# *1st International Caucasian Symposium on Polymers and Advanced Materials*

# ICSP&AM 1

Iv. Javakhishvili Tbilisi State
University

11-14 September 2007
Tbilisi Georgia

# *1st international Caucasian Symposium on Polymers and Advanced Materials*

### Scientific Program

## 10 September

13:00–17:00 Registration
17:30–19:30 Welcome reception

## 11 September

10:00–10:20 Opening ceremony
10:20–10:50 Opening lecture (Prof. Omar Mukbaniani, Prof. Marc Abadie)

## Session "Polymers"

***Co-chairmans:*** Alexander Rusanov, Rinat Iskakov

**11:00–11:30** H. Tenhu (University of Helsinki, Finland) – "Responsive polymers and their biological and drug release applications".

**11:30 –12:00** F. Komarov[1], A. Kupchishin[2], T. Shmygaleva[2], A. Togambaeva[2] ([1]Belarusian State University; [2]Al-Farabi Kazakh National University) – "The Modelling of the formation processes of nanoporous structures in Si, irradiated of Si-iones".

*Lunch break*

**13:30–14:00** O.Yu. Prikhodko, Sh.Sh. Sarsembinov, A.P. Ryagusov, S.Ya. Maksimova, E.S. Stefanova and D.V. Medvedkov (Al-Farabi Kazakh National University, Kazakhstan) – "Electrical and optical properties of metallized polyimide films prepared by different methods".

**14:00–14:30** R. M. Iskakov, B. A. Zhubanov, V. D. Kravtsova (Institute of Chemical Sciences; Kazakhstan) – "Peculiarities of the Modification of Alicyclic Polyimides as New Thermostable Materials"

**14:30–15:00** V. Tskovrebashvili, L. Kemkhadze, G. Tsintskaladze (Iv. Javakhisvhili Tbilisi State University) – "Polymerization of the dimethylorgano-cyclosiloxanes in the presence of zeolite catalyst"

*Coffee break*

***Co-chairmans:*** Vazha Tskovrebashvili, Heikki Tenhu

**15:30–16:00** A.L. Rusanov[1], L.G. Komarova[1], M.P. Prigozhina[1], S.A. Shevelev[2], M.D. Dutov[2], O.V. Serushkina[2], A.Kh. Shakhnes[2], V.Yu. Voitekunas[3] M.J.M. Abadie[3] ([1]A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, Moscow, Russia; [2]N.D. Zelinskiy Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia; [3]Universite Montpellier 2, S.T.L., Montpellier, France) – "TNT-based condensation polymers: synthesis, properties, applications"

**14:30–15:00** E.O. Batyrbekov, T.N. Akylbekova, B.A. Zhubanov* (Institute of Chemical Sciences, Almaty, Kazakhstan) – “Application of Natural Polysaccharides for Controlled Release of Local Anesthetic Kazkain”.

## Session “Advanced Materials/Eco & Bio Materals”

***Co-chairmans:*** Nodar Lekishvili, Irina Razumovskaja

**11:00–11:30** M.J.M. Abadie & L. K. Widjaja (France & Singapore) – “State of the Art of Stents”.

**11:30 –12:00** M. Gurgenishvili, G. Papava, Z. Molodinashvili, I. Chitrekashvili, Z. Tabukashvili **(**Georgia**)** – **“**New fillers for preparation of antifriction polymer composites”.

*Lunch break*

**13:30–14:00** J. Aneli (Iv. Javakhishvili Tbilisi State University, Georgia) – **“**Electrical Conducting Polymer composites: modern and conceptions”.

**14:00–14:30** T.Z. Akhmetov, A.P. Kurbatov, A.K. Galeyeva, O.Yu. Prikhodko. (Kazakh State University, Almaty, Kazakhstan) – “Kinetic of metallization of polyimide films by electrochemical methods”.

**14:30–15:00** G.G. Meskhi (Iv. Javakhishvili Tbilisi State University, Georgia) –**“**Emission of clusters during solid surface bombardment by atomic and molecular ions”.

*Coffee break*

***Co-chairmans:*** Marc Abadie, Tleuken Akhmetov

**15:30–16:00** N.A. Kavtaradze, A.V. Kiriakidi, N.V. Jalabadze, R.V. Chedia (Georgian Technical University & P.Melikishvili Institute of Physical and Organic Chemistry) – "Synthesis of Nanocrystaline Powders of Inorganic Compounds by Using Polymeric Matrices".

**16:00–16:30** N. Lekishvili, L. Arabuli, T. Beruashvili, T. Lobzhanidze, Kh. Barbakadze,
M. Kezherashvi (Iv. Javakhishvili Tbilisi State University, Georgia) - "Antibiocorrosion coatings based on various bioactive organo-metallic complexes".

**16:30–17:00** I.V. Razumovskaja[1], L.L. Muhina[1], V.N. Koptsev[1] , S.K. Kudaikulova[2], R.M. Iskakov[2], T.Z. Akhmetov[3], B.A. Zhubanov[2], M.J.M. Abadie[4] ([1]Department of Solid State Physics, Moscow State Pedagogical University, [2]Institute of Chemical Sciences (ICS), Almaty, Kazakhstan; [3]Center of Physico-Chemical Analysis , al-Farabi Kazakh National State University, Almaty, Kazakhstan; [4]Laboratory of Polymer Science & Advance Organic Materials,Montpellier University 2 Montpellier, France) – "The structure and physical properties of the surface layers in the new metallized polyimide films with high electrooptical performances"

## 12 September

## Session "Polymers"

***Co-chairmans:*** Dmitriy Sapozhnikov, Sevan Davtyan

**10:00–10:30** R. Katsarava, D. Kharadze[1], D. Tugushi[2] ([1] Technical University of Georgia, Center for Medical Polymers and Biomaterials; [2]Iv.

Javakhishvili Tbilisi State University, Department of Chemistry, Georgia) – "New Non-conventional Macromolecular Systems on the Basis of Naturally Occurring Amino Acids".

**10:30–11:00** S. Strandman, S. Hietala, V. Aseyev, S.J. Butcher, H. Tenhu (University of Helsinki, Finland) – "Amphiphilic star diblock copolymers. Syntheses and solution properties".

**11:00–11:30** M.J.M. Abadie[1], D.A. Sapozhnikov[2], V.Yu. Voytekunas[2], T.V. Volkova[2], A.A. Sakharova[2], R.G. Gasanov[2], Ya.S. Vygodskii[2] ([1]Université Montpellier 2, Montpellier, France; [2]A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences Russia) – "Acrylates Photopolymerization in the Presence of Polyheteroarylenes".

**11:30–12:00** S.P. Davtyan, A.O. Tonoyan (State Engineering University of Armenia) – Hybrid Nano Composites, Synthesis and Properties

*Lunch break*

***Co-chairmans:*** Ramaz Katsarava, Anahit Tonoyan

**13:30–14:00** O. Mukbaniani, T. Tatrishvili (Iv. Javakhisvhili Tbilisi State University). – "Polymethylhydrosiloxane As a Matrix for Macromolecular Grafting of Dienes "

**14:00–14:30** Ya. S. Vygodskii, T.V. Volkova, O.N. Pashkova, M.N. Ilina, Ya.V. Zubavichus, O.V. Afonicheva, I.A. Garbuzova, V.V. Kireev (A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Russia) – "The

Characterization of Grafted Copolymers of Nylon-6 and Aromatic Polyimides of Different Structure”.

**14:30–15:00** M. A. Semsarzadeh, M. Hasannejad, B. Nateghian (polymer group, Tarbiat modares university, Tehran, Iran; petrochemichal R&T of NPC(Tehran center), Tehran, Iran and polymer group, Tarbiat modares university, Tehran, Iran)– “The effect of external donors on the complex of Ziegler-Natta catalyst in the polymerization of ethylene”

*Coffee break*

**15:30–16:00** E. Gavashelidze, G. Papava, N. Maisuradze, N. Dokhturishvili, N. Gelashvili **(**P.Melikishvili Institute of Physical and Organic Chemistry, Georgia**) – “**Polyurethanes on the basis of card-type diols”.

**15:30–16:00** S.P. Davtyan, A.O. Tonoyan (State Engineering University of Armenia) – The Technological Aspects of Frontal Polymerization

**16:00–16:30** V. Grushina, I. Papisov, D. Sapozhnikov, Ya. Vygodskii (Moscow car and road institute (State Technical university) & Institute of organoelement compounds RAS, Russia) – “Matrix process as a Way of Obtaining Nanocomposites Based on Polysilicic Acid and Polymethyl Methacrylate.”

## Session “Advanced Materials/Eco & Bio Materals”

***Co-chairmans:*** Oleg Figovsky, Vitali Lipik

**10:00–10:30** J. Aneli (Iv. Javakhishvili Tbilisi State University, Georgia) – “Electrical Conducting Polymer composites: modern and conceptions”.

**10:30–11:00** B. Zhubanov, M. Umerzakova, G. Meirova, N. Kurmankulov, A. Zainullina (Institute of Chemical Sciences, Almaty, Kazakhstan) – “New Bioactive polymers based on Sodium alginate and styromal”.

**11:00–11:30** M. Yoelovich, A. Leykin and O. Figovsky ([1]Nano-Add Ltd, Migdal HaEmek, Israel; [2]Polymate, Migdal HaEmek, Israel) – “Nano-Cellulose and its Application”.

**11:30–12:00** V.T. Lipik[1], M.J.M. Abadie[2] ([1]State Technological University of Belarus, Department of Industrial Ecology; [2]University Montpellier 2, Laboratory of Polymer Science & Advanced Organic Materials, S. T. L.) – “Polyester waste recycling at the melted state”.

*Lunch break*

***Co-chairmans:*** Jimsher Aneli, Mir Mohammad Alavi Nikje

**13:30–14:00** O.L. Figovsky (Israel Research Center Polymate) – “New Nanostructured Matrixes for Fibre Reinforced Composites”.

**14:00–14:30** L. Nadareishvili (Cybernetics Institute, Georgia) – “Gradient oriented state of polymers”.

**18:00 – 19:00 Cultural Program.**

## 13 September

**Excursion in old capital of Georgia, Mtskheta or Gori (Stalin museum, etc.).**
**& Gala Dinner.**

## 14 September

12:00 – 15:00 Poster session (**“Polymers” and** “**Advanced Materials/Eco & Bio Materials”**)

*Coffee break*

15:30 – 16:00 closing lecture

## *Farewell*

# Reponsive polymers and their biological and drug release applications

*Heikki Tenhu*
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Water soluble and amphiphilic polymers may respond to various stimuli in aqueous solutions. Changes in the dimensions or the degree of aggregation may find use in several applications.

Thermally responsive polymers like poly(N-isopropylacrylamide), PNIPAM, poly(vinylcaprolactam), PVCL, and poly(vinylmethylether), PVME, have been extensively investigated during the last decade. These polymers dissolve in cold water but phase separate upon increasing temperature at a certain critical temperature. Polymers either precipitate or, in very dilute solutions, form colloidally stable particles. Crosslinked polymers (gels) collapse upon heating at the critical temperature but reswell upon cooling. PVCL microgel particles, for example, may find use as drug carriers and in controlled drug release. For this application it is beneficial to stabilise the particles against coagulation.

Polyelectrolytes respond to changes of pH and ionic strength. As an example, the synthesis and properties of amphiphilic star diblock copolymers will be described. In these stars, the outer block of the arm is a polyelectrolyte whereas the inner one is hydrophobic. Aggregation and self assembling of these polymers is affected by the number of arms, as well as by changes in the solvent composition.

# Polymethylhydrosiloxane: As a Matrix for Macromolecular Grafting of some Cyclic Dienes

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Polysiloxanes are characterized by a number of interesting properties, e.g. excellent heat resistance, low toxicity, biocompatibility, high oxygen permeability, poor wettability, extremely low surface tension, low melting point and glass transition temperature, resistance to radiation, special rheological properties, outstanding electrical isolating properties and others [1, 2]. Polydimethylsiloxanes in which some methyl groups are replaced by reactive organofunctional groups are widely used. They have attracted much research and found useful applications, because it is a simple way to add new properties to the exceptional properties of silicones. Functional groups may be used to obtain new organic-silicone architectures. If the functional groups are distributed along the main chain, graft copolymers are obtained [3]. Macromolecular grafting is a synthetic approach that involves the functionalization of a preformed polymer backbone containing reactive groups with an appropriate reagent. There is an increasing interest in catalytic grafting of polyhydrosiloxane as to an alternative route for the synthesis of organic–inorganic hybrid polymers, owing to the complexities involved in direct generation of well-defined linear hybrid polymers [4]. Besides the process of equilibration, the hydrosilylation process is the most widely used method of preparing organofunctional polymethylsiloxanes starting from poly(methylhydro)siloxanes [5, 6]. Selectivity is also important consideration in the hydrosilylation of alkynes because in addition to regioisomers and stereoisomers as legitimate products there is also the probability of obtaining diaducts. Hydrosilylation of alkynes offers a greater synthetic challenge of the triple bond and the potential for a broader product distribution. The majority of functionalized polysiloxanes were designed to undergo thermally induced cross-linking, and cure by hydrolytic processes or photochemically induced polymerization [1]. Hydrosilylation is a general term used, for the addition reaction of organic and inorganic silicon hydrides to molecules and macromolecules containing multiple bonds. The universal character of the process is reflected in the wide spectrum of usable unsaturated moieties, which consist of the addition sites (C=C, C≡C, C=N, N=N, C≡N, N=O). It is no surprise that this reaction has developed into the second most common method in synthetic organosilicon chemistry and technology.

The aim of our presentation is to report new effective conditions of grafting, especially based on platinum precursors, of poly(methylhydro)siloxanes with selected conjugated and non-conjugated dienes, predominantly with tricyclodecadiene and cyclohexadiene-1,3 in order to devise a facile procedure for synthesis of soluble polysiloxane coupling agents containing organofunctional (unsaturated) groups in the side chain as well as to characterize the modified poly(methylorgano)siloxanes prepared under the optimum condition. For prediction of hydrosilylation reaction direction quantum-mechanical half empiric AM1 method, in modelling hydrosilylation reaction of methyldimethoxysilane to conjugated and non conjugated dienes also will be considered

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## The Modelling of the formation processes of nanoporous structures in Si, irradiated of Si-iones

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An ionizing radiation effect on solid has number of the features caused by properties of a solid state: a regularity of structure (cristalline and defective), electronic interactions between particles of solid, difficulty of diffusions for large particles, etc. At radiating initiation physical processes and chemical transformations proceed not only on a surface and in near-surface layers, but also in volume of a crystal, and first of all in nano and microdefects areas. With ionic beams help it is possible to influence purposefully on physicochemical, physicomechanical and magnetic properties of irradiated substances, to create in superficial layers such structures which cannot be get traditional methods - new solid solution, chemical compounds, metastable and amorphous phases.

