop a universal method for the preparation of PDMS with different functional groups, capable of independently entering into chemical interaction with the corresponding functional groups, easily modifiable, differing in the structure and mutual arrangement of functional groups, as well as having different molecular mass characteristics.

We studied the process of obtaining of 3-azidopropylmethyldimethoxysilane, its hydrolytic polycondensation and copolymerization of the products of hydrolysis with octamethylcyclotetrasiloxane (D4) to obtain copolymers containing from 5 to 20 % 3-azidopropylmethysiloxane units, and also without D4 to obtain polymer containing 100 % of 3-azidopropylmethysiloxane units. Also we studied the copolycondensation of chloropropyl- and vinylalkoxysilanes in the presence of a tetramethylammonium siloxanolate catalyst.

The structures of the obtained products were confirmed by ¹H NMR spectroscopy and gel-permeation chromatography. We also investigated their solubility.

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P-60

**INVESTIGATION OF HYDROLITIC POLYCONDENSATION OF
TITANIUM CHEMICAL COMPLEXES WITH
DIORGANODICHLORSILANES
IN THE ACETONE-CARBAMIDE SYSTEM**

Polshchikova N.V.^a, Bokova K.V.^b, Trankina E.S.^a, Kononova E.G.^a, Tokazova R.U.^a, Zavin B.G.^a
^a *FGBUN Institute of Organoelement Compounds (INEOS RAS), Moscow, Russia*

^b *Moscow Technology University, Moscow, Russia*

E-mail: cherkun4ik@gmail.com

Recently, there has been growing interest in new alternative methods of hydrolytic polycondensation (HPC) in homogeneous "non-aqueous" media [1-3]. In contrast uncontrolled water-dispersion processes, in these methods the water required for hydrolysis is generated during the reaction at intermediate stages of the process. Thus, in the system ketone-carbamide-chlorosilane, water is formed by condensation of ketone (acetone, acetylacetone) and carbamide in the presence of acid (organochlorosilane) [2, 3]. The reactions running in such systems are the "paired": hydrolysis of chlorosilane provides the condensation of ketone and carbamide with the release of water, which, in turn, participate in hydrolyze process of chlorosilane. Moreover, the number of HCl and H₂O molecules is determined by the ratio of the initial reagents in these systems. And this in turn determines the formation of cyclic or linear type of oligoorganosiloxanes obtained. These processes offer a wide range of possibilities for controlling the condensation reactions not only chlorosilanes, but also other compounds, including organometallic monomers, that cannot be obtained by common hydrolytic polycondensation.

Now, carrying out condensation in such mediums with the use of chlorosilanes and titanorganic monomers is of considerable interest.

In the present study, we investigated the hydrolytic co-polycondensation of chelate complexes of titanium with diorganodichlorosilanes, in particular methylphenyldichlorosilane and bis(acetylacetonate)dichlorotitanium, in nonaqueous organic solvents (toluene, dioxane, acetone). The water necessary for hydrolysis was obtained in situ by interaction of carbamide (CA) with acetone (AC). The ratio of the initial reagents MePhSiCl₂: TiCl₂(acac)₂:CA:AC ranged widely from 5:1:24:12 to 5:1:72:108. Colored viscous liquid, which is titanosiloxanes with

MM=2000÷6000 a.u., was obtained as a result.

The composition, structure and molecular mass characteristics of the resulting products were analyzed by various physical methods - GPC, GLC, ¹H- and ²⁹Si- NMR and IR-spectroscopy and elemental analysis.

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P-61

New Poly(arylene-thiophenes)

Elena N. Rodlovskaya, Valerii A. Vasnev

*Nesmeyanov Institute of Organoelement Compounds,
119991 Russia, Moscow, Vavilov st., 28*

E-mail: rodlovskaya@mail.ru

Development of fundamental principles for the synthesis of new monomers and polymers, for the production of ordered organo-hybrid assemblies, based on thiophene and ferrocene derivatives [1]. Interest in such derivatives is due to the fact that thiophene including polythiophene are π -conjugated photo- and electrically conductive compounds, and ferrocene besides the structural features of the molecule, has one of the low oxidation potentials. Moreover, the oxidation of its molecule is not destructive, but is associated only with a change in the valence of the iron entering into its composition, that is, Fe (2+) is oxidized to Fe (3+), which causes specific electrophysical properties. Thus, the photovoltaic, paramagnetic, and nonlinear optical properties of the new thiophene and ferrocene derivatives of low-molecular compounds and polymers will be studied.

