

**MATERIALS FOR THE NEW MILLENNIUM-  
SYNTHETIC INORGANIC, SEMI-INORGANIC,  
AND ORGANIC-INORGANIC HYBRID POLYMERS**

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The properties of mineralogical and covalent inorganic polymers are briefly described in the introductory part. Glass is an important polymer made up of rings and chains of silicate units which contain negatively charged oxygen atoms neutralized by positive metal ions. Glass and few other mineralogical types of inorganic polymers, like aluminum oxide, could be fabricated into fibers and used as insulating materials, and as reinforcing fibers in composite materials. Most rocks, bricks, concrete and ceramics belong to mineralogical polymers which are of great importance as construction materials, but their application is often limited because they are not flexible, elastomeric and resistant to impact. The most important covalent polymers are poly(organosiloxanes) and poly(organophosphazenes). Poly (organosiloxanes) contain chains of silicone-oxygen atoms with two methyl groups attached to silicon atoms. Silicone polymers have low glass transition temperature of  $-130\text{ }^{\circ}\text{C}$ . Temperature of elasticity of silicone rubber is from  $-30\text{ }^{\circ}\text{C}$  to  $250\text{ }^{\circ}\text{C}$ . They strongly repel water and are used as corrosion inhibitors of metals. An important field of application of silicones is in medicine and in preparation of medical devices. In continuation, there are briefly described the properties and application of poly(phosphazenes) and poly(sulfur nitride). After that, several examples of organic-inorganic hybrid polymers are listed, illustrating the variety of existing and possible new commercial applications of these new materials. The following applications of hybrid polymers are described: silane block copolymers for contact lenses, acrylate tin copolymers for marine antifouling coatings, scratch resistant automotive coatings and preparation of microporous silica.

**Key words:** *synthetic inorganic polymers, mineralogical polymers, covalent inorganic polymers, inorganic-organic polymers, organic-inorganic hybrid polymers, poly(organosiloxanes), poly(organophosphazenes), poly(sulfur nitride)*

**Materijali za novo tisućljeće - Anorganski, polu-anorganski i organsko-anorganski hibridni polimeri.** U referatu je naglašeno da iako su mnogi anorganski sintetski polimeri otkriveni prije organskih sintetskih polimera, anorganski polimeri značajno zaostaju u razvoju u usporedbi s organskim polimerima koji se proizvode na osnovi petrokemijskih sirovina. Međutim i pored prednosti koje imaju organski sintetski polimeri u usporedbi s anorganskim polimerima, oni se ne mogu primjeniti u mnogim područjima visokih tehnologija u kojima se zahtijevaju materijali otporni na visoke temperature uz uvjete korodirajuće atmosfere. Očekuje se da će mnogi problemi povezani s primjenom organskih polimera biti savladani razvojem nove generacije anorganskih polimera. Od posebnog su značaja polu-anorganski polimeri koji sadrže anorganske elemente u glavnom lancu, a organske skupine kao bočne grane, te organsko-anorganski hibridni kopolimeri, koji su se počeli razvijati u zadnje vrijeme. Anorganski polimeri klasificiraju se na razne načine, a najčešće kao mineraloški i kovalentni anorganski polimeri. Staklo predstavlja mineraloški tip anorganskih polimera u kojima su postrane skupine negativnih kisikovih atoma neutralizirane pozitivnim nabojima metalnih iona natrija, magnezija ili kalcija. Od kovalentnih anorganskih polimera značajni su poli(organosiloksani) ili silikoni, poli(organofosfazeni) i poli(sumpor nitridi). Molekulska masa silikona iznosi  $2 \times 10^6$ , a  $T_g$   $-130\text{ }^{\circ}\text{C}$  uz područje elastičnosti od  $-30\text{ }^{\circ}\text{C}$  do  $250\text{ }^{\circ}\text{C}$ . Silikonski polimeri mogu se proizvoditi jednostavnim tehnološkim postupcima iz jeftinih laganog dostupnih sirovina. Silikoni se koriste za izradu predmeta od keramike, stakla, gume, građevinskog materijala, te u medicini. Značajna je primjena silikona za zaštitu metala od korozije. Poli(di-trifluoretoksifosfazen) se lagano oblikuje iz otopine, tali se kod  $242\text{ }^{\circ}\text{C}$ , a  $T_g$  iznosi  $-66\text{ }^{\circ}\text{C}$ . Novo područje anorganskih polimera su anorgansko-organski hibridni polimeri koji se upotrebljavaju za proizvodnju kontaktnih leća, za zaštitu površine metala od korozije i mehaničkih oštećenja od grebanja, te za sprječavanje nakupina na ljusku broda u moru.

