

Inorganic and Organometallic Polymers: A Review

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ABSTRACT

Inorganic polymeric materials comprise a very unique area of polymer science. These macromolecules which contain inorganic elements as part of their main chain structure or as pendent group, attract considerable attention as speciality materials with unique properties and novel applications. Two main classes of these compounds: inorganic and organometallic polymers, which represent a growing field of research, have found broad diverse applications. As, organic and inorganic components with countless combinations are found in these classes of polymers they offer a wide range of interesting properties and applications. In this paper, the main properties of some more important classes of these compounds, including wholly inorganic polymers inorganic-organic polymers, organometallic polymers and hybrid organic-inorganic networks are discussed on the basis of their structural features, and some examples of the novel applications of these materials are presented.

Key Words:

organic-inorganic polymers;
organometallic;
structural features;
properties; applications.

INTRODUCTION

High polymers with inorganic elements in their backbone or as pendent group offer a new area with broad opportunities for material scientists and technologists who are looking for new classes of compounds that are attracting attention as high-

technology materials, biomedical polymers, and electrical conductors [1-2]. The main reasons for scientists to be interested in inorganic-based macromolecules are connected with their unique property profiles that make them different from their total-

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ly organic counterparts. among these are the following main features [3-5]:

- The number and variety of elements found in these polymers (well over 40 elements in addition to those typically found in commercial organic elements),
- The relative high abundance of inorganic elements in the earth's crust (e.g., oxygen 50%, silicon 26%),
- Stronger bond formation, which are more resistant to cleavage reactions (Si-O 110, P-N 140, and C-C 85 k cal/mol),
- Different valencies for attachment of side groups,
- Stability at high temperature, and;
- Tailoring new and interesting structures with many variations, which seem endless.

Thus, inorganic polymers provide an opportunity for expansion of fundamental knowledge, development of new materials assisting in the advancement of technology, and stimulating the thought of what might result if organic and inorganic chemistry are combined in polymer science [6].

In this paper, attempt is made to provide a perspective to the field of inorganic polymers by focussing on some more important features and applications of these interesting materials.

DISCUSSION

Inorganic and organometallic polymers represent a rapidly growing field of chemical research and already have many applications and any classification is necessarily somewhat arbitrary. For simplicity and convenient a classification is used here which may be far from perfect. In the following, we will focus on four main classes of inorganic polymers which are: wholly inorganic polymers, inorganic-organic polymers, organometallic polymers, and hybrid organic-inorganic polymers [7].

Wholly Inorganic Polymers

Inorganic polymers in this class constitute the major components of soil, mountains and sand, and they are also employed as abrasives and cutting materials (diamond, silicon carbide (carborundum), fibres (fibrous glass, asbestos, boron fibres), coatings, flame retardants, building and construction materials (window glass, stone, Portland cement, brick and tiles), and lubricants and catalysts (zinc oxide, nickel oxide, car-

bon black, silica gel, aluminium silicate, and clays).

Among the polymers in this class a few of the more well-known wholly inorganic polymers will be introduced in the following:

Portland Cement

Portland cement is the least expensive, most widely used modified inorganic polymer. It has a complex structure (short-range morphological order with long-range morphological disorder), three-dimensional structure. A typical cement paste contains Portland cement, sand, gravel, and about 75% water. There are many specialty cements including reinforced concrete, lightweight concrete, prestressed concrete, calcium-aluminate cement, magnesia cement, and gypsum [8].

Limestone additions to Portland cement have significant effect upon its physical properties, as it is recognized that finely divided limestone incorporated in masonry cements have a beneficial influence on mortar plasticity and water retention [9,10]. White and coloured cements are employed for decorative purposes [11] and soil cement which is a densely compact mixture of portland cement, soil/aggregate and water is used primarily as a base material for pavements construction[12].

Silicon Dioxide

Amorphous silicon dioxide-intensive materials (Figure 1) include a wide variety of glasses such as fibre-glass, window glasses, Vycor glasses, borosilicate glass, which can be shaped by drawing, pressing, casting, and blowing. Colourless optical glasses, lumines-

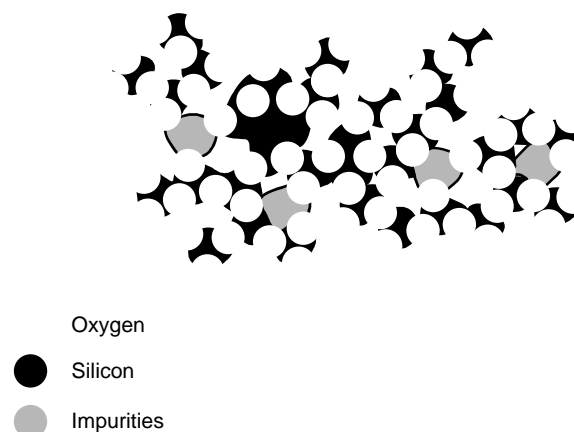


Figure 1. Structure of a typical silicon dioxide intensive glass [8].

cence and laser glasses are produced by using rare earth elements as components of these special glasses [13]. A scintillating glass with fluorescence properties uses PbO-Bi₂O₃ heavy-metal oxides based materials [14]. A new superionic glasses (solid electrolyte) based on silver iodide with organic monomer ions is reported [15], which exhibits high ionic conductivity comparable to that of oxides based superionic glasses, but 10 to 10000 times larger than of typical Li⁺ polymer electrolytes.

Polyanionic glasses including titania- and aluminosilicate glasses in the systems Na₂O-TiO₂-SiO₂, CaO-Al₂O₃-SiO₂, R₂O-(RO)-Al₂O₃-SiO₂-TiO₂ (R= Mg, Li, Na) are characterized by an unusual combination of properties and of their composition interdependencies. Examples of practical use of this model are for synthesis of glasses with certain combination of properties, namely with temperature coefficient of ultrasonic velocity near to zero [16]. The formation, structure and properties of alkaline earth, specially those of barium family, gallogermanate glasses, which are excellent candidates for infrared optical applications, are discussed [17].

Silicon dioxide also exists in crystalline forms that form the basis of many rocks, sands, and soils. Quartz is one of three crystalline forms which is the most abundant mineral of the Earth's crust.

Polymeric Carbon

Polymeric carbon exists in two common forms as diamonds and as graphite, the latter being thermodynamically more stable. Diamonds are almost entirely pure carbon, where each carbon is at the center of a tetrahedron composed of four other carbon atoms. It is the hardest known natural material. Diamonds are commercially synthesized for industrial use as cutting and shaping agents.

Polycrystalline diamond (PCD) efficiently is used in the machining of metal matrix composites [18] and PDC compact cutters increase penetration rates and cumulative footage through abrasion, impact, interface strength, thermal stability, and fatigue characteristics improvement [19]. Diamond saws are also used for cutting trees[20] and CVD diamond which can be prepared as loose grit, thin films deposited on a substrate or thick free-standing sheets is used in a wide range of applications such as grinding wheel polishing compound, coatings of twist drills, machine tools, wire dies

and nozzles [21,22].

