9th International Workshop on Silicon-based Polymers

ISPO-2013

Moscow,
September 22-25, 2013
Workshop Chair

Aziz M. Muzafarov

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ISPO-2013 PROGRAM
### Sunday, Sept 22

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<th>Time</th>
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<tr>
<td>16:00 – 19:00</td>
<td>Registration</td>
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<td>Welcome reception</td>
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<td>/INEOS RAS: ul. Vavilova 28, Moscow/</td>
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### Monday, Sept 23

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<thead>
<tr>
<th>Time</th>
<th>Event</th>
<th>Authors/Institutions</th>
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<tbody>
<tr>
<td>09:30 – 09:50</td>
<td>Opening Ceremony</td>
<td>Aziz M. Muzafarov, Vladimir S. Papkov, Michael P. Egorov INEOS RAS, Russia</td>
</tr>
<tr>
<td>09:50 – 10:25</td>
<td>New approach to synthesis of functionalized polysiloxane microspheres</td>
<td>Julian Chojnowski, Witold Fortuniak, Stanislaw Slomkowski, Piotr Pospiech, Jan Kurjata, Urszula Mizerska Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Poland</td>
</tr>
<tr>
<td>10:25 – 11:00</td>
<td>Structured Silicones: Assembly Through Physical and Click Linkages</td>
<td>Michael A. Brook, John B. Grande, Laura Dodge, Amanda S. Fawcett McMaster University, Canada</td>
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<tr>
<td>11:00 – 11:30</td>
<td>Coffee-break</td>
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<tr>
<td>12:05 – 12:35</td>
<td>Glassy siloxane-containing polynorbornenes – novel materials for hydrocarbon membrane separation</td>
<td>Maria Leonidovna Gringolts¹, Maksim Vladimirovich Bermeshev¹, Alexandr Vladimirovich Syromolotov¹, Ljudmila Erikovna Starannikova¹, Valentin Georgievich Lakhtin², Eugene Shmerovich Finkelshtein¹, Yurii Pavlovich Yampolskii¹ ¹A.V. Topchiev Institute of Petrochemical Synthesis RAS, Russian Federation; ²State Scientific Center of the Russian Federation “State Research Institute for Chemistry and Technology of Organoelement Compounds”</td>
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<tr>
<td>12:35 – 14:00</td>
<td>Lunch</td>
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<td>14:00 – 14:35</td>
<td>Silicon-based magnetic elastomers with giant magnetic response</td>
<td>G.V. Stepanov¹, V.S. Molchanov², A.S. Semisalova², N.S. Perov², Elena</td>
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Tuesday, Sept 24

**Chair: Michael A. Brook**

<p>| Time       | Session | Title                                                                 | Authors                                                                                           | Institutions                                                                                   |
|------------|---------|----------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| 09:30 – 10:05 | I-6     | 1D- 2D- and 3D-Coordination Polymers Containing Organosilicon Linkers | Paul D. Lickiss, Rob P. Davies, Karen Robertson, Andrew J. P. White                               | Imperial College, United Kingdom                                                              |
| 10:05 – 10:40 | I-7     | Functional polysiloxanes and nano-devices                            | Wlodzimierz Andrzej Stanczyk, Krzysztof Jasek, Tomasz Ganicz, Jan Kurjata, Tomasz Makowski, Adam Tracz | 1Department of Engineering of Polymer Materials, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Poland; 2Military Academy of Technology; 3Department of Physics, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences |
| 10:40 – 11:10 | Coffee-break |                                                                      |                                                                                                   |                                                                                                 |</p>
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<th>Time</th>
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<tr>
<td>11:45 – 12:05</td>
<td>O-4</td>
<td>New composites based on highly gas permeable addition poly(3-</td>
<td>Maxim Vladimirovich Bermeshev¹, Ludmila Starannikova¹, Pavel</td>
<td>A.V. Topchiev Institute of Petrochemical Synthesis RAS, Russian Federation; Semenov Institute of Chemical Physics RAS; Mendeleyev University of Chemical Technology of Russia</td>
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<td>trimethylsilyltricyclononene-7) and substituted calixarenes</td>
<td>Chapala¹, Viktor Shantarovich², Nataliya Gavrilova³, Yuriii</td>
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<td>Yampolskii¹, Eugene Finkelshtein¹</td>
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<td>12:05 – 12:25</td>
<td>O-5</td>
<td>An efficient route for synthesis of ethoxysilanes and processes</td>
<td>Jan Kurjata, Krystyna Rozga-Wijas, Wlodzimierz Stanczyk</td>
<td>Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Poland</td>
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<td></td>
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<td>occurring on condensation of methyltriethoxysilane in aqueous</td>
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<td>12:25 – 14:00</td>
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<td>R. Schmidt</td>
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<td>and Alcohols</td>
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<td>permeable 1,2-disubstituted polyacetylenes</td>
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<td>15:15 – 15:35</td>
<td>O-8</td>
<td>Self-assembled oligothiophenesilanes for monolayer organic</td>
<td>Elena V. Agina¹, Alexey S. Sizov¹², Daniil A. Anisimov¹², Oleg V.</td>
<td>ISPM RAS, Russian Federation; MSU, Russian Federation</td>
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<td>electronics</td>
<td>Borschchev¹, Maxim A. Shcherbina¹, Artem V. Bakirov¹, Dmitry Yu.</td>
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<td>Paraschuk², Sergey N. Chvalun⁴, Sergey A. Ponomarenko¹</td>
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<tr>
<td>15:35 – 15:55</td>
<td>O-9</td>
<td>Model Silicone Contact Lenses as Drug Delivery Devices to Ocular</td>
<td>Frances Jacqueline Rosemary Lasowski, Genevieve Conant, Heather</td>
<td>McMaster University, Canada</td>
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<tr>
<td>15:55 – 16:25</td>
<td>Coffee-break</td>
<td><em>Chair: Richard Weidner</em></td>
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<tr>
<td>16:25 – 16:45</td>
<td>O-10</td>
<td>The carbodiimide sol-gel process - recent advances in synthesis, structures and understanding of a sol-gel route to non-oxide materials</td>
<td>Edwin Kroke</td>
<td>TU Bergakademie Freiberg, Germany</td>
</tr>
<tr>
<td>16:45 – 17:05</td>
<td>O-11</td>
<td>Metal-Free Click Assembly of Amphiphilic Silicone Architectures</td>
<td>Talena Rambarran, Ferdinand Gonzaga, Michael A. Brook</td>
<td>McMaster University, Canada</td>
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<tr>
<td>17:25 – 17:45</td>
<td>O-13</td>
<td>Rhodium catalysts supported on polysiloxanes for hydrosilylation</td>
<td>Marek Jaroslav Cypryk(^1), Piotr Pospiech(^1), Krzysztof Strzelec(^2)</td>
<td>1^Center of Molecular and Macromolecular Studies, Poland; 2^Technical University of Lodz</td>
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<tr>
<td>17:45 – 18:05</td>
<td>O-14</td>
<td>Synthesis and ionic conductivity of siloxane based polymer electrolytes with pendant propyl acetoacetate pendant groups</td>
<td>Jimi Nikoloz Aneli(^1), Omari Vasili Mukbaniani(^1)(^2), Eliza George Markarashvili(^1)(^2), Tamara Nuzgar Tatrishvili(^1)(^2), Maia Zurab Chigvinadze(^4)</td>
<td>1^Iv. Javakhishvili Tbilisi State University; 2^Institute of Macromolecular Chemistry and Polymeric Materials, Iv. Javakhishvili Tbilisi State University</td>
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20:00 – 23:00 **Cruise on the Moscow River (Conference Dinner)**

**Wednesday, Sept 25**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
<th>Presenter(s)</th>
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<tr>
<td>09:30 – 10:05</td>
<td>I-10</td>
<td>Supramolecular interactions in ladder oligosilsesquioxane materials.</td>
<td>Anna Kowalewska</td>
<td>Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Poland</td>
</tr>
<tr>
<td>10:05 – 10:40</td>
<td>I-11</td>
<td>New Applications of Cyclic Silanols</td>
<td>Masafumi Unno, Hisayuki Endo, Chika Kuramochi, Nobuhiro Takeda</td>
<td>Gunma University, Japan</td>
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<tr>
<td>10:40 – 11:10</td>
<td>Coffee-break</td>
<td><em>Chair: Alan R. Bassindale</em></td>
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<td>Time</td>
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<tr>
<td>11:10 – 11:45</td>
<td>I-12</td>
<td>Silicone Surface Science</td>
<td>Michael James Owen, Michigan Molecular Institute, United States of America</td>
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<tr>
<td>11:45 – 12:20</td>
<td>I-13</td>
<td>Silicon-based nanoparticles for biomedical applications</td>
<td>Victor Yurevich Timoshenko, Moscow State Lomonosov University, Russian Federation</td>
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<tr>
<td>12:20 – 12:30</td>
<td>Closing</td>
<td>Closing remarks</td>
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<td>12:30 – 14:00</td>
<td>Lunch</td>
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**Poster Session (Monday, Sept 23, 16:00-18:00)**

**P-1. Synthesis and properties of nanostructured cuprous chloride**
Nicolay Yu. Adonin¹, Sergey A. Prikhodko¹, Anton Yu. Shabalina¹, Igor P. Prosvirina¹, Vladimir I. Zaikovskii¹, Evgeny A. Monina², Irina A. Bykova², Petr O. Martynova², Sergey L. Rusakova²
¹G.K. Boreskov Institute of Catalysis SB RAS, Russian Federation; ²State Research Institute for Chemistry and Technology of Organoelement Compounds, Russian Federation

**P-2. New organosiloxane coatings with methylene phosphine groups**
Alexey Anatolevich Amelichev, Elena Nikolaevna Rodlovskaya, Boris Aleksandrovich Izmailov, Valery Aleksandrovich Vasnev
Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russian Federation

**P-3. Siliconorganic backbone as a matrix for solid polymer electrolyte membranes**
Jimi Nikoloz Aneli¹,², Omari Vasili Mukbaniani¹,², Tamara Nugzari Tatishvili¹,², Eliza George Markarashvili¹,², Natia Amiran Jalagania¹
¹Iv. Javakhishvili Tbilisi State University, Georgia; ²Institute of Macromolecular Chemistry and Polymeric Materials, Iv. Javakhishvili Tbilisi State University

**P-4. The approaches to the synthesis of siloxane rotaxanes**
Anton Anisimov, Yuriy Kononevich, Dmitriy Arkhipov, Aleksandr Peregodov, Olga Shchegolikhina, Aziz Muzafarov
INEOS RAS, Russian Federation

**P-5. Synthesis polymolybdenophenylsiloxane containing molybdenum atoms in oxidation state +6**
M.I. Balanov, A.V. Ermolaeva, V.V. Vasilieva, A.V. Alikovsky
Far Eastern Federal University, Russian Federation
P-6. Investigations on structural properties and reactivity of novel aryl substituted silanes

Judith Binder, Kristina Schrempf, Ana Torvisco, Roland Fischer, Frank Uhlig
TU Graz, Austria

P-7. Luminescent organosiloxane nanocomposites

Oleg Borschchev$^{1,2}$, Maxim Skorotetcky$^{1,2}$, Nikolay Surin$^{1,2}$, Elena Tatarinova$^1$, Aziz Muzafarov$^1$, Sergei Ponomarenko$^{1,2}$

$^1$ISPM RAS, Russian Federation; $^2$«Luminescent Innovation Technologies» LLC, Russian Federation

P-8. Thermal and oxidation degradation of metallasiloxanes

Boris Zavin, Mikhail Buzin, Ilya Volkov, Natalia Sergienko, Ekaterina Trankina, Natalia Cherkun, Vladimir Papkov
INEOS RAS, Russian Federation

P-9. Influence of Si-substitution on photovoltaic properties of thiophene-based copolymers

Fedor Drozdov, Ekaterina Myshkovskaya, Michail Surin, Abderrahim Yassar, Sergej Ponomarenko
ISPM RAS, Russian Federation

P-10. POSS-containing, Reactive Siloxane Resins as Polymer Modifiers

Michal Dutkiewicz$^{1,2}$, Mariusz Szolyga$^3$, Hieronim Maciejewski$^{2,3}$, Bogdan Marciniec$^{1,2}$

$^1$Advanced Technology Centre, Adam Mickiewicz University of Poznan, Poland; $^2$Poznan Science and Technology Park, Adam Mickiewicz University Foundation, Poland; $^3$Faculty of Chemistry, Adam Mickiewicz University of Poznan, Poland

P-11. The Synthesis of High Molecular Weight POSS-Polymers Using ATRP

Adrian Franczyk$^1$, Krzysztof Matyjaszewski$^2$, Bogdan Marciniec$^{1,3}$

$^1$Adam Mickiewicz University in Poznan; $^2$Carnegie Mellon University; $^3$Adam Mickiewicz University in Poznan, Centre of Advanced Technologies

P-12. Synthesis of polysiloxanes microcapsules containing phase change materials

Witold Fortuniak, Chojnowski Julian, Pospiech Piotr, Kurjata Jan, Slomkowski Stanislaw
Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, Poland

P-13. Polycondensation of Methylbenzylidethoxysilane in Acetic Acid

Aleksandra Kalinina$^1$, Sergey Milenin$^1$, Vadim Gorodov$^1$, Natalia Vasilenko$^1$, Nina Demchenko$^1$, Aziz Muzafarov$^{1,2}$

$^1$ISPM RAS, Russian Federation; $^2$INEOS RAS, Russian Federation
P-14. Synthesis polymolybdenophenylsiloxanes and investigation of their thermostatic the stabilizing properties
S.G. Krasitskaya, A.V. Alikovskiy, V.V. Vasileva, M.I. Balanov
The Far Eastern Federal University, Russian Federation

P-15. Novel fluorine-containing polyorganosiloxane for the protective antireflection coatings
Elena Ladilina¹, Tatiana Lyubova¹, Kirill Sidorenko², Vladimir Semenov³
¹G. A. Razuvaev Institute of Organometallic Chemistry RAS, Russian Federation; ²Research Physico-Technical Institute, Lobachevsky Nizhegorodsky State University, Russian Federation

P-16. Novel water-soluble polysiloxanes for the biomedical applications
Elena Ladilina¹, Tatiana Lyubova¹, Swetlana Lermontova¹, Yury Klapshin², Vladimir Semenov³
¹G. A. Razuvaev Institute of Organometallic Chemistry RAS, Russian Federation; ²Lobachevsky State University of Nizhny Novgorod, Russian Federation

P-17. Kinetic studies of condensation of α,ω-siloxane diols with aminoalkyl(alkoxy)silanes
Magdalena Łubkowska¹, Włodzimierz Stańczyk², Krystyna Różga-Wijas²
¹Chemical Plant "Silikony Polskie" Ltd., Nowa Sarzyna, Poland; ²Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Poland

P-18. Bithiophenesilane-based dendritic macromolecules: synthesis and properties
Yuriy N. Luponosov¹, Sergei A. Ponomarenko¹, Nadezda.N. Rasulova¹, Nikolay M. Surin¹, Dmitriy A. Lupenko², Eugeni I. Maltzev², Aziz M. Muzafarov¹
¹Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences, Russian Federation; ²Institute of Physical Chemistry and Electrochemistry of RAS, Moscow Russia

P-19. Hydrophobic Materials Based on Fluorocarbofunctional Spherosilicates
Joanna Karasiewicz¹, Hieronim Maciejewski¹,², Michal Dutkiewicz²,³, Bogdan Marciniec²,³
¹Faculty of Chemistry, Adam Mickiewicz University of Poznan, Poland; ²Poznan Science and Technology Park, Adam Mickiewicz University Foundation, Poland; ³Advanced Technology Centre, Adam Mickiewicz University of Poznan, Poland

P-20. Synthesis of hyperbranched polymethylsilsesquioxanes
Ivan Borisovich Meshkov
ISPM RAS, Russian Federation

P-21. Synthesis of the polymethyl(vinyl)silsesquioxane nanogels with different core-shell structures through the condensation of the hyperbranched polymethyl(vinyl)siloxanes
Dmitry Migulin, Elena Tatarinova, Ivan Meshkov, Michail Buzin, Aziz Muzafarov
P-22. Synthesis of some new siloxane hyperbranches
Sergey Alexandrovich Milenin, Denis Igorevich Shragin, Aziz Mansurovich Muzafarov
ISPM RAS, Russian Federation