**Ključne riječi:** *sintetski anorganski polimeri, mineraloški polimeri, kovalentni anorganski polimeri, organsko-anorganski polimeri, organsko-anorganski hibridni polimeri, poli(organosiloksani), poli(organofosfazeni), poli(sumpor nitridi)*

## INTRODUCTION

A large number of new materials with new properties, designed for specific applications have been developed during the last Century. Some of these materials are based on naturally occurring raw materials like metals, wood, minerals and many other natural products: wool, silk, rubber. Presently however, of special interest are various synthetic materials like synthetic organic polymers, inorganic polymers, high performance organic composites, nanocomposites for special devices, electroconductive and photo-image processing materials, drug carriers, materials for artificial organs and biomedical uses.

In the previous article published under the title: "Synthetic Organic Polymers with Special Emphasis on Their Comparison with Metals", D. Fleš, *Metalurgija*, 39 (2000) 3, 157-163 [1], a review of the development of synthetic organic polymers during the last fifty years, and the main advantages of plastics in comparison with metals, wood, glass, paper and other natural materials was described. The present paper will briefly describe the preparation, properties and application of inorganic, semi-inorganic and organic-inorganic hybrid polymers.

Many inorganic synthetic polymers have been discovered before the discovery of synthetic organic polymers. However, due to the ready availability of organic monomers from the petrochemical industry, nearly all synthetic plastics and elastomers in use today, are organic polymers. But the fact remains that few organic polymers can be heated above 150 °C for a prolonged period of time. Many of the problems associated with the use of organic polymers are expected to be solved by the development of inorganic polymers which are stable at extremely high temperatures in a corrosive environment. At the same time, inorganic polymers can withhold tensile strength, are electroconductive, have thermoinsulating properties, and are incombustible and stable to solvents and chemicals.

Although the intrinsic thermal stability of many inorganic polymers is good, a variety of difficulties should be overcome before a usable inorganic polymer can be obtained. For this reason, large efforts have been undertaken in order to synthesize semi-inorganic polymers, which contain inorganic elements in the main chain, and organic elements as side groups. The third group of inorganic polymers, often called organic-inorganic hybrid polymers, have been commercially used since 1950s, but only recently these copolymers which represent molecularly linked organic-inorganic blocks, have attracted a large attention.

## CLASSIFICATION OF INORGANIC POLYMERS

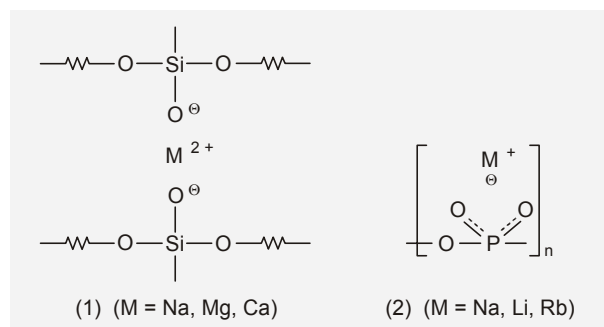
A literature search indicates that there is no agreement concerning the definition and classification of inorganic polymers. In broad terms, as an inorganic polymer may be

considered any substance containing a large number of repeating units, involving elements other than carbon, connected by various types of chemical bonds. This definition covers all inorganic solids, but also includes the compounds which have organic groups linked to inorganic back-bonds [2-3].

Difficulties in the systematization of inorganic polymers arise because the developments in inorganic macromolecular field involve contribution from the researchers working in mineralogy, general inorganic and organic chemistry, and various fields of processing technologies. Recently, an attempt has been made to establish a uniform system for characterization of inorganic polymers, but nevertheless, inorganic polymers are usually divided into: mineralogical types of inorganic polymers, and covalent inorganic polymers [4].