Perspective matrix for nano-sized wires and crystallites are crystals of silicon. For Si nano- structuring the slow and fast ions irradiation can be used.

Processes of an irradiation of crystal silicon by ions of silicon in a energy range 100 - 1000 keV are considered and analysed. Calculations of sections of interaction and selection of approximation factors are made (see Table.1), on the basis of which cascade-probability functions calculation depending on depth of penetration and number of interactions is executed, concentration of radiating defects is carried out. Mechanism of behavior of cascade-probability functions and concentration of radiating defects depending on various factors are obtained. Areas of result finding are found.

Comparison of KPF behavior and concentration of the radiating defects calculated for energy (100 - 1000 keV) is made.

Table 1 – approximated parameters for silicon in silicon

| $E_0$ | $\sigma_0 * 10^8$ | A | $E_0'$ | k |
|---|---|---|---|---|
| 1000 | 0,0090309 | 0,003807 | 1,2887 | 253,42 |
| 800 | 0,0087111 | 0,0038471 | 1,0105 | 238,54 |
| 500 | 0,44703 | 0,17285 | 0,81656 | 291,78 |
| 200 | 0,0057614 | 0,0069751 | 0,10581 | 91,763 |
| 100 | 2,2195 | 0,35734 | 0,42616 | 775,67 |

# Synthesis and Investigation of New σ-π Conjugated Organosilicon Polymers

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The σ-π conjugated organosilicon polymers composed of an alternating arrangement of organosilanylene and p-conjugated units are of a great interest, because of the variety of their possible applications in polymer light emitting diodes, photovoltaic cells, photo- and electro-luminescent materials, due to their unique optical, electrical and mechanical properties [1-3]. In this research we present the synthesis and investigation of new σ-π conjugated organosilicon polymers via hydrosilylation polymerization. We have carried out hydride polyaddition reactions between methylphenylsilane and 1,1-diethynyl-2,3,4,5-tetraphenyl-1-germanium-cyclopendadiene-2,4 (1), 1,4-bis(dimethylsilyl) benzene and 1,1- diethynyl-2,3,4,5-tetraphenyl-1-germanium-cyclopentadiene-2,4 (2), methylphenylsilane and dianizyldiethinylsilane (3), 1,4-bis (dimethylsilyl)benzene and dianizyldiethinylsilane (4). All reactions were done in the presence of Karstedt's catalyst under inert atmosphere. The structure and composition of synthesized products were established by elementary analysis, $^1$H NMR and FTIR spectroscopy. Obtained polymers were characterized by photolumiscent (PL), UV/Vis and electron paramagnetic resonance spectroscopy, gel-permeation chromatography, differential scanning and thermogravimetric analyses.

By GPC analyses we have established that during polymerization via side reactions are obtained branched polymers, which are characterized by polymodal molecular weight distribution. Obtaining of branched systems is caused by proceeding of intermolecular hydride addition. Bellow we present values of weight average molecular weights and polydispersities: polymer (1) - $M_{\omega}=4,25x10^3$, $\overline{M}_n=1,43x10^3$, D=2,97; polymer (2) - $M_{\omega}=$ $9,26x10^3$, $\overline{M}_n=1,64x10^3$ D=5,64 and polymer (3) - $M_{\omega}=$ $13,39x10^3$, $\overline{M}_n=2,85x10^3$ D=4,70.

For synthesized polymers by PL spectroscopy were found absorption and emission values: polymer (1) - $\lambda_{abs.}=350$ and $\lambda_{em.}=500$ nm; polymer (2) - $\lambda_{abs.}=350$ and $\lambda_{em.}=500$ nm; polymer (3) - $\lambda_{abs.}=320$ and $\lambda_{em.}=440$ nm;

For synthesized polymers the specific surface conductivity varies in the range of $\rho=5\cdot10^9-8\cdot10^{11}$ om·cm$^{-1}$ and the activation energy - E=2,1-2,5 ev, showing that given polymers pertain to the polymeric semiconductors.

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# Modification of Phenolic Composite Material With Thienyl-Containing Silicon Organic Oligomers

*D. Gventsadze, E. Markarashvili, L. Gventsadze, G. Mindiashvili, N. Megrelidze*

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The work is devoted to the effect of modification of the polymer composites based on resol-phenotic resins filled with thienyl-containing silicon organic compounds (tetrol, oligotetrol and linear methylthienylsiloxane oligomers). Insertion of 2% of these modifiers leads to increasing of physical-mechanical and tribological properties of composites. So, the strengthening of all composites at compression increases on 35%. Shock viscosity of these composites increases to some extent. All these composites are electro conductive materials. However effect of modification on conductivity of composites doesn't display. Modifiers mentioned above display essential effect on tribological properties of investigated composites. Namely, at high rates the friction coefficient decreases sharply and wear resistance increases too, especially in case of composite, modified by olygotetrol, this parameter increases 5 times more.

# Polymers on the base of dichloranhydride of 2,9-dioxycarbonyl-1H,10H-benzo/e/pyrrolo/3,2-g/ indole

*M.V. Trapaidze, N A.. Kuprashvili, N.M. Iashvili, Sh.A. Samsoniya**

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Polymers that comprise the indole fragments as well as macromolecules in the chain are known [1,2]. Of particular interest are those comprising free β positions of pyrrole rings of an indole fragment. Likewise the polymers, conversion of the later can lead to formation of polymer analogs of well-known physiologically active indole compounds having durable action.

By use of the method of low temperature polycondensation, synthesis of polyesters and polyamides on the base of dichloranhydride of 2,9-dioxycarbonyl-1H,10H-benzo /e/pyrrolo/ 3,2-g/ indole, diamines and bisphenols has been accomplished. 4,4'-diaminodiphenyloxide, 4,4'- diaminodiphenyl methane, piperazine, 2,2-bis(4-hydroxyphenyl) propane, 1,1- bis(4-hydroxyphenyl)cyclohexane were employed as diamines and bisphenols. For the purposes of determination of optimality condition for reaction of polycondensation, effects of temperature, nature and amount of solvent, catalyst and succession of introduction of the source reagents into the reaction have been studied. Dimethyl formamide, hexamethyl phosphorus triamide, and N-methyl-2-pyrrolidone were employed as solvent-acceptors.

As differed from the dichloranhydrides, the activated diesters are characterized by availability, stability, and minor contribution to attendant processes. Therefore, dichloranhydride of 2,9-dioxycarbonyl-1H,10H-benzo/e/pyrrolo /3,2-g/ indole was transformed into corresponding activated diesters. 2,9-di(2,4-dinitrophenoxycarbonyl)-1H,10H-benzo/e/pyrrolo/ 3,2-g/ indole was choosed as a monomer in the syntheses.

Under the condition of low temperature polycondensation, passage of by-products is not observed. But for all that polyamides and polyesters with the yields of 95% and 77% respectively, and reduced tenacities of 0.22 and 0.2 dl/g respectively have been obtained.

The thermal stability of the polymers has been studied by the method of the thermogravimetry on the Paulic derivatograph at the heating rate of 10 $^0$C/min. Weight losses of 10% are observed within the temperature limits of 100-270 $^0$C.

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2. Sh.A. Samsoniya, Nguen Khiu Din, N.N. Suvorov. Bulletin of the Academy of Sciences of the Georgian SSR, 1982, v. 108, № 1, pp. 81-84.

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# Polyesters, polyamides and polyamines on the base of 2,2-dihydroxycarbonyl-bis(5-indolyl)oxide and 2,2-dihydroxycarbonyl-bis(5-indolyl)sulfon

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Polymers that comprise the indole fragments can be of two types: those comprising indole fragments in the form of lateral substituents [1, 2]; and those comprising indole rings in the chain of macromolecules [3, 4].

Reviewed are methods of synthesis of various polymers comprising indole rings in the chain of macromolecules with free reactive centers in β positions of the indole rings.

There have been synthesized complex polyesters and polyamides on the base of dichloranhydrides of 2,2-dihydroxy-carbonyl-bis(5-indolyl)oxide and 2,2-dihydroxycarbonyl-bis(5-indolyl)sulfon under the low temperature acceptor-catalytic polycondensation. Relative reactivity of synthesized dichlor-anhydrides in the acceptor-catalytic polyesterification process has been studied. Synthesis of activated phenyl diesters as well as polyamides on the base of the same has been accomplished.

Methods for obtaining water soluble polyamides on the base of synthesized activated diesters and N,N'-di (tri-methylsilyl)lysine as well as water soluble polyamides on the base of 2,2'- diethoxycarbonyl-3,3' – di(brombenzyle)-bis(5-indolyl)-sulfon and various diamines.

Judging by the powder patterns, the synthesized polymers basically have amorphous structure. Characteristic viscosity of the polyesters, polyamides and polyamines changes within the limits of 0.18 - 0.59 dl/g. The polyesters lose 10% of their masses under the conditions where the temperature changes within the limits of 250 – 400 $^0$C, and the polyamides - under the conditions where the temperature changes within the limits of 200 – 400 $^0$C.

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# Molecular and supramolecular photoluminiscence tuning of new polyazomethines with triphenylamine core

*D. Sek B. Kaczmarczyk, Z. Mazurak, B. Jarząbek*
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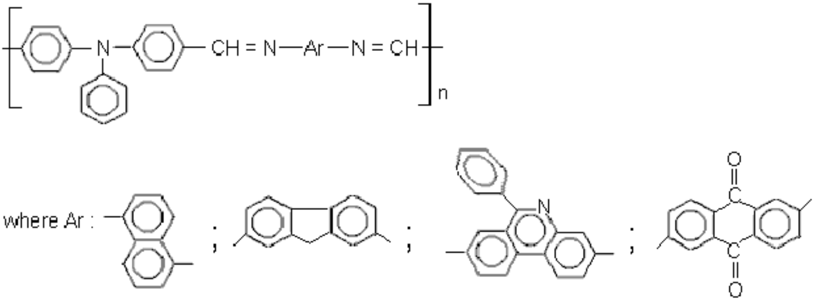
Understanding a relationships between chemical structure of polymer chains and their properties is a fundamental tool for tuning the desired properties of polymeric materials. This approach, being called "molecular engineering" is widely used in practice. However, in the case of conjugated polymers containing imine group –CH=N-, another possibility of properties modification, called "supramolecular engineering", can be applied. It is due to the fact that lone electron pair of imine nitrogen atom can be protonated with Bronsted acids, complexed by Lewis acids or can form H-bond, which effect on electron conjugation in polymer chain and influence on polymer properties.

In our work the both approaches were used for tuning optical properties of novel polyazomethines bearing triphenylamine core in the main chain. The polyazomethines were synthesized in the reaction of 4,4'-diformyltriphenylamine with various diamines. Structures of the polymers are presented below:



The polyazomethines emit blue light being in the range of 460-478 nm in dependence on the polymer structure. Protonation of the polyazomethines with methanesulphonic acid caused little hypsochromic shift of the emission wavelength and influenced on increase of luminescence intensity. The novel polyazomethines form transparent films on glass and other supports and can be considered as blue light emitting materials.

This work was financially supported in the frame of expenditure on science (2006-2007)
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## Synthesis and Investigation of Properties of Diphenylsilyl Containing Bis-Acenapthyls

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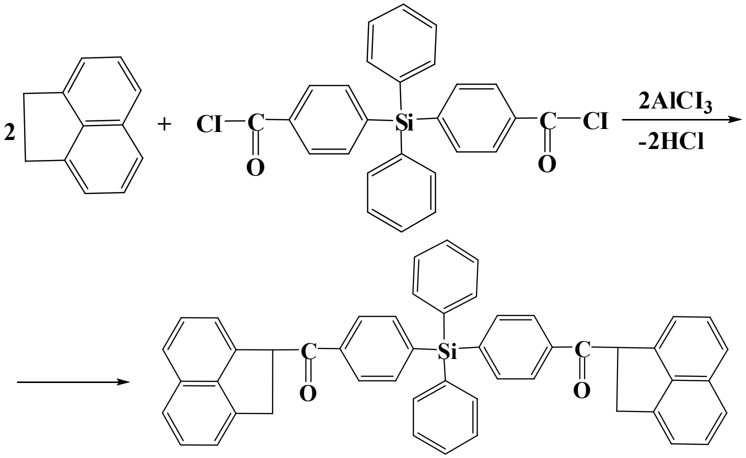
By Friedel-Crafts condensation reaction of diphenylbis(n-karboxyphenyl)silane chloroanhydride with acenaphtene the diphenylsilylcontaining bis-acenaphtyl has been obtained according to the following scheme:



The condensation reaction was carried out in organic solvent, in the presence of Aluminum chloride as a catalyst. During the reaction the modificated Friedel-Crafts acylation reaction techniques was used. By such modificated techniques the bis-acenaphtyl derevatives with a high yields are obtained. As a solvent during reaction tetrachloroetane as a solvent was used. The condensation reaction was carried out at 0.5$^0$C, with rising of temperature up to 60-70$^0$C at continuously stirring during 4 h, at 2:1:2,1 ratio of acenapthene, diphenylbis(n-karboxyphenyl)silane chloroanhydride and Aluminum chloride accordingly the yield of bis-acenaphtyl was about 62%.

The structure and composition of obtained bis-acenaphtyl was determined by means of elementary and functional analyses, IR and NMR spectra data.

By preliminary investigation it was astablished that via oxidation and dehydration of diphenylsilyl containing bis-acenaphtyl corresponding diphenylbis((4,5-dicarboxynapht-1-)keto-n-phenyl))silane dianhydride is obtained, which gives possibility to receive polyheteroarylenes with diphenylsilyl fragments in the main chain.

# Electrical and optical properties of metallized polyimide films prepared by different methods

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One of the actual problems of the space material science technology is the preparation of new high reflectance film coatings, and polymer metallized films with a big surface conductivity are very perspective for this purpose. Such films are also perspective for application in microelectronics as subtract in the production of semiconductor structures. It was known that silver coatings have high reflectance and conductivity. At the same time formation of initial mirror surfaces from silver with good conductivity on the polyimide films is very complicated because of bad silver adhesion to polyimide surface. Special polyimide surface preparation by plasma-chemical etching, ionic or electron bombardment and also photolytic methods does not increase adhesion. The using of metal compounds, such as salts or coordination complexes, directly in solution at the preparation procedure of polyimide films, with consequent silver reduction by thermal diffusion, doesn't form homogeneous and strong conducting metal coating with high reflectance.

In this paper the electrical and optical properties of silver metallized polyimide capton films were studied. The films metallization was carried out by different physical techniques, such as thermal evaporation in a vacuum and ion-plasma sputtering. The capton surface was activated before silver condensation.