P-23. Synthesis of Carbosilane Dendrimer Derivatives Containing Linear Ethylene Oxide and Dioxolane Groups in the Outer Layer
Natalia Alexandrovna Novozhilova, Yurii Nikolaevich Kononevich, Elena Anatolievna Tatarinova, Aziz Mansurovich Muzafarov
ISPM RAS, Russian Federation

Natalia Alexandrovna Novozhilova, Olga Anatolievna Serenko, Aziz Mansurovich Muzafarov
ISPM RAS, Russian Federation

P-25. Synthesis and properties of new tetrafunctional cyclosiloxanolates
Maria Nowacka, Anna Kowalewska
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Poland

Maria Nowacka, Anna Kowalewska, Adam Tracz, Tomasz Makowski
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Poland

P-27. Self-assembly of ladder oligo(phenylsilsesquioxanes) into spherical structures.
Maria Nowacka, Anna Kowalewska, Adam Tracz, Tomasz Makowski, Przemysław Sowiński, Marcin Florczak, Beata Wiktorska
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Poland

P-28. Synthesis of trimethylsiloxane derivatives of polymethylsilsesquioxane
M. A. Obrezkova, A. M. Muzafarov
N.S. Enikolopov Institute of Synthetic Polymeric Matherials of RAS / Russian Federation, Russian Federation

P-29. How sticking efficiently silicone elastomers on metals?
Loic Picard, Francois Ganachaud, Etienne Fleury
INSA Lyon, France

P-30. Synthesis of functionalized microspheres for immobilization of catalyst
Piotr Pospiech, Julian Chojnowski, Witold Fortuniak, Marek Cypryk
P-31. Siloxane copolymers containing hydrolytically degradable poly(L-lactide) blocks.
Krystyna Rozga-Wijas, Jan Kurjata, Wlodzimierz Stanczyk, Witold Fortuniak, Stanislaw Slomkowski
Centre of Molecular and Macromolecular Studies, Poland

P-32. Synthesis of methyltriethoxysilane and their application as material for soil modification
Krystyna Rozga-Wijas, Jan Kurjata, Wlodzimierz Stanczyk
Centre of Molecular and Macromolecular Studies, Poland

P-33. Aryl Substituted Silanoles as Precursors for Novel Polysiloxanes
Kristina Schrempf, Judith Binder, Vera Dopona, Ana Torvisco, Roland Fischer, Frank Uhlig
TU Graz, Austria

P-34. Exchange reactions of the framework metallasiloxanes
Boris Zavin, Natalia Sergienko, Natalia Cherkun, Ekaterina Trankina, Alexandr Korlyukov
INEOS RAS, Russian Federation

P-35. Nanometallocarbosilanes: synthesis, physicochemical properties, structure
Galina Igorevna Shcherbakova, Mariya Khristoforovna Blokhina, Dmitriy Vladimirovich Zhigalov, Valery Vladimirovich Shatunov
SSC RF FSUE «GNIICHTEOS», Russian Federation

P-36. Synthesis and Properties of Fluorine-containing Carboxilane Dendrimers
Natalya Sheremetyeva¹, Elena Tatarinova¹, Viktor Myakushev¹, Michael Buzin², Aziz Muzafarov²
¹ISPM RAS, Russian Federation; ²INEOS RAS, Russian Federation

P-37. New luminescent crosslinking agents for functional organosiloxane polymers
Maxim Skorotetcky
Enikolopov Institute of Synthetic Polymer Materials RAS, Russian Federation

P-38. Preparation of honeycomblike porous films by Breath figures method from epoxy binder modified with fluorocontaining organosilicon oligomers
Mikhail Alexandrovich Soldatov, Natalya Alexandrovna Sheremetyeva, Aziz Mansurovich Muzafarov
ISPM RAS, Russian Federation

P-39. Synthesis of hyperbranched polyphenylsilsesquioxanes
M.N. Temnikov¹², D.I. Shragin¹², M.I. Buzin², M.A. Muzafarov¹²
¹ISPM RAS, Russian Federation; ²INEOS RAS, Russian Federation
P-40. Polyethylene-silicon dioxide composites with the structure of semi-interpenetrating networks
Elena Trofimchuk1, Ivan Meshkov2, Ekaterina Nesterova1, Nina Nikonorova1, Valentina Kazakova2, Aziz Muzafarov2, Nikolay Bakeev1,2
1Moscow State University, Russian Federation; 2Institute of Synthetic Polymer Materials RAS, Russian Federation

P-41. New heat-resistant oligoorganoelementsilazanes with a tantalum-, hafnium fragments
S.V. Zhukova, O.G. Ryzhova, P.A. Storozhenko, A.N. Polivanov
State Research Institute for Chemistry and Technology of Organoelement Compounds, Russian Federation

P-42. The preparation of microchannel silicon rubber
Natalia Vadimovna Zolotareva, Vladimir Viktorovich Semenov, Viktor Nikolaevich Myakov
G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Russian Federation
INVITED LECTURES
New approach to synthesis of functionalized polysiloxane microspheres

J. Chojnowski, W. Fortuniak, S. Slomkowski, P. Pospiech, J. Kuriata, U. Mizerska

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences
*e-mail: jchojnow@cbmm.lodz.pl

Cross-linked polysiloxane microspheres containing a large number of silanol groups are synthesized using polyhydromethylsiloxane (PHMS) as starting material. This polymer is cross-linked and functionalized in aqueous emulsion using a combination of three reactions of its Si-H groups, i.e., hydrosilylation of vinyl groups of cross-linker, hydrolysis and dehydrogenative condensation with Si-OH groups formed in the hydrolysis. All these reactions are catalyzed by the same catalyst which is the Karstedt platinum Pt(0) complex. A solution of PHMS with 1,3-divinyltetramethyldisiloxane (DVTMDS) containing the Pt(0) complex is mechanically emulsified with water containing a non-ionic surfactant. Preliminary partial hydrosilylation of DVTMDS is usually carried out prior to the emulsification in order to graft vinyl functions on the polymer, while the cross-linking by the hydrosilylation of these functions takes place in droplets of the emulsified polysiloxanes. The hydrolysis of Si-H occurs in parallel producing Si-OH groups on the polymer which partly enter into the condensation reaction with the Si-H groups thus contributing to the polymer cross-linking.

Fig. 1A. SEM Micrograph of microspheres,

Fig. 1B. Schematical representation of a microsphere

The morphology of the isolated microspheres is studied by SEM and their chemical structure by $^{29}$Si and $^{13}$C MAS NMR and by FTIR. Particles have regular spherical structure with average diameters ranging from 1 μm to 40 μm. They may contain up to $7 \times 10^{-3}$ mol/g of SiOH groups which are located in the bulk and surface of microspheres. The reaction with Me$_3$SiCl in the presence of Et$_3$N allows the silylation over 80 % of the silanol functions thus rendering microspheres hydrophobic. The average size, density of cross-linking as well as the content of Si-OH and Si-H functions of microspheres may be tuned by the variation of parameters of their synthesis and by a modification of the precursor structure. The reactions of the Si-OH groups with reactive silanes containing organofunctional groups (known as promoters of adhesion) can be used for the further functionalization of these microspheres. These procedures allows the introduction of a large number of functions, such as vinyl, amine, glycidoxy1 and others to the bulk and surface of the microspheres.

This work was supported from the National Centre of Science (project NCN 2011/01/B/ST5/06662).
Polymer properties arise from their 3D structures and distribution of functionalities. A desirable, narrow range of properties requires, of course, narrow molecular weight polydispersity and excellent control over the distribution of functional groups in the molecule. To achieve this objective with silicones has proven challenging. Normally silicones are prepared by equilibration, which leads to broad polydispersity: narrow polydispersity is achieved by ring opening polymerization, which is synthetically tricky. For functional materials, aside from $\alpha,\omega$-functional linear silicone polymers, the distribution of functional groups is not generally well controlled. The control of 3D structures is even less well elaborated. We are interested in developing new routes to control the behavior of silicones both through precise syntheses, and also through the use of new strategies for crosslinking.

Coumarin undergoes reversible 2+2 photocycloaddition. The compound was incorporated along the backbone of a linear silicone chain 1. Prior to photocycloaddition, it was surprising to learn that association of the aromatic groups converted the silicone oil into a thermoplastic elastomer. Further reversible photocrosslinking of the silicone was possible.

Lewis acids/base complexation provides a different mechanism to structure silicones. Boronic acids are weak Lewis acids that form strong bonds with amines. We will discuss their incorporation onto silicone oil backbones 2. The materials have interesting surface properties in their own right. In addition, crosslinking with aminopropylsilicones was facile.

A few beautiful, heroic syntheses of silicone dendrimers have been reported. The methods generally involve acidic or basic conditions that, through equilibration, can lead to scrambling of precise structures. Both divergent and convergent strategies, and a combination of Piers-Rubinsztajn condensation and hydrosilylation, can lead to large (>10,000 MW) polymers with precise 3D structures and optionally, high functionality 3.

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Silicon-based magnetic elastomers with giant magnetic response

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Magnetic field controlled elastomers based on highly elastic polymeric matrices filled with magnetic nano- and microparticles have attracted much attention nowadays. The novel feature of these materials is the ability to change their properties in magnetic fields and thus, they are perspectives for design of various magnetic field controlled devices. During the last years mainly mechanical and viscoelastic properties of magnetic elastomers (ME) based on magnetically soft fillers have been studied and improved. Developed ME have demonstrated:
- a huge magnetorheological effect. Up to three orders of magnitude increase of the elastic modulus as well as the loss modulus was observed in the magnetic field of 3 kOe.
- an enormous magnetodeformational effect in homogeneous as well as in gradient magnetic fields;
- a high responsiveness to alternating magnetic field at the frequency up to 40 Hz;
- a magnetic field induced plasticity, or memory effect.

In this work we focus on the rheological behavior of the ME based on magnetically hard magnetic filler and compare it with that of magnetically soft MR. Besides, we examine the effect of an external magnetic field on the permittivity of the ME. The MR used in this work were synthesized on the basis of silicone rubber filled with magnetically hard FeNdB particles and were magnetized in the fields of 3 and 15 kOe. We have shown that due to high residual magnetization the materials demonstrate well pronounced non-elastic behavior already in the absence of any external magnetic field. In particular, in contrast to magnetic elastomers based on soft magnetic fillers their elastic modulus is strain-dependent. Under the influence of external magnetic field the storage and loss moduli of magnetic elastomers with hard magnetic filler can both increase and decrease tremendously.

We also report for the first time on a giant magnetodielectric effect of the developed ME with up to 150% increase of the permittivity in the magnetic field of 10 kOe. The influence of the chemical nature, size and concentration of the magnetic particles is studied in details and a model of the magnetodielectric effect is proposed.

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Conjugated organosilicon materials for organic electronics and photonics

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Organic electronics is a fast growing field of science and technology, which relies upon (semi)conducting, luminescent or light harvesting properties of conjugated organic materials. As opposite to conventional electronics based on silicon or other inorganic semiconductors, organic electronics allows obtaining light weight, large area, flexible and transparent electronic devices by inexpensive solution processing, printing or roll-to-roll techniques. Albeit their characteristics nowadays are inferior to conventional electronics devices, rapid progress in this field indicates that the future of electronics has organic nature.

Conjugated organic materials containing organosilicon groups often show better characteristics in organic electronic devices than their organic analogs or allow preparation of novel types of organic electronic devices. That is why during the last years conjugated organosilicon materials became a hot topic in organic electronics. Many of them possess their high thermal and oxidation stability, good solubility and processability necessary to preparation of stable and inexpensive organic electronic devices.

Our group has developed an approach to functional organosilicon derivatives of oligothiophenes capable to self-assembly into 2D crystalline monolayer with excellent semiconducting properties. Such molecules have a flexible aliphatic spacer between the semiconducting oligothiophene core and the functional chlorosilyl group. Electronic circuits of different complexity have been made based on these organosilicon materials.

Direct linking of different conjugated units to silicon atoms allows creation of branched or dendritic organosilicon macromolecules with the so-called “molecular antennae effect”. Such molecules possess high molar extinction coefficient in a wide spectral region, highly efficient transfer of the excitation energy from the periphery to the center of the molecule and emit the light in the narrow spectral region. They can be used as functional materials in organic light emitting diodes or as “nanostructured luminophores”, combining activator and spectral shifter in a new generation of plastic scintillators.

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Simple disiloxanes containing pyridyl groups can form coordination polymers with a range of metals such as Mn(II), Co(II), and Cu(II) [1]. The utility of such ligands for coordination polymer formation is based on their flexibility in the case of the disiloxanes, and upon the ease of synthesis of novel ligands containing several organic ligating groups via simple synthetic steps at tetrahedral Si-centres to give compounds of the type RₙSi(p-C₆H₄CO₂H)₄₋ₙ (n = 0, 1, or 2; R = Me, Et, Ph etc.).

Treatment of both transition metal salts and main group element precursors with Si(p-C₆H₄CO₂H)₄ affords a variety of MOFs that contain either the [Si(p-C₆H₄CO₂)₄]⁺ or [Si(p-C₆H₄CO₂)₃(p-C₆H₄CO₂H)]⁻ anion as the linker [2, 3]. More complicated arylsilanes such as C₆H₄-p-[Si(C₆H₄CO₂)₃] and [CH₂Si(C₆H₄CO₂H)₃] also give rise to the formation of novel framework materials when treated with metal salts. For example, the scheme below shows the use of a hexa-acid to form a MOF isoreticular to MOF5, but with alternate corners occupied by Si rather than by Zn₄O⁺ clusters as shown below [4].

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Functional polysiloxanes and nano-devices

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A number of current nano-devices for optoelectronics, laser technology, sensing and field effect transistors includes silicon containing materials. Our interest in this area started some years ago with modification of silicon wafer surface with lateral, covalently attached liquid crystalline polymers1 as an element of laser light switches and studies of liquid crystalline polycarbosilanes as coatings for acoustic wave sensors2.

The current presentation shall be devoted to side chain polysiloxanes bearing conjugated aromatic substituents as shown below:

Novel Cage Silsesquioxanes and Their Potential in Materials Science

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The presentation briefly covers two aspects of our recent work in silsesquioxane (POSS) chemistry.
We are interested in the use of tailored POSS molecules as additives to organic polymers such as LDPE. We have already determined the X-ray crystallographic structures of a series, Si₈O₁₂((CH₂)ₙCH₃)₈, where n is 2-10. Here, our attention turned to similar examples where n is 13-17 where we could not grow crystals suitable for single crystal X-ray measurement. We used state-of-the-art time-resolved Small- and Wide-angle X-ray scattering (SAXS/WAXS), thermal and optical techniques to elucidate the morphology of these molecules. The effect of these longer-chain-substituted silsesquioxanes on the crystallisation of low density polyethylene will also be reported.

Fig. 1. SAXS of pure POSS cages

The second study describes a new class of F⁻@T₈ with Group 1 metal ions encapsulated by crown ethers.

Fig 2  F⁻@T₈ with a K⁺ cation encapsulated by two 10-c-5 crown ethers.

Potential uses of these salts will be discussed.
Silicone resins continue to attract significant attention due to their attractive optical, thermal, insulating and surface properties. New applications are being realized in new markets such as in lighting (LED), in communications (optical interconnects), in photovoltaic devices, in composites, nano-composites, high quality films, etc. Determining the process-structure-property relationships, which govern their performance in applications continuous to be a challenging endeavor. In this presentation we will describe characterization experiments on model and commercial silicone resins at the molecular pre-polymer, polymer and cured network levels and we will offer interpretations on the material properties in prototype complex systems and devices.
Supramolecular interactions in ladder oligosilsesquioxane materials

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It has been noted that some oligomeric silsesquioxanes (LPSQ) of linear double-chained backbone are capable of formation of interesting supramolecular structures. The phenomena stem from the silsesquioxane chain morphology and associative interactions between side substituents.

Fig. 1. The synthesis of oligomeric LPSQ using cyclotetrasiloxane precursors.

Owing to the backbone rigidity and \( \pi-\pi \) interactions between side substituents, oligo(phenylsilsesquioxanes) self-assemble into nanometer sized spherical objects in template-free systems. Such microspheres can have a significant potential as templates to synthesize macroporous materials. Modification of other simple organic functions [Vi, \((CH_2)_3Cl\) and formation of more complicated systems can be achieved via thol-ene addition or “click chemistry” protocols. Oligosilsesquioxanes bearing such moieties have good film-forming properties. They can provide unique, nanostructured synthetic surfaces of varied morphology and interesting physiochemical properties.