## MINERALOGICAL TYPES OF INORGANIC POLYMERS

A number of mineralogical inorganic polymer systems have been used for a long time. Glass is, for instance, an important polymer made up of rings and chains of repeating silicate units. Glass fibers can be made by the extrusion of molten glass through spinarettes and they can be used for fabrication of textiles or insulation mats. Glass belongs to the mineralogical type of inorganic polymers in which the side-group oxygen atoms bear negative charges which are neutralized by positively charged metal ions such as sodium, magnesium or calcium ions (1).



Several other mineralogical-type inorganic polymers have also been fabricated into fibers by high-temperature techniques. Aluminum oxide monofilaments can be produced by melt extrusion. The fibers are stable up to 1400 °C and are used in thermal insulation or in filtration. One widespread use of mineralogical fibers is as reinforcement fillers in crosslinked organic matrices.

Well known mineralogical polymers are phosphate polymers (2) which contain a backbone of alternating phosphorous and oxygen atoms. Metal ions in structure (2) are sodium, lithium and rubidium. A problem in the application of some phosphates is that treatment with water causes breakage of chains, thus decreasing the molecular weight of polymers.

Most rocks, bricks, concrete and ceramics are three-dimensional inorganic polymers held together by a combination of covalent and ionic bonds, and they are the fundamental construction materials since the dawn of civilization. However, their use is limited for many modern applications because of the difficulty in fabrication, and because they are not flexible, elastomeric, or resistant to impact.

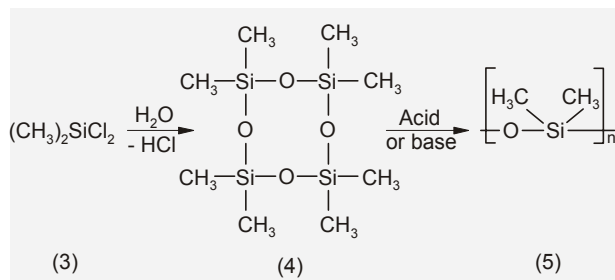
### COVALENT INORGANIC POLYMERS

The limitation of the technical application of mineralogical-type of inorganic polymers is the need that elements which make the backbone should be linked together through covalent bonds. For this reason, the search for useful inorganic polymers has concentrated on the covalent main group elements: boron, aluminum, silicon, germanium, tin/nitrogen, phosphorus, arsenic, oxygen, sulfur, selenium, and tellurium.

Several examples which illustrate the synthesis, properties and application of covalent-inorganic polymers are described in this paper.

#### Poly(organosiloxanes) or (Silicone polymers) [4a, 5-6]

The poly(organosiloxane) (5) is the most widely used silicone. It contains chains of alternating silicon and oxygen atoms with two methyl groups attached to each silicon atom. The starting material for the preparation of polymer (5) is octamethylcyclotetrasiloxane (4), which is obtained by the hydrolysis of dimethyldichlorosilane (3):



The molecular weight of the polymer (5) may be as high as  $2 \times 10^6$ , corresponding to 25000 silicon-oxygen repeating units per chain. The mechanism of siloxane polymerization follows an ionic mechanism. Beside the dimethylsilane, also other substituent groups have often been introduced: vinyl, ethyl, fluoropropyl, p-cyanoethyl, propyl and biphenyl. The introduction of various substituent groups improves strength, toughness, flame resistance, and compatibility with organic polymers.

Poly(organosiloxanes) or silicone polymers are polymers with the low glass transition temperature of  $-130^\circ\text{C}$ . The temperature range of elasticity of silicone rubber is from  $-30^\circ\text{C}$  to  $250^\circ\text{C}$ . Silicone rubber strongly repels water and is used as a corrosion inhibitor of almost all

common metals (iron, aluminum, zinc) [4a]. In industrial application it was established that silane coupling treatment of metals improves their corrosion performance after printing. Recently however [7] (Figure 1.), it was shown that, protection of metals with silane coupling agents can be obtained even without paint coatings. The best results of corrosion protection of metals are obtained by coupling vinyl silane (6) with bis-1,2-(triethoxysilyl)ethane (7).