Graphite occurs as sheets of hexagonally fused benzene rings (Figure 2). The bonds holding the fused benzene rings together are covalent bonds, while the bonding between the sheets results from the weak overlapping of π electron orbitals. Thus, many of the properties of graphite are anisotropic. The weak forces holding the graphite sheets together are responsible for its [slipperiness]. Graphite is commercially made from charcoal or coke.

Graphite as an active material is employed for negative electrode in lithium ion batteries with large capacity of lithium intercalation with low average voltage [23]. It is also used in secondary lithium ion battery applications with high rate of dischargeability [24]. Flexible graphite is found to be more effective than conductive-filled silicone materials for electronic applications such as electro-magnetic interference (EMI), gasketing, resistive heating, vibration damping, and heat dissipation. The flexibility and compliance of flexible graphite in addition to its electronic and thermal behaviour are effective for these applications [25,

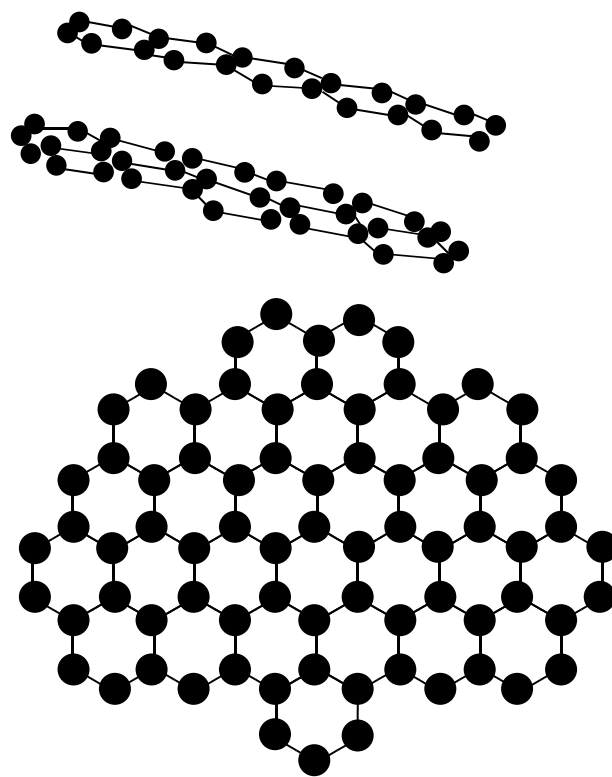


Figure 2. Structure of graphite emphasizing the layered (top) and sheet (bottom) nature of graphite[8].

26]. The expanding form of metallized graphite, as flakes of nickel-plated, and copper-plated were obtained by thermal treatment and characterized by electron microscopy [27], and it was found that the pore structure of expanded graphite makes it an excellent materials for biomedical applications. The expanded graphites were also obtained at different temperatures by electrochemical treatment with a peak pore diameter value from 500 to 4000 nm which makes it a good new biomedical material [28]. Graphite/metals bondings are developed for fusion reactor applications. layers of W and Mo on the graphite and some brazing agents were produced and used in the first wall components of fusion machines which are found to be more resistant to thermal shocks than simple junctions [29]. An advanced graphite composite structure is designed for high speed rotating machines which results in significant weight savings [30].

Poly(sulphur nitride)

This polymer contains planar chains of alternating sulphur and nitrogen atoms (Figure 3). It is the first reported non-metallic covalent polymer, with electronic conductivity properties comparable to that of metal, and is the first example of a polymeric superconductor. Poly(sulphur nitride) is a crystalline, fibrous malleable material. Its films have a lustrous golden colour which are very striking in appearance [8].

Poly (sulphur nitride) has found many interesting applications. It is used as conductive materials in the manufacturing of a plasma display panel [31] and in electrically conductive plastic light sources such as battery-powered flash lights and lanterns. Tail cap, battery housing or head assemblies for light sources are formed from electrically conductive polymers such as poly(sulphur nitride) (inherent/doped) [32]. A dry etching method is achieved while providing sidewall protection effects by using a sulphur nitride based compound which is composed mainly of poly (sulphur

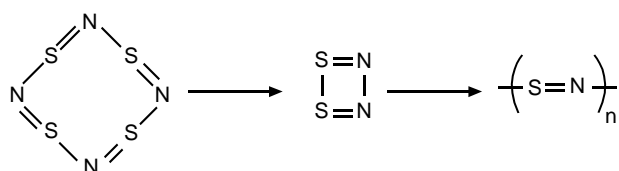


Figure 3. Representation of chain structure of alternating sulphur and nitrogen in poly(sulphur nitride) [2].

nitride), polythiazyl(SN)_x, which causes no particle pollution, because it can be removed through sublimation or decomposition [33]. A dry etching method is also achieved using a polythiazyl (SN)_x coating formed during the etching process which acts as an etching mass. This process emits no carbon to etching system [34].

Inorganic-organic Polymers

In this section we focus on inorganic polymers containing organic portions attached to inorganic elements in their backbone. The area of inorganic-organic polymers is very extensive, thus the more important classes are discussed here [35,36].

Polysilanes

The polysilanes are linear polymer based on chains of silicon atoms (Figure 4), which show unique properties resulting from easy delocalization of sigma electrons in the Si-Si bonds.

The interaction between adjacent silicon orbitals is relatively large which is also important, leading to energy splitting and as the number of silicon atoms increases the energy of the electronic transition decreases [37].

Polysilanes are useful as precursors to silicon carbide ceramics (Figure 5), as photoresists in microelectronics, as photoinitiators for radical reactions and as photoconductors.

The polysilanes are different from all other high polymers, in that they exhibit sigma-electron delocalization. This phenomenon leads to special physical

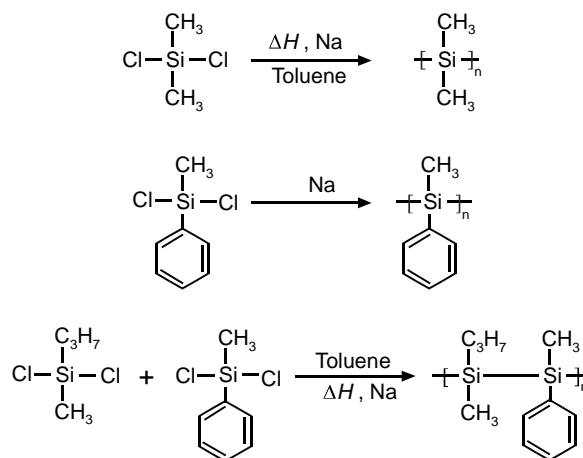


Figure 4. Polysilanes with chains of silicon atoms [7].