It was found that the temperature dependence of the specific resistance in the metallized films at the temperature from

20 up to 200°C was in the well agreement with linear law. The specific resistance at 20 °C and temperature coefficient showed low values and was ~ $2\cdot10^{-6}$ Ω·cm and $(3\text{-}70)\cdot10^{-3}$ $K^{-1}$, respectively. The film reflection coefficient in visible spectrum field at wavelength of 530 nm was 94 % and essentially enlarged with wavelength increasing.

The parameters of studied films are compared with those of the films metallized by chemical modification of the polyimide film surface.

*This work is supported in part by ISTC in the framework of K-1117 grant.*

## Peculiarities of the Modification of Alicyclic Polyimides as New Thermostable Materials

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In the last decade there are broadly growing interest on the modification of polymers by both low- and high-molecular weight substances. A perspective way for the development of new polymer materials with high physico-mechanical performances and appropriate processing, including polyimides, is to prepare polymeric blends of both similar and non-resembling types. Alicyclic polyimides are perspective materials for various fields of technics, such as materials of interlayered dielectrics in multi-integral chips, enamel-wires, film isolation, metallized films with high surfacial electroconductivity and high volume dielectricity.

A series of alicylic dianhydrides those based on benzene and its substitutes with maleic dianhydride has been developed.

However, the synthesized polymers shows less performances than those of aromatic ones, particularly on physico-mechanical properties. To improve the performances a various polymeric blends were produced on the basis of the synthesized polyimides through their blending modification. Peculiarities of alyciclic polyimide modification with acrylic polymers, such as poly(acrylic acid), poly(methacrylic acid), their esters, poly(amic acid) of aromatic and alicyclic structures, epoxyde compounds and polyurethanes have showed that new polymeric blends manifest performances those remarkably different from that of the initial one.

A study of basic properties of new polymeric systems, forming through a mechanical blending of alicyclic polyimide solutions with various modifiers and polymers in the presence of their catalytic amounts, has shown that the maximal characteristics is reached for aromatic poly(amic acid). It is demonstrated that modified alicyclic polyimides is characterized with appropriate casting processing, where breaking durability of the films is about 180÷190 MPa, elongation at breakage 45÷50%, thermostability of new materials maintains intact.

## The Technological Aspects of Frontal Polymerization

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Concrete approaches for the obtainment of various polymeric items are discussed based on the analysis of peculiarities of frontal polymerization of liquid and solid (crystalline) monomers in the reactors of periodic and non-stop (continuous) action. Aggregate state of the produced polymers (viscous, solid-crystalline) was also taken into consideration.

1. Frontal radical polymerization of solid and liquid monomers makes nano fillers to distribute evenly throughout the volume of polymer binder.
2. Technology developed to carry out frontal polymerization in tubular reactor of non-stop (continuous) action. The developed technology allows producing profiled armored items from glass- and carbon-plastics possessing enhanced physical-mechanical properties.
3. Frontal radical polymerization of methylmetacrylate in cylindrical and spherical reactors with radial-symmetrical fluxes of initials and products are investigated theoretically and experimentally. Cylindrical reactor's optimal work regimes are identified creating stable conditions for the frontal polymerization to proceed evenly. The mean molecular mass of the polymer comprises more than $10^5$, poly-dispersity is in between 2.3–2.5; while conversion is 93–95 per cent.

## Hybrid Nano Composites, Synthesis and Properties

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The various polymeric superconducting and hybrid nanocomposites are obtained. Based on the radical polymerization of acrylamide, ε-caprolactam and methylmethacrylate in the presence of nano powders $SiO_2$ as well as Co, Mn, Ni-containing metal-complex monomers with high temperature superconducting ceramics powder it was shown that the use of surfactant active materials permits to de-agglomerate and evenly distribute nano particles in the initial reaction media. In case of frontal polymerization regime the initial condition of nano additives in the monomer area is fixing also in the polymeric matrix.

The morphology of interphase layer, thermo-chemical and physic-mechanical properties were investigated. It was shown that the properties of obtained composites strongly depend on the stability of frontal waves distribution. The boundaries of stable front velocity were determined.

## Polymerization of the Octamethilcyclotetrasiloxane in the presence of zeolite catalyst.

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A large number of research works have been devoted to the use of the modified and metal-containing forms of natural zeolites, as catalysts of different organic and inorganic reactions. However, the polymerization reaction of organocyclosiloxanes on natural zeolites has not yet been studied.

In spite of large information flow, there are at present no data about the catalytic activity of natural zeolites in the polymerization reactions of organocyclosiloxanes.

The catalytic activity of modified high-silicone clinoptilolite of Khekordzula layer in the polymerization reactions of octamethylcyclotetrasiloxane is investigated. During the experiment the effective catalysts of this reaction are revealed.

It is possible to conclude, that highly crystalline clinoptilolite of Khekordzula layer, modified into the H- form through the processing of initial clinoptilolite 1N and 2N by hydrochloric acid or the termal treatment $NH_4$- form, represents the active catalyst of the polymerization reaction of octamethylcycloteterasiloxan ($D_4$). On the studied catalysts, with the temperature interval of100-150°C, during $D_4$ polymerization it is possible to obtain polydimethylsiloxane with the molecular weight equal of $0,5\cdot10^5$-$2,31\cdot10^5$.

$D_4$ polymerization reaction has cathion nature. It goes in the Brünsted acid centers. In this process acid centers also manifest catalytic activity, locating on the surface of the crystal phase of clinoptilolite. Results of X-ray structural and infrared spectral analysis and also the electron-microscopic scanning of catalyst surface area confirm our conclusion.

In particular this is the H-form of clinoptilolite, obtained by action on initial zeolite 1N and 2N by the solution of hydrochloric acid and by following thermal treatment, and also by termal treatment $NH_4$- form of clinoptilolite. The optimal conditions of conducting the reaction and its supposed mechanism are selected. On the given catalysts, at temperatures between 100 and 150°C , the possibility of obtaining of polydimethylsiloxane with large output is demonstrated, with a molecular weight of 0,510-2,310.

The study of the possibility of applying natural zeolites as the catalyst in the polymerization reactions of organicyclosiloxanes and the clarification of possible reaction mechanism is the purpose of this work.

# The Structure and Stabilization of Two Stage Reactions in Frontal Polymerization Processes

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The structure of heat waves occurring in reagents flow in cases of both consecutive and concurrent reactions in frontal polymerization processes is considered in approach of narrow zones

The distribution of heat fields and positional relationship of reaction zones in frontal polymerization reactor are obtained on the basis of numerical solution of thermal conductivity equation for stationary waves of two stage reaction in the condensed substances flow.

The possibilities of regulation of wave structure and polymerization regimes are studied. It is shown that the reaction interdependency limits the possible structure changes of polymerization waves. For example, in case of consecutive reactions the inversion of reaction zones is impossible, while for concurrent reactions the control regime is impossible, and the intercapture of reaction zones in wide range of front temperatures is typical.

# TNT-based condensation polymers: synthesis, properties, applications[1]

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*A.Kh. Shakhnes**,*
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Extremely available and inexpensive explosive material – 2,4,6-trinitrotoluene (TNT) – was transformed in the frames of demilitarization and conversion program into different difunctional compounds – dinitrocompounds and diamines useful for the preparation of new condensation polymers.

TNT-based aromatic dinitrocompounds containing electrone -withdrowing groups were used for the preparation of new aromatic polyethers via the aromatic nucleophylic nitrodisplacement reactions.

TNT-based aromatic diamines were used for the preparation of aromatic polyamides and polyimides containing bulky side groups. These polymers combine solubility in organic solvents with large "windows" between softening and degradation temperatures.

Polymers developed may be used for the preparation of high performance materials; of especially great interest are low K polyimides useful as interlayer dielectrics in microelectronics and sulfonated polymers useful as proton-exchanging membranes for fuel cells.

[1] *This work was supported by NATO (grant № 981762)*

# "New Non-conventional Macromolecular Systems on the Basis of Naturally Occurring Amino Acids"

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α–Amino acids are one of the main building blocks of the animate nature. They form important molecules of the life like peptides, polypeptides, and proteins. The orientation of amino acids in these molecules is *conventional* – directional. This orientation determines the primary and secondary structures of the said bio-polymers that, in turn, determines their biochemical properties including *immunogenicity*. This along with costly manufacturing processes and products standardization complexity substantially restricts practical applications of α–amino acids' based naturally occurring polymers as biomedical biomaterials.

At the same time α–amino acids' based polymers are of high interest for biomedical applications, especially as biodegradable biomaterials since after biodegradation they can supply the organism with physiological building blocks – α-amino acids including essential amino acids that can actively participate in regenerative processes by metabolic means.

In the light of the said above synthetic amino acid based polymers look more promising as compared with naturally occurring analogous. Virtually unlimited number of the synthetic polymers can be synthesized on the basis of 20 naturally occurring α–amino acids. The orientation α–amino acids in synthetic polymers can be both *conventional* and *non-conventional*. Polymers with non-conventional orientation of α-AAs we call as Amino Acid Based Bioanalogous Polymers – AABBPs. A large variety of AABBPs were synthesized and studied. Those are hetero-chain polymers like polyamides, polyurethanes, polyureas, poly(amide urethane)s, polyesters, polycarbonates, poly(imino carbonate)s, poly(ester amide)s, poly(ester urethane)s, poly(ester ureas)s. The general idea for the synthesis of polymers containing various types of chemical linkages and having non-conventional orientations of α-amino acids in the backbones is that such architecture (primary structure) of macro-chains provides with "non-natural" secondary structure that is expected to impart *low immunogenicity* to the polymers by "Confusing the Nature".

To render AABBPs biodegradable with reasonable rates of biodegradation easily hydrolizable chemical sites, e.g. ester bonds, should be incorporated into the backbones. It is also important for other building blocks, used for the construction of AABBPs, to be non-toxic. From this point of view poly(ester amide)s [1-3], poly(ester urethane)s [4] and poly(ester urea)s [4,5] entirely composed of naturally occurring α-amino acids and nontoxic building block like fatty dicarboxylic acids and diols are one of the most promising representatives of biodegradable AABBPs. The said polymers undergo both *in vitro* and *in vivo* biodegradation with desirable rates [4-7] and reveal high biocompatibility [7,8]. Some of them were successfully used for constructing various medical devices like medicated artificial skin a drug eluting micro-particles [9,10], stent coatings [8,11], vaccine delivery systems [12], etc.

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# Synthesis of polymer nano-composites by the method of frontal polymerization

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The aim of this work was to obtain polymer nano-composites by the frontal polymerization method. One of the main objectives was the problem of nano-size particles conservation, their deagglomeration and uniform distribution in the polymeric matrix.

Different surface active materiales have been tested to prevent the agglomeration of nanoparticles during polymerization. The uniform distribution of nanoparticles in polymeric matrix was obtained by the method of frontal polymerization.

Nano-scaled particles of $TiO_2$ have been obtained using the different surface active materiales and by the method of frontal polymerization.

Optimal concentration of surface active materiales which preventing the agglomeration of nanoparticles was found. Also were investigated the conditions where the stable front can exist.

# Amphiphilic Star Diblock Copolymers. Syntheses and Properties in Aqueous Solutions

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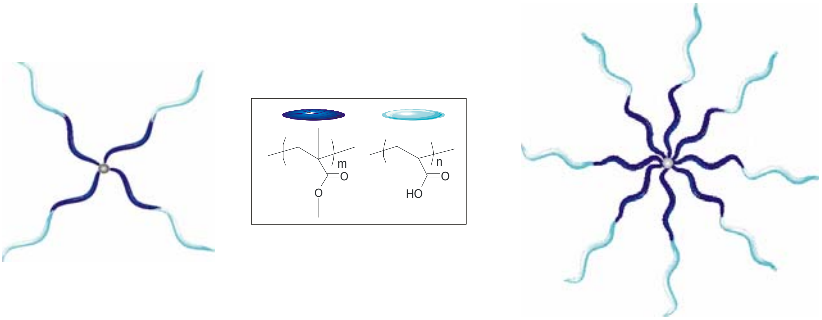
Self-assembling of amphiphilic block copolymers provides an interesting way to obtain various nanostructures in solution. In the current work, we have synthesised star block copolymers having poly(methyl methacrylate) core and poly(*tert*-butyl acrylate) shell using two types of resorcinarene-based initiators that give stars with 4 or 8 arms. [1,2] Amphiphilic star block copolymers have been prepared by selective hydrolysis of *tert*-butyl ester groups to obtain poly(acrylic acid) shell. The self-assembling behaviour of the amphiphiles has been investigated in aqueous solutions, in which they form micelle-like aggregates. The balance between attractive and repulsive forces that govern the micellisation can be disturbed by the addition of salt or by changing the pH of the solution, leading to changes in micellar morphologies. [3,4]



Scheme 1. Amphiphilic PMMA-*b*-PAA star block copolymers

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# Thermosensitive Liquid Crystal Polymer Films

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Creation of the thermosensitive liquid crystal structures are very important for using the liquid crystal materials in thermoindication.

At present, it is known that the thermosensitive polymer films containing the mixtures of cholesterol esters. Due to a low photochemical stability of the cholesterol esters the temperature dependent color characteristics of these films changes in time.

There have been developed a new kind of thermosensitive liquid crystal chiral-nematic polymer films, containing the mixtures of different nematic substances and optically active dopant-tigogenin caprate. The films are obtained by the method of microcapsulating based on polyvinyl alcohol with the use of the suitable emulsifying agents.

It was investigated the influence of chiral-nematic components ratio, amount of emulsifying agents on the temperature range and intensity of coloration of the films, was studied temperature dependent color characteristics and photochemical stability of chiral-nematic and cholesterol esters films respectively.

The result of our study shows that the integrated intensity of chiral-nematic films coloration is higher than of films containing the mixtures of cholesterol esters, especially in the long wavelength range of the visible spectrum. Photochemical investigation shows that chiral-nematic films are photochemically more stable as compared with to cholesterol esters films.

New thermosensitive liquid crystal chiral-nematic polymer films obtained by us have the increased photochemical stability and improved temperature dependent color characteristics, therefore the films may find wide application in various fields of thermoindication. In particular
the films can be used for the following purposes:

- obtaining a panoramic pattern of the thermal field on the surface of various articles in
studying aerodynamic heating and other thermophysical effects;
- determination of overheating zones in radio and electric equipment;
- visualization of invisible IR and microwave radiation;
- diagnosing of inflammatory sites in medicine;
- manufacturing of medical and household thermometers.

# Polyurethanes on the Base of Card Group Containing Diols

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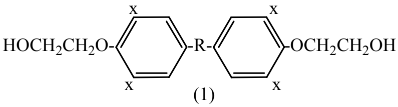
Homogeneous, linear polyurethanes have been synthesized on the base of card type diols. Diols containing cycloaliphatic – cyclopentane, cyclohexane, norbornane, adamantane and cycloaromatic – phthalide, flourene and anthrone card groups were used for the synthesis of polyurethanes. Methods of synthesis of primary and secondary diols were developed. Primary diols (1) were obtained by interaction of bisphenols and ethylene oxide, while the secondary diols (2) were obtained by interaction of bisphenol with propylene oxide in alkaline medium.