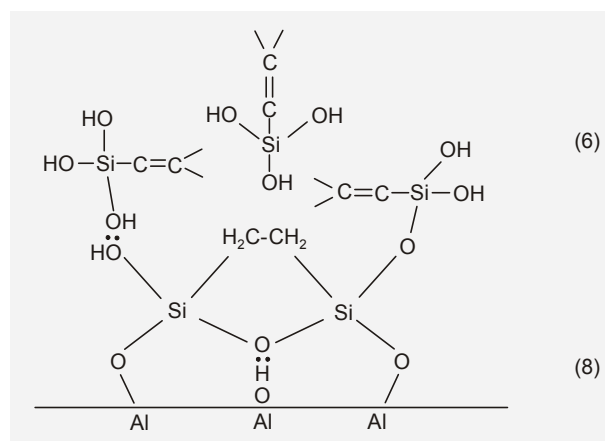


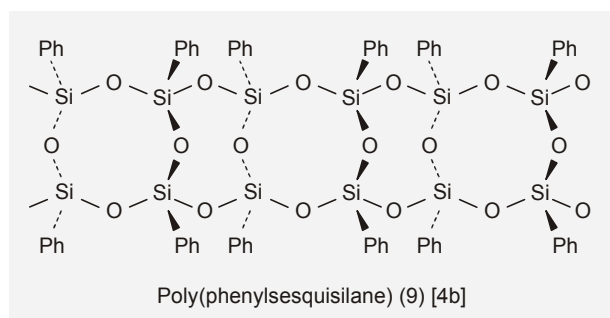
Figure 1. Sheme which indicates the formation of a double-layer crosslinked film on the surface of aluminum by coupling of bis-1,2-(triethoxysilyl) ethane (8) with vinyl silane (6)

Slika 1. Shema koja pokazuje nastajanje dvoslojnog umreženog filma na površini aluminija povezivanjem bis-1,2-(trioksetil) etana (8) s vinil silanom (6)

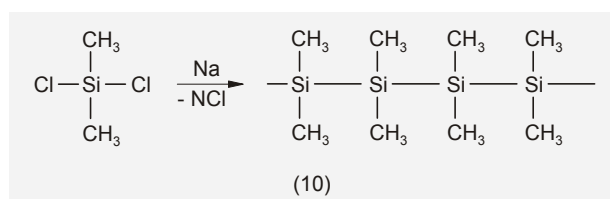
Bis-1,2-(triethoxysilyl)ethane (7) easily hydrolyzes with water producing bis-1,2-(triethoxysilyl) ethane,  $(\text{HO})_3\text{Si-CH}_2\text{CH}_2\text{-Si(OH)}_3$  (8), which can react with weakly basic hydroxyl group on metal-oxide surface, thus forming a film of 50-100 nanometers thickness. By coupling hydroxy groups on this film with vinyl silane (6), a double layer crosslinked film is formed. This film protects metal against corrosion even without any subsequent painting. A specially important field of application of silicone polymers is in medicine and in preparation of biomedical devices. There is practically no part of human body or in the surgery where silicone polymers have no application. One of the important applications of silicone polymers in medicine is the use of vulcanized silicone for the preparation of the artificial skin. Artificial skin is produced from the crosslinked animal skin, collagen and chondroitine- $\beta$ -sulphate and silicone. Due to the pronounced permeability for oxygen, silicone layer in contact with atmosphere enables the healing of damaged skin. Copolymers of silicone and urethane are extremely flexible, tough, impact resistant material compatible with human and animal tissues and they represent the most important synthetic materials for artificial heart valves and experimental heart by-pass pumps. Copolymers of silicone and acrylates are an important material for the production of contact lenses.

Poly(organosiloxanes) are resistant to oxidation at temperatures up to 200 °C, but at the temperature above 250 °C, siloxane chains breakdown and depolymerize to form rings, thus losing the advantageous properties of polymer. In order to solve this problem, research of a new class of siloxanes called "silicone ladder polymers" is under way.

An example of this type of polymer is poly(phenylsesquisiloxane) (9) [4b]. The double chain structure of this polymer restricts the mobility of the silicon-oxygen bond, thus forming a high melting, non-elastomeric material. Ladder polymers are stable up to a temperature of 300 °C.