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This work was supported by the Russian Foundation for Basic Research (project no. 18-03-00892).

P-62

Synthesis of Organoalumoxanes Modified by Mg and Si Compounds

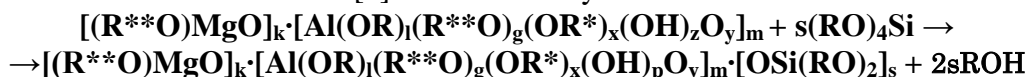
G.I. Shcherbakova^a, A.S. Pokhorenko^b

^a State Scientific Center of the Russian Federation "State Research Institute for Chemistry and Technology of Organoelement Compounds" (SSC RF "GNIChTEOS")

^b Federal State Budgetary Educational Institution of Higher Education Moscow Technological University (MITHT)

E-mail: galina7479@mail.ru

We have studied the interaction of foreceramic organomagnesiumoxanealumoxanes that were first synthesized at GNIChTEOS [1] and tetraethoxysilane. General reaction time:



where R – C₂H₅; R* – C(CH₃)=CHC(O)OC₂H₅; R** – C(CH₃)=CHC(O)CH₃

The optimum conditions for the synthesis of organoalumoxanes modified with magnesium and silicon compounds have been determined. Physicochemical properties of the prepared organomagnesiumoxanealumoxanesiloxane oligomers were analyzed by ¹H, ¹³C, ²⁷Al, ²⁹Si NMR, IR, SEM with EDS (Fig. 1), TGA and elemental analysis.

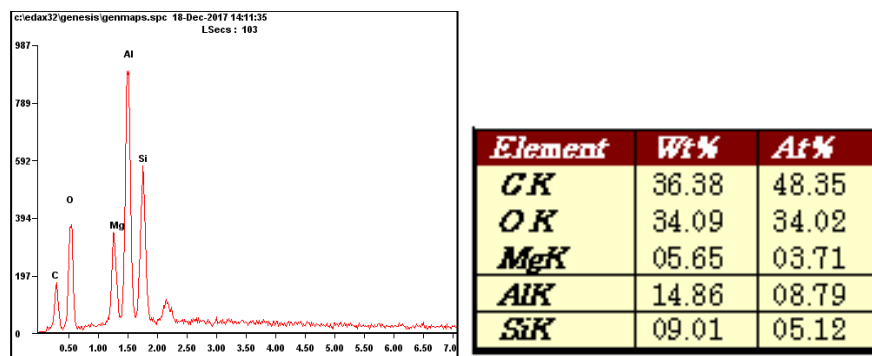


Fig. 1. X-ray elemental microanalysis

Foreceramic organomagnesiumoxanealumoxanesiloxane oligomers can be employed as precursors of the components of high-purity ceramics based on magnesium, aluminum and silicon oxides.

Oxide systems of xMgO–yAl₂O₃–zSiO₂ have low dielectric losses and a low coefficient of thermal conductivity, and therefore they are used as high-frequency, radioelectronic, electroinsulating materials, as well as in the processes accompanied by a temperature differential [2].

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P-63

Investigation of polymethylsilsesquioxanes by methods of viscometry and size exclusion chromatography with light-scattering detector

N.L. Shikut^a, F.V. Drozdov^a, I.B. Meshkov^a, A.M. Muzafarov^b

^a N.S. Enikolopov Institute of synthetic polymeric materials, Russian Academy of Science, Profsoyuznaya st. 70, 117393, Moscow, Russia

^b A.N. Nesmeyanov Institute of Organoelement, Russian Academy of Science, Vavilova st. 28, 119991, Moscow, Russia

E-mail: nshikut@yandex.ru

Gel-permeating chromatography (GPC), as a case of size-exclusion chromatography, is one of most universal and express method for measurement of polymers' molecular weights. Their disadvantage is the necessity of calibration according to polymer standards, which have well-defined molecular weight and narrow weight distribution. Nowadays, one of the most convenient for GPC calibration standards, which widely used also for investigation of silicon-based linear polymers, are polystyrene standards. However, molecular weights of branching silicon polymers, which were determined by GPC with polystyrene standards and other methods, often are not in strong correlation to different polymer's nature. In present work, we propose to use polymethylsilsesquioxane (PMSQ) to produce a new GPC universal standard for silicone branching silicon polymers and dendrimers.