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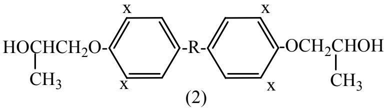

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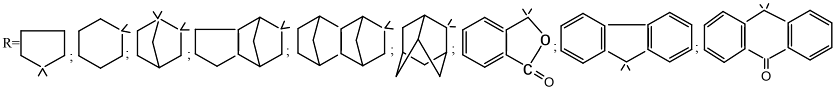

X = H, $CH_3$, Cl

Polyurethanes were synthesized on the base of diols, aliphatic and aromatic di-iso-cyanates. Synthesis proceeds by migration polymerization mechanism. The main kinetic regularities of polymer formation have been studied. Optimal conditions were defined for obtaining polyurethanes. Relationship of polyurethanes properties and the chemical structure of polymer chain was studied.

Polyurethanes synthesized on the base of card type diols are characterized by high heat resistance and good solubility in organic solvents. These properties of polyurethanes are conditioned by the presence of card type cycles bounded to the central hydrogen atom between oxyphenyl nuclei of diol component.

Study of card group containing polyurethanes showed that heat resistance of card group containing polyurethanes is far high than heat-resistance of industrial polymers obtained on the base of aliphatic diols, as well as that of polymers not containing card groups which stand close to polyurethanes by their chemical structure.

Heat resistance of polyurethanes obtained on the base of primary diols is higher than that of polyurethanes obtained on the base of secondary diols, which is explained by the presence of methyl group in secondary diol molecules.

Polyurethane properties are also affected by the diisocyanate structure. At the substitution of aliphatic diisocyanate with aromatic one, heat resistance is increased markedly. Roentgenostructural analysis proved that polyurethanes synthesized on the base of card type diols have amorphous structure.

Dynamic thermogravimetric analysis proved that decrease of mass of the synthesized polyurethanes starts at 280-300$^{o}$C, while intense mass decrease within the interval 300-400 $^{o}$C.

# Quantum-Chemical Estimation of Relative Reactivity of Dimethylthienylvinylsilane and Dithienylmethylvinylsilane in the Reactions of Radical Co-polymerization

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Last time besides experimental searches all relative reaction ability of monomers which participate in reactions of co-polymerization, great attention is paid to their quantum-chemical calculation with a view to establish parameter values of reaction ability.

The aim of the presented work is to study the reactions of radical co-polymerization of dimethylthienylvinylsilane(DMTVS) and dithienylmethylvinylsilane(DTMVS) with styrene and methylmetakrilate(MMA) and to determine their relative reactivity in this reactions.

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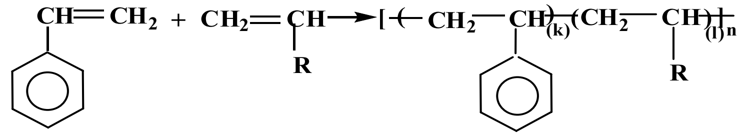

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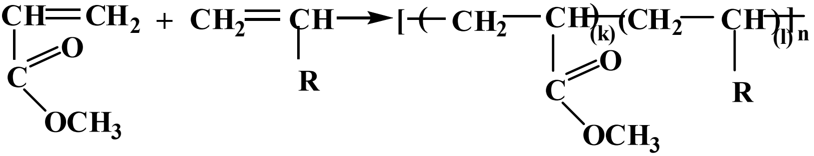

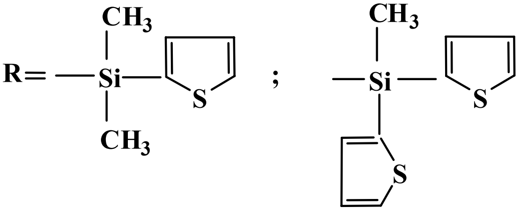

In order to study quantum-chemical parameters of molecules of DMTVS and DTMVS we have make complete optimization geometry of their molecules.

On the base of quantum-chemical researches of molecules of as well their exited condition and simplicificate α-radicals is determine sequence of their activity in chemical reactions:

DMTVS<DTMVS<Styrene,

This is proved by comparing with experimental data.

## Hydrosilylation Reactions of Polymethylhydrosiloxanes To Allyloxytriethoxysilane And Allyloxytrimethylsilane

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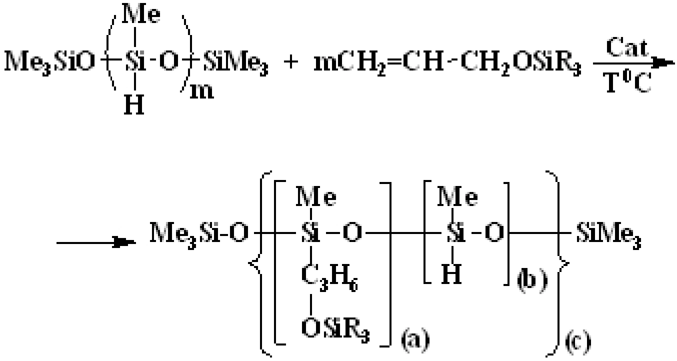
Polysiloxanes attract the widest interest among the organic-inorganic polymers. Modification of polymethylhydrosiloxane via hydrosilylation reaction still remains as an interesting way for obtaining of new siliconorganic polymers

For purpose of obtaining comb-type organosilicon oligomers with propyloxytriethoxysilane and propyloxytrimethylsilane fragments in the side chain the hydrosilylation reactions of α,ω-bis(trimethylsiloxy)methylhydrosiloxane to allyloxytriethoxysilane and allyloxytrimethylsilane in the presence of 0.1 M solution of platinum hydrochloric acid in tetrahydrofuran.

Initial products allyloxytriethoxysilane and allyloxytrimethylsilane have been obtained by heterofunctional condensation of allyl alcohol with tetraetoxysilane and trimethylchlorosilane accordingly.

Hydrosilylation reaction of α,ω-bis(trimethylsiloxy)methylhydrosiloxane to allyloxytriethoxysilane and allyloxytrimethylsilane in the presence of catalyst platinum hydrochloric acid have been studied at 1:35 ratio of initial components, in inert atmosphere, at various temperature ($60\text{-}80^0$C). The reaction mainly proceeds according to the following scheme:



Where: [(a)+(b)](c) = m $\approx 35$: $R=OC_2H_5$, $I^1$ ($60^0$C), $I^2$ ($70^0$C), I ($80^0$C); R=Me, II ($80^0$C).

Synthesized oligomers are transparent liquides well soluble in ordinary aromatic type organic solvents. For oligomers FTIR, $^1$H, $^{13}$C NMR. TGA and wide angle X-ray analyses have been carried out.

For prediction of reaction direction quantum-mechanical half empiric AM1 calculations for modelling hydrosilylation reaction of methyldimethoxysilane to allyloxytrimethylsilane have been carried out. The obtained results are in conformity with NMR spectra data.

***We acknowledge*** *Georgian National Science Foundation (Grant #GNSF/ST06/4-070) for financial support.*

# The Charakterization of Grafted Copolymers of Nylon-6 and Aromatic Polyimides of Different Structure

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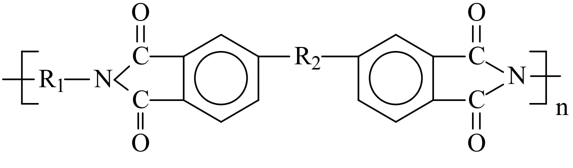
The copolymers were obtained [1] by graft anionic copolymerization of ε-caprolactam with 5 mass. % PI



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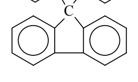
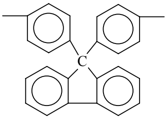
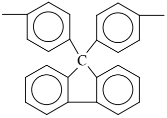
where R$_1$=  , $–C_6H_4–C(CF_3)_2–C_6H_4–$, $–C_6H_3(SO_3H)$-, R$_2$=$-C(CF_3)_2$-, -O-, having ηinh in chloroform 0.32-1.4 dl/g. The grafting was realized via rupture of 5 membered PI cycles under the action of MgBr- ε-caprolactam – the catalyst of lactam polymerization.

The copolymers synthesized are not dissolved in usual organic solvents and swell in m-cresol (gel-fraction content 69 – 96 %), formic and sulfuric acids, that is evidence of cross-linked structure. Their prolonged treatment in acids is accompanied by linkages destruction. The copolymer of nylon 6 with PI at $R_1$=–$C_6H_4(SO_3H)$ – и $R_2$=–$C(CF_3)$ – (ηinh 0.64) is an exclusion, that was also characterized by the greatest gel fraction content in m-cresol. In copolymers IR – spectra along with the Amide - 1, Amide – 2 bands and the band of valence NH vibration of nylon 6 the weak carbonyl and aromatic PI structure signals were present.

According to X-ray data the crystallinity of the copolymers synthesized changed in interval of 66 – 82 %. Their diffraction patterns were of the same type and differed in contributions of four diffraction characteristics, that were among α–, γ– and amorphous nylon 6 phases. The thermomechanical curves of copolymers of nylon 6 with PI (ηinh 0.84) at $R_1$=  and $R_2$=–O– in contrast to nylon 6 and studied copolymers with PI of another structure were characterized by presence of rubber-like elasticity region above Tm of nylon 6. On the thermomechanical curves obtained at variable load of nylon 6 and their copolymers with PI at temperatures from – 100 to 230 – 2700C (depending on PI) the reversible deformation was noted. It amounts 2.6 – 9.6 %, is higher for copolymers than for nylon 6 and depends on PI chemical structures; Tg transition was accompanied by increase of mentioned deformation. It marked also the correlation of the reversible deformation and nylon impact strength, that reached the largest value (>50 kJ/m2) at $R_1$=  and $R_2$=–O–.

On the TGA evidence the thermal resistance of the copolymer synthesized on 38 – 650 surpasses the nylon one. The study of copolymer frictional properties showed the increase of their friction contact temperature (on 5 – 270), the wear (on 25 – 28%) and the constant of friction (on the value up to 60%) in comparison with nylon 6.

Authors express one's thanks to M.I. Buzin for TGA copolymer study.
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## The effect of external donors on the complex of Ziegler-Natta catalyst in the polymerization of ethylene

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The effect of silane donors has been investigated as external donors in Ethylene/1-butene copolymerization. Cyclohexyl methyl dimethoxy silane and dicyclopenthyle dimethoxy silane have been used as external donors in Ti/$MgCl_2$ Ziegler-Natta catalytic system. Polymerization was repeated in four molar ratio of donor to co-catalyst from zero to 1:15 and three states:

homopolymerization and copolymerization with 50gr and 200gr of comonomer

Results from characterization of products show that:Yield of polymerization has decreased with increasing comonomer and donor concentration. Melting point($T_m$) and crystallinity have decreased with increasing comonomer concentration. Effect of donor concentration on crystallinity in copolymerization with 200g 1-butene is more clear than 50gr 1-butene. Poly dispersity index has increased with increasing comonomer, while it has decreased with increasing donor concentration.

## Synthesis of Inorganic Nano Composites Based on Polyacrylamide

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Polymer nano composites based on acrylamide with the additives of nano- scaled particles of $Fe_2O_3$ homogeneously dispersed in the polymer mixture have been obtained.

It is shown that deagglomeration of nano particles and their uniform distribution in the monomer mixture can be achieved when nano powder is pretreated with the sufficient surfactants. Uniform distributed initial mixture was fixed by the frontal polymerization method.

The influence of the nano aditives amount’s variation on the structure of heat waves and front propagation velocity has been investigated. It has been shown that the nano aditives amount's variation leads to non- monotonous changes of front velocity and the limiting temperature of heat waves.

# Matrix process as a Way of Obtaining Nanocomposites Based on Polysilicic Acid and Polymethyl Methacrylate

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The main idea of the matrix process is that monomer molecules are coordinate upon the matrix polymer chain length by Coulomb's and hydrogen bonding with following producing daughter polymer chain as a result.

This affect was studied on the example of synthesis of nanocomposites derived of polysilicic acid (PSA) and polymethyl methacrylate (PMMA), which were obtained by hydrolysis of tetraacetoxy silane in benzene solution of PMMA with the following polycondensation of obtained silicic acid. The calculate quantity of water was introduced from gas phase. The hydrolysis of tetra(acetoxy silane) (TAS) in wet benzene followed with rapid polycondensation of *in situ* formed silicic acid results in the formation of insoluble networked poly(silicic acid). Similar process conducted in dilute benzene solutions of PMMA and at low initial TAS: PMMA ratios (from 0,5:1 to 1:1 mole/ground mole) result in formation of the clear solutions. The increasing of TAS amount in solution led to formation of insoluble precipitate.

The solubility of the obtained composites is a result of interaction between PSA and PMMA chains, after which great parts of polymer chain are kept free and retained forming complexes in solution.

In all products obtained via template processes, the presence of Si-O-Si bonds was detected by IR-spectroscopy. It was also shown that mechanical mixing PSA and PMMA don't produce a composite material.

As it was shown from the results of thermogravimetric analysis on air the maintenance of hydrogen groups in the samples is much more then the one in the pure PSA, that indicates the formation of more linear and less cross linked structure of PSA.

The forming particles have a spherical shape and diameter about 20-40 nm, that was shown by electronic microscopy analysis. It should be noted, that PSA doesn't form particles of regular size and shape.

The viscosity of the systems obtained was higher then the one of plain PMMA at the same concentration.

The films of the synthesized material were transparent, and appear to be more rigid and brittle, than PMMA films.

## Acrylates Photopolymerization in the Presence of Polyheteroarylenes

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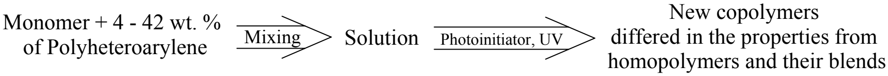
The kinetics of unsaturated monomers radical polymerization in the presence of polyheteroarylenes & nbsp;

  (polyimides, polyarylates)     and corresponding model compositions was& nbsp;  studied by differential scanning photocalorimetry and infrared spectroscopy& nbsp; & nbsp; methods.

The combination of cited research methods with the infrared spectroscopy, nuclear magnetic resonance,    size exclusion chromatography, thermogravimetric and    elemental analysis investigations allow to make the conclusion that the radical polymerization of vinyl monomers& nbsp;   (methyl methacrylate and ethyl acrylate) in the presence of aromatic polymers resulted in the formation of copolymers due to reactions of transfer and/ or& nbsp;   termination& nbsp;  of chain onto corresponding polyheteroarylene. Electronic paramagnetic resonance measurements combined with kinetic study  & nbsp;justified  the mechanism previously proposed [1] included the interaction of radicals with functional  & nbsp;groups of polyheteroarylenes (imides & nbsp; cycles and ester  groups) introduced & nbsp; into the monomer.