A relatively new class of silicon-containing polymers are polycatenasilanes which contain silicon atoms only in the backbone (10). These polymers are prepared by the action of alkali metal on dimethyldichlorosilane:

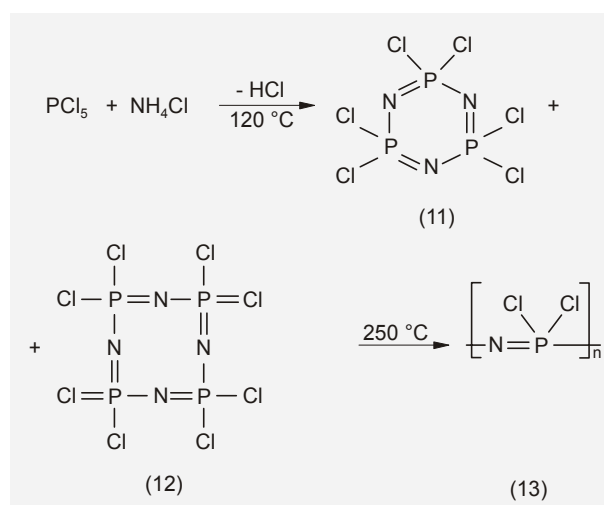


Instead of the compound (10), cyclic oligomer (SiMe<sub>2</sub>)<sub>6</sub> is more frequently formed. Pyrolysis of cyclic oligomers can lead to the formation of higher oligomers known under the name of silicon-carbide polymers. Because the backbone structure of these compounds shows extensive electron dislocation, the electrical properties of these polymers are of importance. In some respect they behave like metals.

It is of interest to note that silicon-based compounds can be produced from simple sources like sand, rice hull and ethylene glycol without an expensive, high-temperature processing and toxic by-products. Currently, most polymers are produced from petroleum-based chemicals, although petroleum comprises less than 1 % of the Earth's natural sources. Silicon sources, on the other hand, accounts for some 25 % of the minerals on the planet [8].

**Polyphosphazenes.** The first phosphazene derivative, hexachloro-cyclophosphazene (NPCl<sub>2</sub>)<sub>3</sub> (11), was synthesized in 1834 by Liebig and Wöhler [9] by reacting phosphorous pentachloride with ammonium chloride. The principal products are trimer (11), tetramer (12), and polymer

(13). The side groups, beside halogen could be: amino, alkyl, aryl, alkoxy or aryloxy:



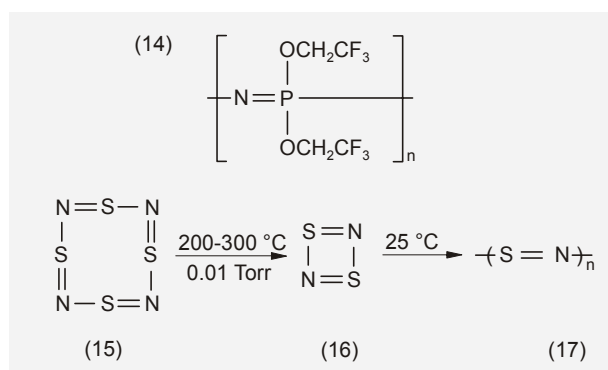
The cyclic trimer (11) is soluble in organic solvents and polymerizes at a temperature of 230 - 300 °C to a transparent rubber-like product (13). Poly(dichlorophosphazene) (13) has relaxation properties better than natural caoutchouc, and remains elastomeric up to the glass transition temperature of -63 °C, and is thermally stable up to 350 °C. Its molecular weight can be as high as 2x10<sup>6</sup>. Although poly(dichlorophosphazene) has excellent properties, it is not technologically useful material, because it slowly reacts with atmospheric moisture yielding phosphoric acid, ammonia and hydrochloric acid. Replacement of chlorine by organic groups improves stability of phosphazenes. An example of polyphosphazene in which chlorine is substituted with trifluoroethoxide is poly[bis(trifluoroethoxy)phosphazene] (14).