Fig. 2. TEM photograph of Ph-LPSQ microspheres.

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Cyclic silanols, or cyclooligosiloxanes with hydroxyl groups, were originally prepared by hydrolytic condensation from chlorosilanes. Among them, isopropyl-substituted cyclic silanol possesses both stability and reactivity, and has been serving as a potential precursor of well-defined silsesquioxanes (Scheme 1).

However, because of four possible stereoisomers and incapability of the separation by chromatography, yield of this cyclic silanol was not very good. In 1996, Pozdnyakova's group reported the isolation of potassium salt of cyclic silanols and transformation to cyclic silanols. This method enables the access to cyclic silanolates with various substituents in high yields.

In this presentation, we show the application of these cyclic silanols and silanolates as the starting unit for well-defined silsesquioxanes. In addition, recent isolation of new cyclic silanols is also shown.

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Silicones are the most industrially important “semi-inorganic” polymers produced today with polydimethylsiloxane (PDMS) being the dominant material. The fundamental characteristics of PDMS that account for its pre-eminent position among organo-inorganic polymers are: low intermolecular forces between methyl groups, compact size of the methyl groups, high siloxane backbone flexibility, high siloxane bond energy, and partial ionic nature of the siloxane bond. Most commercial applications of silicones exploit the surface properties and behavior of silicones such as low surface energy, hydrophobicity and oleophilicity that result from this set of fundamental characteristics. These properties will be briefly reviewed using water and n-hexadecane contact angles as indices of hydrophobicity and oleophilicity, respectively. Surprisingly, there is no consensus regarding the correct value for the contact angle of water on PDMS. Originally, fluorosilicones were developed to reduce the swelling by hydrocarbon oils and solvents that occurs with PDMS. The introduction of aliphatic fluorocarbon groups onto the siloxane backbone might be expected to produce even lower surface energy polymers than PDMS. However, this is not the case for the most commonly available fluoroilicone, polymethyltrifluoropropylsiloxane (PMTFPS). In particular, its liquid surface tension is significantly higher than that of PDMS. The surface energy, hydrophobicity and oleophobicity of PMTFPS will be compared and contrasted with the behavior of PDMS. The surface properties of more highly fluorinated fluorosilicones will also be examined (Figure 1).

Fig. 1. Dispersion force component of surface energy versus fluorinated side-chain length for fluorosilicones

Silicon-based Nanoparticles for Biomedical Applications

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Silicon (Si) nanostructures (nanocrystals, nanoparticles, porous layer, nanowires) are known to be biocompatible and biodegradable [1]. Combined with unique optical properties [2], Si nanoparticles (NPs) look very promising for bioimaging, drug vectoring, photodynamic and ultrasonic therapy [3-5]. Luminescent porous Si NPs can be produced by electrochemical etching of c-Si in hydrofluoric acid solutions [1,2]. Laser ablation in gaseous and liquid environment emerged as a "green" physical alternative to the conventional chemical or electrochemical methods [6,7]. The ablation in clean aqueous environment (e.g., de-ionized water) can be used to form colloidal Si NP solutions [8]. Ultra-short laser pulses were used to produce stable solutions of pure low-size-dispersed, size-tunable NPs with remarkable fluorescence and singlet oxygen releases [9], which make them important candidates for applications in cancer theranostics. Currently Si nanowires (NWs) formed by metal (Ag)-assisted chemical etching (MACE) [10,11] are of great interest because of their potential applications in various fields as electronics, optoelectronics, photonics, photovoltaics, bio- and chemical sensors. In particular, Si NWs exhibit a strong optical absorption and rather low reflectance in the visible spectral range [11] as well as the room temperature photoluminescence (PL) [12].

In our work Si NPs were prepared by electrochemical etching of bulk c-Si in HF-based solution followed by mechanical grinding of the obtained porous materials [6,7]. Si NWs with diameter of 10-100 nm were prepared by MACE of p-type double-side polished (100)-oriented c-Si wafers with specific resistivity of 1-10 Ω·cm. The length of Si NWs was controlled in the range from 0.1 to 10 µm by MACE duration. The etching was done at room temperature. The NW arrays were additionally immersed in concentrated nitric acid to remove residual Ag nanoparticles. Finally the samples were rinsed in de-ionized water and dried in air at room temperature. The obtained layers were transformed into powders and aqueous suspensions by mechanical grinding. The samples were studied by using transmission electron microscopy (TEM), dynamic light scattering and optical spectroscopy techniques. PL properties were investigated by using both conventional spectroscopic equipment and confocal fluorescent microscopy. Fig.1 shows typical TEM images of the obtained samples, which illustrate their nanostructure. The Si NPs and NWs are found to consist of Si nanocrystals with minimal sizes of 1-5 nm.

![Fig.1. TEM images of different kinds of Si NPs obtained by electrochemical etching (a) and laser ablation (b) as well as Si NWs prepared by MACE (c).](image)

PL spectra of Si NPs and NWs exhibit maximum varied from 1.2 to 1.8 eV, depending on the conditions of preparation and storage. The PL spectra of 3C-SiC NPs suspended in water consist of a broad band with maximum at 2.2-2.5 eV, depending on the NP size and excitation energies.
The PL properties of NPs and NWs are interpreted as a result of the radiative recombination of excitons confined in small nanocrystals – quantum dots (QDs), which consist in the prepared NPs and NWs. In oxygen ambient the PL intensity of Si QDs was found to decrease strongly in comparison with that in vacuum (or in oxygen-free water). The PL quenching in oxygen ambient is maximal at 1.63 eV due to the photosensitization of singlet oxygen generation [5]. In vitro experiments demonstrated that photoexcited Si NPs suppressed the proliferation of cancer cells. Besides the photochemical reaction of Si NPs they could be used as sonosensitizers of local ultrasound-induced hyperthermia and cavitation to destroy cancer cells and tumors in vitro and in vivo, respectively.

For fluorescent bioimaging the aqueous suspensions of NPs and NWs were added to cancer cells in vitro. Fig.2 shows typical fluorescent images of the cells in the presence of Si NPs and NWs. The incorporation of NPs and NWs inside the living cells was monitored over several hours. Under the optical excitation, the NPs marked by red color are rather bright in order to be distinguished from the autofluorescence background of cells. An analysis of the depth profile of the NP fluorescence signal shows that NPs are localized inside the cells, while Si NWs are located mainly on the cell membranes. Finally, the obtained results demonstrate that Si-based nanomaterials are promising for biomedical applications as diagnostics, drug delivery and PDT. The highly luminescent, stable, and biocompatible Si NPs can be applied for fluorescence imaging.

![Fluorescent images of cancer cells with Si NPs obtained by electrochemical etching](image)

**Fig. 2.** Fluorescent images of cancer cells with Si NPs obtained by electrochemical etching (a), laser ablation (b), as well Si NWs (c). The Si QD emission and cell nuclei are colored by red and blue, respectively.

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**References**

ORAL TALKS
Glassy siloxane-containing polynorbornenes – novel materials for hydrocarbon membrane separation

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Separation of hydrocarbon vapors from their mixtures is hardly solved in industrial scale but important problem. Membrane materials used for this purpose are polymers with solubility controlled gas permeation. For a long time highly permeable polyacetylenes formed the only group of glassy polymers, for which the solubility controlled permeation was observed. We have realized synthesis and polymerization according to addition and metathesis mechanisms of norbornenes and tricyclononenes with different number of Me₃Si-substituents. This led to discovery of new highly permeable glassy polymers - addition silicon-substituted polynorbornenes. Along with the high permeability they demonstrated the solubility controlled gas permeation like polyacetylenes and capability to separate hydrocarbon gases.

Herein we demonstrate a new approach to affect purposefully the gas separation properties of glassy polymers by introducing Si-O-Si-containing substituents. With this aim we synthesized new polynorbornenes containing in each monomer unit several Me₃Si-groups bonded to the carbocycle via flexible Si-O-Si bonds and studied their gas permeation properties. The corresponding monomers were synthesized by stereospecific [2σ+2σ+2π]-cycloaddition of quadricyclane and (trichlorosilyl)ethylenes followed by siloxanation with Me₃SiONa. The tricyclononenes were obtained as a single isomer having a preferable for polymerization exo-position of the cyclobutane fragment.

It was found that introduction of Si-O-Si-containing substituents not only increased hydrocarbon gas permeability of addition polynorbornenes (APTNSi) but made metathesis polynorbornenes (MTNSi) more permeable and reversed selective, e.g. having higher permeability for heavier hydrocarbons. Thus a new class of membrane materials, Si-O-containing metathesis polynorbornenes, with solubility controlled permeation was created.

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“Self-healing” silicone additives for sealing applications

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Silicones are outstanding elastomers that are more and more used in more conventional, lower-cost applications than aeronautics, e.g. in the automotive industry. For instance, seals commonly used in connectors are made of Liquid Silicone Rubbers (LSR) with remarkable elasticity, solvent resistance and water sealing. The main drawbacks of these materials lie in the poor tear strength that they develop and sometimes also in their weak compression set.

To fight against the first type of failure, we have developed a strategy aiming at repairing the material after it has been torn. Most self-healing systems reported in the literature were not relevant here, either because of the thin envelope of material to repair (≠ microcapsules), or of the polarity of the solvent/water atmosphere (≠ ionomers, supramolecular chemistry via hydrogen bonding). Blocked-isocyanate silicone additive has been retained as thermally-active, fast crosslinking material. A thorough literature survey has been done on the subject and recently published.¹  The experimental work to generate the different additives tested here is given in the scheme below. Two different molecules, i.e. 3,5-dimethylpyrazole and methylethylketoxime, were chosen to block a model diethoxypropylcyanato-silane. This latter was then engaged in polycondensation reaction with a PDMS to generate the final additive.

Real industrial tests on connectors showed no leaks on normal rework tests after the additive has been worked out by temperature, and a decrease of 70% of leaks for seals that were harshly torn. This work has been patented recently.²

Scheme: strategy of deblocking/crosslinking reaction involving a home-made temperature-sensitive additive.

Hetero-phase polymerization of vinyl monomers in the presence of silicone surfactants


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One of the promising areas of heterophase polymerization process is synthesis of functional polymer suspensions with a narrow particle size distribution. Most of the known methods for their preparation are technologically complex, multi-step, expensive and difficult to reproduce. Thus development of new methods for producing polymer suspensions with a narrow particle size distribution is an important issue.

In this report studies of vinyl monomers polymerization in the presence of oligodimethylsiloxanes with chain length from 6 to 60 siloxane units containing carboxydecylic, aminopropyllic and glicydoxypropyllic groups at the both ends of the polymer chains will be presented.

It was shown that the water-insoluble silicone oligomers form direct emulsions. Their distinctive feature is the ability to lower the interfacial tension at the monomer / water interface to 4-30 mJ/m², as well as the ability to form strong interfacial layer on the surface of the polymeric particles, ensuring their stability.

The heterophase polymerization of styrene and methyl methacrylate in the presence of functional siloxane oligomers leads to the formation of polymeric microspheres having a narrow particle size distribution (Dw/Dn<1.050) with diameters from 0.2 up to 2.0 microns. It should be noted that the particles formed by polymerization, contain functional groups on the surface and may subsequently be modified by various chemical reagents, proteins, quantum dots and others.

Thus in this presentation we propose a concept of the interfacial layer, stabilizing the surface of the polymer particles since the early stages of the polymerization. Particular characteristics of vinyl monomer polymerization in the presence of the siloxane surfactants can be summarized as follows: particle size is independent of monomer conversion; high stability of emulsion during synthesis at low surfactant concentrations; a narrow particle size distribution; a large particle size as compared with particles formed in the presence of ionic surfactant, the ability to adjust the size of polymeric particles by using surfactants with different chain lengths and the nature of functional groups; amount of the functional groups on the particle surface may be customized by changing the concentration of surfactant and pH.
New composites based on highly gas permeable addition poly(3-trimethylsilyltricyclononene-7) and substituted calixarenes

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Earlier we have developed some tools of macromolecular design for synthesis of highly permeable polymers based on norbornene and its derivatives. As a result, addition silicon-containing polytricyclonones were obtained. They belong to the class of the most permeable polymers and possess good mechanical properties and thermal stability. In this work we tried to find ways for a membrane selectivity control. For this purpose we prepared the composites based on addition poly(3-trimethylsilyltricyclononene-7) (PTCNSi1) and substituted calixarenes (Figure 1). PTCNSi1 was used because of its high gas permeability and good film-forming properties. The choice of calixarenes was due to the positive influence of such additives in pervaporation membrane processes. Furthermore, the organic nature of calixarenes should result in a good miscibility with an organic polymer matrix.

Fig. 1. The structure of the polymer matrix and calixarenes used in the work.

As a result a new series of such composites were obtained and the systematic investigation of their gas permeation parameters was done. Relationships between the structure of a calixarene (the macrocycle size and the nature of substituents at the rims) introduced into the polymer matrix and gas permeability values of the composite were found. It was shown that the introduction of calixarenes gave a positive influence in respect to the selectivity values while gas permeability coefficients decreased. For example, for the pairs of gases He/N2, H2/CH4, H2/N2 in a number of cases an increase of selectivities by several times in comparison with the similar parameters for the polymer matrix was observed. It was found that an increase of a calixarene concentration in a composite resulted in higher values of gas separation factors. The composites were also studied by means of BET, TEM, WAXD, positron annihilation spectroscopy and the corresponding data will be discussed.

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An efficient route for synthesis of ethoxysilanes and processes occurring on condensation of methyltrimethoxysilane in aqueous systems

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Alkoxysilanes are widely used as intermediates for manufacturing silicones and silicone-based materials. The common method of synthesis of a silyl ether linkage is alcoholysis of Si-Cl bonds. Recently we have described\(^1\) an environmentally friendly synthetic methodology that allows for preparation of alkoxysilanes from the respective chlorosilanes, with high yields and to provide a semi-stable emulsion, based on alkoxysilanes, as a hydrophobic and soil hardening reagent. The synthetic process involves so-called “reverse addition” - where an appropriate chlorosilane is introduced to the reaction flask containing alcohol under the surface of the liquid. This method limits the contact of alkoxysilanes with traces of water and hydrochloric acid, which usually leads to subsequent reactions. The side product (HCl) was removed from the reaction by passing nitrogen and absorbed in water. The reactions were carried out at room temperature. Chlorosilanes were introduced at the rate of 2.5 mL/min. It allowed for over 90% yield of alkoxy compounds with small addition of condensation products: dimer and trimer as shown by GC and GC/MS. The developed water emulsion consisted of alkoxysilanes, a surfactant and an emulsifier. Samples of the medium sand, treated with water emulsion of alkoxysilane, having diversified hydrophobicity were obtained. \(^{29}\)Si NMR and MS analyses have shown that the polymer/soil system is contains two types of units \(T^0_2\) and \(T^0_3\).

A detailed studies of a model system, involving hydrolysis of MeSi(OEt)\(_3\) in water, demonstrated that low molecular silanols are stable in the aqueous mixture for a long time and can be detected by \(^{29}\)Si NMR, MS and IR. The presence of silanol species in the aqueous emulsion of methyltriethoxysilane, which are capable to form covalent bonds with OH group on the surface of inorganic materials, rationalizes, the fact that such emulsion are extremely effective in hydrophobization of minerals and soil.

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\(^1\) Kurjata, J.; Rozga-Wijas, K.; Stanczyk, W.; Lefik, M; Wojciechowski, M; Baryla, P. 2012, Polish Patent Appl. P.401246
Direct Synthesis of Alkoxysilanes by the Reaction between Silicon and Alcohols

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The direct synthesis of chlorosilanes and their further reaction with alcohols have been the basic method for producing alkoxysilanes. In addition to that it is a multistage process, the main disadvantage of this particular scheme consists in large quantity of liberating corroding hydrochloric acid wastes and the need of installation of rectifying columns with extremely high number of theoretical plates.

Significantly more effective is manufacturing of alkoxysilane by the direct synthesis based on interaction between silicon and alcohols in presence of various catalysts. This method possesses many advantages: it is environmentally friendly and more practically feasible due to lower number of stages. However, in this case both trialkoxysilanes and tetraalkoxysilanes are generated, so the problem of achieving high selectivity for desirable product arises. There are many literature sources (mainly patents) describing the production of alkoxysilanes¹,²,³. Most of them describe direct process in liquid phase. On the other hand, the gas/solid phase option seems to be more promising since it uses no additional organic solvents.