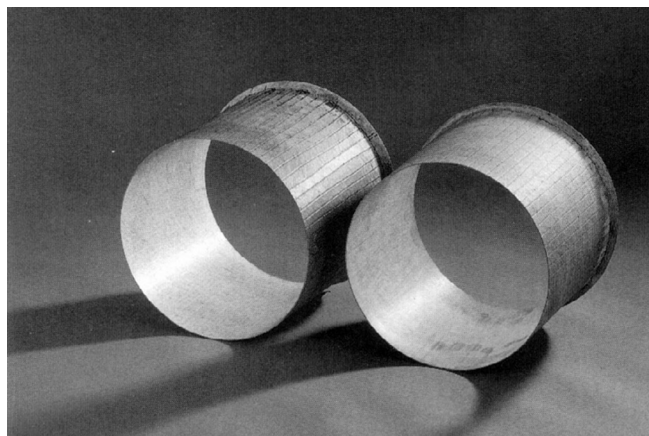


Figure 5. Ceramic matrix composite based exhaust nozzle [38].

properties: strong electronic absorption, conductivity, photoconductivity, photosensitivity [39]. These interesting properties provide materials for extremely important applications such as semiconductors, photoconductors and non-linear optical materials. The followings are some examples of polysilanes broad and diverse applications:

Poly(carbosilane) is obtained from poly(dimethylsilane) via thermolysis at 400-450°C, which after fractionation and melt-spun is converted to fibres.

The resulting fibres are oxidized at the surface in air at 350°C (cross-linking reaction occurs) to provide rigidity, then pyrolyzed at 1300°C (under nitrogen) to give crystalline β -SiC fibres with very high tensile strength (350 kg/mm²):

The spectroscopic, electronic and structural properties of a diaryl polysilane, poly[bis(p-n-butylphenyl)silane] (PBPS) were examined and improvements were observed in the electro-luminescence (EL) characteristics compared with light-emitting diodes (LEDs) based on conventional polysilanes [40]. Colloid formation of Au on polysilane film pre-exposed to UV-light process are reported [41,42] and its possible application in a new optical recording system for recordable (CD-R) and read-only-memory (ROM) is demonstrated. The intrinsic photosensitivity of a family of poly(alkyl)(aryl) silanes and poly(hydrido-phenyl) silane is investigated to develop photoimprinted waveguide devices [43]. Polysilanes' unique application as imaging materials in the printing technology or display devices, focusing on UV photodecomposition due to photochemical nature of Si-Si bonds, is demonstrated [44]. A system

composed of a photoresist overcoated with a thin layer of poly(cyclohexyl methylsilane) is studied for its unique material for certain lithographic applications, particularly those utilizing multilayer techniques [45].

Polysiloxanes

Polysiloxanes or silicones are the popular term used to describe a whole family of organo-silicon compounds based on a backbone or molecular chain of alternate silicon and oxygen atoms (Figure 6).

Depending on the length of the chain and the organic groups attached to silicon atoms, these compounds range all the way from water thin through heavy oil-like fluids to greases, gels, rubbers and solid resins [46-48]. Main structural features of these polymers are as follows:

- The strength of Si-O bonds (about 22 kcal/mol more than C-O bonds) gives the siloxane polymers considerable thermal stability, which is important for their use in high performance applications.

- The length of Si-O bond (1.64 Å in comparison to 1.53 Å for C-C bond) results in diminishing of interferences or intramolecular congestion. The small oxygen skeletal atoms are disencumbered by side groups, and

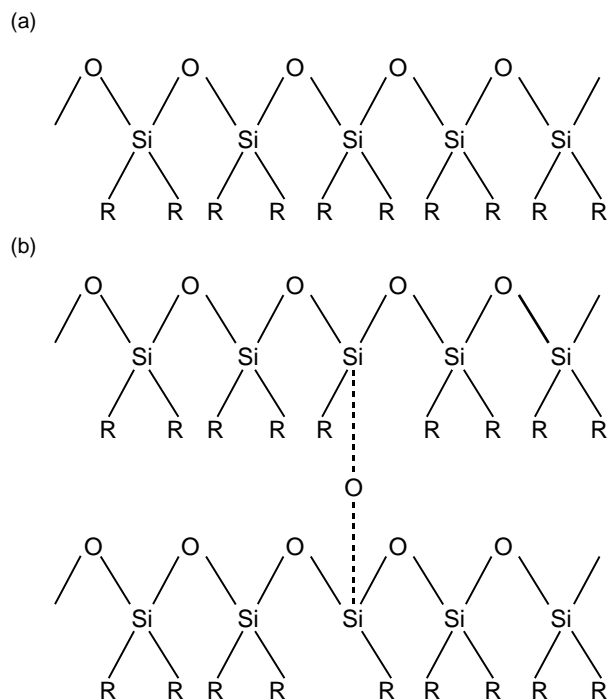


Figure 6. Polysiloxane's chain structure of alternating silicon and oxygen (a) one linear polymer, (b) two-linear polymers with cross-linking [49].

still have the divalency needed to continue a chain structure.

- The Si-O-Si bond angle ($\sim 143^\circ$ in comparison to $\sim 110^\circ$ for usual tetrahedral bonding) and torsional rotations can occur without incurring serious energy penalty.

These features make siloxane backbone the most flexible polymer.

The major route to produce polysiloxane is Rochow process in which ground silicon is reacted with chloromethane using a catalyst, such as copper. These compounds react with water forming dihydroxysilanes that in turn will be condensed, splitting out water, eventually forming polysiloxanes.

Siloxane polymers have numerous medical applications [50] such as: prostheses, artificial organs, facial reconstruction and tubing and catheters take advantage of the inertness, stability, and pliability of these polymers; artificial skin, contact lenses, and drug delivery systems utilize their high permeability as well. A wide range of medical-purpose items were manufactured using vulcanizates of unsaturated siloxane rubbers with silicon hydrides of various structures (Figure 7). These materials are biologically-compatible with a high complex of medical and engineering properties [51].

A composition of siloxane rubber and ultra-high molecular weight polyethylene is characterized for its rheology, vulcanizational and the physico-mechanical properties and was found that these materials combine elasticity and strength, and may be used as polymer inserts for new generation of endoprosthetic applications for hip joints [52]. A series of polyimide siloxane copolymers for blood compatibility were investigated using platelet adhesion/platelet activation analysis. Scanning electron microscopy (SEM) and light

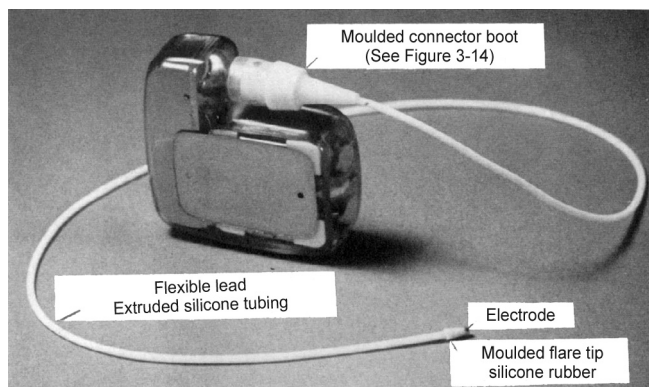


Figure 7. Siloxane artificial pacemakers[54].