General scheme of this process is



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# Tea Leaf Polyvitamin Extractive Oil

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Beside of the century-old history of Tea, practically lipofolar substances of tea leaf are left without consideration. But according to the analysis exactly these lipofilar substances consist of more valuable biologically active components for the organism than the "classic" extract of Tea. Tea leaf oil extractive contains (mg%) : carotina- 750-800 (in "Oleum Hippoheae" 180-200); tocopherols – 1500-1600 (in "Oleum Hippoheae" 110-120); chlorophylls – 750-800 (more than oil of Eucalipty), unsaturated fatty acid nearly to 60%, 45% - vitamin F (Linol and Linolen acids).

Our product can compete not only with "Oleum Hippoheae" but also with analogous preparations in the world market. There is no problem for the raw materials in Georgia. We have studied and elaborated Tea Leaf oil extractive (temporal pharmaco article numb.: 186/96) prepares on its basis, we have patents on inventions, and according to recommendation of Georgian pharmacological committee the are allowed to be used in Medical practice.

It is established that mentioned pharmaco-production can be used as an untiulcered remedy when damage of stomach. Immediate laying of these preparations on the skin with cancer tumor causes interruption of production of cancer cell and their gradual desrtuction.

Pharmacotherapeutical activity oil extractive of tea leaf is 3-5 times large than well known "Oleum Hippoheae". Besides, known analogous foreign preparations are more expensive and less effective than aforesaid preparation.

As we have calculated prime-cost of 50 ml "Tiol" for 1000 flacon is 100 USD, when the cost for the same amount "Oleum

Hippoheae" is not less than 1800 USD (cost of "Oleum Hippoheae" in world market is 40 dollar/kg).

Skaki Tseretaly State University is able to organize small production with productivity – 250 kg tea raw middle per day, where 24 workers will get a job – employees with middle monthly pay equivalent of 150 dollars. Necessary expenses for the realization of small production are not 4…5 months and annual profit is more than 800 thousand dollar.

Georgian corresponding structures and Pharmaceutical industry must take an interest in oil extractive of tea leaf and in phitomedicine "Tiol", prepared on its basis. By all means, foreign institutions will show an interests, as treatment of malignant tumours still remains as problematic and vital question for modern medicine. We carry on active consultations with the world leading pharmaceutic firms.

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# Preparation and Properties of Polyimide/Siloxane Hybrids

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Performance of polyimide (PI) can be broadened by inclusion of inorganic materials, such as silica[1] and clay[2]. Inclusion of the inorganic compounds into PI provides improved thermal and mechanical properties, but the hybrids become brittle. In these circumstances, the range of polymer properties can be broadened by combining with another polymer. Poly(imide-siloxane) shows many properties such as low water absorption, impact resistance and flexibility. Previously we prepared novel PI-hybrids from PI-clay-polydimethylsiloxane (PDMS) aiming to improve the properties of PI and overcome drawbacks of PI-clay nanocomposites [3]. In this study, we developed a new type of hybrid, PI-silica-PDMS, through in-situ sol-gel process to enhance performance of PI. PI-clay and also PI-clay-PDMS hybrids were made for comparison.

Poly(amic acid) (PAA) was prepared from the reaction of BPDA and PDA. Diethoxydimethylsilane (DEDMS) and tetraethoxysilae (TEOS) were used as a source of PDMS and silica as shown in Scheme 1. Organically modified clay (OMMT) or silica content was fixed to 3% and PDMS 5% .

1. *Preparation of PI- hybrid films*

PI-clay nanocomposite and PI-silica-PDMS hybrid films were transparent. On the other hand, PI-clay-PDMS hybrid films were opaque. Inorganic particle size was observed by SEM. In case of PI-clay-PDMS hybrids, the particles size of PDMS was 50-80nm, whereas the size is about 20-25nm in case of PI-silica-PDMS hybrids (Figure 1). Aggregation of inorganics made the PI-clay-PDMS hybrid opaque

2. *Properties of PI- hybrid films*

The tensile properties of various films are shown in Table 1. Reinforcement effect of OMMT increased the tensile modulus but decreased elongation. Hybrid from of PI-silica-PDMS showed higher tensile performance than others because of the toughening effect of PDMS and high rigidity of silica

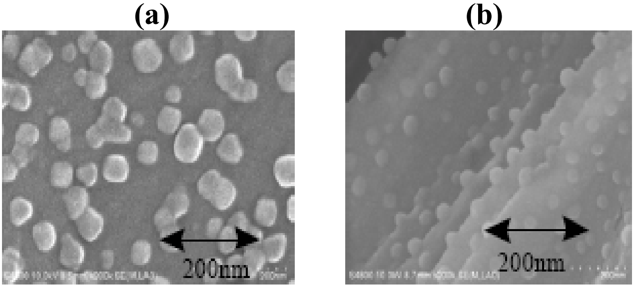

Figure 1. SEM images of (a) PI-clay-PDMS and (b) PI-silica-PDMS hybrids

Table 1. Tensile properties of different PI-films

| Type of PI | Tensile modulus (GPa) | Tensile Strength (MPa) | Elongation at break (%) |
|---|---|---|---|
| PI | 8.5 | 201 | 16.9 |
| PI-clay | 10.5 | 198 | 7.3 |
| PI-clay-PDMS | 10.6 | 179 | 17.5 |
| PI-silica-PDMS | 11.2 | 335 | 19.9 |

Dynamic mechanical analysis (DMA) of films revealed that $T_g$ from tanδ of the pristine PI was 320°C, which became 376, 364, 344°C in case of PI-clay, PI-clay-PDMS, PI-$SiOB_2$-PDMS hybrids accordingly. The reinforcement effect of OMMT and silica or silica-PDMS network limited the motion of PI chain and provided higher $T_g$ of all hybrids

The thermal stability of the hybrids were checked by TGA. The 5 and 10% weight loss temperatures were increased in the hybrids than the pristine PI because of the higher thermal stability and insulating effect of the inorganics. The increase of weight residue (%) at 800°C proved that the inclusion of inorganics enhanced flame retardent properties of PI.

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# ADVANCED MATERIALS

## State of the Art of Stents

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The concept of the stent came out directly of the problems with angioplasty balloons. In a small percentage of cases, the artery would collapse after the balloon was deflated, and around 30% of all coronary arteries began to close up again after balloon angioplasty. One such solution for those problems was the stent, a metal tube or "scaffold" that was mounted on a balloon and could be opened once inside the coronary artery. But while stents virtually eliminated many of the complications of sudden artery closure, bare metal stents still experienced reblocking in about 25% of cases. Researchers began testing a variety of drugs that were known to interrupt the biological processes that caused restenosis. Stents were coated with these drugs, sometimes imbedded in a thin biodegradable polymer for time-release, and clinical trials were begun. In the data gathered so far, the drug-eluting stent has been extremely successful in reducing restenosis from the 20-30% range to single digits. However, there is some evidence that drug-eluting stents may be susceptible to an event known as "late stent thrombosis", where the blood-clotting inside the stent can occur one or more years post-stent.

This is where biodegradable stents come into place. With the capability to completely disappear after a certain period of time, “late stent thrombosis” will not be a problem anymore. Furthermore, biodegradable stents will also eliminate the need to do surgery for taking out stent which is not needed in the body anymore. To this end, researchers have explored biodegradable, fully polymeric stents. The Igaki–Tamai stent is a self-expanding biodegradable stent ; however, the self-expansion can be achieved only by heating to 70 ºC, which may cause some trauma to cells during deployment. In the other hand, researchers from NTU have also developed fully degradable multi-layer stent with elastic memory. But such stents are still not ideal, in that the memory effect is not optimized due to the viscoelastic nature of the biodegradable polymer used.

Based on the previous research on biodegradable stent, we are targeting to create a stent that has a superior performance in the following properties : biocompatibility, biodegradability, drug release mechanism, shape memory and radio opacity.

## Kinetic of metallization of polyimide films by electrochemical method

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For the giving of the functional properties to polyimide films (reflectivity, electroconductivity, environmental protection) the precipitation of the secondary coating on the silver-sputtered polyimide films was carried out.

Nickel, cobalt, gold, rhodium and platinum coatings were used as modifying coatings. The tracing of the secondary coating was conducted by galvanic precipitation of those metals on the silver layer surface.

The optimization of the plating method was carried out by the matching of electrolytes composition and electrolysis conditions, like the temperature, current density etc. At the plating of the secondary coating the exfoliation may be a main problem, which hampers the progress. The evident exfoliation occurs in alkaline electrolytes and strong-acid medium. It is because the electrolyte influences on the underlying modifying coating through the pores in metal coating. The changes in it are caused to exfoliation.

The essential complication was appeared with the gold and rhodium extracting from the standard electrolytes.

The investigations of the exfoliation nature of metal coatings in electrolytes were conducted. The strong influence of the complexing additives on this process was detected.

As a result of the electrolyte composition and plating conditions optimization the secondary nickel, cobalt, rhodium and gold coatings were obtained. At the same time high-grade nickel, gold and rhodium coatings were received. Those coatings had stable characteristics of electroconductivity and reflection coefficient dependences on temperature. It was failed to obtain glare cobalt coatings with good reflecting properties.

The influence of the precipitable metal quantity on the reflection and conductivity characteristics was studied.

It was shown that the change of conductivity characteristics at the secondary precipitation is concerned with discontinuous primary metal layer and precipitable metal conductivity. At the same time the reflecting properties are fully determined by the conditions of the secondary layer precipitation and the epitaxy taking into account.

Proper resistance of virgin silver film distinctly influences on precipitation process uniformity along the sample length and leads to the local internal stress in the coating.

# Emission of clusters during solid surface bombardment by atomic and molecular ions.

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Clusters are form of matter intermediate between atoms (or molecules) and the solids with a well defined number n (the number of atoms – size of clusters) of constituents, they allow study of the evolution of a physical and chemical property from the atom towards the solid surface. Cluster (fullerene) of each size has an inspected expressive individuality. Physical and chemical properties (geometric and electronic structure, superconductivity and magnetism, chemical reactivity and catalysts, absorption etc.) can change drastically (by a few orders of magnitude) from one cluster size to the next. Consequently, it's important to get high intensity of different cluster flux for their investigations and interactions with matters.

In the presented work at UHV ($1.10^{-9}$ torr) conditions $A_n^+$($n = 1,2,3,\ldots,7$) clusters emission during $N^+$, $N_2^+$, $O^+$, $O_2^+$, $Ar^+$ primary ions bombardment of the C, NaCl, Mg, Al, Si, S, Cu, Ti, GaAs surfaces were investigated at different experimental conditions using SIMS method [1]. Mass and energy distribution measurements of emitted clusters at different primary ions initial energy ($E_o = 5$ - $50$ keV), intensities ($I_o$ = nA – μA on $cm^2$), angles of incident ($\alpha = 0$ -$45)^o$ and at various oxygen partial pressure ($p = 1.10^{-9}$ - $1.10^{-6}$ torr) were performed.

The emission of light clusters ($n \leq 10$) takes place during first ps after ion impact on surface, they are in internal (vibrational) excitation states (≈ eV/atom) and before detection (a tent of μs) cluster suffers fragmentation, ionization, relaxation and therefore, it's very difficult to determine mechanisms of their formation and emission from solid surfaces, consequence the experimental investigations here is very important.

For example, the yields of $Al_2^+$ and $Al_3^+$ clusters at molecular ($N_2^+$, $O_2^+$) ions bombardment are about one order of magnitude large, than in $N^+$, $O^+$ - Al case. Different way of surface interaction leads to formation various excitation states of clusters and they will be dissociated by a sundry manner. Each way of decay is corresponded by fixed probabilities. Besides, according to modeling of Betz and Husinsky [2] in suggestion of “double collision” model simultaneous impact by molecular ion (ion + atom) leads to more efficiency creation dimers and trimers from neighbour atoms of Al surface. Difference between the yields of $Al_2^+$ and $Al_3^+$ clusters is sensitive to either atomic ($N^+$,$O^+$) or molecular ($N_2^+$,$O_2^+$) projectiles are used. Two possible explanations for this difference are suggested: i) the formation of dissociative excitation states of emitted clusters and ii) the effective production of dimers and trimers from neighbour atoms of surface in a simultaneous impact of molecular ion (ion + atom).

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## Synergistic Effect in Conductivity of the Polymer Composites Based on Phenol-formaldehyde Resin

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At present the intensive works on creation of polymer composites with high electro-conductivity and stable exploitation properties for production of electrical engineering elements have been conducted. High interest of researches to this problems explained by possibility of obtaining of conductive materials with conductivity values of which is changed in the interval between insulators and metals. The conductivity and other useful properties of the conductive polymer composites (CPC) may be changed by use of relatively simple technological conditions. Very interest results have been obtained in the case of conducting polymer composites (CPC) including two different fillers (fillers may be conducting or one of them may be conducting and second one - insulator). Some composites display such called synergistic effect - nonadditive increasing (decreasing) of important properties of CPC at increasing of contain of fillers at change of proportion of ones. This phenomenon allows change the conductivity of composites in wide range of values.

The investigation of some peculiarities of dependence of conductance on filler type and amount in the polymer composites have been conducted. It is established, that conductivity of composites based on phenolformaldehide resin essentially depends on proportion of double fillers: graphite + carbon black, graphite+ andesite, contained in composites. It was shown, that these composites characterized by synergistic effect – non additive influence of fillers concentration on the conductivity and other properties of composites. Some other properties of composites contained binary fillers (effect of temperature, pressure on conductivity) have been investigated.

# Effect of Filler Modification by the Siloxane Compounds on the Properties of Composites Based on Epoxy Resin

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It is well known that modification of carbon chain polymers by some silicon-organic compounds leads to change their physical and chemical properties.

In the presented work dihydroxylphenilsiloxan (silphen) and tetraetoxysilane (TEOS) as modifying substances in composites on the basis of epoxy resin have been used. There were investigated the mechanical strengthening at compression, softening temperature and water absorption of obtained composites. The experimental results allow make following conclusions.

1. The dependence of mechanical strengthening of compounds based on dian epoxy resin on the content of silphen has extreme character with maximum at content of 5% mas % of this siloxane. This maximum is almost two time higher than in case of pure hardened epoxy resin; this composite containing 5 mass % of siloxane is characterized also by increasing of softening temperature and decreasing of water absorption nearly one order in comparison with hardened epoxy resin.
2. Mechanical and other physical properties of composites on the basis of epoxy resin with modified by TEOS (3 and 5 mass %) bentonite particles increase essentially in comparison with analogical composites containing same but unmodified filler. This result is explained by increasing of compatibility of filler particles with polymer matrix.