![Fig. 1. Scheme of the interaction of silicon/copper contact mass with alcohols.](image)

The aim of the current study was to develop a novel technique for production of trimethoxysilane with high selectivity at satisfying silicon conversion.

Principal possibility and general regularities of obtaining of the organoalkoxysilanes by the reaction of elemental silicon with several organic precursors (first of all alcohols and ethers) were investigated. Trialkoxysilanes, tetraalkoxysilanes and alkyl trialkoxysilanes were the main products of the reaction. They were identified by means of elemental analysis, NMR- and IR spectroscopies, chemical analysis. Primary kinetic regularities were investigated as well.

The direct process was carried out in 5 different reactor types: flask-like liquid-phase; tube-like gas/solid-phase; flask-like gas/solid-phase with strong UV irradiation; a microwave device, and an autoclave.

As a result of optimization we obtained both HSi(OAlk)₃ and Si(OAlk)₄ with very high selectivity (> 90 %).

Pretreatment of the silicon and contact mass was found to be important factor as well. Optimization of this step allowed us to significantly increase silicon conversion.

The data seems to be very promising in terms of development of new chlorine-free alkoxysilanes production techniques.

³ Pat. US 2002010354 A1 Freshly precipitated CuO as catalyst for the trialkoxysilane synthesis, 2001
Functional properties and submolecular organization of high permeable 1,2-disubstituted polyacetylenes

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Silicon-containing disubstituted polyacetylene poly(1-trimethylsilyl-1-propyne) (PTMSP) exhibits the highest gas and organic vapor permeability and selectivity during recovery of C3+ from mixtures with permanent gas. Unique properties of PTMSP and a number of other high-permeable disubstituted polyacetylenes are provided by a specific organization of nanospace in these polymers, namely, extremely high fractional free volume and interconnected free volume elements. The specific structure is formed by rigid backbone containing C=C bonds and bulky substituents. The unusual high selectivities of recovery of higher hydrocarbons from vapor-gas mixtures are attributed to predominant sorption of organic vapor (e.g. butane) in nanosized pores (free volume holes), and therefore subtle variation of structure on nanolevel can provide means of developing novel effective polymer materials. Detailed investigation of synthesis of Si-containing polyacetylene PTMSP and its Ge-containing analogue poly(1-trimethylgermyl-1-propyne) (PTMGP) in the presence of catalytic systems based on Nb and Ta pentachlorides has shown that by varying synthesis conditions, e.g. cocatalyst, solvent polarity and temperature of polymerization process, one can regulate the geometric structure of macrochains, i.e. the ratio of units of cis- and trans-configuration, that determines macrochains packing and submolecular organization of the polymer. It was shown that functional properties of disubstituted polyacetylenes such as transport characteristics as well as stability towards organic solvents are controlled by the geometric structure. In this study disubstituted polyacetylenes PTMSP and PTMGP with different specific geometric structure (calculated from the 13C NMR spectra) were synthesized by methods of stereospecific polymerization with the use of catalytic systems based on Nb and Ta halides. An investigation of submolecular organization, utilizing PALS, N2 sorption and AFM, for PTMSP and PTMGP with different geometry was performed. All techniques indicate that polymers depending on the microstructure have distinct dissimilarities in free volume holes or pores. The PALS shows that polymers are composed of two types of free volume holes (τ3 and τ4) and it reveals differences both in amount and in structure of hole free volume in polymers with the same chemical structure (both PTMSP and PTMGP) but with different cis-/trans- composition. It was observed that polymers with bigger hole free volume demonstrate higher n-butane permeability as well as n-butane/methane mixed-gas selectivity in permeability experiments carried out for n-butane/methane mixtures (content of n-butane 1.6 mol.%). According to low-temperature nitrogen adsorption BET measurements the sorption capacity as well as the surface area of polymers with higher permeability and mixed n-butane/methane selectivity is greater than for polymers with lower permeability. AFM shows that the surface topography of polymer films consists of clusters with different lateral size. The observed correlation between increasing the size of cluster and enhancement of permeability as well as a mixed n-butane/methane selectivity indicates that the size of clusters influence on polymer packing density which governs gas transport through polymer matrix. This work was supported by RFBR (project № 11-03-00343-a).

Self-assembled oligothiophenesilanes for monolayer organic electronics

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Nowadays one of the most important problems of organic electronics is a development of the techniques for fabrication of semiconducting self-assembled crystalline monolayers (SAMs). Topicality of this problem connected with the fact that SAMs application as an active layer in organic field-effect transistors (OFETs) allows to reduce a consumption of organic semiconducting materials up to ten times without affecting its electrical properties.

The aim of this work is to study morphology, structure and electrical properties of the self-assembled monolayers obtained by Langmuir-Blodgett technique on the base of different organosilicon derivatives of oligothiophenes.

It has been shown that Langmuir-Blodgett technique employed under the optimal conditions is a very promising method for formation of the self-assembled crystalline monolayer films of the linear oligothiophene-silanes and siloxanes with vertical orientation of the oligothiophene fragments. It should be noted that with increasing the transfer pressure both growing of the substrate coverage and change of the internal structure of the monolayer associated with the tilt of the oligothiophene fragments take place. It is necessary to emphasize that Langmuir-Blodgett technique does not result in a monolayer formation for non-functional linear oligothiophenes (i.e. for α.α’-dialkyloligothiophenes), so, the presence of silane or siloxane functional groups plays a significant role for further development of functional π-conjugated oligomers for SAMFETs.

The efficient monolayer organic field-effect transistors with charge carrier mobilities up to $10^{-2}$ cm²/Vs and on/off ratio up to $10^6$ based on silane and siloxane derivatives of oligothiophene have been fabricated by LB technique (Fig.1) and their functionality in integrated circuits under normal air conditions has been demonstrated. The performance of oligothiophene LB monolayer OFETs is close to those of the SAMFETs prepared by solution self-assembly technique. The LB process allows rapid monolayer OFETs fabrication and appears to be promising technique for solution-processed organic electronics.

This work was supported by RFBR (project № 11-03-01137a) and The President of Russian Federation (grant for young scientists MK-6878.2013.3).
Model Silicone Contact Lenses as Drug Delivery Devices to Ocular Tissues

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Topical administration of eye drops remains the most prevalent method of delivering drugs to the eye, though a more effective drug delivery method is desirable. Silicone contact lenses represent an attractive option as an alternative vehicle for wide range of therapeutics. A model contact lens delivery system for the ocular drugs timolol maleate, roscovitine and atropine was investigated. The effects of drug loading and material composition were analyzed to further understand the drug-hydrogel interactions that govern the release kinetics and critical material properties.

Model lens materials were based on combinations of dimethylacrylamide (DMA), hydroxyethyl methacrylate (HEMA) and methacryloxypropyltrimethoxysilane (TRIS). These were synthesized by UV with the crosslinker ethylene glycol dimethylacrylate. The materials were prepared with and without the direct addition of roscovitine at 0.5 wt%, timolol maleate at 0.5 wt% and atropine at 0.5 wt% and 1.5 wt%. Release studies were performed into PBS solutions using UV spectroscopy and HPLC to quantify release of each drug. Swelling, extraction, NMR, TEM and contact angle studies were done to characterize the materials and their domain formations.

The HEMA/TRIS materials have shown greater amounts of drug released than the DMA/TRIS materials. Timolol and atropine has higher release percentages than roscovitine from the model materials. Figure 1 shows the release kinetics from 80% DMA:20% TRIS materials, where the modified silicone causes a faster release profile.

Contact lenses provide a feasible method to deliver a variety of drugs to ocular tissues. The modification of the silicone components in the lenses can alter the drug release from these materials.

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The carbodiimide sol-gel process - recent advances in synthesis, structures and understanding of a sol-gel route to non-oxide materials

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Molecular, oligomeric and polymeric silylcarbodiimides of the type \( R_3Si(\text{NCN})SiR_3 \), \([R_2Si(\text{NCN})]_n\) and \([RSi(\text{NCN})]_m\) (with \( R = \text{alkyl, aryl} \)) have been described in the literature. \(^{[1]}\)

Non-oxide gels are obtained when bis(trimethylsilyl)carbodiimide (\( (\text{H}_3\text{C})_3\text{Si-NCN-Si(CH}_3)_3 \)) (BTSC) is reacted with \( \text{SiCl}_4 \), trichlorosilanes and related compounds:

\[
n \text{R}_x\text{SiCl}_{4-x} + \text{ex. (H}_3\text{C})_3\text{Si-NCN-Si(CH}_3)_3 \rightarrow [\text{R}_x\text{Si(\text{NCN})(4-x)/2}]_n + n(4-x)(\text{H}_3\text{C})_3\text{SiCl}
\]

\( R = \text{aryl, alkyl, H; } x = 0, 1, 2 \)

These studies lead to a pseudo-water concept, which is based on BTSC reacting as a pseudo-water molecule, containing the NCN unit as a pseudo-oxygen atom and trimethylsilyl-groups as pseudo-hydrogen atoms. The latter concept is supported by spectroscopic, structural and reactivity-related characteristics of silyl-carbodiimides. The carbodiimde sol-gel process can be applied to prepare non-oxide hybrid materials, glasses and ceramics. These include binary carbides SiC and B\(_4\)C, ternary as well as multinary nitride-based phases such as B/C/N, and Si/B/C/N and Si/C/N/O materials. \(^{[2]}\) The latter were obtained by incorporation of the hetero-elements into the molecular precursors.

Among other studies we investigated silanol-analogous silicon-carbodiimides. Attempts to isolate “pseudo-silandiols” were not successful, but the corresponding macrocyclic condensation products were obtained in good yield. \(^{[3,4]}\) For example, the 16-membered ring c-[\( \text{Ph}_2\text{Si-NCN-} \)]\(_4\) as well as the 14 and 12 membered dimers c-[\( \text{Ph}_2\text{SiNCNSiPh}_2(\text{C}_2\text{H}_4) \)]\(_2\) and [\( \text{Ph}_2\text{Si-NCN-SiPh}_2\text{-O-} \)]\(_2\) were comprehensively analysed including single crystal X-ray analyses.

A summary of the current status of the carbodiimide-sol-gel process will presented, followed by a discussion of the advances gained in recent years. Limitations and prospects of the BTSC-pseudo-water concept will be considered including an analysis of most promising future applications.

Silicone oils (polysiloxane) and elastomers are a class of hydrophobic polymers with an extensive range of uses. While the high hydrophobicity can be beneficial in a variety of applications, it is not universally the case. Modification strategies for both fluid and elastomeric polydimethylsiloxane (PDMS) must be employed to create silicones with the desired properties, including enhanced hydrophilicity. Derivatization of PDMS leads to functional silicones with unique properties and added value.

Recently, we showed that the thermal Huisgen 1,3-dipolar cycloaddition ('click' chemistry) can be used to functionalize and crosslink mixtures of alkyne- and azido-functionalized polysiloxanes. This new methodology allows extensive control over the curing time and temperature, avoids the use of precious metal or copper catalysts, and facilitates subsequent derivatization with hydrophilic polymers such as poly(ethylene glycol) – PEG. 

We now extend this methodology to the preparation of functional polysiloxanes and elastomers containing multiple grafted hydrophilic macromolecules (either pendant on the PDMS backbone or within an elastomeric network). Azido-functionalized polysiloxanes undergo sequential modification with different alkynyl compounds to create PDMS graft copolymers. For example, it is possible to functionalize the azido-PDMS with less than stoichiometric amount of PEG- alkyne, and then functionalize or crosslink the product with different alkynes, which enables the straightforward preparation of novel silicone architectures. The synthesis of the precursor molecules, sequential modification, crosslinking and the resultant properties of the various amphiphilic structures will be discussed.

Novel electrical insulation and anti-corrosion materials based on linear and branched sol-gel hybrid polymers

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In a recent report we described very promising pyromellit diimde-bridged alkoxysilane precursors for electrical insulating coatings.[1] Here we present aminoalkylalkoxysilane modified s-triazines which were prepared to obtain single source precursors that can be used for the electrical insulation of fine copper wires and as anti-corrosion materials.

Scheme 1: Aminoalkylalkoxysilane modified s-triazine and its tested applications.

The molecular precursors were comprehensively analyzed using FT-IR, $^1$H, $^{13}$C and $^{29}$Si NMR spectroscopy. The initial stages of hydrolysis and condensation reactions under acidic conditions were examined with solution $^{29}$Si NMR spectroscopy.

The precursors were applied on fine copper wires using industrial coating and curing techniques. The applied hybrid coatings were tested by different analytical methods including electrical breakdown, pin hole and mechanical strength as well as FT-IR spectroscopy and thermogravimetric methods.

The anti-corrosion behavior of the s-triazines precursor was studied by using coated steel samples. Coating properties were determined using electrical impedance spectroscopy with respect to different hydrolysis and condensation rates, curing temperatures and coating thicknesses. For both potential fields of application (electrical insulation and anti-corrosion) promising results were obtained.

Unique physicochemical features of polysiloxanes such as chemical and thermal stability, extreme chain mobility and solubility make them interesting potential supports for transition metal catalysts. Soluble polymer-supported catalysts attract considerable attention. Such catalysts may have similar catalytic activity and stereoselectivity as the homogeneous parent system. When the reaction is completed, the catalyst can be separated by either solvent or heat precipitation, membrane filtration, centrifugation, or size-exclusion chromatography. Methods for the synthesis of functional polysiloxanes with controlled structure by ring-opening polymerization of cyclosiloxanes as well as their modifications by the reactions involving specific side groups (to introduce metal-anchoring ligands) are discussed. In particular, the immobilization of rhodium complex on polysiloxanes having various ligands and molecular architecture and the catalytic activity of so-prepared catalysts in the model hydrosilylation reaction are presented (Scheme 1).

Scheme 1. Model hydrosilylation reaction

The effect of a support structure and of the functional groups on the rate and selectivity of hydrosilylation in different solvents is discussed. Rhodium complexes supported on polysiloxanes show high activity and interesting selectivity, dependent on the structure of the support. Unfortunately, they are unstable and loose activity after one or two reaction cycles and therefore cannot be recycled.

Synthesis and ionic conductivity of siloxane based polymer electrolytes with pendant propyl acetoacetate pendant groups

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A polymer electrolyte is a polymer with a salt mixture which can support ionic conductivity. The polysiloxanes, with very low glass transition temperatures and extremely high free volumes, are expected to be good hosts for Li⁺ transport, when polar units are introduced into the polymer backbone.

The hydrosilylation reactions of 2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane (D₄H) with allyl acetoacetate catalysed by Karstedt’s catalyst, platinum hydrochloric acid (0.1 M solution in THF) and platinum on the carbon have been studied and fully edited product D₄R has been obtained. The reaction order, activation energies and rate constants have been determined for hydrosilylation reactions in the presence of Karstedt’s catalyst. Ring–opening polymerization reaction of D₄R in the presence of catalytic amount of powder-like potassium hydroxide has been carried out. Linear methylsiloxane oligomer with regular arrangement of propyl acetoacetate groups in the side chain has been obtained. The synthesized D₄R and oligomers were studied by FTIR, ¹H, ¹³C, ²⁹Si NMR spectroscopy. Comb-type oligomers were characterized with wide-angle X-ray, gel-permeation chromatography, and DSC analyses.

The synthesized oligomers are vitreous liquid products, which are well soluble in organic solvents with specific viscosity ηₛₚ ≈ 0.14 - 0.2. During polymerization reaction of D₄R in the presence of potassium hydroxide the reaction rate constants and activation energy of polymerization reaction at various temperatures were determined.

Via sol-gel processes of doped with lithium trifluoromethylsulfonate (triflate) or lithium bis(trifluoromethylsulfonyl)imide polymer systems solid polymer electrolyte membranes have been obtained. The dependence of ionic conductivity as a function of temperature and salt concentration was investigated. The electrical conductivity of these materials at room temperature belongs to the rather wide range of electrical conductivity magnitudes (10⁻¹⁰ - 10⁻⁴ S · cm⁻¹) and depends on the structures of grafted anion receptors and the polymer backbones.