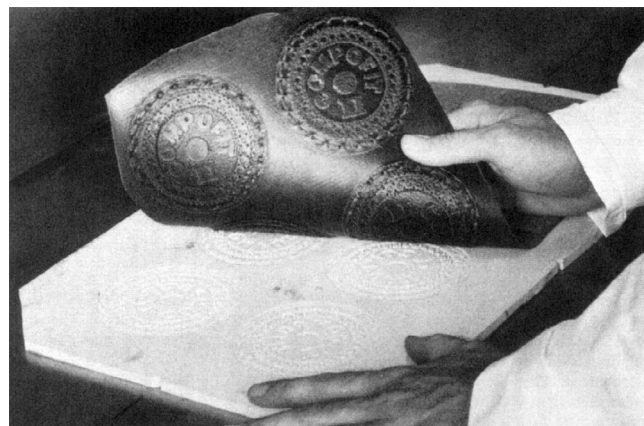


Figure 8. A polysiloxane rubber mould being used to make vinyl sheet with detailed surface[42].

microscopy with image analysis (LM-IA) results indicate a two dimensional change in the platelet response [53].

Typical non-medical applications include high-performance elastomers, membranes, electrical insulators, water repellents, antifoaming agents, mould-release agents, adhesives, protective coatings, release control agents for agricultural chemicals, encapsulation media, mould-making materials (Figure 8), layers in high-tech laminates, and hydraulic, heat transfer, and dielectric fluids[6]. Some examples of these materials are as follows:

Silicone rubber compounds which are high-consistency rubber products are developed for moulding high-voltage (HV) insulators, surge arresters and weather sheds are developed and designed to deliver outstanding tracking resistance over a wide voltage range [55]. Silicone rubber (RTV) coatings, which are designed to replace greasing and cleaning of insulators, increase the flashover voltage of contaminated insulator. These coatings have been used in China to prevent pollution flashover of insulator due to their long service life and convenience [56].

Polyphosphazenes

Polyphosphazenes or phosphonitrilic polymers are the most interesting and commercially promising inorganic polymers with backbone of alternating phosphorus and nitrogen atoms and with inorganic or organic side groups attached to each phosphorus (Figure 9).

Polycarbophosphazenes which contain phosphorus, nitrogen and carbon in the backbone and polythiophosphazenes with sulphur atoms in the skeleton in addition

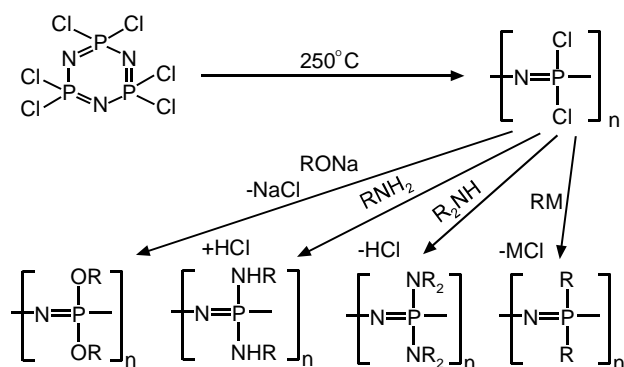


Figure 9. Polyphosphazene's backbone of alternating phosphorus and nitrogen atoms [48].

to the normal phosphorus and nitrogen atoms are examples of the new polymer systems that will be investigated in the coming years [6].

The most important feature of polyphosphazene chemistry is the method of synthesis that allows the side group to be varied over a very broad range. Different side groups generate different properties such that the characteristics may vary from those of elastomers to glasses, from water-soluble to hydrophobic polymers, from bioinert to bioactive materials, and from electrical insulators to conductors [57-59].

Applications based on structure-property correlations in technology or medicine are as follows:

- Advanced elastomers, design for a rechargeable lithium battery based on the conductivity of lithium triflate in solid poly[bis-(methoxyethoxyethoxy) phosphazene],
- Solid, bioinert polyphosphazenes such as poly[bis(trifluoroethoxy)phosphazene] are useful biomaterials at the present time,
- The extreme hydrophobicity of the surface minimizes the "foreign body" interactions that normally occur when non-living materials are implanted in contact with living systems, including blood.
- Solid polymers with hydrophilic or bioactive surfaces such as poly[bis(butylamino)-phosphazene] fabricated by solution casting for membrane experiments, with hydrophilic surface character are deliberately designed to stimulate tissue adhesion or infiltration or to generate a biochemical response.
- Hydrogels water soluble, bioactive polymers such as lightly cross-linked poly[bis-(methoxyethoxyethoxy)-

phosphazene] absorbs water to form a hydrogel which is a good candidate for use as intracular lenses, soft tissue prostheses or as hydrophilic coatings for biomedical devices.

Some examples of biomedical and advanced applications are the followings:

Solid polymer electrolytes have been extensively investigated for their potential applications in high-energy density batteries. Poly [bis(amino)-phosphazene], and lithium perchlorate, which is of the phosphazene elastomer in this group, has received considerable attention for its good conductivity and good mechanical stability at room temperature[60]. Poly(organo-phosphazenes) are linked to biactive molecules through Schiff base linkages and are used as chemotherapeutic models[61].

Polyphosphazenes are also used as carrier species for biologically active agents by linking steroidal residues to polyphosphazene chain via the sodium salt of the steroidal dihydroxy functions [62]. Poly[(amino acid alkyl ester) phosphazenes] have been synthesized by the interaction of poly(dichlorophosphazene) with amino acid esters and it was anticipated that the polymers could be biocompatible as solids or biodegradable to the harmless hydrolysis products, amino acid, phosphoric acid, and ammonia, and they could possibly be used as plasma extenders or carrier molecules for chemotherapeutic drugs [63].

An approach to the preparation of membranes and hydrogels that may be of interest as biomedical materials are discussed. The amphiphilic polyphosphazenes as membrane materials have been synthesized by sequential replacement of chlorine in $[NPCI_2]_n$ by trifluoroethoxide or phenoxide and methylamine [64].

Poly(organo-phosphazenes) with alkyl ether alkoxy side groups attached to the phosphorus atoms of the skeleton have been synthesized. Some mixed substituent polymers have been prepared which are of interest as membranes and biomedical materials [65]. Bioerodible polymers have been extensively used for drug delivery systems. Polyphosphazene's membrane or microcapsules bearing amino acid side groups are used to entrap antibacterial or anti-inflammatory drugs, useful in periodontal tissue regeneration which release in vitro and in vivo at a rate that ensure therapeutic concentrations in the surrounding tissue [66]. Poly bis-(carboxylatophenoxy)-phosphazene) when it is treated

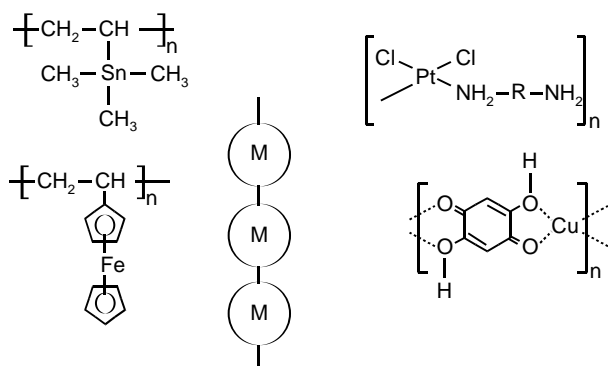


Figure 10. Different structures found in organometallic polymers [7].

with salts of divalent cations forms hydrogels which might entrap proteins or 30 mm polystyrene beads and allow their release in a controlled manner. The ability to tailor this polymer system, combined with mild conditions of encapsulation, makes these synthetic hydrogels potentially suitable as a drug delivery system e.g., for parenteral and oral vaccine delivery [67].