Fractions of PMSQ with narrow weight distribution were obtained by preparative GPC from earlier synthesized PMSQ.

The characteristic viscosity $[\eta]$ was determined by viscometry. The dependence of reduced viscosity on concentration was plotted, hydrodynamic radii for each case were calculated by using the Einstein equation for viscosity of solid spheres. Diffusion coefficients D of every fraction were calculated according to data of GPC with light-scattering detector. Using obtained results, we defined the hydrodynamic radii of PMSQ by Stokes-Einstein equation.

Summarized all the results, we calculated molecular weights for each PMSQ fraction. The dependence of molecular weight on retention time was plotted. The applicability of obtained calibration for analysis of silicon dendrimers is shown.

P-64

Study of Operating Conditions Influence on the Properties of Abrasion-Resistant Coatings Based on Organosilicon Composition and Designed for Heatproof Organic Glazing

P.A. Storozhenko, A.N. Polivanov, T.I. Fedotova, A.V. Levchuk, V.A. Vlasova,
K.E. Smirnova*

SSC RF JSC GNIChTEOS

*e-mail: fedotova@eos.su

We have synthesized samples of organosilicon composition for the preparation of abrasion-resistant coating on the polycarbonate sheets designed for heatproof organic glazing. The samples were prepared by sol gel method on the basis of alkoxo technology.

The organosilicon composition samples were applied on the polycarbonate samples, sheets of 100 * 100 * 3 mm size, by unilateral pouring method, and then cured in a heat chamber at a temperature of 125 - 130⁰C.

Test results of the produced abrasion-resistant coatings are presented in the table:

Table

Sample No, viscosity mm ² /s	No 1, 5.3 mm ² /s	No 2, 12.6 mm ² /s	PC without coating
Adhesion according to GOST 15140-78, item 4, score	1	1	-
Abrasive resistance, cotton-wool No 00	Is not chafed	Is not chafed	Is chafed, hazy
Pencil hardness, H (Elcometer 3086, load 7.5H)	4	4	F
Heat- and moisture resistance (t- +60 ⁰ C, φ= 95% - 48 hours), frost resistance (- 40 ⁰ C for 6 hours)	Coating without any change	Coating without any change	No change
Light-resistance (UV irradiation for 100 h)	Coating without any change	Coating without any change	No change
Integral visible light transmission factor at 6 mm sample thickness, %	<u>86.9</u> 86.2-87.0	<u>86.9</u> 86.2-87.0	86
Tensile yield limit, MPa	<u>69.0</u> 68.7-69.3	<u>68.3</u> 68.3-68.3	<u>68.7</u> 68.5-68.8
Elongation at break, %	<u>136.4</u> 119.1-146.4	<u>142.7</u> 115.6-178.5	<u>139.6</u> 117.4-162.5

We are thankful to I.V. Mekalina and M.K. Aizatulina employees of FSUE VIAM for testing the samples.

P-65

Electrorheological properties of montmorillonite suspensions, modified with siloxane modifiers

D. Yu. Stolyarova^{a,b}, N.M. Kuznetsov^a, V.V. Gorodov^b, S.I. Belousov^a, M.A. Sokolov^a,
N.V. Nemanova^a, D.I. Shragin^b, A.M. Muzafarov^b, S.N. Chvalun^{a,b}

^a *NRC «Kurchatov Institute», Akademika Kurchatova pl., 1, Moscow, Russia*

^b *ISPM RAS, Profsoyuznaya st. 70, Moscow, Russia*

E-mail: stolyarova.d@gmail.com

Electrorheological (ER) fluids are smart materials that have been attracting interest of researchers in various scientific fields for over than 50 years. Common ER fluid consists of solid particles carrying charge which provide dipole-dipole interactions, and a carrier solvent – dielectric dispersion medium [1]. In the presence of external electric field particles in ER fluids form continuous structures that leads to drastic changes in the rheological properties of the material and its transition from viscous to viscoelastic fluid [2]. The appearance of the electrorheological effect in the montmorillonite-based ER fluids consisted of aluminum silicate clay particles in polydimethylsiloxane (PDMS) oil, is related to the presence of polar functional groups at the interphase interface. Owing to its high anisotropy (that is close to 500) and large surface area (800-1400 m²/g) the use of montmorillonite as a filler allows to get ER response at relatively low concentrations (1-8 wt%) of the filler. It is worth mentioning that to obtain stable ER response montmorillonite particles must have good compatibility with the dispersion medium that would also provide the sedimentation stability of suspension.