Phosphazene (14) can be solution cast from acetone or methyl ethyl ketone yielding a colorless, flexible film, which can be oriented by stretching and resembles to polyethylene (4c). Polymer has a low glass transition temperature of -66 °C and remains flexible from T<sub>g</sub> up to its melting point at 242 °C. Similar to silicones, polyphosphazenes decompose above 200 - 250 °C causing the formation of small rings. Since the depolymerization process is highly disadvantageous, the blocking of thermal depolymerization of inorganic polymers is one of the main challenges for research of inorganic polymers.

Most of the current technological applications of many organophosphazenes depend on their oil resistance, ultraviolet light resistance, nonflammability and low glass transition temperature (T<sub>g</sub> -80 °C). Organophosphazene elastomers are mostly used as fuel liners, hoses, gaskets, O-rings, and as nonburning foam rubber articles. Polyphosphazenes are also used as biomedical polymers which degrade in the body to phosphate, ammonia and amino acids released from the side groups [4c].



Poly(sulfur nitride) or polythiazyl [4d] is formed by the sequence of reactions (15), (16) and (17).



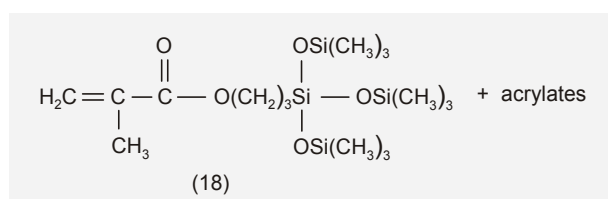
Tetrasulfur tetranitride (15) is prepared from elemental sulfur and liquid ammonia. The cyclic tetramer (16) is an orange-yellow crystalline solid, melting at 178 °C. Poly(sulfur nitride) (17) is a new type of metal which has a metallic appearance and exhibits metallic-type electrical conductivity at room temperature. At 25 °C its electrical conductivity is similar to that of mercury and bismuth. The conductivity increases by lowering temperature, and at 4.2 K it is 200 times higher than at 25 °C. However, at 0.3 K the polymer behaves as a superconductor.

## ORGANIC-INORGANIC HYBRID POLYMERS

Hybrid organic-inorganic polymers have been commercially used for more than 50 years, but only recently the understanding of organic-inorganic structure-property relationship has enabled the creation of new hybrid materials that display unique desired properties. Several examples which illustrate the successful application of organic-inorganic hybrid polymers listed in this article show the variety of existing and possible commercial applications of these new materials.

Contact lenses represent a successful application of hybrid technology based on acrylate-functional silane copolymers. Parameters which have been achieved by hybrid copolymers based on acrylate-silane compounds are permeability and equivalent oxygen percentage.

The first methacrylate-silane hybrid which was widely commercialized for rigid gas-permeable lenses is based on the technology discovered by Gaylord [10]. The process is based on the copolymerization of methacryloxypropyl-tris(trimethylsiloxy)silane (18) with various acrylates:



## Acrylate-functional tin copolymers: marine antifoulant coatings

Among the largest volume of hybrids are tributyltin-methacrylate copolymers used as marine antifoulant coatings [11]. The potential savings from using antifoulant coatings can be illustrated by the following example: A large cargo container ship operating at 15 knots for 300 days/year consumes more than \$ 7 million of fuel. Increased drag caused by marine fouling can easily increase fuel consumption by 30 % - more than \$ 2 million per year.