Organometallic Polymers

Organometallic polymers are made of over 40 elements including main group of metals (Si or Ge), transition metals or rare earth elements in addition to the 10 elements (C, H, N, O, B, P, halides) which is found in organic polymers (Figure 10).

The variations of organometallic polymers seem endless. Organometallic polymers are new materials which combine the low density and structural variations and functional group varieties of organic materials with electrical conductivity and the high temperature stability features of inorganic compounds[68].

Metals may be present as in polymerization products of vinylcyclopentadienyl manganese tricarbonyl (Figure 11a), π -(benzylacrylate) chromium tricarbonyl

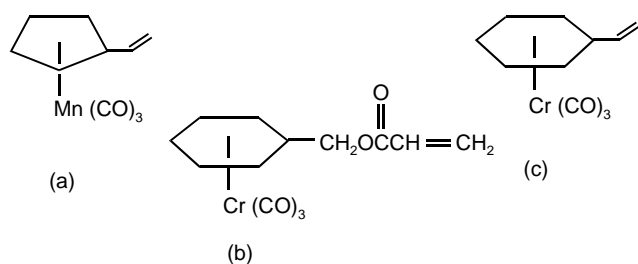


Figure 11. Typical organometallic polymers with metals as pendent groups[69].

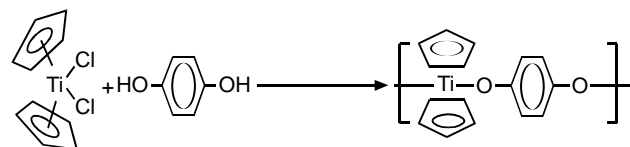


Figure 12. Structure of titanium polyether with metal in the main chain [70].

(Figure 11b) and styrene tricarbonyl chromium (Figure 11c) [69].

Metals may be present in the main chain as found in titanium polyether, a product of interfacial polycondensation (Figure 12).

The structure of some other examples of organometallic polymers are shown in Figure 10. A variety of organometallic polymers have been synthesized. Some more important examples are as follows:

Coordination polymers are polymers with covalent bonds in the repeating unit. Considerable work has been done in this area. Among variety of applications of coordination polymers are thermally stable and conducting or semiconducting materials, and water based coatings which are environmentally friendly materials in comparison with solvent based coatings.

There are two kinds of inorganic polymers: In one type the coordination bonds are an integral part of the polymer backbone. In the second type, which is best described as polymeric chelates, the chelating metal is only linked to the overall polymer structure and breaking the coordination bonds would not rupture the polymer backbone.

The reaction product of tetracyanoethylene with copper is a polymer having a phthalocyanine type sheet-like structure (Figure 13).

An example of the polymeric chelate type of polymer is obtained from 5,5'-methylene bis(salicylaldehyde)

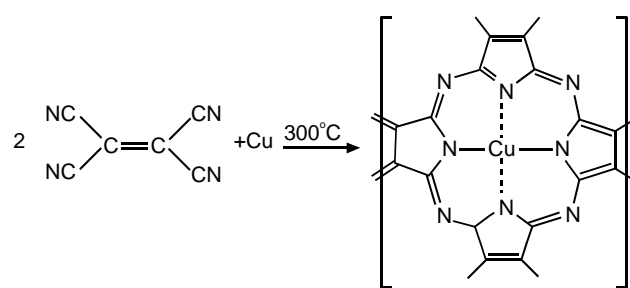


Figure 13. Phthalocyanine-type coordination polymer [3].

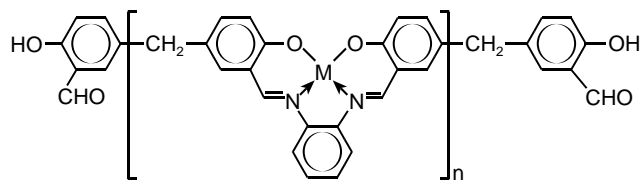


Figure 14. Chelate-type coordination polymer [3].

hyde) and *o*-phenylenediamine complexed with divalent metal (Figure 14).

This type of polymeric chelates has been prepared from a variety of transition metals [3,68]. Organometallic condensation polymers as dyes or pigments resist bleeding, blooming or plate-out.

An example is the reaction product of fluorescent or sulphophthalein dyes with dicyclopentadienyldichlorotitanium or organostannanes (Figure 15). Such polymers adhere to surface so much better than the monomeric analogs[70].

In addition to these dyes, a series of high quality absorbers-dyes in polymeric host material using the reverse saturable dye chloroaluminium phthalocyanine (CAP) with different host materials is developed and it is investigated in terms of solubility, integrity of the dye molecules in the polymer host, hardness of the resulting polymer, ease of polishing to the production of a good optical finish, induced stress, and non-linear absorption performance [71].

Polymers containing metalloporphyrin have been studied due to their unique electronic structures and optical properties. Monomers and polymers with the structures shown in Figure 16 have been successfully synthesized [72] and it was observed that the electronic, optical and magnetic properties of these polymers

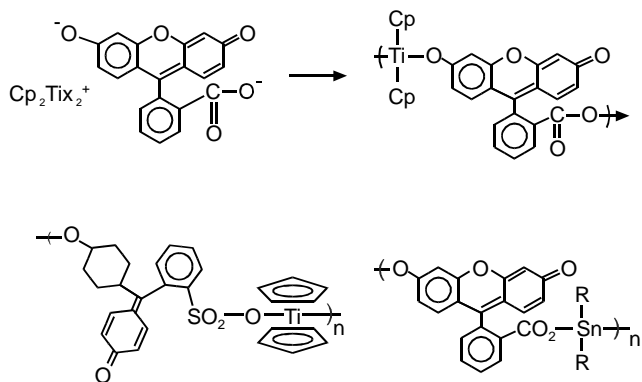


Figure 15. Structure of organometallic dyes [70].

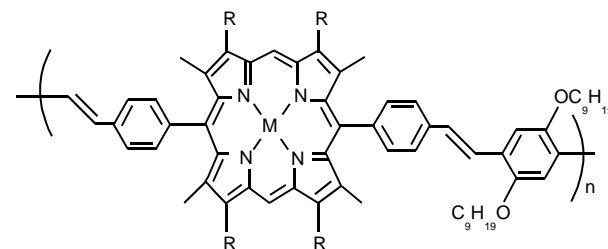
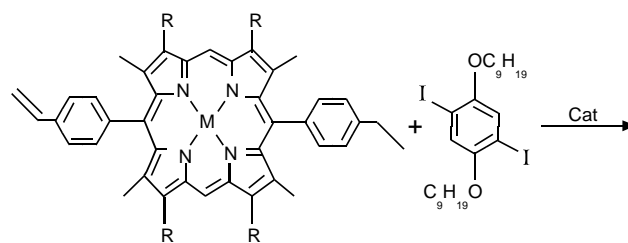


Figure 16. Metalloporphyrin polymers with different substituents [72].

can be turned by changing different substituents and by incorporating various metal ions into the porphyrin units.

