

# **SILOXANE-BASED COMPOUNDS AS PRECURSORS FOR NANOMATERIALS**

**Petru Poni Institute of  
Macromolecular Chemistry,  
Iasi**

**National  
University Research  
Council**

## **PNCDI II – *IDEAS* Program**

**Project ID\_233**

**Contract no. 5/28. 09.2007**

**Running period: 1 oct. 2007 – 30 sept. 2010**

**Total budget (initial): 750 000 RON**

**Total budget (approved): 632 700 RON**

***Principal investigator: Dr. Carmen Racles***

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## Project team

**Dr. Carmen Racleş** - principal investigator

**Dr. Maria Cazacu**

**Dr. Vasile Cozan**

**Dr. Aurelia Ioanid**

*PhD students:*

**Mihaela Alexandru**

**George Stiubianu**

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## Project abstract

Starting from the incompatibility of polysiloxanes with most of the organic polymers, the project aims to increase the knowledge on tailoring the biphasic morphology in siloxane-containing systems, in order to obtain nanostructured materials with special properties and potential top-field applications. We will try to bring new insights into the structure-morphology - properties relationships of siloxane-containing multifunctional materials. New organo-siloxane systems (copolymers, polymer blends, polymer-dispersed systems) will be obtained and studied to observe nano-organization in solid state, in melt or in solution and to understand the influence of the biphasic morphology over bulk and surface properties. The synthesis of siloxane-containing copolymers with various architectures will be realized by polycondensation or polyaddition reactions, starting from preformed macromers. The structures will be confirmed by spectral methods (NMR, FT-IR) and their properties will be investigated by DSC, DMA, UV-VIS spectroscopy, polarized light POM. The biphasic morphology and nanostructuration will be evidenced by TEM, SEM, AFM, XRD and XPS. The potential of siloxane based surfactants or liquid crystals as nanoreactors or nanocontainers will be investigated. We will test the preparation of nano-objects, including polymeric nanoparticles, by nanoprecipitation or polymerization / polycondensation reactions in nanoreactors consisting of biphasic organo-siloxane supramolecular assemblies. The results will be evaluated for subsequent use as disperse phase in polymer blends and as delivery vehicles. Mostly biocompatible / biodegradable materials will be designed and water-based formulations for medical and personal care use will be explored.

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**General objective:** *the increase of knowledge on tailoring the biphasic morphology in siloxane-containing systems, in order to obtain nanostructured materials.*

**Specific objectives:**

- to synthesize new bi/multiphase siloxane-containing systems (copolymers, polymer blends, polymer- dispersed systems) and to study them from the morphological standpoint, in order to understand the influence of biphasic morphology over bulk and surface properties;
- to test unconventional approaches such as siloxane-based nanoreactors for the synthesis of nano-objects;
- to use polymeric nanoparticles (nano-objects) for unconventional purposes (for example as disperse phase);
- to explore water-based formulations containing siloxane-based nanoreactors and nano-containers for targeted applications, such as drug delivery systems, coatings, paints, personal care.

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## PROJECT BUDGET (RON)

NR.	Budget Chapter	TOTAL VALUE 2007 (RON)	TOTAL VALUE 2008 (RON)	TOTAL VALUE 2009 (RON)	TOTAL VALUE 2010 <sup>2</sup> (RON)	TOTAL VALUE (lei)
1.	PERSONNEL COSTS	29000	120000	84211	100000	333211
2.	INDIRECT COSTS	18571	71428	36875	42550	169424
3	MOBILITIES	0	10000	1146	3000	14146
4.	LOGISTICS	17429	48572	25268	24650	115919
5.	TOTAL	65000	250000	147500	170200	632700

1- Aproved Budget

# SILOXANE-BASED COMPOUNDS AS PRECURSORS FOR NANOMATERIALS

2007

## Proposed objectives

1. Synthesis of multifunctional siloxane compounds
2. Characterization of the organo-siloxane compounds

## Results

- New organic mesogenic presursors;
- Organo-siloxane copolymers with chelate groups;
- Siloxane copolymers with functional pendant groups;
  - obtained by condensation reactions on the backbone;
  - obtained by addition reactions (hydrosilylation);
- Multifunctional nanoporous compounds.
  
- Structural characterization by spectral methods;
- Thermal / thermotropic characterization.