In this work PDMS oil was used as a dispersion medium, whereas a dispersed phase was presented by Na-montmorillonite, modified with quaternized PDMS. The concentration of modified filler was varied from 1 to 8 wt%. The rheological and electrorheological properties of obtained samples were studied.

It was demonstrated that in the absence of EF suspensions with the filler concentration of up to 2 wt% exhibit properties of Newtonian fluids. The further increase of the filler concentration leads to the appearance of yield stress, which value depends on the concentration of filler. In the presence of electric field ER fluid begins to demonstrate a plastic behavior. Moreover, the yield stress dramatically rises although only slight increase of the viscosity can be observed. It is further shown that ER effect in the studied samples appears only at the certain intensities of the applied electric field. The minimum intensity of electric field, at which ER effect can be observed, depends on the filler concentration. In turn, the maximum intensity, when ER effect vanishes, is determined by the value at which on electric breakdown happens (nearly 7 kV/mm). Additionally, it is established that the sedimentation stability of the modified montmorillonite suspensions depends on the dispersed phase concentration.

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P-66

**Study of the Properties of the Hydrophobic Coating Obtained with
the Use of Fluoro-organosilanes**

P.A. Storozhenko, A.N. Polivanov, T.I. Fedotova, N.V. Tyurikova*, V.G.. Lakhtin,
V.A. Vlasova, T.I. Shulyat'eva
SSC RF JSC GNIChTEOS
*e-mail: fedotova@eos.su

One of the most common methods of surface modification is its hydrophobization. As is known, organochloro(alkoxy)silanes and products of their hydrolysis are successfully used for hydrophobization of various object surfaces, including products made of silicate glass. In order to investigate in the framework of this work the possibility of increasing the contact angle of the silicate glass wetting by hydrolytic copolycondensation based on C-fluorinated organosilanes, (C₁₀-F) trichlorosilanes and trialkoxysilanes, samples of the compositions were synthesized to obtain hydrophobic coatings (samples FC №2, FC №1, respectively).

Compositions were applied on the samples of silicate glasses of 60 * 60 * 3 mm size, the coatings were examined by the following parameters:

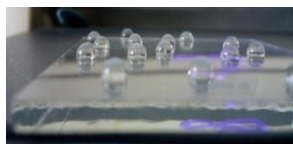
- appearance,
- light transmission coefficient, T%, within the range of 0.40-0.74 micron wave length,
- limiting wetting angle,
- dynamic dust resistance (T min = - 65⁰C, T max = +60⁰C).

Test results of the coatings based on water-repellents are presented in the table:

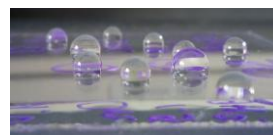
Table

Sample	Appearance of the coating	**Light transmission coefficient , T %, within the range of 0.40-0.74 micron wave length	Limiting wetting angle, C	**Dynamic dust resistance according to T min = - 65 ⁰ C, T max = +60 ⁰ C)
FC №1	Colorless , clear	91.9	111-113	Resistant without visible changes
FC №2	Colorless , clear	91.4	107-109	Nonresistant

**We are thankful to L.N. Solov'eva, an employee of SRC ORPE "Technologiya" named after A.G. Romashin for testing the samples.



FC №1



FC №2

P-67

The synthesis and research of new renewable siloxane-methylenedithiol copolymers based on limonene

Victoria V. Velikorodnaya^a, Fedor V. Drozdov^b, Georgiy V. Cherkaev^b, Nina V. Demchenko^b, Mihail I. Buzin^c, Aziz M. Muzafarov^{b,c}

^a *Moscow Technological University (Fine Chemical Technologies Institute), Vernadsky Avenue, 119454 Moscow, Russia*

^b *N.S. Enicolopov Institute of Synthetic Polymeric Materials, Profsoyuznaya street, 117393 Moscow, Russia*

^c *A. N. Nesmeyanov Institute of Organic element Compounds, Russian Academy of Sciences, 119991, Moscow, Russia*

E-mail: missviktorija61@gmail.com

Over the past twenty years, polymers obtained from renewable sources have been attracting great attention mainly for two reasons: first, because of environmental problems associated with the processing and disposal of synthetic polymers, and secondly, because of the possibility of using renewable natural compounds instead of oil resources [1-2].