A series of polymers (Figure 17) having (η^5 -cyclopentadienyl) cobaltacyclopentadiene moieties in the main chain and flexible aliphatic, electron-donating, or electron-withdrawing groups in the main chain or (and) in the side chain have been synthesized and characterized [73]. These kinds of polymers have become of interest owing to their physical properties

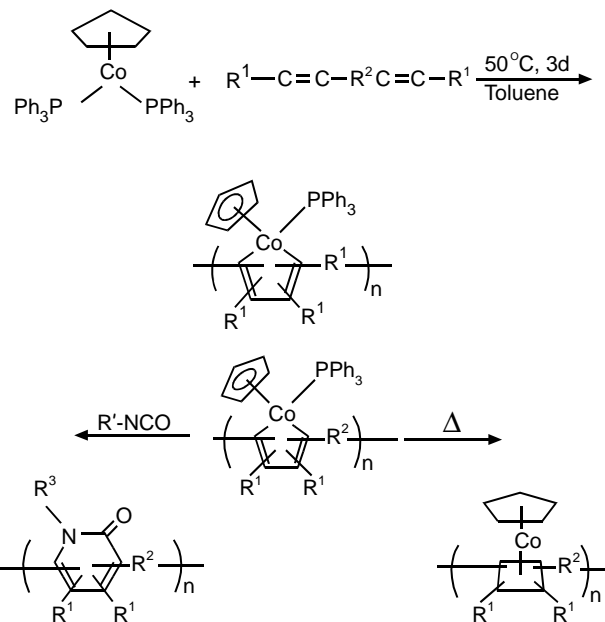


Figure 17. Organometallic polymers having cobaltacyclopentadiene in the main chain [73].

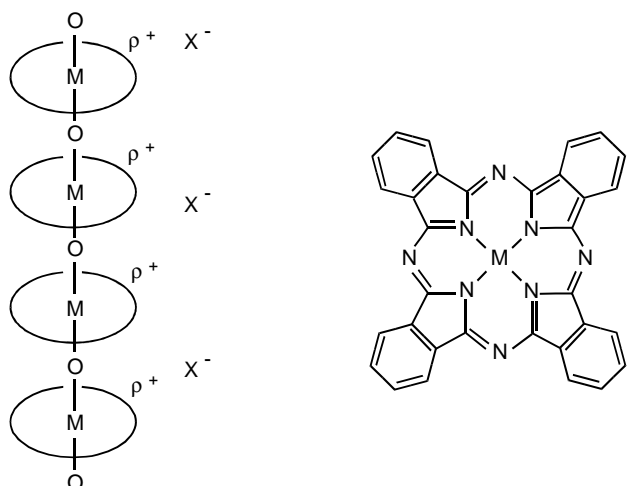


Figure 18. Representation of a molecular metal [79].

and reactivities based on the carbon-metal bonds.

The cofacially joined phthalocyanine polymer, $\{[\text{Si}(\text{Pc})\text{O}]_n\text{x}_y\}$ represents a molecular metal where band filling is widely tunable (Figure 18). This is an example for polymers which their electrical, optical and magnetic properties are a delicate function of complex architectural and structural interactions [74].

A series of organometallic poly-yne polymers with general formula shown in Figure 19 have been prepared. They are soluble in most organic solvents and form thin films that are suitable for photophysical measurements [75].

Polymeric copper phthalocyanine containing peripheral carboxyl groups (Figure 20) is converted into polyimides through polycondensation with aromatic diamine to obtain a processable material for potential application in the fabrication of electronic devices [76].

Several organometallic main-chain, side-chain and guest-host materials based on polymeric ferrocene derivatives (Figure 21) have been prepared and were

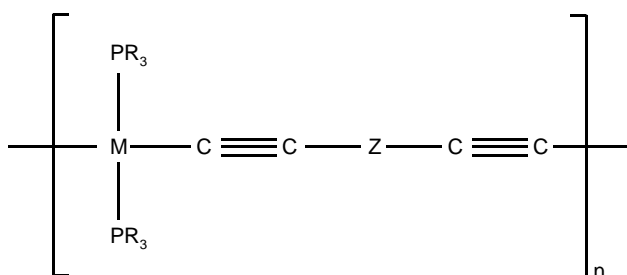


Figure 19. The general formula for the rigid-rod poly-yne polymers [75].

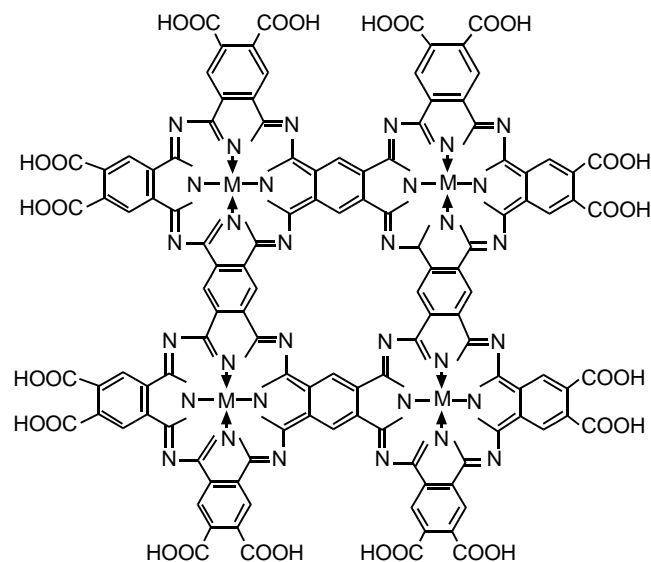


Figure 20. Structure of cyclic oligomeric phthalocyanine; M: Cu [76].

investigated for their non-linear optical (NLO) properties. Studies are continuing involving the synthesis and evaluation of organometallic NLO polymers and supermacromolecular organometallic assemblies [77].