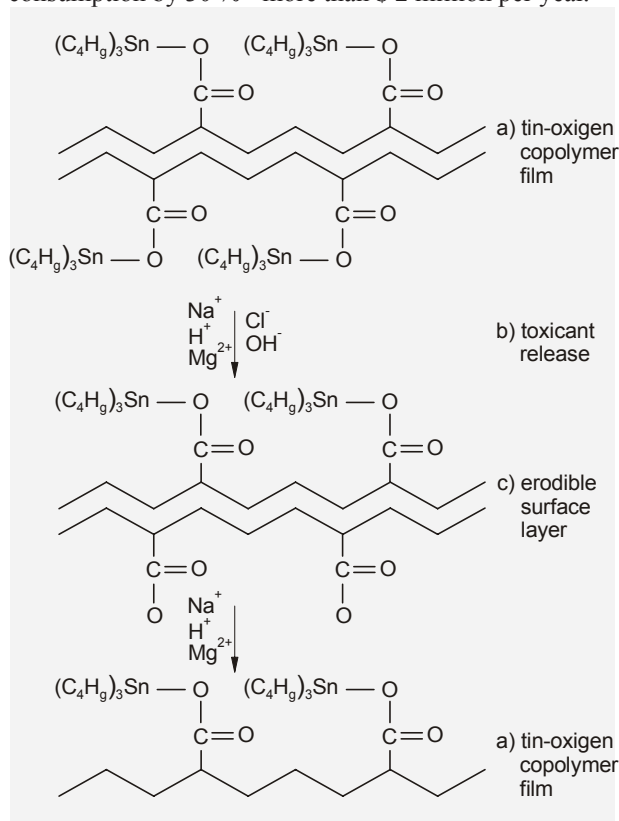
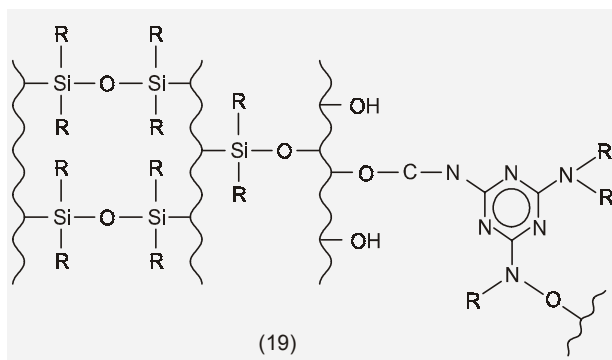


Figure 2. Organotin antifoulant coatings present an organic polymer base film with tin-oxygen copolymer film (a) which can be hydrolyzed by sea water under the release of tin toxicant (b) and formation of erodible layer (c) under the recovery of hydrolyzable tin-oxygen copolymer film (a).  
Slika 2. Organo-stanum prevlake koje sprječavaju nakupljanje nečistoća predstavljaju osnovni stanum-kisik kopolimerni film (a) kojega može hidrolizirati morska voda uz oslobađanje otrova (b) i nastajanje razgradljivog sloja (c) i uz regeneriranje hidrolizirajućeg stanum-kisik kopolimernog filma (a).

The success of organotin copolymer (Figure 2a) is attributed to the slow electrolyte-catalyzed hydrolysis of the surface layer of copolymer under the release of toxicants:  $(\text{C}_4\text{H}_9)_3\text{SnCl}$  and  $[(\text{C}_4\text{H}_9)_3\text{Sn}]_2\text{O}$ . The removal of toxicants from the copolymer surface forms a hydrolyzable erodible layer which by the action of sea water removes the erodible film and recovers the marine bio-fouling tributyltin-methacrylate copolymer surface.

### Clear, scratch-resistant automotive coatings

A patented procedure for automotive coatings combines two hybrid polymer systems that cross-link simultaneously during the cure from a partly grafted, partly interpenetrating polymer network (19) [12].



The superior scratch resistance and environmental etch resistance of methacryloxy-propyltrimethoxysilane led to their acceptance as topcoats for 8 of the 10 top selling automobiles in 1997, including Ford Taurus, Toyota Camry and Honda Civic del Sol. This application represents a dramatic new high volume use of hybrid organic-inorganic polymers in automobile industry.

### Preparation of microporous silica from polyoxazoline-silica block copolymers

Another example of organic-inorganic hybrid polymer is the block copolymer of polyoxazoline (POZO) with  $\text{SiO}_2$  terminated with 3-aminopropyl-triethoxysilane (Figure 3.) [13]. The homogeneity of the obtained composite gel is due to a chemical bonding at the end of POZO and to the interaction between the amide group in POZO and silica through the hydrogen bonding. POZO segments from the