In this work new biodegradable siloxane-methylenedithiol copolymers based on limonene were synthesized. Due to the introduction of the limonene, which is a biodegradable hydrocarbon of the terpenic group, to the polymeric siloxane molecule, the obtained polymers have all the properties and characteristics of siloxanes. Moreover, we presumed, that introduction of limonene's moiety renders them biodegradability.

In this work, six new copolymers as viscous liquids were produced and characterized. These copolymers were synthesized by using hydrosilylation and hydrothiylation reaction. We also studied the influence of the ratio of siloxane and methylenedithiol blocks on the physical properties of copolymers, such as viscosity, rheology, thermal and phase properties.

The obtained results showed that the viscosity and molecular weight of siloxane-methylenedithiol copolymers, linearly changes with the increasing of methylene spacer, but in the case of the copolymers, which do not contain siloxane fragments, viscosity and molecular weight were changed insignificantly.

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P-68

New Oligoboronorganosilazanes and Their High-Temperature Pyrolysis Features

A.Ya. Yakimova^a, O.G. Ryzhova^a, P.A. Storozhenko^a, P.A. Timofeev^b, A.N. Polivanov^a, I.A. Timofeev^b, M.G. Kuznetsova^b, A.I. Drachev^b, S.N. Dugin^b, E.L. Gurkova^b.

^a SSC RF GNIChTEOS, Moscow

^b JSC "Kompozit» Moscow region, Korolev city

E-mail: djiolta@mail.ru

We have studied new oligoboronorganosilazanes (OBOSs) prepared by nitrogen-containing silicon compounds (NCSC) interaction with a boron-containing modifier – amine borane (BH₃•NH₃). Organocyclosilazanes, organodisilazanes, amine silanes, oligoorganosilazanes were used as nitrogen-containing silicon compounds.

It is found that the thermal and oxidation stability of the OBOSs obtained is determined by the Si/B ratio. Thus, when the Si/B ratio is 1/3, amine borane acts both as a modifier of nitrogen-containing silicon compounds, and as a cross-linking agent of OBOSs, obtained during the modification process. The modification process is accompanied with molecular weight increase, and, as a consequence, an increase in the viscosity characteristics of the OBOS and the yield of the inorganic residue after pyrolysis up to 1100 °C in an argon atmosphere. The presence of boron in oligomethylhydridesilazane provides: an increase in the thermal stability of the OBOSs; reduction of mass loss, as well as nitrogen retaining in ceramics during heat treatment in argon up to 1500 °C.

An increase in the thermal-oxidative stability of the OBOSs is observed only when Si/B ratio ≤ 3. The TGA curves, therewith, in argon and in air in the temperature range of 0 - 1100 °C completely coincide, which indicates the absence of oxidizing processes in the OBOS within the analyzed temperature range. Moreover, the loss of mass after thermal treatment at 1800 °C decreases to 40 wt % as compared to 70 wt % typical for OBOS at Si/B ≥ 3.

It is shown that when NCSC, containing vinyl and hydride groups, interacts with amine borane at a temperature ≥ 90°C amine borane acts as a catalyst for OBOSs formation. Moreover, during the interaction, the addition of boron to vinyl group carbon atom bonded to silicon is observed. OBOSs production without vinyl groups occurs with the participation of N-H and B-H bonds. This mechanism of the reaction is confirmed by 1H NMR spectroscopy.

Quasicrystalline ceramics obtained by pyrolysis of OBOSs at a temperature of 850 °C is sequentially transformed into the ceramics of SiBCN composition during thermal treatment at temperatures of 1350, 1500 °C.

The increase of heat treatment temperature in this interval is accompanied by a gradual decrease in the content of carbon and nitrogen. The IR spectrum of the ceramics obtained after heat treatment at 1500°C contains the absorption bands of Si-C and B-N bonds typical for ceramics of silicon carbide and boron nitride, and there are no Si-N bond absorption bands typical for silicon nitride and silicon carbonitride in IR spectra.

OBOSs were studied by the following chemical analysis methods: MMD; TGA, DTA; ²⁹Si, ¹H, ¹¹B NMR spectroscopy; IR-spectroscopy. The morphology and elemental composition of silicon nitride ceramics, obtained by their pyrolysis, were investigated by X-ray phase analysis, X-ray crystallography, SEM, and X-ray microanalysis.