The cyclometallation reaction is employed to obtain organometallic acrylic monomers suitable to afford side chain organometallic polymers containing

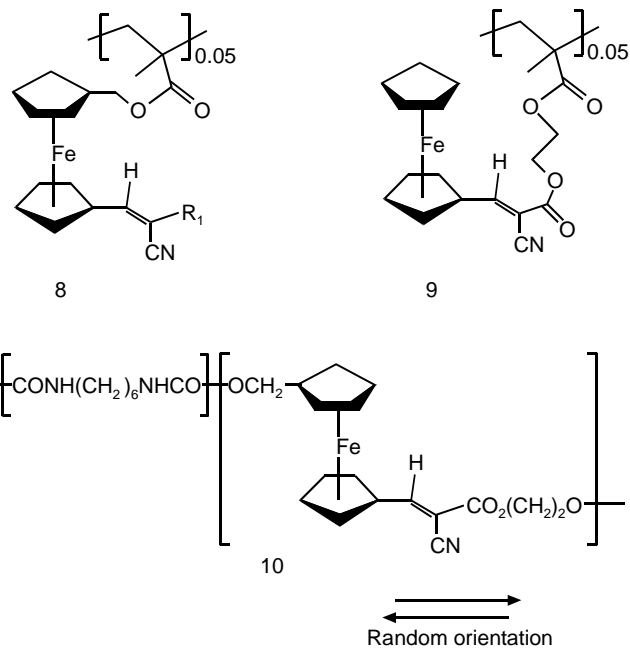


Figure 21. Organometallic polymers and copolymers with NLO properties [77].

cyclopalladated fragments as pendants which are potentially second order NLO active materials [78].

A large number of organometallic polymers have been utilized as catalytic systems with the advantages of both homogeneous catalysis and the ease of catalyst recovery of heterogeneous catalysis.

The polymer bound Ni(0) analog of $(PPh_3)_2NiBr_2$ and $NaBH_4$ has been used for selective dimerization of butadiene in high yield [79]. A series of the polymer anchored catalysts of nickel, rhodium and ruthenium were used for catalytic reactions such as cyclooligomerizations, hydrogenations and hydroformylations and the effect of catalyst anchoring on rates was discussed [80,81].

The arenechromium carbonyl complexes were anchored to commercial resins as macromolecular support leading eventually to polymer-attached catalysts [82]. Various π -conjugated polymers with well-defined structure are prepared via organometallic polycondensation reactions (Figure 22). These polymers are useful materials for electrical and optical devices [83].

Hybrid Organic-inorganic Networks

Hybrid organic-inorganic networks, prepared via sol-gel process, are multi-functional materials offering a wide range of interesting properties. Since there are countless different combinations of the organic and

inorganic moieties, a large number of applications are possible by incorporation of inorganic building blocks such as silica networks, porous materials and metals [84-86].

Sol-gel process allows to adjust the degree of interpenetration of organic and inorganic components from sub-micronic range to the nano scale level, providing an easy method to synthesize different classes of hybrid materials [87-89].

Sol-gel processes based on inorganic polymerization reactions are a way to make dispersed materials through the growth of metal oxo-polymers in a solvent. Metal oxo-polymers can be obtained through hydrolysis and condensation of molecular precursors such as metal alkoxides $M(OR)_z$. Sol-gel/epoxy resin hybrid coatings (Figure 23) display enhanced mechanical strength such as hardness and abrasion resistance in addition to excellent adhesion on metal surfaces [90-92].

Epoxy polysiloxane hybrid protective coatings, which are prepared by chemical modification of inorganic polysiloxane backbone with functional organic aliphatic epoxy groups, achieved advances such as significant improved weathering and outstanding corrosion resistance, excellent flame resistant and reduced effect on health, safety and environment. The epoxy polysiloxane is easy to apply by spray, brush or roller and this hybrid coating is compatible with a wide range of primers and intermediate coatings [93].

Siloxane-anchored organic films have been obtained on stainless steel surfaces. The surface of the material was initially treated with tetraalkylorthosilicate to obtain a thin layer of SiO_2 . This layer anchors the subsequent attachment of octadecyltrimethoxysilane. The films created in this fashion can contain a

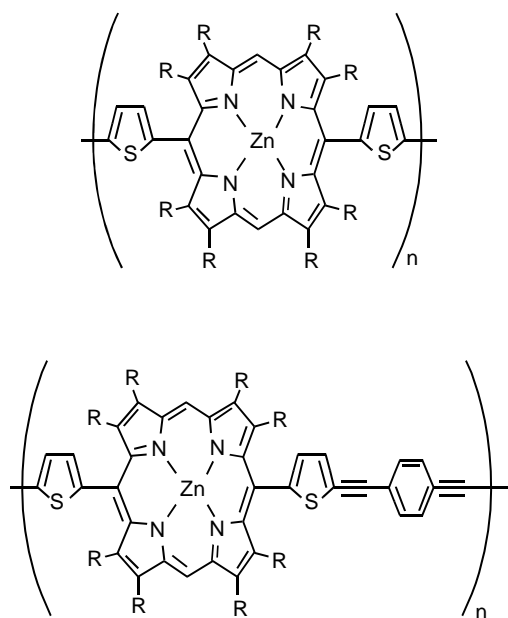


Figure 22. π -Conjugated polymers prepared via organometallic condensation reactions [83].

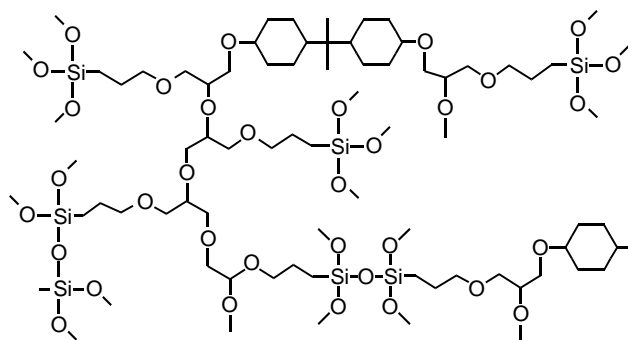


Figure 23. Structure of a sol-gel/epoxy resin hybrid network [86].

variety of functional end groups at the alkyl chains and can thus impart a range of chemical and physical properties to the coated surface [94].

An amino functionalized alkoxy silane was used as condensation catalyst and the nanocomposite material such as silica or alumina sols was thermally cured after flow or spray coating on pretreated polycarbonate substrates. The coatings used for transparent plastic glazing displayed excellent adhesion which was shown by cross cut and tape test [95].

To evaluate the relative performance of clear coatings such as the acrylic varnish, a hybrid sol-gel coating, and some hard coatings, the wear resistance of the three types of protective layers was investigated with linear scratch and abrasion tests. Great improvements were achieved in wear resistance of decoration brass profiles by applying the hybrid sol-gel clear coatings [96].

Sol-gel derived protective coatings based on inorganic-organic copolymers for use in outdoor bronze substrates was developed and adjusted to optimize adhesion and resistance against weathering. The main components of the starting materials were 3-glycidoxypropyltrimethoxysilane and γ -methacryloxypropyl trimethoxysilane [97].

Hybrid SiO_2 sol-gel coatings on metals for clinical applications have been prepared and evaluated for electrochemical behaviour and the results of preliminary in vivo tests indicate that by combining an inner SiO_2 hybrid film acting as barrier against corrosion with an outer coating containing bioactive glass particle, a pronounced improvement in the electrochemical behaviour is observed [98].

For improvement of resistance to oxidation and wet corrosion sol-gel driven films on metals have been studied. It was found that the deposition technique is an important aspect of the application of sol-gel method for coating metallic objects [97].