This work has been fulfilled by financial support of Science & Technology center in Ukraine (Grant #5055).
Synthesis and properties of nanostructured cuprous chloride

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Reaction of silicon with chloromethane or alcohols proceeding in the presence of copper catalyst, so called “direct synthesis, plays an important role in production of organosilane compounds possessing unique properties and widely used in different fields1. Many efforts have been made to develop efficient copper-based catalysts for “direct synthesis” and to investigate their catalytic mechanism2. Nevertheless, the reaction mechanism is still debatable and good catalytic performances for industrial purposes are mostly achieved empirically. Therefore, development of efficient catalysts for “direct synthesis” is actual problem3. In present work, we developed a method for preparation nanostructured cuprous chloride by reductive thermolysis a mixture of CuCl2 with Cu(OH)2 in glycerol.

Fig. 1. Structure of a cuprous chloride aggregate with a size about nm consisting of globules with a diameter of about 200 nm, which are comprised of nanoparticles with a size about 20 nm (left); a single dense globule CuCl with a dispersed particles on the surface (right).

The obtained samples of nanostructured CuCl were characterized with infrared spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, and transmission electron microscopy (see Fig. 1).

The prepared samples demonstrated high catalytic activity in “direct synthesis” of triethoxysilane.

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NEW ORGANOSILOXANE COATINGS WITH METHYLENEPHOSPHONE GROUPS

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The creation of fibrous multifunctional materials with a complex of specified properties is a promising and actual direction of the investigation. One of the most interesting classes of high molecular compounds are polymers, containing in its composition aminomethyleneephosphonate groups, giving the materials sorption properties, as well as fire resistance and incombustibility and other properties of practical importance.

The present investigation is devoted to the developing of the lamellar molecular assembly method on the surface of cotton, wool and glass fibers of the grafted organosiloxane coatings with hydrophilic aminomethyleneephosphonate groups, conducted in two stages. On the first stage the immobilization to the surface of the oligo(chloromethyl)ethoxysiloxane fibers was carried out, when ethoxy groups of the oligomer react with OH-groups of the fiber with formation of the organosiloxane coating with chloromethyl groups (scheme 1):

Scheme 1

\[
\begin{align*}
\text{OH} + & \text{EtO Si} \quad \text{CH}_2\text{Cl} \quad \text{OEt} \\
\text{CH}_2\text{Cl} & \quad \text{O} \\
\text{OEt} & \quad \text{m} \\
\text{-(m+2)EtOH}.
\end{align*}
\]

On the second stage the immobilization of amino(dimethyleneephosphonate) acid was carried out (scheme 2):

Scheme 2

\[
\begin{align*}
\text{Si} \quad \text{O} \quad \text{CH}_2\text{Cl} \quad \text{O} \\
\text{O} & \quad \text{HN} \quad \text{CH}_2\text{P(O)}(\text{OH})_2 \\
\text{HN} & \quad \text{CH}_2\text{P(O)}(\text{OH})_2 \\
\text{O} & \quad \text{Cl} \\
\text{CH}_2\text{P(O)}(\text{OH})_2 & \quad \text{I} \\
\text{(NH}_4)_2\text{CO}_3 & \quad \text{II}
\end{align*}
\]

For the organosiloxane coatings obtained their composition and structure were determined and their sorption properties were investigated.

This work was supported by RFFI (project № 11-03-00577).
Siliconorganic backbone as a matrix for solid polymer electrolyte membranes

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Polysiloxanes attract the widest interest among the inorganic backbone polymers. The reason lies in properties of polysiloxanes such as strong heat resistance, elastomeric behavior, biocompatibility, thermal-, UV- and oxidative stabilities, low surface energy, good weather ability, low melting points and glass transition temperatures, convenient rheological properties and outstanding electrical properties. The polysiloxanes, with very low glass transition temperatures, extremely high free volumes, are expected to be good hosts for Li\textsuperscript{+} transport, when electron donor units are introduced into the polymer backbone.

The hydrosilylation reactions of \(\alpha,\omega\)-bis(trimethylsiloxy)methylhydrosiloxane with allyl di-(tri)ethyleneglycol monomethyl ether and vinyltriethoxysilane at 1:28:7 ratio of initial compounds in the presence of Karstedt’s catalyst, platinum hydrochloric acid (0.1 M solution in THF) and platinum on the carbon catalyst in 50\% solution of anhydrous toluene have been studied. Dependence of reaction rate and active ≡Si-H bonds’ conversion depth on the catalyst activity was investigated. The reaction order, activation energies and rate constants for hydrosilylation reactions in the presence of Karstedt’s catalyst have been determined.

The synthesized oligomers are vitreous liquid products, which are well soluble in organic solvents with specific viscosity \(\eta_{sp} \approx 0.05 - 0.06\). The synthesized oligomers were analysed with FTIR, \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{29}Si NMR spectroscopy. Synthesized polysiloxanes were investigated with wide-angle X-ray, gel-permeation chromatography, and DSC analyses.

Via sol-gel processes of doped with lithium trifluoromethylsulfonate (triflate) or lithium bis-(trifluoromethylsulfonyl)imide polymer systems solid polymer electrolyte membranes have been obtained. The dependence of ionic conductivity as a function of temperature and salt concentration was investigated and the activation energies of conductivity for all obtained compounds are calculated.

This work has been fulfilled by financial support of Science & Technology center in Ukraine (Grant #5055).
The approaches to the synthesis of siloxane rotaxanes


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Rotaxanes are molecules possessing one of the most unusual structures existing in the supramolecular chemistry. The direction develops actively:

- development of new strategies of similar structures,
- new building blocks are synthesized for self-assembly of rotaxanes,
- techniques of rotaxanes separation from the reaction medium are improved.

In this work the approaches to the synthesis of new rotaxane systems are presented. It is siloxane rotaxanes based on stereoregular siloxane macrocycles (as cyclic fragment of rotaxane 1) and polydimethylsiloxane with narrow molecular weights distribution (as linear fragment of rotaxane 2). Due to the combination of interesting properties of both components (1 and 2) in one macromolecule - the systems which can be prepared should demonstrate unique physical-chemical properties.

This work was supported by the grant of the Presidium of RAS (project OX-6).
Synthesis polymolybdenophenylsiloxane containing molybdenum atoms in oxidation state +6

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Synthesis polymolybdenophenylsiloxane was performed according to the methods previously described for obtaining of metallosiloxanes containing in its composition molybdenum +5 oxidation state, as follows:

$$2[(\text{PhSiO}_{1.5})\text{O}_{0.5}\text{Na}] + \text{MoO}_2\text{Cl}_2\cdot2\text{DMSO} \rightarrow [(\text{PhSiO}_{1.5})_2\text{MoO}_3] + 2\text{NaCl} + 2\text{DMSO}$$

The synthesis was carried out in a solvent system of benzene-DMSO at the boiling point of the solution. On the basis of elemental analysis of the isolated compounds, the ratio of silicon to molybdenum is different from the set value, depending on the fraction is very different. In this case, the fraction (frac.1) with a high content of molybdenum in the IR spectrum has a very narrow absorption band, responsible for Si-O bond, according to Powder X-ray diffraction (XRD) (Fig. 1) is not revealed peaks corresponding to interplanar distances as polyphenylsiloxane (PPS) and molybdenum oxide (VI) MoO$_3$. Thus on the basis of these data we can conclude that major structural chain in this fraction is not siloxane fragment but molybdenum-oxygen fragment.

![Figure 1. Spectrum XRD](image.png)

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Investigations on structural properties and reactivity of novel aryl substituted silanes

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Hydrogen rich arylsilanes, RSiH₃ and R₂SiH₂, are important precursors for the generation of di-, oligo- and polysilanes with arylsubstituents. Arylpolysilanes show interesting photoreactive properties and have great potential for applications in optoelectronic devices owing to their unique electronic structure, attributed to the σ-electron delocalization in the Si-Si backbone and the π-electron systems of the aryl substituents.¹,²

Here we report on the synthesis and characterization (NMR, GC-MS, UV-VIS, single crystal X-ray diffraction) of secondary silanes prepared via Lithiation or Grignard reaction (Fig. 1) to form the halosilanes which were treated with LiAlH₄ to give Anthracenyl₂SiH₂, 2,6Xylyl₂SiH₂, (Fig. 2) and p-Butylphenyl₂SiH₂ in moderate yields. In addition, 1-Naph₂SiH₂, first reported by West ³ was prepared and recrystallized from toluene (Fig. 2).

The reactivity of prepared secondary arylsilanes, R₂SiH₂, in the presence of transition metal catalysts, such as Cp₂TiMe₂, in order to form compounds of higher molecular weight was investigated and compared to the corresponding primary arylsilanes, RSiH₃. Photoreactivity studies were performed by irradiation of the compounds in the range of 190-600nm. Specifically, Anthracenyl₂SiH₂ undergoes structural changes, which has been reported in literature for similar compounds.⁴ Furthermore, the thermal stability of the arylsilanes and resulting materials and their potential formation of inorganic-organic hybrid materials when being thermolysed under inert gas atmosphere was tested.

Luminescent organosiloxane nanocomposites

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A wide range of unique physical and chemical properties of polyorganosiloxanes allows their use in various fields of science and technology. They are employed for the production of lacquers, enamels and press compositions, adhesives, protective coatings for microelectronics and so on.

In this work we developed new luminescent crosslinking agents and organosiloxane nanocomposites based on them. The new luminescent crosslinking agents are branched oligoarylenesilane molecules with fluorescent groups in the center and at the periphery, which has additional reactive end groups. In these compounds different chromophores are combined within one dendritic molecule that lead to the so called “nanostructured organosilicon luminophores” with an intramolecular directional energy transfer from their external chromophores to the center (a molecular antenna effect). Photoluminescence study of the new luminescent crosslinking agents has shown an efficient absorption in a wide spectral range and luminescence quantum yield up to 88%. These molecules can be used as the spectral shifters, which absorb UV light and emit in the blue, yellow or red region of spectrum. Stability of the new luminescent crosslinking agents was checked by TGA method, which showed that they are thermostable up to 450 °C.

Presence of the reactive vinyl groups in the periphery of new functional crosslinking agents makes it possible to obtain luminescent organosiloxanes nanocomposites by hydrosilylation reaction. Various methylphenylsiloxane oligomers with residual hydridesilyl groups were used as a matrix.

Promising properties of new luminescent organosiloxane nanocomposites allow of their application in the brand-new technologies, such as flexible, thermally and radiation stable luminescent lacquers, which are in high demand in radiation control, space and medical diagnostics technologies.

At the present work a relation between the properties of nanocomposites and the structure of new luminescent crosslinking agents as well as their concentration in the matrix is discussed.

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Thermal and oxidation degradation of metallasiloxanes

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Metallasiloxanes (MOS) are of interest as potential precursors for metal-oxide and silicon-oxide ceramics. In this work the peculiarities of formation of ceramics on pyrolysis MOS were studied. The MOS has been obtained from tri-functional organosiloxanes under the general scheme:

\[
\text{PhSi(OEt)}_3 + \text{NaOH} + \text{H}_2\text{O} \rightarrow (\text{PhSiOONa})_n + \text{MCl}_2 \rightarrow [(\text{PhSiO}_2\text{M})_n
\]

According to this scheme the crystalline individual compounds – frame organometallasiloxane (FMOS) can be prepared at certain conditions - in addition to the polymer metallasiloxanes (PMOS). Some of these compounds are described by the general formula \([\text{PhSiO}_2]_6\text{M}_6[\text{PhSiO}_2]_6 (\text{M} = \text{Cu, Ni, Mn}).\)

In addition to monometallic Cu-FMOS, bimetallic “alkaline” derivatives (Cu, M’)-FMOS, wherein M’ are ions Na were also obtained. They are described by formulas \([\text{RSiO}_2]_6\text{Cu}_4\text{Na}_4[\text{RSiO}_2]_6 (\text{where } R = \text{Ph, Me}.\) The latter reacts with metal chlorides \(\text{MCl}_2\) to form bimetallic “neutral” FMOS of formula \([\text{RSiO}_2]_6\text{Cu}_4\text{M’}_2[\text{RSiO}_2]_6 (\text{M’} = \text{Mg, Mn}).\)

Pyrolysis of FMOS was investigated by TGA, DSC, XRD, XPS, optical and electron microscopy. It was found that the degradation of FMOS at inert atmosphere occurs in two stages. First proceeds at temperature range 300-400 °C. Already on this stage break-away of organic groups from the silicon atoms is observed. It is accompanied by partial or complete reduction of metal atoms and forming of a metal and metal oxide phases. On the second step (T> 400 °C) occurs complete removal of organic groups and further formation of a metal oxide and a metal phase, followed by simultaneous increase in their sizes. In a case of Na-containing FMOS at temperatures above 800 0C a transformation of pyrolysis products into crystallized SiO2 occurs.

The second step at oxidizing atmosphere leads to the formation of a strong monolithic thermostable ceramic based on SiO2, which includes interspersed microphase of metals and their oxides. Thermo-oxidative destruction occurs as a single step in the 300-400 °C and is accompanied by considerable heat release.

On comparison with FMOS the decomposition of PMOS occurs at temperature on ~ 50 °C lower, however, the general patterns (weight loss on similar stages, nature of exothermic effects) remain similar.
Influence of Si-substitution on photovoltaic properties of thiophene-based copolymers

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Organic photovoltaics is one of the outstanding and fast growing field of modern science and alternative energy technologies. During the last 20 years power conversion efficiency (PCE) up to 10\% has been achieved in polymer-based photovoltaic cells, in comparison with less than 1\% in 90\textsuperscript{th}. For the sake of further improvement of polymer solar cells PCE, new high efficient copolymers need to be developed. Besides of high charge carriers mobility and narrow band gaps, the new copolymers should absorb solar light in the widest possible range of the solar spectrum and have the absorption maximum near the sun emission maximum. Moreover, it is desired, that new copolymers will have high molecular weights which render them better semiconducting properties. Also synthetic methods for preparation of these copolymers must be simple and lead to the products with high yields.

Cyclopentadithiophene (CPDT) – is one of the promising building blocks for narrow band gap copolymers design. Insertion of a heteroatom with d-orbitals (Si, Ge) in the methylene bridge of CPDT can dramatically alter the absorption spectra of the corresponding copolymers and, as a consequence, increase PCE. Furthermore, synthesis of Si-containing CPDT monomers – dithienosiloles (DTS) – is rather simple. That is why it was important to compare photovoltaic properties of the CPDT-based copolymers with their DTS analogues, as we did in the case of the four new copolymers (P1-P4) synthesized either with dialkyl-DTS or dialkyl-CPDT donor monomers units and 4,4’-difluoro-CPDT as acceptor monomers units [1]:

![Chemical structures](image)

UV-vis spectroscopy measurements of the copolymers synthesized have shown that all of them possess a broad absorption in the range of 400-700 nm. Further investigations revealed that $\lambda_{\text{max}}$ of P3 was bathochromically shifted on 60 nm relative to those of P1 that can be explained by the influence of the carbon substitution with the silicon in the CPDT ring. Photovoltaic properties of P1-P4 were investigated in bulk heterojunction solar cells with the active layer, consisting of a mixture of [60]PCBM as an acceptor and the copolymer as a donor in the ratio of 1:1. After varying the preparation conditions (thickness of the active layer and annealing temperature) PCE of Si-containing copolymer P4 was measured as high as 2.4\%, while it was only 1.24\% for its carbon analog P1.

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POSS-containing, Reactive Siloxane Resins as Polymer Modifiers

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Along with technological development of all branches of industry, the demand for higher processed materials of improved physicochemical properties is constantly increasing. In many cases such materials can be obtained on the basis of well-known products that have been present on the market for a years, by their modification with appropriate modifiers. Nowadays polyhedral oligomeric silsesquioxanes (POSS), especially T₈ derivatives, have become a group of compounds most extensively explored as modifiers and nanobuilding blocks. Their attractiveness stems from useful physicochemical properties, ease of chemical modification, reactivity and nanometer size¹,²,³. Development of new and effective methods of POSS synthesis with various functional groups influences the number of their possible applications. Particularly important from the point of view of chemical synthesis are the POSS with reactive functional groups in example hydrogen atoms, vinyl, amino, epoxy, methacryloxy or hydroxypropyl groups. Despite the development of methods for the synthesis of these compounds and the growing number of their potential applications their prices are still high and availability is quite low. An alternative for those well define, attractive but still expensive compounds may be to use a lot cheaper siloxane/silsesquioxane resins of type and structure described in this contribution.  