P-69

Полиимид-кремнийорганические композиции для термостойких покрытий и слоистых композиционных материалов

Светличный В.М.^a, Ваганов Г.В.^a, Мягкова Л.А.^a, Попова Е.Н.^a, Сапрыкина Н.Н.^a,
Елоховский В.Ю.^a, Мешков И.Б.^b, Татарина Е.А.^b, Юдин В.Е.^a

^a Федеральное государственное бюджетное учреждение науки Институт
высокомолекулярных соединений РАН, Санкт-Петербург

^b Федеральное государственное бюджетное учреждение РАН Институт
синтетических полимерных материалов им. Н.С. Ениколопова, Москва

E-mail: e-mail: mila_myagkova@mail.ru

e-mail: valsvet@hq.macro.ru

Синтезированы гибридные полиимид-кремнийорганические полимерные композиты на основе полиимида (ПМ-ОДА) - продукт поликонденсации диангирида пиромеллитовой кислоты (ПМ) и 4,4'-оксианилина (ОДА), а также полиимида (ИДА) - продукт поликонденсации диангирида 3,3',4,4' -дифенилоксидтетракарбоновой кислоты и бис(4-ацетамидо)дифенилоксида и модифицированных MQ-смола. На основе полиимида ПМ-ОДА 8 модифицированных MQ-смола (непленкообразующих кремнийорганических сополимеров) были получены самонесущие гибридные пленочные образцы при содержании в композиции от 40 до 60 мас.% кремнийорганического компонента. Пленки обладают высокими физико-механическими и термическими показателями: E до 1,76 ГПа, σ_p до 99 МПа, ϵ_p до 71%, T_c до 398 °C. Синтезированные композиты демонстрируют предельно высокую термостойкость (τ_5) в инертной среде и на воздухе до 587 °C и 572 °C, соответственно.

Разработаны гибридные полиимид-кремнийорганические связующие при использовании полиимида ИДА и полифенилсилоксанов, на основе которых были приготовлены слоистые композиционные материалы - углепластики и стеклопластики. Изучение свойств композиционных материалов показало, что введение полифенилсилоксанов в связующее ИДА приводит к получению материалов, обладающих высоким уровнем межслоевой вязкости разрушения, прочности при изгибе и модуля упругости.

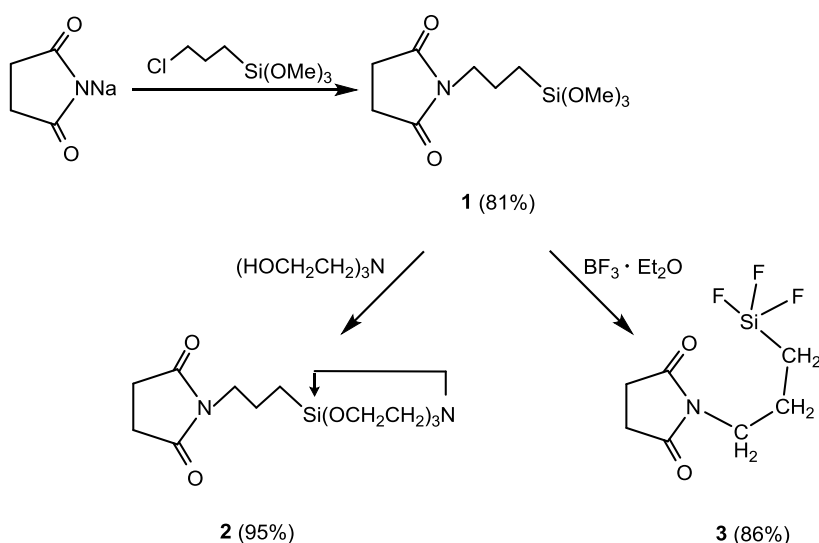
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New organosilicon derivatives of pyrrolidine-2,5-dione

Bolgova Yu., Grebneva E., Trofimova O., Borodina T., Albanov A., Smirnov V.
A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of
Sciences, 1 Favorsky Str., Irkutsk, 664033, Russia
E-mail: omtrof1@irioch.irk.ru

A series of new tetra- and pentacoordinate organosilicon derivatives of pyrrolidine-2,5-dione (**1-3**) has been synthesized.