# SILOXANE-BASED COMPOUNDS AS PRECURSORS FOR NANOMATERIALS

2008

## Proposed objectives

1. Study of the morphology of biphasic polymers containing siloxane units;
2. Synthesis of amphiphilic siloxane compounds
3. Characterization of siloxane surfactants

## Results

- Electron microscopy and AFM observations for siloxan-organic segmented copolymers and amphiphilic co-networks;
- Synthesis and characterization of new siloxan-organic amphiphilic compounds – potentially non-ionic surfactants – having various architectures (linear or cyclic macromers, copolymers with pendant functional groups) and hydrophilic units derived from monosaccharides or THMAM;
- Investigation of water soluble amphiphilic compounds regarding their surface properties and their potential for nanoparticles stabilization (preliminary tests by nanoprecipitation and chemical reactions).

# SILOXANE-BASED COMPOUNDS AS PRECURSORS FOR NANOMATERIALS

2009

## Proposed objectives

1. Preparation of polymeric nanoparticles by physical methods
2. Polymer syntheses in siloxane nanoreactors
3. Dimensional characterization of the obtained nanoparticles

## Results

- Metal complex nanoparticles, as a result of self-assembling of siloxane-containing segmented copolymers in selective solvents
- Study of chemical reactions in aqueous medium, in the presence of siloxane surfactants with original structures, in order to obtain nanoparticles
- Dimensional and stability investigations of particles obtained in different surfactant – polymer systems.



## Young researchers (PhD students)

**MIHAELA ALEXANDRU** (Ph.D. Student starting 2006), PhD without attendance, with 100% involvement degree (2007-2009).

**Thesis title:** Siloxane-organic siloxane-inorganic crosslinked structures obtained by sol-gel technique.

### Results within the project

1. M. Cazacu, A. Vlad, A. Airinei, M. Alexandru: Silica encapsulating lanthanum complexes using the sol-gel technique, *Polym. Int.* 57: 1067-1074, 2008.
2. C. Racles, M. Alexandru, M. Cazacu, A. Ioanid, T. Hamaide: Obtention des elastomeres silicones en nanoreacteurs siloxane-organiques; *Rev. Roum. Chim.* –2009, 54(7), 583–588.
3. Maria Cazacu, Carmen Racles, Anton Airinei, Mihaela Alexandru, Angelica Vlad: Association Phenomena of the Ferrocenylsiloxane Polyamide in Solution, *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 47, 5845–5852 (2009)
4. M. Alexandru, C. Racles, M. Cazacu : Siloxane-organic hybrids. Evaluation of some surface properties by tensiometry, *Journal of Optoelectronics and Advanced Materials - Symposia*, Vol. 1, No. 6, 2009, p. 1095 - 11002.
- 5) M. Alexandru, M. Cazacu, C. Racles, C. Grigoras: Amphiphile polydimethylsiloxane-based networks reinforced with in situ generated silica- submitted to *Polymer Engineering and Science*
- 6) Mihaela Alexandru, Carmen Racles, Maria Cazacu: Siloxane-organic hybrids. Evaluation of some surface properties by tensiometry *Comunicare - International Conference on Materials Science and Engineering, February 26-28, 2009, Brasov, Romania*

**GEORGE STIUBIANU** (PhD student starting 2007) – PhD without attendance; involvement degree 100% (nov.2007-2009).

**Thesis title:** Hybrid materials based on siloxanes and ligno-cellulose derivatives

**Results within the project:**

- G. Stiubianu, C. Racles, M. Cazacu, B. C. Simionescu: Silicone-modified cellulose. Crosslinking of the cellulose acetate with poly[dimethyl(methyl-H)siloxane] by Pt-catalyzed dehydrogenative coupling, *J. Mater. Sci.* - accepted
- George Stiubianu, Cristian Grigoras, Carmen Racles, Maria Cazacu: New materials developed on the cellulose and siloxane derivatives. Preparation and properties evaluation Comunicare - *International Conference on Materials Science and Engineering, February 26-28, 2009, Brasov, Romania*