Series of siloxane resins with POSS Q₈ structures as network nodes containing reactive Si-H bonds in the siloxane bridges linking silsesquioxane units was obtained in hydrolytic condensation process. The influence of reactants stoichiometric ratio (POSS/dichloromethylsilane) on the structure of final product was investigated. In the next step attempts to addition of Si-H groups present in siloxane bridges to multiple bonds of olefins were performed in order to obtain organofunctionalized materials of different organic group content. As a final result numerous reactive siloxane/silsesquioxane resins, capable to chemically interact with organic polymers were obtained. The authors idea was that material of this type could be an interesting, fully functional and cheaper alternative to typical mollecular POSS compounds and serve as various polymer modifier or reactive filler.  

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Synthesis of polysiloxanes microcapsules containing phase change materials

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The coemulsification method was used for the synthesis of polysiloxane microcapsules filled with a phase change material (PCM) destined for the application as additive in textile industry for the thermoregulation of clothes. The PCM polysiloxane microcapsules are formed in aqueous emulsion by the precipitation of n-eicosane together with modified polyhydromethylsiloxane from a common solvent which is miscible with water. The microcapsules formed in the aqueous emulsion are stabilized by the in situ cross-linking of polysiloxanes shell. Before the coemulsification linear polyhydromethylsiloxane is modified by hydrosilylation of 1,3-divinyltetramethyldisiloxane to graft vinyl groups on the polymer chain. Further hydrosilylation leading to the polymer cross-linking occurs in the microcapsule shell in the aqueous emulsion following the formation of the capsule. Karstedt Pt(0) catalyst used in the hydrosilylation also promotes hydrolysis of SiH groups in the polymer producing a large number of silanol groups. Some of these groups undergo the Karstedt catalyzed dehydrogenocondensation with remaining SiH groups thus forming siloxane bridges between the polymer chains, which increases the density of cross-linking. The microcapsules were analyzed by DSC, SEM, optical polarized microscopy and thermooptical analysis (TOA).

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The Synthesis of High Molecular Weight POSS-Polymers Using ATRP

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Polyhedral oligomeric silsesquioxanes (POSS)i with empirical formula (RSiO1.5)n are among the most intriguing examples of well-defined, nanostructured building blocks for the synthesis of novel, high-performance, hybrid materials.ii Their unique, three-dimensional structure is based on the inorganic, ceramic in nature core (with dimension < 1 nm), made up of silicon atoms linked by oxygen atoms and covalent bonded with organic groups which are symmetrically situated at the periphery of the framework. Polymerization at the single reactive “X” site results in a polymer containing nanosized cube pendent to an organic polymer backbone. Our research is focused on the synthesis of polymethacrylates containing Si-O cage in the structure. So far that type of polymers was prepared by the conventional radical techniques (RP)iii as well as living and controlled methods (LCP) such as atom transfer radical polymerization (ATRP)iv, reversible addition–fragmentation chain-transfer polymerization (RAFT)v or anionic polymerization (AP)vi. Poly(POSS-MA) with the highest polymerization degree DPn= 104iii was obtain by RP process, however when living systems were employed only oligomers were formed. Due to these information we decided to performed detailed kinetic studies of polymerization of POSS-MA using ATRP method and define the reason of the formation only low molecular weight polymers in controlled process. Results of our work led to the developing an efficient method, which allowed for the first time synthesis of high molecular weight, linear POSS-methacrylate homopolymers with polymerization degree DPn>500.

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Use of organoalkoxysilanes instead of organochlorosilanes as initial monomers for organosilicon synthesis tends to grow into a new trend in the chemistry of organosilicon compounds. Polycondensation of organoalkoxysilanes in the active medium (the excess of acetic acid) has been recently proposed as an universal chlorine-free method for the synthesis of polyorganosiloxanes of different structure. The investigations of the process have shown its prospects to obtain both branched and polycyclic [1], and linear and cyclic structures [2, 3].

In recent years an active research of Grignard reaction was conducted in order to obtain alkoxysilanes with different organic substituents [3], including methylbenzyldiethoxysilane. To the best of our knowledge data on obtaining linear or cyclic polymethylbenzylsiloxanes is missing in the literature.

The aim of the work was to study polycondensation of methylbenzyldiethoxysilane in active medium and to find conditions allowing to selectively obtain linear or cyclic products (fig. 1).

**Fig. 1. Scheme of polycondensation of methylbenzyldiethoxysilane in acetic acid.**

The results of the study including characteristics of the products by GPC, NMR, IR-spectroscopy will be discussed in the presentation.

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Synthesis polymolybdaenphenylsiloxanes and investigation of their thermostatic the stabilizing properties

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Polymolybdaenphenylsiloxanes (PMoPS) with a ratio of silicon to metal equal to 1, 3 and 6 were synthesized by reacting sodium polyphenylsiliconate with MoOCl$_3$·2DMSO in the previously described conditions as follows:

\[ n\text{MoOCl}_3 \times 2\text{DMCO} + n\text{NaOSi≡} \rightarrow \text{Mo}(\text{OSi≡})_n + n\text{NaCl} \]

The metal content in the polymer was controlled by changing the ratio of Si/Na in the starting polyphenylsiliconates. PMoFS are solids, infusible up to the decomposition temperature, are well soluble in most organic solvents, insoluble in saturated hydrocarbons. According to the SEC all PMoFS have molecular weight = 5000 and does not contain low molecular weight compounds. PMoFS have been investigated by elemental analysis, IR spectroscopy, X-ray diffraction analysis.

PMoFS heat stabilizing effect has been investigated by introducing them to a polydimethylsiloxane rubber (SKTN) at a concentration of 1%. It was established that all PMoFS have thermally stabilizing effect and increasing metal content in the polymer enhances the effect. It is estimated, that polymolybdaenphenylsiloxane with Si/M ratio equal to unity has the greatest heat stabilizing effect. These results agree well with the data obtained with earlier investigations of polyferrophenylsiloxanes, where by a polymer with a high metal content in the main chain (Si/Fe = 1) has the highest heat stabilizing effect.

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Novel fluorine-containing polyorganosiloxane for the protective antireflection coatings

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Novel organosilicon monomer was synthesized by the reaction:

\[(\text{EtO})_3\text{Si}-\text{NH}_2 + \text{O} = \text{C} \rightarrow (\text{EtO})_3\text{Si}-\text{NH}-\text{C} = \text{OH}\]

This monomer gives polymer by the intermolecular condensation:

\[
\begin{align*}
\text{(EtO)}_3\text{Si}-\text{NH}-\text{C} = \text{OH} & \quad \text{HO} \quad \left[ \begin{array}{c}
\text{OEt} \\
\text{CF}_3
\end{array} \right] \\
\text{CF}_3 & \quad \text{CF}_3 \\
\text{CF}_3 & \quad \text{CF}_3 \\
\text{CF}_3 & \quad \text{CF}_3 \\
\text{CF}_3 & \quad \text{CF}_3
\end{align*}
\]

\[n = 3–4\] for the low molecular mass fraction and \[200-450\] for the high molecular mass fraction.

The hydrolysis of this polymer by air moisture yields polysiloxanes coating directly on the substrate. The films surface found to be sufficiently smooth; the height of the relief is less than 2 nm. The value of the arithmetic mean roughness \(R_a\) 0.24 nm. The surface of coating is hydrophobic, and the contact angle for water is 88°. Studied samples are low energy polysiloxane with the value of total surface energy of 13.16 mJ/m². At the same time polymer has low surface polarity \((\gamma_p/\gamma_s=0.14)\), which is characteristic of organofluorine polymers, as well as linear polysiloxanes with fluorinated substituents. Absorption bands in UV, visible, and near IR region are not observed for the obtained polysiloxane. Ellipsometric measurements show that polymer has low refractive index over a wide wavelength range. The minimum value for the sample achieves 1.300–1.305.

![Fig. 1. The dependence of the refractive index of the polymer coating on the wavelength](image1.png)

![Fig. 2. The transmission spectra of thin film of polymer on a quartz substrate: the transmission of pure quartz substrate (1), polymer (2).](image2.png)
Novel water-soluble polysiloxanes for the biomedical applications

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Novel organosilicon monomers have been prepared:

\[
\begin{align*}
(\text{EtO})_2\text{Si} & \quad \text{NH} \quad \text{NH} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH}
\end{align*}
\]

1

\[
\begin{align*}
(\text{EtO})_2\text{Si} & \quad \text{HN} \quad \text{NH} \\
\text{C} & \quad \text{O} \quad \text{SiO}_1.5 \\
\text{HO} & \quad \text{H}
\end{align*}
\]

2

The one-pot sol–gel process gives cross-linked polymers 3 and 4:

\[
\begin{align*}
\text{HO}_2\text{C} & \quad \text{CH}_2\text{OH} \\
\text{CH}_2\text{OH} & \\
\text{CH}_2\text{OH} & \\
\text{NH} & \quad \text{C} \quad \text{O} \\
\text{HO} & \quad \text{SiO}_{1.5} \quad \text{H}
\end{align*}
\]

3

\[
\begin{align*}
\text{HO} & \quad \text{C} \quad \text{O} \\
\text{F}_2\text{C} & \quad \text{CF}_2 \\
\text{F}_2\text{C} & \quad \text{CF}_2 \\
\text{F}_2\text{C} & \quad \text{C} \quad \text{O} \\
\text{NH} & \quad \text{SiO}_{1.5} \quad \text{H}
\end{align*}
\]

4

They are readily soluble in water and lower alcohols, contains multiple donor primary amide groups which can efficiently bind metal complexes and dyes. The water suspensions of europium benzoyl trifluoroacetone (III) based on polymers 3 and 4 show efficient emissions (pic.1a).

Fig. 1. The photoluminescence spectra of complex Eu³⁺ with polymers 3 (1a) и 4 (2a) and porphyrin with polymers 4 in water by the addition serum (1b) and albumin (2b).

Investigations of the luminescent properties of siloxane-based particles doped porphyrin showed a strong red fluorescence enhancement in an aqueous solution of serum and of human albumin (main serum protein) (pic.1b). This probably reflects effective conjugation of nanoparticles with protein molecules. These water-soluble fluorescent polymers are suitable for biological applications such as in sensors and imaging agents.

This work was supported by RFBR (project № 12-03-31489 мол_а) and Ministry of Education and Science (state contract 14.132.21.1673).
Organopolysiloxanes bearing aminoalkyl substituents, often referred to as aminosiloxane oils, are a group of one of the most widely applied functionalized organopolysiloxanes\textsuperscript{1,2,3}. Because of their unique properties, they have been used in both textile and hair care applications for decades. These organoreactive silicones have gained also a large importance in such areas as treatment of metal and mineral surfaces.

Scheme 1. Reaction of siloxane diols with aminoalkylalkoxy silanes

The problem of optimization of reaction was approached by kinetic studies of condensation, involving the respective model (aminoalkyl)alkoxy silanes and individual, well defined oligosiloxanediols. In this study the conversion rate of aminosilanes in condensation with silanediols was described and revealed the second order kinetic dependence in substrates\textsuperscript{4}.

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Bithiophenesilane-based dendritic macromolecules: synthesis and properties

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Dendrimers are unique organic materials, which combine highly branched regular arrangement of functional organic moieties within one macromolecule having typical dimensions of 1 to 10 nm. Oligothiophenesilane dendrimers are known for their efficient molecular antenna effect¹, as well as intensive photoluminescence in the violet-blue region, the quantum yields of which are significantly higher than those measured for their constituent luminophores themselvesii. The main drawback of the high-molecular weight dendrimers is their multistage synthesis, which limits their practical applications. This problem may be solved by the synthesis of dendronized polymers. These unique materials combine the properties of both dendrimers and polymers. They are currently are under intense investigation with respect to various applications, including the synthesis of hierarchically structured materials, catalysis, applications in the biosciences, such as ion channel mimics and DNA compactization, as well as optoelectronic applicationsiii. We report here the synthesis and investigation of several generations of bithiophenesilane-based dendrimers and dendronized polymersiv as well as the results of preliminary tests of the most perspective molecules as functional materials in organic light-emitting diodes.

Fig. 1. Schematic structures of bithiophenesilane-based dendritic macromolecules

This work was partially supported by the Presidium of Russian Academy of Sciences (program P-24) Russian Foundation of Basic Research (project № 03-13-01315а) and Russian Ministry of Education and Science (project 11.G34.31.0055).

Hydrophobic Materials Based on Fluorocarbofunctional Spherosilicates

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Fluorine-containing materials have been the subject of studies by many researchers, not only because of their influence on hydrophobic or oleophobic properties of various materials¹, ². They can be applied to the synthesis and modification of fabrics, new efficient catalysts, optical materials, and polymers and also in biotechnology and nanotechnology³, ⁴. As a natural extension of the most recent interests of modern science to the fields of nanotechnology and fluorine-containing materials, fluorinated silsesquioxanes have emerged as a new class of compounds. POSS (polyhedral oligomeric silsesquioxanes) of the empirical formula (RSiO₁.₅)ₙ with different possible structural representations have recently become the subject of growing interest in many branches of chemistry. In this presentation, the syntheses of fluorocarbofunctional silsesquioxanes (spherosilicates), as well as their selected surface properties were presented⁵, ⁶.

Previously obtained octakis(dimethylsiloxy)octasilsesquioxane was used as a starting material in the hydrosilylation process of functional olefins leading to a synthesis of POSS. This method enabled us to synthesize functional silsesquioxanes containing mixed functional groups at different stoichiometric ratios via tandem (successive) hydrosilylation of two respective olefins, e.g. fluorocarbofunctional allyl ether and allyl-glycidyl ether or vinyltrimethoxysilane⁵, ⁶. Depending on obtained derivative processes were conducted in THF, toluene as solvents. The contribution of our research team to the above field was the application of highly effective rhodium siloxide complex to the synthesis of various fluorocarbofunctional spherosilicates compounds. Proper choice of solvent as well as catalytic system results in high yield of obtained products.

The hydrophobisation method involves the condensation reaction of the hydroxyl groups on the modified surface with reactive groups in the organofunctional compounds. The obtained fluorocarbofunctional organosilicon derivatives are good precursors for the synthesis of highly hydrophobic materials and coatings. The measure of hydrophobicity is contact angle determined by drop profile tensiometry. Values of contact angles exceeding 150° are typical of superhydrophobic surfaces. Such results were obtained for the glass surfaces modified by the above compounds together with silica nanoparticles using dip coating method or chemical vapour deposition.

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⁵ Marciniec B., Maciejewski H., Dutkiewicz M. PCT/PL 2011/050053.
Synthesis of hyperbranched polymethylsilsesquioxanes

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Polymethylsilsesquioxanes are suitable fillers for introduction into the various polymer matrix and extensively used in cosmetics. In this paper will be presented the modification of hyperbranched polymethylethoxysilsesquioxane by condensation in acetic acid in various condition.

By such method we can obtain polymethylsilsesquioxanes, terminated by trimethylsiloxy groups in various ratios. If we use in this reaction another termination agent, in example tetramethyldivinyldisiloxane, we can obtain functionalized polymethylsilsesquioxanes and use them for further transformations. Obtained products was characterized by various methods. As shown DSC analysis when we increase time of condensation before adding termination agent so we increase the ratio [MeSiO] and [Me2SiO], glass transition temperature also increases. And in GPC curves we can see increase of molecular mass in this series. We also measured the Langmuir isotherm and we saw that all terminated polymethylsilsesquioxanes have low surface energy, lower than PDMS. So they may be also used as surfactants.

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Synthesis of the polymethyl(vinyl)silsesquioxane nanogels with different core-shell structures through the condensation of the hyperbranched polymethyl(vinyl)siloxanes.

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The annual number of publications devoted to the study and application of the hyperbranched silicone containing polymers reflects the increasing interest to such systems in recent years.

In this work the hyperbranched polymethyl(vinyl)siloxanes were used as a starting material in the process of the “macromolecule-nanoparticle” transition.

Due to the high functionalities of hyperbranched polyorganosiloxanes their acyclic structure can be easily transformed into the polycyclic structure of the polyorganosilsesquioxane nanogel with the ability to control the size and functionality of the latter. And variation of the chemical nature of the starting hyperbranched polyorganosiloxane and the end-capping agent leads to the formation of the polyorganosilsesquioxane nanoparticles with different core-shell structures.

Thus, the introduction of the functional vinyl groups capable of chemical modification into the shell of the resulting polyorganosilsesquioxane nanoparticles leads to the formation of the polysilsesquioxane nanoparticles that can be used as highly compatible organic-inorganic nanocomposite materials. While the integration of functional groups into the core of globular molecule of polyorganosilsesquioxane nanogel yields the polyorganosiloxane matrix that has a potential ability of acting as a nanoencapsulating agent.