This phenomenon is the main reason of increasing of softening temperature and decreasing water absorption of these composites;

3. Analogical results were obtained in case of composites based on epoxy resin and modified and unmodified by TEOS diatomite particles. However some differences in properties of described above composites have been obtained; so, the composite containing diatomite filler is characterized by low specific weight and relatively high water absorption because of high porosity of filler particles (last properties is essential at high concentrations of the diatomite); although the strengthening of this material remain high at sufficiently high content of the filler.
4. On the basis of obtained experimental results some structural models of obtained composites have been proposed.

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## Effect of Vulcanization Technique on Electrical Conductivity of Filled Silicon-organic Rubbers

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It is known that vulcanization conditions affect electroconductive properties of the polymer composites. To clear up the effect of vulcanization technique on electrically conducting and some other properties of composites four methods of vulcanization were used: additive, peroxide, radiation and polymerization filling. Rubbers were essentially obtained on the basis of polydymethylvinilmethylsiloxane and carbon-graphite materials.

Analysis of experimental data allows make following conclusions:

1. During additive vulcanization cross-linking of macromolecules proceeds by the end groups with further formation of comparatively mobile three dimensional network preserving diffusion parameters of macromolecular segments, i.e. the medium with relatively low viscosity, that promotes filler macro-diffusion and formation secondary conductive structure, characterizes by relatively high conductivity.
2. Vulcanization initiated by peroxides forms more branched system of cross-links between macromolecules due to disclosure of non-saturations with further cross-linking of macromolecules which leads to formation of the system characterized by relatively low conductivity.
3. Radiation vulcanization forms the cross-linking between chemically active groups of carbon black particles and macromolecular free radicals. Such bonds reduce the cohesion forces inside the carbon black particles that reduce their coagulation. This process promotes formation of new reserves of conducting bridges and the increase of total composite conductivity.
4. The highest conductivity is displayed by composites produced by polymerization filling. Initial liquid medium promotes to homogeneous distribution of filler particles in polymer matrix and maximal usage of the “building” material current conducting channels and, consequently, the conductivity of composites increases at relatively low content of the filler. This fact is the main reason of low percolation threshold in these composites that have important practical meaning.

# Electrical Conducting Polymer Composites: New Coceptions and Perspectives

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Investigations of molecular and supermolecular structure effects on physical and physico-chemical properties of heterogeneous polymer systems show that the structurization is one of the main processes in formation of electrically conducting properties of conducting polymer composites (CPC). Growth of ECPC conductivity with the increase of conducting filler content is the rule without exclusions. The specific feature of this dependence is a jump-like increase of conductivity at definite (for a particular composite) threshold filler concentration, induced by an insulator-conductor transition. This transition conforms to the so-called threshold of proceeding, or percolation. In this case the conductivity is stipulated by formation of a continuous chain of filler particles in the polymer matrix - the infinite cluster. Resulting the increase of filler content the probability of occurrence of associates of these particles in the composition, or the so-called isolated clusters, grows. Further increase of the filler content promotes the juncture of isolated clusters into greater associates up to occurrence of an infinite cluster, i.e. a continuous electrically conducting channel in CPC. Continuous growth of the filler concentration may induce a situation, when all isolated clusters are included into an infinite cluster.

There are many mathematical expressions describing the dependence of conductivity of conducting polymer composites (CPC) on content of conducting filler. But nearly all these functions are suitable for only separate composites at various assumptions. Main reason of this situation may be explained by disregarding of proportion between physical interactions of three types: macromolecule-macromolecule, macromolecule-conducting filler particles and between lasts. Taking into account these interactions the expression reflecting the dependence conductivity-filler content will be correspond to experimental data more exactly for most CPC.

There are proposed some expressions describing the dependence of electrical conductivity of CPC on content of binary conducting fillers. Some peculiarities of effects of different physical factors (Temperature, pressure) on conductivity of CPC are considered too.

## Synthesis of Nanocrystalline Powders of Inorganic Compounds by Using Polymeric Matrices

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Receiving of nanocrystalline powders is one of the significant problems in modern technologies. Among the methods are known, sol-gel method makes possible to receive wide spectra of inorganic compounds. We have suggested synthesis of compounds by using polymeric matrices, which have special designation. That 2-200 nm size particles are possible to get by using polymeric matrices was established.

Receiving nanocrystalline powders by using polymers are possible by using following methods: I. adding polymers in reaction area and II. producing polymers in reaction area.

Polymeric matrices are oxidized and gases released while pyrolisis of gel produced by sol-gel method which is favorable factor for getting powders of mono dispersed inorganic compounds. Organic-inorganic hybrid compounds are produced by adding polyfunctional substances in sol-gel process. Pyrolisis of these compounds gives desirable product. Adding of carbochain or heterochain polymers in sol-gel process causes adsorption of reaction area components in various places of macromolecules, their separation from one another and powders of polyphase compounds are produced. Adding of polymers in sol- gel process is suitable, when oxides or oxide-ceramic compositions are obtained. It is possible to receive silicates, germinates, titanates, oxides and multicomponent ceramic compositions by using various type of methalorganic compounds.

The synthesis have been successful when siliconorganic polymers were used, which made possible get rare earth metal compounds ($Lu_2SiO_5$, $Lu_2Si_2O_7$, $LuTiO_5$, $Lu_2Ti_2O_7$, $Nd_2SiO_5$, $Yb_2Si_2O_7$).

We have elaborate technology of receiving of $SiO_2$, $TiO_2$, $Al_2O_3$ and other oxides containing special designation composition materials. Nowadays we have received $Lu_2SiO_5/SiO_2$, $LuSi_2O_7/SiO_2$, $LuAlO_3/Al_2O_3$, $Lu_3Al_5O_{12}/$ $Al_2O_3$, $Lu_2TiO_5/TiO_2$ and $Lu_2Ti_2O_7/TiO_2$ containing compositions, which are perspective ceramic scintillation materials.

## Tensile properties of the LDPE + Boehmite composites

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Composites of low density polyethylene reinforced with micrometric Boehmite powders were studied in combination with two silane coupling agents VTMES - SCA 972 and 3MPS - SCA. Samples were prepared via melt mixing followed by compression and injection molding. Morphology and mechanical behavior of the composites were investigated. Tensile tests show that the modulus increases with increasing contents of micrometric Boehmite particles while strain at break decreases for a certain loading range. ESEM examinations reveal formation of fibrous structures upon the addition of the treated micro fillers. Apparently the main factor of the fibrillation of the LDPE phase is an increase of the matrix viscosity. The most effective coupling treatments improving modulus and strain at break are those based on VTMES. Improvement in the tensile properties is attributed to a homogeneous dispersion and good interfacial adhesion between the fillers and matrix, seen in SEM.

## Tribological and thermal properties of blends of LDPE + Boehmite composites

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Tribological and thermal properties of composites of low density polyethylene reinforced with 1, 5, 10, 20 wt. % micrometric Boehmite powders were studied in combination with two silane coupling agents: VTMES - SCA 972 and 3MPS - SCA. We have determined sliding wear by multiple scratching along the same groove using a micro scratch tester [1]. Instantaneous penetration depth is lowered by the filler addition to LDPE. However, there is less viscoelastic recovery and the residual (healing) depths increase with increasing Boehmite concentration. Microindentation hardness increases along with higher powder content. Friction determined with a pin–on–disk tribometer using silicon nitride and steel balls as a function of Boehmite concentration shows a minimum. The result is explained in terms of surface morphology seen in scanning electron microscopy. At the same time, all samples friction values are lower than for neat LDPE. Wear determined in the pin–on-disk tribometer decreases along with the powder concentration increase. The results attributed to improved interfacial adhesion between the treated powder and the polymer matrix.

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## Chemical Modification and Characterization of Boehmite Particles

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We see increasing use of ceramic oxide fillers in the development of polymer composites. One thus obtains composites with better mechanical, thermal, electrical or other properties. The properties are strongly influenced by the nature of the filler/matrix interface, in particular by adhesion between the filler particles and the polymer [1 - 3]. The main problem here is the incompatibility of hydrophilic ceramic oxide fillers and hydrophobic polymer matrix, which yields composites with poor properties. Thus, control and/or manipulation of the surface properties of the particles are of great importance. We know that during the preparation process formation of covalent bonding between organic polymers and inorganic components contributes to the enhancement of the compatibility in the composites. This can be achieved through the grafting of a polymerisable group onto the oxide surfaces via hydroxyl groups followed by its copolymerization with organic monomers [4]. Among others, silane coupling agents have been used to improve dispersion, adhesion and compatibility in such materials [5].

The purpose of the present work is modification and characterization of Boehmite aluminum oxyhydroxide (AlOOH) powder through grafting of polymerisable organic silane molecules 3-(trimethoxysilyl)-propylmethacrylate (3MPS) and vinyltri(2-methoxyethoxy)silane (VTMES) onto surfaces of ceramic oxide powders via hydroxyl groups on the oxides. In order to obtain organic-inorganic hybrid “macromonomers”, effects of grafting conditions have to be carefully determined to optimize the process.

Experiments were conducted on (SCA) modified Boehmite powders. These hybrid macromonomers were blended with low density polyethylene (LDPE). Investigation of the effect of powder loading and powder morphology on the thermal, mechanical and tribological properties of the resulting materials contributes another paper.

This paper is one of a series dealing with polymer + ceramic oxide powder composites. Our other papers address free – radical copolymerization of the modified $SiO_2$ oxides with methylacrilic monomers and the characterization of resulting organic – inorganic hybrids [6-8].

Polymerisable organic silane molecules 3-(trimethoxysilyl)-propylmethacrylate (3MPS) and vinyltri(2-methoxyethoxy)silane (VTMES) have been grafted onto surfaces of high purity Boehmite (trade name HiQ alumina) via hydroxyl groups on the oxides in order to obtain organic-inorganic hybrid "macromonomers". Changes of surface characteristics and quantification of grafting have been determined using thermogravimetric analisis (TGA) and Fourier-transform infrared spectroscopy (FTIR). The influence of the type of silane used and grafting conditions have been determined.

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## Synthesis and Characterization of Poly(methyl acrylate) + $SiO_2$ Hybrids

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For the past decade, organic + inorganic composites prepared by the sol-gel process have attracted much attention, especially in the fields of ceramics, polymer chemistry, organic and inorganic chemistry, and physics [1 - 5].

Organic + inorganic materials prepared by the sol-gel process can be generated using different synthetic techniques by incorporating various starting inorganic and organic components with varied molecular structures [6 - 8].

Incorporation of organic/inorganic/polymeric materials into organic + inorganic networks by the sol-gel process makes it possible to optimize selected properties independently. Specifically, the introduction of organic groups into an inorganic network leads to new structure – property variation, thereby promoting new potential applications for the resulting composite materials [1, 2, 9 - 11].

The objective of this work is synthesis and characterization of poly(methyl acrylate) (PMA) + $SiO_2$ hybrid composites via a sol-gel reaction. Therefore, we have prepared acrylic based copolymers with a content of alkoxysilane groups by co-polymerization of methylacrylate (MA) with 3-(trimethoxysilyl)-propylmethacrylate (3MPS) and viniltrimethoxysilane (VTMS). The products were co-condensed with tetraethylorthosilicate (TEOS) [12].

We have used a variety of techniques to characterize our PMA + $SiO_2$ hybrid materials, including Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and environmental scanning electron microscopy (ESEM). Since our study involves also bioactivity, a test of bioactivity in the simulated body fluid (SBF) and the characterization the surface changes of the composites in a physiological solution is in progress.

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# Antibiocorrosive Covers and Conservators Based on some Arsenic Compound Derivatives

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The arsenic organosilicon oligomers, aromatic derivatives and complex compounds have been obtained and studied. The adamsite derivatives have been synthesized by Grignard reaction; arsonium salts-10-brom-ethylene-izo-propyl-5,10-dihydrophen-arsazines bromides have been synthesized by alkylation of Adamsite derivatives with 1,2-dibromethane. The Zink, cadmium, cobalt- and nickel-containing complexes based on adamsite derivatives, iodm- ethylene trialkylarylarsonic compounds have been synthesized. Synthesized compounds are solid, non-evaporating substances soluble in usual organic solvents (acetone, diethylether, ethanol, DMF, etc.), and insoluble but dispersed in water.

By using of the data of elemental, functional and IR spectral analysis, the composition and structure of the synthesized compounds have been established.

For investigation of the bactericide and fungicide properties, as testing systems, some anaerobic and aerobic bacteria and mushrooms have been used.

It was shown that all synthesized compounds characterized with the active bactericide and fungicide properties. It was established that the synthesized compounds can be used against phyto-pathogen microorganisms, also some anaerobic and aerobic bacteria and mushrooms. The synthesized compounds were doped into polymer matrix on the basis of silicon-organic film-forming adhesive polymers with easily hardening functional groups, also various organic hetero-chain polymers. Antibiocorrosive covers and conservators for archaeological samples and materials from plastics, rubbers, and leather have been manufactured.

## The structure and physical properties of the surface layers in the new metallized polyimide films with high electrooptical performances

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ICS[2] have developed new methods to metallize PI films, which yield conductiing materials with high reflectivity, but without damaging the films in the process. The surface layers of films represent composite material in which metal nanoparticles strengthen the polymer. The high adhesion and reflection coefficient in visible spectrum part, caused by this specific structure, makes these films prospective for new technicues.

The structure and physical properties of the surface layers were investigated by RSA, DSK, TGA methods and by measurements of the microhardness, reflectivity and the electrical conductivity.

The microhardness (MH) method (according to Vickers) was used as an express method for estimation the depth of metal particle penetration in experimental films: on this depth two curves (for untreated films and films after modification) coincide together. On the whole these values correspond to the data of the electron microscopy.

Because the value of MH is essentially less in comparison with such of pure metal, evidently we deal with composite material in which metal nanoparticles strengthen the polymer.

For Kapton hardening of the surface layers was observed especially for Co. At the same time, Umplex film is more hard and elastic and the MH of original and modified films is essentially larger, than it for Kapton. The MH of original film is larger, than the same of modified. Probably for this solid film the diffusion during modification initiates the structure loosening and MH reduction. X-ray structural analysis confirmed the possibility of the effect from metal particles implanting to polymer matrix structure. X-ray analysis was carried out with using diffractometer in transmission mode (Cu $K_{\alpha}$, Ni-filter). For small angles analysis was used 18-kW Rigaku X-ray generator and detector “Bruker AXS”. The experiment detected the crystal Ag peaks are clear for the examples PI-Ag, but for PI-Co only the light presence of β-Co occurs.

At the same time for examples with Ag polymer matrix did not change and for with Co ones it became more amorphous. X-ray structural small angles analysis in approximation of the spherical particles estimated the middle Co particles size as 200 nm when the wide distribution of particles size. Middle Ag particles size estimated from peaks width is near 2 000-4 000 nm.