The composition and structures of the synthesized compounds **1-3** were confirmed by elemental analysis, IR and NMR spectroscopy and mass spectrometry. The X-ray crystal analysis of 1-[3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undec-1-yl)propyl]pyrrolidine-2,5-dione (**2**) shows a distorted trigonal-bipyramidal coordination at silicon.

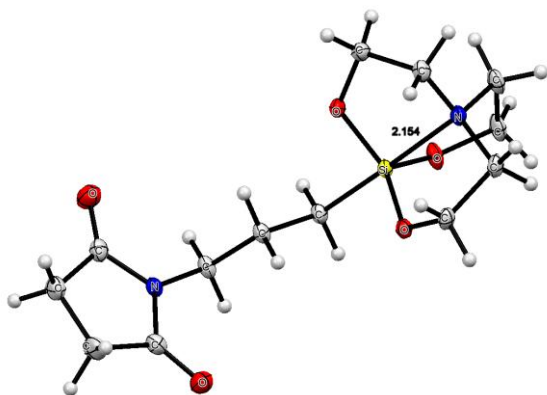


Fig. 1. Molecular structure of **2**

According to the PASS program, compounds **1-3** possess potential antineoplastic activity and can be promising of phobic disorders treatment.

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**Functionalization of 2-mercaptobenzothiazole
with iodomethyl derivatives of silanes**

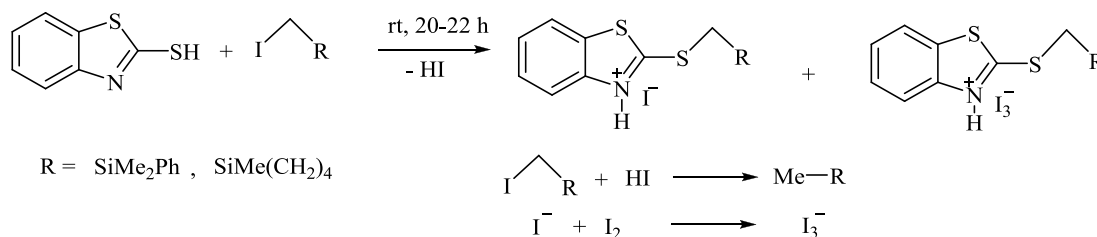
Yarosh N.O., Zhilitskaya L.V., Shagun L.G., Dorofeev I.A.

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk,

Russian Federation. Fax: +7 3952 419 346; E-mail: yarosh.nina@irioch.irk.ru

Bicyclic molecules, containing two heteroatoms, as a rule, have several types of biological activity of a wide pharmacological spectrum of the action [1]. In industry, their derivatives are used in the leather and rubber industries to produce automobile tires, rubber threads and footwears. Despite a large number of studies in this field, organosilicon derivatives of 2-mercaptobenzothiazole remain poorly understood. Such compounds are of interest primarily due to their potential ability to give industrial products elasticity, strength, chemical inertness and biocompatibility [2].

We have firstly studied the reaction of 2-mercaptobenzothiazole with iodomethylsilanes containing exocyclic and endocyclic silicon atoms [(iodomethyl)(dimethyl)phenylsilane and 1-iodomethyl-1-methylsilolane in the molecule.



When the reaction temperature is increased up to 90°C, its running time is decreased 3 times, however, under these conditions in case iodomethyl(dimethyl)phenylsilane partial splitting of the Si-C_{sp}² bond occurs in the targeted products under the action of the selected hydrogen iodide. The iodosilane formed in this case easily is hydrolyzed in the course of its isolation, forming diiodide bis(benzothiazolylthiomethyl(dimethyl)silyl)siloxane.

The by-products of the reaction in the presence of iodine were polyiodides 1,2-(benzothiazol-2-yl)-1,2-bis[(dimethyl(phenyl)silyl)methyl]- and 1,2-di(1,3-benzothiazol-2-yl)-1,2-bis[(1-methyl-lanil)methyl]disulfonium. Their yield is increased by counter synthesis from bis(benzothiazolyl)disulfide and iodomethylsilanes in the presence of a two-molar amount of elemental iodine. Organosilicon polyiodides are the first representatives of stable organosilicon disulfonium-dications, which can be used as electrophilic reagents to obtain various classes of elementorganic compounds in reactions with C-nucleophiles.

References

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