In the present study new hyperbranched polyvinyl(methyl)sirolxane polymers and polyorganosilsesquioxanes with two different core-shell structures were obtained and investigated.

Figure 1. Synthetic scheme of the preparation of the polymethyl- and polyvinylsilsesquioxane nanogels and their end-capping with divinyltetramethyldisiloxane and hexamethyldisiloxane respectively.

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Synthesis of some new siloxane hyperbranches

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Noted processes of hyperbranched siloxane structures formation, are accompanied by the formation of cyclic fragments owing to the cycle formation reactions.\textsuperscript{1,2}
We have proposed an approach to produce ethoxysiloxane hyperbranched polymers by one-pot synthesis from one monomer, which containing both one type of reactive groups, namely hydro- and ethoxysilane, by reaction Pierce-Rubinstein. Such a scheme, allows to obtain a molecules with a high degree of branching, without the formation of intermolecular cross-linking appears, to be very promising. This paper will present the results of studies on the reactions of monomers AB3 and AB6 type. [Fig. 1].

Fig. 1 Scheme of hyperbranches synthesis from monomers AB2 and AB6 type


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Synthesis of Carbosilane Dendrimer Derivatives Containing Linear Ethylene Oxide and Dioxolane Groups in the Outer Layer

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Dendrimers are brand-new class of polymers, distinguished by nearly perfect, highly – branched architecture of a molecule. Thanks to their outstanding properties such as definite size and certain shape of a molecule, low polydispersity, controllable functionality, dendrimers caught the imagination of chemical community. As of today, there is a great variety of dendrimers with different structure and chemical nature of a core and an external layer. On the basis of carbosilane dendrimers there was created a wide array of functional and nonfunctional derivatives e.g. hydrophilic polyhydroxyl systems, hydrophobic and oleophobic fluoro-containing systems, polysiloxane derivatives and even dendrimers containing mesogenic external groups. Given that, outer layer of a dendritic molecule includes not only, at least, the half of a molecule structure but also this is a part of a molecule where intermolecular interactions take place, no wonder, that physical properties turn out to be determined by chemical nature, structure and density of the outer layer.

So, in order to get insight into the problem of «structure – property» relationships, there should be a row of new macromolecular objects which distinguish by the level of intermolecular interactions and flexibility of the external structural fragments.

At the present research synthesis of carbosilane dendrimers containing flexible ethylene oxide linear structural fragments distinguished by polarity (fig. 1, a) and rigid dioxolane external groups (fig. 1, b) is considered. Also, influence of the nature and density of outer layer on physical properties of carbosilane dendrimers is discussed.

Fig. 1. Carbosilane dendrimers of different generations containing linear ethylene oxide (a) and dioxolane (b) external groups.

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Over the past resent years composite materials filled with nanoparticles attracted a great deal of interest. They owe this attention to a complex of high-performance properties which can be imparted to composites by means of nano-fillers. Carbosilane dendrimers along with silsesquioxane oligomers are the most convenient and promising models of fillers for polymer matrices. They are nanoobjects with precise architecture and strictly defined size of a molecule. Silsesquioxane oligomers, being hybrid organo-inorganic nano-sized particles, consist of a cage-like rigid core and external organic groups, while carbosilane dendrimers are regular hyper-branched structures with a «soft» core and organic outer shell. Besides, high reactivity of functional groups allows for creation a broad variety of organic derivatives on their surface and so, improves compatibility with organic polymeric matrices.

It should be noted that the given macromolecular nano-objects possess narrow MMD and don’t require additional fractionation. Given that, polystyrene was used as polymer matrix, organic external layer of nano-sized macromolecules was modified with hydride silanes, containing polystyrene monomeric unit.

It turned out that the use of hybrid nanoparticles of different sizes makes it possible to raise or lower the glass transition temperature of the composite material on purpose (fig.1). However, structure and rigidity of a core of nanoparticle affect not all the properties of polystyrene-based composite.

At the present study the modification of outer layer of nano-sized particles will be presented. Also, the influence of rigidity of the core, macromolecule architecture and its size on the glass transition temperature, reological and mechanical properties of polystyrene-based composite will be discussed.

![Fig. 1. Influence of dendrimer size on the glass transition temperature of polystyrene-based composite](image)

*This work was supported by RFBR (project № 12-03-00922-A, 12-03-33152-A).*

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Synthesis and properties of new tetrafunctional cyclosiloxanolates

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The synthesis of tetrafunctional cyclosiloxanolates\(^1\) and their use as precursors for the synthesis of 1,3,5,7-tetrahydroxycyclotetrasiloxanes\(^2,3\), or ladder-like silsesquioxanes\(^4\) is known in the literature. Most often these compounds bear at the silicon atom simple organic substituents (Me, Et, Ph etc.). An attempt to synthesize a series of new potassium cyclosiloxanolates with various, reactive functional groups and the corresponding (trimethylsiloxy)cyclotetrasiloxanes has been thus undertaken. The influence of reaction conditions and properties of functional groups on the structure of obtained materials was analyzed (X-ray diffraction and NMR spectroscopy).

\[
\begin{align*}
R & = \text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}, \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2, \text{CH}_2\text{CH}_2\text{CH}_2\text{CN, CH}_2\text{CH}_2\text{CH}_2\text{SH}
\end{align*}
\]

Fig. 1. General scheme for the synthesis of cyclic siloxanolates from functionalized triethoxysilanes

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Nanostructured surfaces by associative interactions in ladder oligosilsesquioxanes.

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Oligomeric silsesquioxanes (LPSQ) of ladder structure of the siloxane backbone and bearing carboxylic acid (CA) functions were prepared by polycondensation of 1,3,5,7-tetravinyl-1,3,5,7-tetrahydroxycyclotetrasiloxanes\(^1\), followed by thiol-ene addition of suitable mercaptans to vinyl moieties.

It was found that the obtained materials are capable of preparation of nano- and microstructured surfaces of designed properties (wettability, bioactivity). They show good film-forming properties and arrange into unique organized layered structures on hydrophilic surfaces, as indicated by atomic force microscopy (Fig. 1). The surface-polymer interactions were analyzed for several supports of different chemospecificity (mica, glass silanized with aminopropylsilane, hydrophilic silicon wafers).

This work was supported by National Science Centre grant DEC-2011/03/B/ST5/02672 „Studies on the preparation and structurization of new hybrid materials”.

\(^1\) Kowalewska A., Nowacka M., Patent Application WIPO ST 101 PL 399575
Self-assembly of ladder oligo(phenylsilsesquioxanes) into spherical structures.

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Linear ladder silsesquioxanes (LPSQ) of regular double-chained structure of the polymer backbone gain growing interest due to their unique physiochemical properties. We have noted that oligomeric LPSQ bearing side phenyl groups (Ph-LPSQ) can self-assemble to form spherical nano- and microstructures (Fig. 1) on precipitation of the solution of Ph-LPSQ into a non-solvent. Such nano-/micrometer-sized solid spheres can be applied as photonic crystals or templates to synthesize microporous materials. There are only few reports concerning homopolymers (not amphiphiles) self-assembling into spherical morphologies and the process of their formation presented here is quite unique, since it refers to rigid molecules with relatively small side substituents.

Fig. 1 SEM (a) and TEM (b) photographs of oligo(phenylsilsesquioxane) microspheres.

Ph-LPSQ were prepared using several methods that resulted in materials of different degree of branching in the backbone (stepwise coupling polymerization of PhSi(OEt)$_3$, condensation of 1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclosiloxane, direct co-hydrolysis and condensation of PhSi(OEt)$_3$ in solution and in bulk). Their structure was analyzed using WAXS, FTIR, triple-SEC, MALDI and NMR techniques. The size and shape of the microspheres were studied using AFM, SEM and TEM microscopies as well as dynamic light scattering. It was concluded that the main factor governing the formation of microspheres is the molecular weight of the oligomer, while the structure of the siloxane backbone is of minor importance.

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Synthesis of trimethylsiloxy derivatives of polymethylsilsesquioxane

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Polydimethylsiloxane is one of the most common polymers in silicones family, which play an important role in different applications because of its unique properties. The variation of polydimethylsiloxane molecular architecture can be used as an effective tool for the controlling its properties. One of the very intriguing example of this kind was given in recent work where the specially synthesized methyl(trimethylsiloxy)-substituted cyclotrisiloxane was polymerized. Possessing the same chemical composition, but different combination of structural units, this new polymer showed different properties, i.e. no crystallinity, higher Tg, etc.

Recently, the same polymer – polymethyl(trimethylsiloxy) silsesquioxane, was prepared by another chemical approach, which was based on the synthesis of polysodiumoxy(methyl) silsesquioxane – polymeric sodium salt prepared by hydrolytic polycondensation of sodiumoxy(methyl)diethoxysilane (Fig. 1).

In this work, we present the synthesis and physical properties of hyperbranched polymethylsilsesquioxane in correlation with its molecular characteristics. (Fig. 2).

The blocking of the ethoxy groups of the hyperbranched polymethylsilsesquioxane allowed to prepare the hyperbranched polymethylsilsesquioxane which was identical in composition of comb-like polymethylsiloxane - polymethyl(trimethylsiloxy)silsesquioxane. The study of the physico-chemical characteristic of hyperbranched polymethylsilsesquisiloxane was performed in comparison with its linear analogues.

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Silicone elastomers are used in different fields, especially in the aeronautic and aerospace industries thanks to their intrinsic resistance properties (against ozone, UV, high temperature and solvents). To manufacture components for the aeronautic industry, adhesion promoter formulations filled with silanes are mainly used because of their chemical compatibility with silicone	extsuperscript{1-3}. One important drawback is the low volume of needed adhesives, which does not provide purchasing continuity. Furthermore, most of the available formulations only bond one type of silicone elastomers (resilient, high damped silicone ...) onto one type of metal surface. The major problem with the use of silanes is to control on the long term several experimental parameters (pH, humidity, nature of the substrate, solvent ...) to master the final properties of the silane film	extsuperscript{1,3} (Fig. 1).

The aim of my Ph. D. project is to understand the mechanisms ruling the adhesion between the different partners of the system (metal, adhesion promoter and HTV silicone elastomer) so as to develop an adhesion promoter that will hopefully bond all kinds of silicone rubbers to various metal surfaces (aluminum, titanium, stainless steel ...) and additionally would not contain any hydrolysis-sensitive molecules. The study was oriented on two commercial adhesion promoter formulations, used as references, and a homemade formulation, and two silicone elastomers (a resilient and a high damped silicone). Different techniques were first used to characterize the coated metal surface such as a mechanical profilometry, atomic force microscopy, contact angle measurements... Then, the work of adhesion of the different formulations onto the various substrates was determined by peeling tests.

![Fig. 1 – EDX analysis of an adhesive formulation filled with silanes used as primer on a steel substrate. On the picture, the red spots represent the silane film and the blue ones the substrate. The complex colored pattern shows the heterogeneous repartition of the adhesive on the steel surface.](image-url)
Synthesis of functionalized microspheres for immobilization of catalyst.

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Unique physicochemical features of polysiloxanes stimulate the continuing interest in seeking the new materials based on them. Their features make them interesting potential carriers for transition metal or enzyme catalysts. Especially cross-linked polysiloxane particles are interesting as support, because they have often a large surface and it can be easily separated from the reaction medium. Unfortunately the catalyst is often bonded to the support only by adsorption in its pores, which can cause leaching of the metal in the subsequent reaction cycles and the loss of catalyst activity.

Polysiloxane microspheres and nanospheres are heat-resistant, they can have tunable elasticity, and are chemically inert. The possibility of introducing a definite quantity of precursor groups (for example: Si-H, Si-OH) on the surface of the particles during their generating allows to control the concentration of functional groups (ligands) that bind catalysts (Figure 1). Simply synthesis, well-defined shape and chemical structure and broad functionalization possibilities open a wide spectrum of abilities to immobilize catalysts.

![Figure 1 Immobilization process: M-transition metal, X-halogen or labile organic group, L-ligand](image)

Our method of the synthesis of microspheres as well as the methods for their modifications (Figure 2) by the reactions involving functional groups are discussed. Processes of modification irregular cross-linked polysiloxanes and microspheres are compared. Preliminary results on their catalytic activity in model reactions are presented.

![Fig. 2. Example of modification of microspheres](image)

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Siloxane copolymers containing hydrolytically degradable poly(L-lactide) blocks.

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Copolymers with polysiloxane and degradable poly(L-lactide) (PLLA) blocks are very interesting not only as candidates for compatibilizers of widely used homopolymers of polysiloxane and polylactide families but also as materials which may have interesting properties by themselves. PLLA often used for biomedical purpose is useful also for a wide range of many other applications including packaging, dust filters in masks, carriers of antimicrobial agents and many others. On the other hand specific properties of poly(dimethylsiloxane) (PDMS), including high thermal stability, low surface energy, high gas permeability, low glass transition temperature and biocompatibility makes PDMS copolymers useful as e.g. biomaterials and elements of electronic and microfluidic devices. Our aim was to clarify how combination in one chain of blocks of PLLA and polysiloxane affects properties of the relevant copolymers. In the paper we present results of our studies on the synthesis of triblock (ABA) poly(L-lactide)-b-polysiloxane-b-poly(L-lactide) copolymers, where the organic block was prepared by ring-opening polymerization of L-lactide monomer carried out in presence of oligosiloxane which did function as a macromonomer and a macrorinitiator. Polymerization of L-lactide was performed using α,ω-hydroxy- or aminopropyl-terminated siloxane oligomers (formula given below) and stannous octoate (Sn(Oct)₂) catalyst.

\[
X-R^1-Si(Me)_2-O-[SiYMe-O]_n-Si(Me)_2-R^2-X
\]

\[
X=H, \quad R^1, R^2=O, \quad Y=CH_3 \text{ or } CH=CH_2
\]
\[
X=NH_2, \quad R^1, R^2=-(CH_2)_3-, \quad Y=CH_3 \text{ or } CH=CH_2
\]
\[
n=0 - 12
\]

In the case of polysiloxane blocks with side vinyl groups copolymers were functionalized by hydrosilylation of double bonds with 3-chloropropylidemethylsilane. Finally, 3-chloropropyl groups were quaternized with N,N-dimetyloctylamine with purpose to obtain a new biocidal poly(L-lactide) block containing copolymers.

In some experiments, the ring-opening polymerization of L-lactide was initiated with α,ω-hydroxy-terminated poly(vinylmethyl siloxane), catalyzed with Sn(Oct)₂ and carried out in presence of N,N-dicyclohexylcarbodiimide used as an agent removing traces of water. Structure and morphology of the final ABA triblock copolymers with diverse segmental chain lengths were determined by MALDI TOF mass spectrometry, IR, ¹H, ¹³C and ²⁹Si NMR spectroscopies and differential scanning calorimetry.

This work was supported by Biopol project - "Technology for obtaining biodegradable polyesters using renewable raw materials" (POIG.01.01.02-10-025/09). The project is implemented under the Operational Programme Innovative Economy 2007-2013, co-funded by the European Regional Development Fund (ERDF)
Synthesis of methyltriethoxysilane and their application as material for soil modification

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The silanes that are typically employed for improving adhesion or surface modification are usually alkoxysilanes. The hydrolysis and condensation of methyltriethoxysilane was studied using various techniques. The main goal of this research was to develop an effective method of preparation of methyltriethoxysilane from methyltrichlorosilane and to provide a semi-stable emulsion, based on alkoxysilane, as a hydrophobic and soil hardening agent. The proposed alcoholysis process of tri-functional chlorosilane (MeSiCl$_3$) can be carried out by a reverse addition (chlorosilanes to alcohol under the surface of the liquid), leading to the respective alkoxysilane. The process is competitive, when compared the substitution of chlorine by alkoxy moiety at silicon atom by means organometallic reagents. Although the latter is commonly used in laboratories, and on a small scale in industry, it is not economic. The important advantage of our process is the lack of side products. The only by-product of the reaction, is hydrogen chloride, which can be effectively and practically utilized as hydrochloric acid when absorbed in water. Alcoholyses were carried at a continuous purge with gas (nitrogen, air) at room temperature. Chlorosilanes were added to ethanol/methanol until the evolution of HCl stopped. Alkoxysilanes were neutralized with calcium monocarbonate and good yields (well above 90%) were obtained. Apart from alkoxysilanes, only small amount of the respective dimmers were found (gas chromatography). The methyltriethoxysilane prepared by this method was used to make an aqueous water emulsion

Hydrolysis and condensation processes taking place during aging of the emulsion were studied by $^{29}$Si NMR.