The temperature dependence of the electrical conductivity (EC) across the film was measured at regime of linear heating (2K/min) in temperature diapason 20 – $257^o$ C. The current strength measured in element with plane-parallel electrodes. Current sensitivity was $1.10^{-15}$ ampere, the constant voltage was 100 V.

As well, as for the MH methods, the matrix determines the basic behavior. The value of the electrical conductivity permits to estimate the thickness of “high conductivity” owing to impurities after chemical modification.

The measurement of TSD current ( prof.G.A.Lutcheikin) detected the presence of the electrical charges, which release higher $120^0$ C. The injection of carriers during the modification process can leads to electron density redistribution in system polymer/ metal nanoclasters.

The reflection coefficient $K_{\text{refl}}$ was measured in MSPU radiophysics laboratory for microwaves on backward-wave tube at 240 GHz frequency ($\lambda \approx 1,2$ mm) for metallized polyimide films on both sides of the films (metallized and non metallized ).

The obtained results open out new application perspectives for dielectric polyimide films modified by metals in microelectronics for semiconductor devices.

# New Bioactive polymers based on Sodium alginate and styromal

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In spite of broad interests for the study in field of syntheses of high-molecular bioactive substances, some aspects of fundamental and applied characters are required still to satisfy current needs of such compounds in pharmaceutics and agriculture.

A series of polymeric bioactive substances on the basis of copolymers of maleic anhydride and several vinyl compounds, such as styrene, acrylic acid, acrylamide, as well as some polysaccharides were synthesized for the application as drug delivery carrier and regulator of controllable plant growth.

Now on some studies on the development of new biopolymers on the basis of sodium alginate and copolymer of styrene and maleic anhydride, or styromal, modified by 1,4-bis-(1,2,5-trimethyl-4-oxypyperidyl-4)-butadiine-1,3, or akpinol as an effective regulator of plant growth, has been carried out. Moreover, some polymeric composites based on sodium alginate and consisting of malachite green and methylene blue has been synthesized to use for photodynamic therapy of cancer.

Optimal conditions for the preparation of these biopolymers are found out. It is shown that fitoactive polymer of styromal is soluble due mainly to the use of low-molecular bioactive substances as hydrochloride. The use of the akpinol leads to its immobilization on polymer-carrier without any catalysts because of hydrochloride form reactivity comparing to its basic form. By means of conductometry, UV-spectroscopy, viscosimetry an interaction between akpinol or malachite on one hand and asodium alginate on the other hand is determined. It is clear that in the case of malachite-alginate system a ratio of the complex is about 2:1, however with akpinol the polysaccharide interacts barely, presumably through hydrophobic interactions.

Experimental tests of the synthesized polymeric systems are on the way now. It is shown that germination capacity of seeds soaked in a solution of fito-styromal exceeds in 21.2% those are soaked in standard solution. Moreover, the use of bioactive polymer leads to intensive growth of plant root systems.

Compositions of malachite dye with sodium alginate possesses remarkable photodynamic properties at cancer treatment. It is established that a value of cancer growth suppression during the photochemical therapy using 1% solution of malachite green is maximal for Erlich's malignant tumor 99% and ovary malignant 85.5% respectively. The use of the developed ointment of 0.1% malachite green causes suppression of malignant tumor with 86-88% for Erlich's ones and 86-87% for ovary tumors respectively. Thus, the application of malachite-containing alginate ointment leads to decrease of photosensibilizer dose by ten times compare to its aqueous solution at the same level of suppression effect during photodynamic tumor therapy. The developed ointment is generally efficient for treatment of cornea neovascularization.

## Nano-Cellulose and its Application

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The new nano-scale cellulose product (NanoCell) with CI crystalline modification was prepared using advanced, environmentally friendly, resource-save and cheap technology. The developed technology permits producing NanoCell in pilot and industrial amounts. NanoCell product can be manufactured in the form of dispersions, high solid paste and dry powder.

NanoCell product was tested by methods of XRD, electron microscopy, Laser-light scattering and viscometry. The investigations showed anisometric particles of NanoCell with length about 150-300 nm and width 20-40 nm. These particles are aggregates of 3-4 individual nano-crystals having length of 40-60 nm and width of about 10 nm.

NanoCell application areas were studied. The most promising application of NanoCell will be cosmetics. Nano cellulose material is suitable for use in a large variety of existing and new cosmetic products for different skin types due to the combination of the following features:

- ✓ NanoCell is a natural product, completely harmless and non-allergic
- ✓ The high sorption ability of nano-particles promotes skin cleaning and opening of the pores by actively absorbing fat from the tiny pores. This effect is enhanced by the small particle size
- ✓ The fine crystalline nano-particles gently and selectively remove dead skin cells (exfoliation) without damage to healthy skin during a peeling procedure
- ✓ NanoCell is a non-abrasive material and contributes to a gentle sensation of peeling
- ✓ Optimally adjusted particle size and ratio between coarse and fine particles provides an excellent peeling effect

NanoCell has excellent compatibility with organic cosmetics ingredients, it gives uniform particle distribution, imparts smooth texture, increases viscosity, water-retention and stability of liquid cosmetic compositions. Introduction of NanoCell into cosmetic compositions permits reducing the amount of thickeners, detergents and other synthetic ingredients and leads to substantial cost-saving in formulations. NanoCell is chemically stable in wide ranges of pH and temperatures, and does not interacts chemically with other active and inactive cosmetic ingredients consequently its efficacy is not compromised.

## New nanostructured matrixes for fibre reinforced composites

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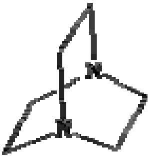
We have elaborated a new type of network interpenetrated polymer as a matrix of nigh shock resistant reinforced plastics. Using as interpenetrating polymer networks principle in production of composite materials provides a unique possibility to regulate their both micro-and nano-structured properties Formulation of a new class of nanocomposite materials is characterized by the absence of contaminants for a network polymers technology. As a main component of such technology we are using branched (dendro)-aminosilanes that at the first stage are curing agents for many oligomers. Additional hydrolysis of aminosilane oligomers creates the secondary nano-structured network polymer that improves service properties of the compound. By using a principle of forming nanostructure by creating nanoparticles during a technological process from a liquid phase, Polymate has elaborated a few of composites based on different kinds of soluble silicates. Significant increasing of silicate matrix strength and toughness was reached by incorporation of special liquid additives, such as TFS, which effect as a microcrystallizing nucleator on the technological stage and later they colmatage the pores of silicate matrix. Our last elaborations are mainly applying a novel type of soluble silicate contained organic cations, for example, the DABCO (  )-based organic alkali soluble silicate.

The problem of modeling of branched cross-linked structures is one of most complicated in composite science. Most existing composite materials have branched cross-linked structure, and their theoretical study is indispensable for their optimal application in practical needs. Conventional methods of description of branched cross-linked structures are numerical and do not allow solution in the general case. Their application needs complicated and long computing and the physical sense of the obtained results is not always clear. Some researchers try application of classical chain models to branched systems, although such approximation is incorrect and may cause serious errors. The problem of modeling of branched cross-linked structures was recently solved by statistical polymer method. This method is based on the consideration of averaged structures (statistical polymers). In such approximation, all reactions in equilibrium are considered as reactions between statistical polymers. The statistical polymer method was tested directly and indirectly. The direct test comprised the exact reproduction of Trommsdorf effect for non-equilibrium polymers, whereas the indirect test allowed the theoretical interpretation of adsorption isotherms for silica and alumina gels. In all cases, the correlation of experimental and theoretical results was very good. The statistical polymer method allows modeling of composites, e.g. materials based on DABCO-based soluble ammonium silicates.

Silica globulas in solution or solid are successfully modeled. Such modeling allows serious reduction (for hundreds-thousands times) of the number of numerical experiments. The proposed statistical polymer method is commendable for description of all kinds of composites with complex structure.

## The effects of multifunctional alcohols in the chemical recycling of polyurethane foam waste

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By attention in the increasing of polymeric materials usage, especially polyurethanes (PU)- due to their versatile characteristics- production of vast volume of wastes is inevitable. Many efforts have been carried out for recovery of valuable materials and reuse for production of new products. Advanced chemical recycling, or chemolysis, is a recycling process where high molecular-weight polyurethanes are broken down into chemical components. In this study PU foam wastes were glycolized by using polyhydric alcohols namely, glycerol and pentaerythritol as destroying agents in the presence of basic catalysts. In all reactions polyol in PU backbone was recovered in high yield and high purity without observation of polyol chain degradation reactions. In another attempts, PU foam wastes were glycolized by using glycerol/ base catalyst system by applying microwave irradiation. In MW assisted reactions the required times for complete foam dissolution were shorter than conventional heating methods. FT-IR, NMR, GPC, viscosity, density and water content of recycled polyol was performed and compared by virgin one. For recycling, industrial samples of flexible cold cure PU foam, derived from the reaction of Daltoflex EC 20240 (formulated virgin polyol) and MDI. The polyol (propylene oxide–ethylene oxide copolyether) was a colorless viscous liquid with Mw ~ 1900, functionality 2 and hydroxyl numbers 59 mg KOH/g. Isocyanate was Suprasec 2027 diphenylmethanediisocyanate (MDI) based prepolymer. Microwave assisted experiments were performed in a Milestone MicroSYNTH "NP" Ethos 1600 microwave oven at atmospheric pressure.

FT-IR spectra were done by using a BRUKER Tensor 27 spectrometer (droplet samples were impregnated on KBr pellets). $^{1}$HNMR and $^{13}$CNMR spectra were done using a BRUKER CRX 300 instrument and deuterated acetone as a solvent and the water contents were measured by Karl Fischer Mettler DL 18 titrator.

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2. Alavi Nikje MM, Nikrah M, Haghshenas M (2007) Polym Bull 59: 91
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# Polyester waste recycling at the melted state

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In this work the results of research on polyethylene terephthalate depolymerisation by the chemical recycling method in the fused state with use of alkalis are submitted. The potential of terephthalic acid and ethylene glycol reception from polyethylene terephthalate with addition of alkalis in the melt is shown. The influence of different alkali reagents on PET depolymerisation was investigated. It is established that calcium hydroxide is the optimal reagent for carrying out the depolymerisation reaction. The research on the property of received terephthalic acid is resulted as well. On the basis of researches the technological process of PET waste treatment with receiving of terephthalic acids is developed. Process of plastic waste treatment includes following stages: crushing of polymer, fusion of polymer with addition of alkali, melt cooling, crushing and hydrolysis of received product, sedimentation of terephthalic acids at pH downturn, washing, filtering and drying of terephthalic acid. This method of chemical recycling does not have the demands of high temperature and pressure, it is realized in a short time and it results in products with the high cleanliness.

# Application of Natural Polysaccharides for Controlled Release of Local Anesthetic Kazkain

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The development of polymeric Drug Delivery Systems is the fundamental direction of polymeric and pharmaceutical technology. Among of the many polymers, natural polysaccharides have been widely used as carriers for Drug Delivery Systems.

The goal of the present work is the evaluation of natural polysaccharides as carriers for controlled release of local anesthetic kazkain. The original synthesis of this drug was firstly carried out by kazakhstanian scientists in the Institute of Chemical Sciences. Immobilization was carried out by means of salt formation with water-soluble natural polysaccharides such as sodium salts of carboxymethylcellulose, alginic or pectic acid. The interaction of analgesic drugs with biodegradable polymers was studied from the viewpoint of thermodynamic behavior. The binding process was examined by an equilibrium dialysis method. The free drug concentration was determined from residual drug concentration; the binding constants were calculated from Klotz equation. The data obtained show that the thermodynamic parameters and their temperature dependence show the existence of electrostatic and hydrophobic interactions between drugs and polysaccharides. The release of drugs into model biological medium at 37°C was studied. The correlation between release rates and binding parameters was determined. It has been shown that dosed release proceeds during 5-7 days and depends on nature of polymers, their concentration, pH of solution and ratio of components.

Calcium-alginate gel beads containing kazkain were synthesized. Release of drug from the alginate gel beads of various mannuronic/guluronic ratios in physiological solution was examined. It was found that discontinuous time of the Fickian diffusion of the drug was followed by a burst release of the remaining drugs. The lag time preceded the burst release depended on mannuronic/guluronic ratio. It was revealed that the burst release of drug was initiated by a swift disintegration of calcium-alginate due to exchange on sodium ions.

The biodegradation process and anesthetic action were studied in experiments on animals. Data of medical-biological and clinical tests show the advantages of polymeric drugs application in comparison with low-molecular drugs.

## Diatomite-Containing Phenoplast Polymer Compositions and Plastic Materials on their Base

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Plastic materials have been obtained by thermal structurization of natural material - diatomite containing phenol formaldehyde (resole and novolac type) polymer compositions.

The major technological parameters of treatment were defined. These are: temperature – 180°C, relative pressure - 60 MPa, treatment duration – 40 sec per mm of object thickness.

When diatomite content in polymer composition is up to 80 mass % the mechanical and dielectric indices of phenoplast are high, but its fluidity decreases significantly, which is the most important factor for the process of treatment of polymer compositions. It was proved that compositions are optimal when diatomite content reaches 40-60 mass %. The table offers physical-mechanical and dielectric indices of phenoplasts obtained on the base of resole and diatomite.

| # | Indices | Diatomite content in compositions, mass % | | | | Industrial marks |
|---|---|---|---|---|---|---|
| | | 30 | 30 | 60 | 80 | |
| 1 | Fluidity, mm | 150-200 | 150-200 | 100-190 | 80-160 | 90-190 |
| 2 | Specific impact strength, kJ/m2 | 4.5 | 6.0 | 7.0 | 4.5 | 4.5-5.5 |
| 3 | Ultimate tensile strength at bending, MPa | 55.0 | 85.0 | 90.0 | 80.0 | 55.0-65.0 |
| 4 | Electric strength, KV/mm | 16.0 | 20.0 | 22.0 | 22.2 | 12.5-16.0 |
| 5 | Relative surface el. resistance, Ohm | $2 \cdot 10^{14}$ | $5.0 \cdot 10^{15}$ | $5.5 \cdot 10^{15}$ | $5.5 \cdot 10^{15}$ | $1 \cdot 10^{13}$-<br>$5 \cdot 10^{13}$ |
| 6 | Specific volumetric el. resistance, Ohm. cm | $1.0 \cdot 10^{14}$ | $2.0 \cdot 10^{15}$ | $2.5 \cdot 10^{15}$ | $2.5 \cdot 10^{15}$ | $1 \cdot 10^{11}$-<br>$5 \cdot 10^{12}$ |

It was proved that in polymer compositions the costly and deficient fillers can be completely replaced by cheaper and accessible local natural mineral material

# Compositions Obtained on the Base of Amide Type Oligomers and Natural Sorbents

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Polymer compositions were obtained on the base of amide aldehyde, namely on the base of carbamide-formaldehyde, thiocarbamide-formaldehyde and melamine-formaldehyde oligomers. Natural diatomite was used as the filler.