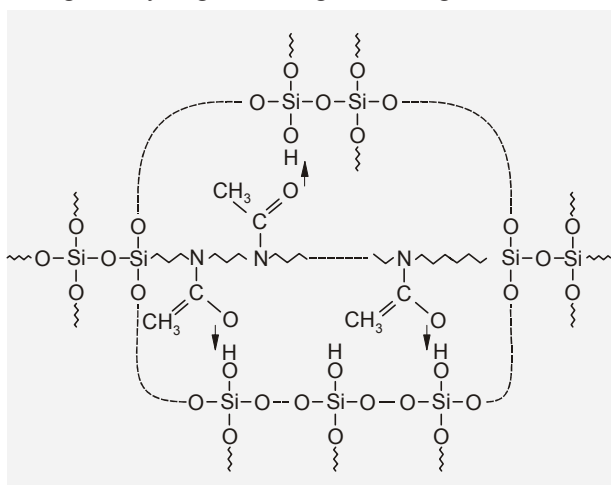


Figure 3. Block copolymer of polyoxazoline with  $\text{SiO}_2$   
Slika 3. Blok kopolimer polioksazolina sa  $\text{SiO}_2$

copolymers illustrated in Figure 3. can be eliminated by the pyrolysis at temperature below the fusion point of silica gel, thus producing a silica having micropores with  $800 \text{ m}^2/\text{g}$  surface area and a  $0.5 \text{ cm}^3/\text{g}$  of pore volume (Figure 4.). The pore volume and surface area of microporous silica could be controlled by the POZO content in hybrid copolymer before the pyrolysis.

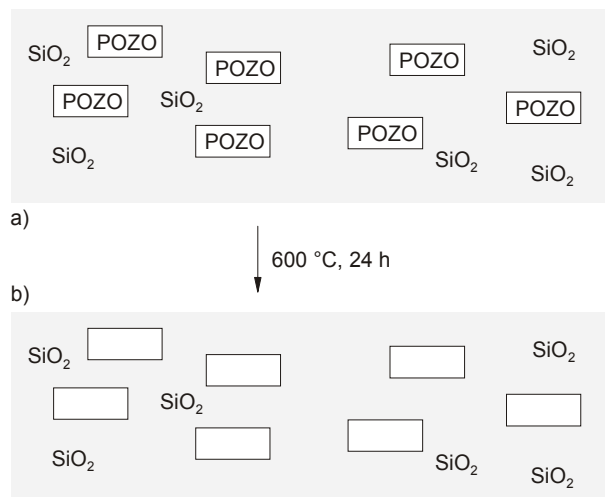


Figure 4. Schematic presentation of block copolymer of polyoxazoline (POZO) with  $\text{SiO}_2$  (a) and porous silica after removal of POZO (b)

Slika 4. Shematski prikaz blok kopolimera polioksazolina (POZO) sa  $\text{SiO}_2$  (a) i porozni silicij nakon uklanjanja POZO (b)

### CONCLUSION

In summary we can conclude that a large number of inorganic polymers has been synthesized, but that with exception of siloxanes and phosphazenes few of these polymers have significant large-volume commercial importance. It is further emphasized that during the last few decades the commercial application of organic-inorganic hybrid polymers is increasing. One of the reasons which prevented the intensive development of commercial application of inorganic polymers is that inorganic polymers are usually considered as substitutes for organic polymers, instead of accepting inorganic polymers as new materials with new properties and a new field of application. In fact it is often more appropriate to compare inorganic polymers with metals, rather than with organic polymers. Another reason for the slow development of technological application of inorganic polymers is a limited knowledge between their structure and properties. And finally, one of the reasons which has caused the slow development of inorganic polymers is related to the fact that in the studies of inorganic polymers have preferably involved organic polymer chemists, which has often resulted in neglecting the

specific properties of main and transition group elements. However, during the last two decades the situation with respect to the application of inorganic polymers has significantly changed.

Inorganic polymers are lately increasingly used in various high-technology fields, specially in electronics, interplanetary technology, robotics, medicine, and as thermo-stable and oil-resistant elastomers. Of special interest is the use of silane coupling agents for corrosion protection of metals, and for clear scratch-resistant automobile coatings.

Recent attention oriented to hybrid organic-inorganic polymers combines the properties of organic and inorganic polymers and metals. Besides, new types of organic-inorganic hybrid polymers enable the production of high tonnage materials by combining high-performance inorganic polymers with commodity polymers like polyethylene, polypropylene and polyurethane. It is evident that hybrid polymer systems will have an ever increasing impact on the marketplace.

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