The evaluation of effectiveness of soil modification was made by measurement of capillary action of water basing the fact that the height of the liquid, depends on interfacial tension.

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Aryl Substituted Silanoles as Precursors for Novel Polysiloxanes

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Siloxanes, especially polydimethylsiloxanes (PDMS), exhibit high industrial importance due to their great stability towards temperature, oxygen, water, UV irradiation, weathering and their high versatility for a broad range of applications. PDMS can be easily gained via ring opening polymerization (ROP) processes based on the monomers hexamethylcyclotrisiloxane (D₃) or octamethylcyclotetrasiloxane (D₄) [1].

In this work we report the preparation of several diorgano substituted dichlorosilanes [2] and subsequent hydrolysis to obtain a wide range of silanediols. Following condensation reactions with amine bases should yield a fully substituted six- or eight membered ring system (see Figure 1) which can be used to perform ring opening polymerization reactions (ROP) to synthesize so far unknown aryl substituted silicon polymers.

Fig. 1: Hydrolyzation of diaryldichlorosilanes and subsequent condensation.

Alternatively, the dichlorosilane species can be reacted with tetramethyldisiloxanedio [4] in order to synthesize diaryltetramethylcyclotrisiloxanes (see Figure 2) for subsequent ROP.

Fig. 2: Condensation reaction of the diaryldichlorosilane species with tetramethyldisiloxane.

The aim of the work is to investigate metal exchange reactions on the example of model compounds - crystal frame metal-organosiloxanes (FMOS).

Traditional path to FMOS by reaction of Na- (K-) silanolate with transient metals salts is a special case of metal exchange. Thus, by partial exchange of Na- (or K-) silanolates with CuCl\(_2\) a number of bimetallic “alkaline” Cu (Na- or K-) FMOS has been synthesized. All of them have a characteristic ratio Si: Cu: M = 3:1:1, but depending on the reaction conditions the compounds of sandwich-like or globular-like structure are formed.

Analogous compounds containing Li or Cs ions could prepared by exchange reaction of “alkaline” (Cu,Na-) or (Cu,K-) FMOS with LiCl or Cs\(_2\)CO. It is found that starting compounds of the structure I reacts in two steps to form an intermediate trimetallic compound of general formula [RSiO\(_2\)]\(_6\)Cu\(_4\)M\(_2\)M\(_1\) where M’ = Na or K; and M’' = Li or Cs ions.

More convenient for the synthesis of (Cu,Li-) and (Cu,Cs-) -phenylsiloxanes are exchange reactions of Li (or Cs) silanolates with the neutral Cu-phenylsiloxane, on the scheme:

Another example is the reaction of metals exchange is the reaction of neutral Cu-phenylsiloxane with alkali acetylacetonates, leading to the formation of alkaline (Cu,M-)phenylsiloxane on the scheme:

Metal exchange reaction allows also to obtain a new bimetallic neutral metallasiloxane, containing different transition metals. In this case two strategies are possible: a) the interaction of “alkaline” sandwich-like metallasiloxanes with MCl\(_2\), according on the scheme:

and b) exchange reaction of neutral metallaphenylsiloxane with complexes M(acac)\(_2\) of transient metals. For example the neutral bimetallic (Cu,Co-)FMOS of different degrees of substitution has been obtained by the interaction of Cu-phenylsiloxane with Co(acac)\(_2\).

As to globular-like “alkaline” Cu-FMOS, they react at alcohol media with CuCl\(_2\) to produce insoluble polymers. But at dioxane or THF in the presence of DMSO the reaction allow obtain product of complete substitution of alkali atoms on CuCl-groups on the scheme:

The structure of obtained FMOS was proved by XRD, element analysis and trimethylsilylation method, followed by NMR\(^1\)H of TMS-derivatives. These examples show possibilities of metal exchange for the syntheses of new different MOS.

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Nanometallocarbosilanes: synthesis, physicochemical properties, structure

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Highly efficient synthesis methods have been developed and characteristics of nanometallocarbosilanes molecular structure were studied by the research team of GNIICHTEOS. Nanometallocarbosilanes were synthesized by thermal co-condensation of oligocarbosilanes and alkyl amides of refractory metals. Zirconium, hafnium, tantalum alkyl amides are highly soluble in aliphatic and aromatic solvents, are ready to lose their organic framing and do not contain harmful to the SiC-ceramic oxygen impurities and chlorine. It is important that alkyl amides of refractory metals interact with oligocarbosilanes before the thermal decomposition stage at room temperature in a solvent, and, therefore, the metal is introduced into oligocarbosilane more gently and completely1,2.

Initial, intermediate, and final products of side reactions were characterized by 1H, 13C, 29Si NMR, and IR spectroscopy, GPC, TGA, TEM, SEM, RES, and elemental analysis.

The proposed method of nanometallocarbosilanes synthesis was found to produce fusible soluble organosilicon oligomers with homogeneous distribution of nanoscale (10-20 nm) metal particles in the oligomer matrix.

Fig. 1. TEM of nanometallocarbosilanes (n-ZrCS; n-HfCS; n-TaCS)

A computational model of the group and element composition of nanometallocarbosilanes was developed; it was shown that they are molecular globules of near-spherical shape and rigid polycyclic structure3.

Nanometallocarbosilanes thermochemical treatment leads to SiC-nanoceramics (a high yield of up to 75 - 80 wt %) modified by metal nanoparticles (20-30 nm), contributing to its stabilization. Preceramic oxygen free nanometallocarbosilanes application will allow to advance in solving the problem of ceramic composite materials with long-term resistance at temperatures above 1500 °C in oxidizing environments.

This work was supported by RFBR (project № 13-03-12014).

Synthesis and Properties of Fluorine-containing Carbosilane Dendrimers

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Synthesis and investigation properties of dendritic systems are actively developing area in the polymer science. Fluorine-containing dendrimers attract much attention due to the combination of the very specific properties, such as low surface energy, chemical inertness and solubility in supercritical CO2. It should be noted that only dendrimers of high generations reveal unusual properties of macromolecules and particle.

In this work, carbosilane dendrimers of several generations were modified via polymer analogous reaction with the different fluorine-containing reagents. The structure and purity of the synthesized dendrimers were confirmed by elemental analysis, NMR-spectroscopy and GPC analysis¹. It was shown the influence of fluoroorganic groups on the thermal, hydrodynamic and surface properties of initial dendritic matrices. The selection of fluorocontaining modifying agents allow to organize different architecture of surface layer of dendrimer’ molecular structure. In case of linear fluorocarbon groups in most cases, insoluble systems were formed due to strong interaction of fluorocarbon groups. The use of branched fluorocarbon substituents lead to the soluble dendrimers with high fluorine content.

![Fluorocontaining dendrimers](image)

The behavior of synthesized dendrimers was compared with irregular hyperbranched polymers of the very same chemical composition. The clear differences in regular and irregular systems behavior in solutions and in bulk were detected demonstrating the importance of molecular structure organization.

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New luminescent crosslinking agents for functional organosiloxane polymers

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There are many ways to crosslink polyorganosiloxanes. For instance, organosilicon oligomer crosslinking is often done by hydrosilylation reaction, which is used also when synthesizing different organofunctional silanes and organic silicon polymers\textsuperscript{1}. However, usually crosslinking agents don’t have any additional properties. We design oligoarylene molecules with fluorescent groups in the center and reactive one in the periphery as the crosslinking agents. In these compounds different chromophores are combined within one dendritic molecule that lead to an intramolecular directional energy transfer from their external chromophores to the center (a molecular antenna effect)\textsuperscript{ii,iii}.

In this work a number of fluorescent linking agents with reactive vinyl groups on the periphery and fluorescent fragments in the center containing bithiophene and thiénylbenzothiadiazole groups were synthesized (Fig. 1). They will allow preparation of organosilicon compositions with completely new optical properties, combining elasticity and high thermal stability of polysiloxanes with luminescent functionality.

Fig. 1. Chemical structures of luminescent crosslinking agents.

Combination of organometallic reactions such as Suzuki, Kumada, direct reaction of lithium and organomagnesium derivatives oligoarylenes with chlorosilanes was used for the synthesis of these compounds. They were purified and isolated as individual compounds. The chemical structures were proved by NMR and UV spectroscopy in combination with analytical GPC. Luminescent properties of the molecules synthesized were investigated by fluorescent UV spectroscopy.

This work was supported by Russian Foundation for Basic Research (№ 12-03-31757) and Foundation of President of the Russian Federation (project MK 6758.2013.3)

\begin{itemize}
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\end{itemize}
Preparation of honeycomb-like porous films by *Breath figures* method from epoxy binder modified with fluorocontaining organosilicon oligomers

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The *Breath figures* method is one of the easiest methods for structured surfaces formation. It has been attracting attention since 1994, when Widawski obtained hexagonal-ordered porous polystyrene films\(^1\). The mechanism of this phenomenon consists in water droplets condensation onto cooled surface of polymer solution while solvent evaporating\(^2\). In almost all of the works concerned with this method there were used polystyrene or its derivatives. But we are unaware for any published papers in which epoxy resins were used. In this work we synthesized fluorocontaining organosilicon oligomers which were used for modification of epoxy binder and for stabilization of water droplets on the film surface. The solutions of epoxy resin with different content of the modifier were casted on mica plates and dried in humid atmosphere. The surfaces of porous films were probed by means of atomic force microscopy.

![AFM images of epoxy film with content of modifier 1% wt.](image)

We found that it’s possible to form ordered porous epoxy films by *Breath figures* method. *This work was financially supported by RFBR (project № 12-03-31331 and 13-03-12230) and HHII-116.2012.3.*

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Synthesis of hyperbranched polyphenylsilsequioxanes

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Up-to-date material science is looking for the brand-new polymers. Polymers with hyperbranched structure, being one of such novelties, attract considerable international attention. Due to their unique properties and simplicity of obtaining, they found industrial application in electronics and microelectronics as well as chemical, textile, paper and oil industry\(^1\).

Polyphenyl(silsequioxanes) is well-known class of organosilicon polymers with high-performance and useful properties. Ladder-like polyphenyl(silsequioxanes) with rigid linear structure are the most popular compounds of this type. Over the recent time, the new synthetic procedures for the creation of hyperbranched polyphenyl(silsequioxanes) of molecular structure appeared. Therefore, obtaining of hyperbranched polyphenyl(silsequioxane) seems to be very promising in terms of solving the «structure-properties» problem.

In the current research, synthetic scheme outlining the synthesis of hyperbranched polyphenyl(silsequioxanes) and their further blocking with hexamethylene disiloxane in the active medium is given (figure 1):

![Synthesis of hyperbranched polyphenyl(silsequioxanes) and their further blocking](image)

Figure 1. Synthesis of hyperbranched polyphenyl(silsequioxanes) and their further blocking.

Also, the obtained compounds were investigated by means of physical methods of analysis.
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\(^1\) Korolev G.V., Bubnova M.L. *Vysokomolekulyarnye soedineniya* 2007, **49**(7), 1357-1388
Polyethylene-silicon dioxide composites with the structure of semi-interpenetrating networks

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Functional polymer-inorganic hybrid nanomaterials are very attractive because they combine the properties of the polymer matrix (low density, chemical inertness) and the second component of inorganic nature (electrical conductivity, sensory properties, etc.). One of the original methods for obtaining nanocomposites with high mutual dispersion of the components is solvent-crazing, which is a type of inelastic deformation of glassy and semi-crystalline polymers. Recently, we developed an approach for the preparation of polymer-silica nanocomposites using crazing for volume filling matrix by a liquid precursor (hyperbranched polyethoxysiloxane), which was further converted into SiO₂ in the volume of nanopores directly¹. The structure of similar composites depends on the content of the second component: from discrete silica nanoparticles (up to 15 wt.% SiO₂) to interpenetrating networks (more than 20 wt.% SiO₂). Similar composites are promising as the materials with special (conductive, thermal, sensor, etc.) properties.

However, such composites are easily converted to the materials with a structure of semi-interpenetrating networks. To do this, its is needed to heat above the melting point of the one component. In the present case, similar a component can only be a polyethylene (PE) matrix. Indeed, the thermal treatment of PE-silica composite at a temperature of 160°C leads to the significant structural rearrangements, while it depends on the environment (air, H₃PO₄, glycerol), wherein heating is carried out (Fig.1).

![SEM-micrographs of surfaces of PE-SiO₂ composites after the thermal treatment at 160°C during 1 h in the presence of (a) air and (b) glycerol.](image1)

**Fig. 1.** SEM-micrographs of surfaces of PE-SiO₂ composites after the thermal treatment at 160°C during 1 h in the presence of (a) air and (b) glycerol.

During heating in liquid media PE melt migrates from volume of a composite to its surfaces. Simultaneously with bleeding of the polymer the liquid medium, which is well compatible with SiO₂, fills the void creating in a volume. The method described allows to fill the composites by H₃PO₄ and proton-conducting membranes with a conductivity of about 3×10⁻² S/cm are received².

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New heat-resistant oligoorganoelementsilazanes
with a tantalum-, hafnium fragments


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One of the promising directions in the development of heat-resistant ceramics is the modification preceramic oligoorganosilazanes by refractory metals. In this work, using TGA and DTA methods, was studied of thermal oxidative stability oligomethylhydridesilazanes (OMHS) modified fragments Si-N-M, where M = Hf (Hf-OMHS), Ta (Ta-OMHS) in a wide range of concentrations.

Analysis of TGA curves in argon showed that almost all the obtained thermogravimetric Ta-OMHS and Hf-OMHS curves can distinguish two stages of weight loss. First, low-temperature, stage occurs in the region 150÷400°C. In this temperature range, the curing process occurs with the participation of end groups, removal of low molecular weight reaction products resulting from thermal decomposition and disproportionation of the organic fragments in the silicon and the heteroatom (Hf, Ta). Second, high-temperature, stage is in the temperature range 400÷700°C corresponding processes of thermal degradation of the main chain. In the temperature range 700÷1000°C the intensity of the destructive process reduced, the weight loss of less than 3% by weight. At 1000°C the smallest value of the inorganic residue yield (52% wt) was observed at a ratio of Si:M = 13:1, and the highest value (90% by weight) at a ratio of Si:M = 2:1, respectively. Introduction into OMHS structure of fragments Si-N-M (where M = Hf, Ta) increases the yield of inorganic residues at each stage weight loss.

DTA method revealed that in the air prevails oxidative processes increasing at temperatures above 400°C. These processes are accompanied by significant exothermic effects resulting interaction of silazane matrix with oxygen, which leads to increased yield of inorganic residues of up to 98% by weight.

By SEM investigated morphology of ceramic obtained by pyrolysis of Ta-OMHS, Hf-OMHS at 850 °C in air (fig. 1 a, b).

Fig. 1. Microphotographies of ceramic obtained in air at 850°C:
  a) Hf-OMGC; b) Ta-OMGC.

Forming ceramics oligomethylhydridesilazanes modified fragments Si-N-M (where M = Hf, Ta) can be used in the preparation of composite materials with high thermal and oxidative stability.
The preparation of microchannel silicone rubber

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The microchannel silicon rubber (MCS) has been obtained from thermosoliﬁcating silicone composition (viscosity 6000-8000 cSt, n_d=1.50) and whiskers of p-aminobenzoic acid (ABA). MCS can be used as scaffolds in medicine. Teflon form was ﬁlled by whiskers and ﬂooded into a liquid composition, kept for 10 h and cured during 1 h at 100°C. Derived silicone matrix after curing is a transparent and does not contain air bubbles. Effective removal of crystals from a matrix was carried out by long ethanol extraction (10-15 h) in a Soxhlet's apparatus. Fig.1 demonstrates the appearance of MCS. Washing of MCS in toluene gives an opportunity to observe the net of microchannels. Toluene is as immersion liquid (fig. 2). Immersion of samples in ethanol solution of Rodamine 6G has shown that 70 - 75 % of channels are open (fig. 3). Joints of whiskers (fig. 4) with widths 10-600 µm and lengths 5-30 mm were obtained from hot water solutions of ABA.

Fig. 1. The appearance of MCS.

Fig. 2. MCS in toluene.

Fig. 3. Dyed net of microchannels.

Fig. 4. Joints of ABA whiskers.