## **Published or accepted articles -ISI**

1. C. Racles, M. Cazacu, A. Ioanid, A. Vlad, Micellization of a siloxane-based segmented copolymer and its use as a tool for metal complex nanoparticles, **Macromol. Rapid Commun.** 2008, 29, 1527–1531
2. M. Cazacu, A. Vlad, A. Airinei, M. Alexandru: Silica encapsulating lanthanum complexes using the sol-gel technique, **Polym. Int.** 57: 1067-1074, 2008.
3. A. Vlad, M. Cazacu, G. Munteanu, A. Airinei, P. Budruga: Polyazomethines derived from polynuclear dihydroxyquinones and siloxane diamines, **Eur. Polym. J.** 44, 2668-2677, 2008.
4. C. Racles, M. Alexandru, M. Cazacu, A. Ioanid, T. Hamaide: Obtention des elastomeres silicones en nanoreacteurs siloxane-organiques; **Rev. Roum. Chim.** –2009, 54(7), 583–588.
5. E. Avram, V. Cozan: Modified polysulfones with N-phenacyl and N-acetoxyalkyl-4,4'-bipyridinium pendant groups, **Materiale Plastice** 45 (3), 2008, 241-245.
6. Carmen Racles, Maria Cazacu, Gabriela Hitruc, Thierry Hamaide: On the feasibility of chemical reactions in the presence of siloxane-based surfactants; **Colloid Polym Sci** (2009) 287:461–470.
7. Vasile Cozan, Mihaela Avadanei, Elena Perju, Daniel Timpu: FTIR investigations of phase transitions in an asymmetric azomethine liquid crystal; **Phase Transitions** 82 (8), 2009, 607 – 619.
8. Maria Cazacu, Carmen Racles, Anton Airinei, Mihaela Alexandru, Angelica Vlad: Association Phenomena of the Ferrocenylsiloxane Polyamide in Solution, **Journal of Polymer Science: Part A: Polymer Chemistry**, Vol. 47, 5845–5852 (2009)
9. Carmen Racles, Anton Airinei, Iuliana Stoica, Aurelia Ioanid: Silver nanoparticles obtained with a glucose modified siloxane surfactant, **J Nanopart Res**;in press DOI 10.1007/s11051-009-9780-1
10. M. Alexandru, C. Racles, M. Cazacu : Siloxane-organic hybrids. Evaluation of some surface properties by tensiometry, **Journal of Optoelectronics and Advanced Materials - Symposia**, Vol. 1, No. 6, 2009, p. 1095 - 11002.
11. G. Stiubianu, C. Racles, M. Cazacu, B. C. Simionescu: Silicone-modified cellulose. Crosslinking of the cellulose acetate with poly[dimethyl(methyl-H)siloxane] by Pt-catalyzed dehydrogenative coupling, **J. Mater. Sci.**\_accepted

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## Book chapters

1. C. Racles: Siloxane-Containing Liquid Crystalline Polymers, in *Advances in Functional Heterochain Polymers*, (M. Cazacu –Ed.), Nova Science Publishers, 2008. ISBN: 978-1-60456-599-7.
2. Carmen Racles: Polysiloxanes and siloxane-organic copolymers for nanotechnologies; in *Functional Polymeric Materials Designed for Hi-Tech Applications*, (M.Nechifor ,Ed.) Ed. Research Signpost, Kerala, India, accepted 2010: ISBN: 978-81-7895-448-6.
3. V. Cozan, M. ciobanu, L. Marin: Aromatic copoly(ethersulfone)s, in *Functional Polymeric Materials Designed for Hi-Tech Application* (M.Nechifor ,Ed.), Ed. Research Signpost, Kerala, India, accepted 2010: ISBN: 978-81-7895-448-6.
4. Carmen Racles, Thierry Hamaide, Etienne Fleury : Siloxane-containing compounds as polymer stabilizers; in *Polymer Research Developments: Amphiphilic Block Copolymers, Polymer Aging, Block Copolymers/Polymer Stabilizers*, (Liudvikas Segewicz, Marijus Petrowsky –Eds.), Nova Science Publishers; [https://www.novapublishers.com/catalog/product\\_info.php?products\\_id=9265](https://www.novapublishers.com/catalog/product_info.php?products_id=9265)

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## Communications

1. C. Racles, M. Cazacu, A. Ioanid, A. Vlad: Synthesis of polymer nanoparticles in siloxane-containing nanoreactors. Oral communication *6th International Symposium Molecular Order and Mobility in Polymer Systems –St. Petersburg, June 2008*
2. C. Racles, M. Cazacu, A. Ioanid: Siloxane-containing surfactants and their use for stabilization of nanoparticles, Poster- *22nd General Conference of the Condensed Matter Division of the EPS (CMD22) Roma, August 2008*
3. Mihaela Alexandru, Carmen Racles, Maria Cazacu: Siloxane-organic hybrids. Evaluation of some surface properties by tensiometry. Oral communication - *International Conference on Materials Science and Engineering, February 26-28, 2009, Brasov, Romania*
4. George Stiubianu, Grigoras Cristian, Carmen Racles, Maria Cazacu: New materials developed on the cellulose and siloxane derivatives. Preparation and properties evaluation. Oral communication - *International Conference on Materials Science and Engineering, February 26-28, 2009, Brasov, Romania*
5. Carmen Racles, Anton Airinei, Iuliana Stoica, Aurelia Ioanid : Nanoparticules d'argent obtenues avec des tensioactifs siloxanes ; Oral communication – *9-eme Colloque Franco-Roumain sur les Polymeres, 27-29 August 2009, Alba Iulia.*