Some kinetic regularities of hardening process of polymer compositions were studied in isomeric conditions at 130, 150, 180 and 200°C temperatures, on the air and under vacuum. The major kinetic parameters were defined. It was proved that the reaction of oligomer structurization is of the first order one. Reaction rate constants, activation energy and probability factors were determined.

It was shown that presence of diatomite in compositions does not change the reaction mechanism, but affects only the structurization reaction rate and depth.

Conversion grade and rate of compositions at heating in vacuum are higher than at heating on the air, which is explained by oxidation of functional groups on the air.

Experiments proved that the process of hardening of compositions containing up to 40 mass % diatomite proceeds till deep conversion, which can be conditioned by two causes: 1) at the hardening of compositions the products possessing less rigid structure are formed, that is, the structure becomes loose, porous and 2) diatomite exerts catalytic effect on the process of hardening. It was shown that the composition is optimal when diatomite content equals to 30-40 mass %. Thermomechanical studies proved that at the increase of diatomite content in the composition, thermal resistance of animoplast is increased. Thus, for example: scratch hardness number, in case of carbamide-formaldehyde oligomer containing composition with 10 mass % diatomite content, equals to 110°C, with 40 mass % content – 130°C, while with 80 mass % content – it raises to 155°C.

Plastic materials which are obtained on the base of such polymer compositions are characterized by high physical-mechanical and dielectric indices.

Compositions obtained on the base of carbamide (1) and melamine (2) *

| # | Indices | 1 | 2 | Industrial mark animoplasts |
|---|---|---|---|---|
| 1 | Relative impact strength, kJ/m$^2$ | 8.8 | 7.9 | 6.4-6.9 |
| 2 | El.strength, kW/mm | 20.0 | 20.0 | 12 |
| 3 | Tensile strength at bending, MPa | 96.0 | 71.6 | 70.4-86.7 |
| 4 | Composition fluidity, mm | 70-150 | 100-195 | 70-160 |
| 5 | Relative surface el. strength : Ohm | $1{,}0 \bullet 10^{14}$ | $4 \bullet 10^{15}$ | $1{,}0 \bullet 10^{12}$ |
| 6 | Relative volumetric el. strength Ohm. cm | $2{,}3 \bullet 10^{14}$ | $2{,}5 \bullet 10^{15}$ | $1{,}0.1^{11}$ |

- Diatomite content in composition – 40 mass %

# New Type Fillers for Obtaining Antifriction Polymer Compositions

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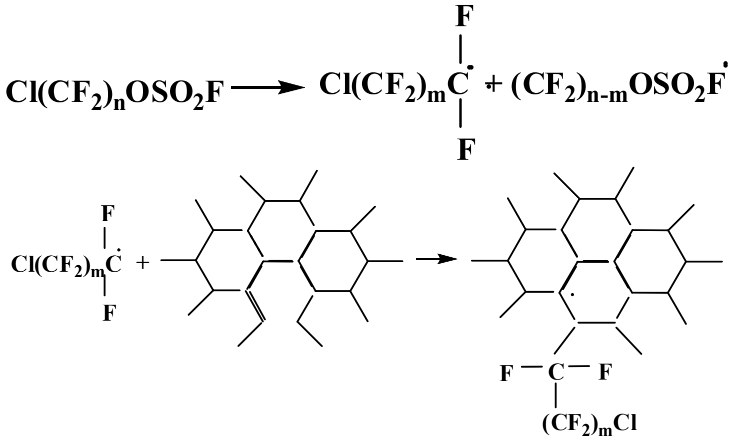
In order to increase the lubricating properties of graphite used as a filler in ant-friction plastic masses the modification was carried out by fluorine-containing oligomer – fluorine alkane (FDS): $Cl(CF_2)_nOSO_2F$, where n=7 –12. Advantage of fluorine alkane to other modifiers was expressed in its good solubility in organic solvents, high temperature of destruction and the opportunity to get highly dispersive compounds by their dispersion ability.

Modification of graphite by FDS was investigated by their joint vibro-dispersion. It was shown that the coefficient of friction of the modified obtained graphite is decreased from 0.16 to 0.03, while the value of free surface energy - from 46.5 to 36.7 J/m$^2$.

Mass-spectral method was used for the study of thermal destruction process, which shows that the mixture "graphite+FDS", in distinct from pure FDS is characterized by marked decrease of "large" products (m/z> 200) and by the increase of number of $(CF_2)_nCl$ ions, which refers to interaction of graphite and FDS during their simultaneous vibro-dispersion.

Electro-paramagnetic resonance analysis (EPR) of graphite and FDS dispersed products revealed that at the dispersion of separate products in the selected conditions the paramagnetic centers (PMC) are not formed. Probably this is connected with swift recombination of the formed radicals, while in the products of vibro-dispersion of a mixture "graphite + FDS" we observel rather significant number of paramagnetic centers.



$$Cl(CF_2)_nOSO_2F \longrightarrow Cl(CF_2)_m\dot{C}F_2 + (CF_2)_{n-m}OSO_2F^{\bullet}$$

Such a scheme of interaction implies the structure where the chlorine atoms in the created products are "outside"

The modified product pbtained by us is used as a filler in various materials of tribochemical designation: in antifriction plastic masses and plastic lubricants, in serial production of ball bearings, which increases their service length by 20%.

## Gradient oriented state of polymers

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For one of the main directions of polymer science of the XXI century is considered as the creation and investigation of materials with the gradient of properties.

In this direction the essential success was achieved in the 70s of the last century. The methods of obtaining of materials with inhomogeneous distributions of properties have been developed.

The heterogenity of composition conditions the gradient of refraction.

By leading in optics of a new parameter - refraction index gradient, the fundament for the theoretical and experimental investigations have been created.

The world practice of development of **GRIN-** optics indicates that the attention of the researchers is concentrated only on the refraction index.

At the same time in opinion of experts of GRIN optics similarly are the perspective materials having other optical properties, in particular, materials of gradient birefringence, too.

By introducing in optics of a new parameter – Gradient Birefringence - a fundament of a new direction of optics was laid which demanded widening of the notion of “Gradient Optics”. Today, the gradient optics covers two independent directions – GRIN–optics and GB-optics.

The ways of formation of GRIN and GB elements are different. The GRIN-elements are received as a result of chemical transformations.

Formation of GB elements is based on ability of great deformations characteristic to linear polymers.

At the same time while realizing great deformations polymer passes on to specific, so called oriented state.

The most widely spread of polymeric orientation is monoaxial orientation stretching. As a result of the orientation the physical and chemical properties of the whole number of exploitation properties of polymers are changed essentially.

With allowance of property gradient, as a strategic mark of development of polymeric science, the oriented state of polymers acquires a new essence which can be qualified as gradiently oriented state.

We think, that introduction of new structural characterization of polymers as new physical characteristics of polymeric nature essentially widen generally the problematic of scientific research of polymeric science principally increase the possibilities of regulation of mechanical, thermal, electric, optical and other properties, will give an impulse to creation of new scientific directions as it has already happened on the example of GB-optics.

For creation of gradient oriented state an uniaxial stretching by means of inhomogeneous mechanical field is used. The form of isotropic polymer sample (i.e. the form of clamps and inter-location) has been selected so that it is provided with preliminary established gradient of relative lengthens in the sample. By means of variation of other parameters (temperature, value, velocity of deformations, etc.) it is possible to regulate gradient oriented state of polymers. Characterization of this state will be effected by means of observation on polarized light through the polarized microscope and studying of birefringence. Thus, the birefringence is a testing characteristic of gradiently oriented state and at the same time it may be itself a purposeful property of the material.

Additional information about gradient oriented state you can see in stand report theses.

## Some possible spheres of GB-elements application

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The usage of gradient oriented polymer systems in the first instance is possible in order to receive classical optical elements such as polarizable compensaters and polarizable interferencive filters, including polarizable-interferencive monochromator. On the point of modern requirement view the usage of gradient oriented polymer systems in holography and photonics is perspective.

Polarized Holography and Photonics: Both in holography and photonics it has become necessary to envisage the polarized characteristics of the light. Generally in this case it is important only the intensity gradation was the reason why dynamic range of the process was sharply limited. In case of fixation of polarization it is already decisive not the intensity gradation (which is limited), but the fixation of practically boundless (infinite) versions of polarization. As a consequence in a given case it becomes necessary to provide with complex space polarized modulation of light. One of the ways for solution of this task is to use the GB elements having the complicated structure which gives possibility to realize the formation of light waves having the specific polarized characteristics.

A special importance is given to applying of GB elements in photonics (in photochemistry), so as for today the investigations are being carried out very intensively for studying both the liner and nonlinear Veigert effects. This time the GB elements will provide with the accurate and simple relation between the linear and nonlinear Veigert effects. In particular, the calibrated (divided) GB elements give possibility to realize the radiation simultaneously by means of all kinds of polarization. This time it is very important that in corresponding sections of polarization the power exposition is absolutely similar, which is automatically realized. And this is particularly important, since it excludes the necessity of labor-intensive and less accurate photometric measurements. In photonics the GB elements will fulfill the function a definite standard polarized modulators.

The Luminescence Analysis: Too interesting are the possibilities of using of anisotrope films in luminescence analysis. In particular, as it is known in oriented organic films as in matrix. Radiation of installed luminescence paints is partially polarized. Besides, this time the degree luminescence (fluorescence) polarization mainly depends on the structure of luminescence material molecule itself and the quality of matrix orientation. In case if the matrix orientation changes along the film, i.e. we have a gradient anisotropic matrix, the luminescence polarization quality is characterized too by definite distribution, i.e. by the gradient to the same direction. If the degree of luminescence polarization, let's say along the X axis, is expressed by $P_1(x)$, and the degree of matrix polarization or distribution of anisotropy - by $P_m(x)$ or $\Delta n(x)$, than the relative value

$$K = P_1(x)/P_m(x) \text{ or } K = P_1(x)/\Delta n(x)$$

in totally with luminescence intensity and spectral characteristics unambiguously should determine

the definite features of given luminescence materials. This approach has definite properties as well for possible broadening of investigation of laser effects.

For development of GB-optics (similarly as of classical optics) processing/development is an universal method which allows us to realize GB-structures of concrete functional destination

by means of creation of various technological equipment and controlling of their technical parameters. e.g. in case of simple one.-dimensional compensators the main determining technological parameters can be the relative lengthens, profile and scale of clamps. And in case of relatively complex two-dimensional compensators to this three main parameters are added the coordinated parameters which mean the simultaneous orientation to the orthogonal or generally to any other direction, too. If we add to it a space modulation of temperature field as well, e.g. gradient heating the obtained GB element configuration can be changed within the wide ranges according to their destination.

# Polarizable properties of polymer films having gradient of birefringence

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Introduction in science of a new specific state of polymer materials and corresponding new physical characteristic – notion of gradientally oriented state essentially widens view on the generally polymer science problems.The results obtained in this sphere will principally increase the possibilities of regulation of mechanical, thermal, electric, optical, acoustic and other properties of polymers, they will give an impulse to formation of a new scientific directions, as it had already happened on the example of GB-optics.

The method of formation of optical polymer elements, having gradient of birefringence (GB-elements) and experimental results of its polarizable properties study are described.GB-elements was made using thin films of PVA (PVA,d=100-150 mk) and Polyethylentherephtalate (PETPh,d=190mk).

A polymer film to be stretched is placed between clamps. The inter-location and/or their form has been selected so, that it is provided with preliminary established gradient of relative lengthens in various sections of polymer sample. By means of variation of other parameters (value, rate and distribution of deformation, temperature, environment, the chemical structure of polymer) it is possible to regulate gradient oriented state of polymers. Characterization of this state will be effected by means of observation on polarized light through the polarized microscope and studying of birefringence. Thus, the birefringence is a testing characteristic of gradient oriented state and at the same time it may be itself a purposeful property of the material.

It is shown, that in the middle of GB-element gradient of birefringence $\Delta n$ increases exponentially across the central axes z, and $\Delta n$ = 0,02 .Increasing of GB-element formation temperature from $80^0$ to $90^0$C improve linearity of the relation $\Delta n$ = f(z), but in the peripheric zone line is broken.

## Some Regularities of Formation of Gradient-Oriented State in Polymers

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In this work we consider some regularities of formation of the gradiently oriented state which is connected with some properties of constructive determinations of corresponding apparatus.

Distribution of the relative lengthen determines by profile of clamps $f_1(x)$ and $f_2(x)$, where independent variable x changes in the $[x_1,x_2]$ interval. $f_1(x)$ undergo parallel displacing across the OY axis and $f_2(x)$ is fixed function. Let us designate the relative lengthen across the OY axis as Φ (x) and the value of parallel transfer as K , then for the distribution of the relative displacing we have:

$$\Phi(x) = K/[f_1/(x) - f_2(x)]$$

In this table is given the various meaning of Φ (x) function:

| Φ (x) | $f_1(x)$ |
|---|---|
| 1) $\Phi(x)=ax+b$ | $f_1(x)=K/(ax+b)+f_2(x)$ |
| $1^1$a=1. b=0 | $f_1(x) = K/x + C$ |
| 2) $\Phi(x)=ax^2+bx+c$ | $f_1(x) = K/(ax^2+bx+c)+C$ |
| $2^1$a=1, b=0,c=0 | $f_1(x) = K/x^2+C$ |
| 3) $\Phi(x)=a/x$ | $f_1(x) = Kx/a + C$ |
| 4) $\Phi(x)=\sin x$ | $f_1(x) = K/\sin x + C$ |

Let us assume that the initial length of the sample in the x point is more than distance between two clamps, i.e. $\Delta x > [f_1(x) – f_2(x)]$ Then for the relative lengthen we have:
$\Phi(x)=K/( f_1(x) – f_2(x)+ \Delta x )$

In this table is given the various meaning of $\Phi$ (x) function:

| $\Phi$ (x) | $f_{1(x)}$ |
|---|---|
| 1) $\Phi (x)=ax+b$ | $f_1(x) = K/(ax+b) + f_2(x)- \Delta x$ |
| $\Phi (x)=ax +b$<br>$f_2(x)=\alpha x+\beta$ | $f_1(x) = K/(ax+b) +C – (\alpha x+ \beta)$ |
| $\Phi (x)= ax^2+bx+c$<br>$f_2(x)=\alpha x+\beta$ | $f_1(x)=K/(ax^2+bx+c) + C – ( x + \beta)$ |
| $\Phi (x)=a/x$<br>$f_2(x)=\alpha x+\beta$ | $f_1(x)=(K/ a) x +C -\alpha x – \beta$ |

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# Advanced materials