Novel inorganic-organic composites (ormocers) have been synthesized using sol-gel process. In this study stable sols are produced by controlled hydrolysis and condensation of an epoxy modified alkoxide, propyl modified alkoxide and an aluminium alkoxide in the presence of fluoride ions and applied by spray-, spin- and dip-coating on metals (Al, Zn, Mg) and cured. The obtained transparent coatings show good adhesion, corrosion and wear resistance [100].

Tetraethoxysilane and polyvinyl alcohol have been

used as the inorganic and organic components to prepare silica-based coating materials by sol-gel method. For improvement of the adhesion between the polymer base film and the coated layer, a silane-coupling agent of vinyltriethoxysilane has been also used. The polypropylene films coated with the hybrid materials have been tested for their morphology, optical transparency and oxygen permeability and promising results have been obtained [101].

Protective coatings based on polyesters and tetraethoxysilane (TEOS) are synthesized for prefinish construction steel and aluminium. The polyester-TEOS system shows an increase in hardness for improved mechanical properties and flexibility for enduring deformation of the metal substrate after coating [102].

Transparent, translucent and opaque hybrid coatings for crystal glassware have been developed and produced recently. Sol-gel type hybrid coatings exhibit several advantages in comparison with conventional organic systems: high abrasion resistance, good adhesion and sufficient stability in dish-washing procedures.

The synthesis and properties of these coating materials and the industrial process are reviewed [103].

Hydrophobic hybrid coating based on 3-trimethoxysilylpropyl methacrylate, tetramethylorthosilicate and methyl methacrylate have been developed and applied on glass objects. Coated glasses display higher strength (more than 50%) than uncoated glass [104].

Summary

There is a wide variety of inorganic polymers. The potential uses are many and include the broad areas of biological, electrical, analytical, catalytic, building, and photo applications.

The bond strength for many combinations are higher than that of many carbon-intensive organic polymers leading to products with superior strength and thermal stabilities.

The number and variety of organometallic polymers and potential applications for these materials are great.

Hybrid organic-inorganic networks offer a new area of material science that has extraordinary implications for developing novel materials that exhibit a diverse range of multi-functional properties.

REFERENCES

1. Kirk-Othmer, *Encyclopedia of Chemical Technology*, John Wiley, 398-411(1978).
2. Allcock H.R., Developments at the interface of inorganic, organic, and polymer chemistry, *C&EN*, March 18, 22-36(1985).
3. Stevens M.P., *Polymer Chemistry: An Introduction*, 2nd ed., Oxford University, 487-508 (1990).
4. Seymour R.B. and Carraher C.E., *Polymer Chemistry an Introduction*, 3rd ed., Marcel & Dekker, 381-401(1992).
5. Rahimi A., Inorganic polymers, polysiloxanes: (1) synthesis and purification of silicon, *Proc. of the Int. Sem. on Polym. Sci. and Techno.*, 3-5 November, 65-8 (1997).
6. Mark J.E., Allcock H.R., and West R., *Inorganic Polymers*, Prentice-Hall, 141-185(1992).
7. Carraher C., Inorganic Polymers in *Ullmans's Encyclopedia of Industrial Chemistry*, A14, 5th ed. VCH, 241-262(1989).
8. Seymour R.B. and Carraher C.E., *Polymer Chemistry, An Introduction*, 3rd ed., Marcel & Dekker, 403-429 (1992).
9. Ingram K.D. and Daugherty K.E., Review of limestone additions to Portland cement and concrete, *First Int. Conf. on Blend. Cem.*, 165-170 (1991).
10. Kelham S., Portland limestone cements, *Concrete* (London), **32**,5,30-31 (1998).
11. Bensted, J., White and coloured portland cements, *World Cement*, **24**, 13-14 and 17-19 (1993).
12. Arman A., Barclay R.T., Casias T.J., Crocker D.A., Adaska W.S., De Graffenreid R.L., Hess J.R., Kuhlman R.H., Mueller P.E., Roof H.C., Super D.W., Winford J.M., and Wissa Anwar E.Z., State-of-the-art report on soil cement, *ACI Mat. J. (Am. Conc. Inst.)*, **87**, 395-417 (1990).
13. Laczka M. and Stoch L., Rare earth elements as components of special glasses, *J. Less-Com. Met.*, **166**, 163-171 (1990).
14. Lu An-Xian and Liu Shu-Jiang, Preparation and properties of a new scintillating glass, *J. Cent. South U. of Technol. (English ed.)*, **9**, 150-153 (2002).
15. Kawamura J. and Hiyama S., New superionic glasses based on silver iodide with organic monomer ions, *Solid St. Ion.*, **53-56**, Part 2, 1227-1231 (1992).
16. Khodakovskaya R. Ya., Polyanionic glasses, the features of properties and structure, *J. Non-Crys. Sol.*, **123**, 275-282 (1990).
17. Jewell J.M., Alkaline earth gallogermanate glasses, *Key Eng. Mat.*, **94-95**, 317-344(1994).
18. Cook M.W., Diamond machining of MMC engineering components, *Ind. Dia. Rev.*, **58**, 15-18 (1998).
19. Mensa-Wilmot G., New PDC cutters improve drilling efficiency, *Oil and Gas J.*, **95**, 64-67 (1997).
20. Jennings M., Cutting trees with diamond saws, *Ind. Dia. Rev.*, **50**, 165-167 (1990).
21. Anthony T.R., Some nonelectronic application of CVD diamond, *Carbon*, **28**, 6, 807 (1990).
22. Sakamoto Y., Kiyama N., and Takaya M., Preparation of fine grain diamond coated WC-Co tools and their cutting performance, *Semitsu Kogaku Kaishi/J. Jap. Soc. for Prec. Eng.*, **63**, 525-529 (1997).
23. Simon B., Flandrois S., Guerin K., Fevrier-Bouvier A., Teulat I., and Biensan P., On the choice of graphite for lithium ion batteries, *J. Power Sou.*, **81**, 312-316 (1999).
24. Liu Z., Yu A., Lee J.Y., Modifications of synthetic graphite for secondary lithium-ion battery applications, *J. Power Sou.*, **81**, 187-191 (1999).
25. Chung D.D.L., Luo X., Chugh R.B., Brain C., Hoi Y.M., Electronic applications of flexible graphite, *J. Elec. Mat.*, **31**, 535-544 (2002).
26. Chung D.D.L., Flexible graphite for gasketing, adsorption, electromagnetic interference shielding, vibration damping, electrochemical applications, and stress sensing, *J. Mat. Eng. and Perform.*, **9**, 161-163 (2000).
27. Ogenko U.M., Fesenko A.V., Zhakarova E.V. and Tsurul M.F., Synthesis, structure and composition of an expanding form of metallized graphite, *Reac. Kin. Cat. Let.*, **50**, 269-272 (1993).
28. Shen W., Wen S., Cao N., Zheng L., Zhou W., Liu Y., and Gu J., Expanded graphite- a new kind of biomedical material, *Carbon*, **37**, 356-358 (1999).
29. Brossa F., Franconi E. and Schiller P., Development of graphite/metals bondings for fusion reactor applications, *J. Nuc. Mat.*, **191-94**, Part A, 469-472 (1992).
30. Rosenwasser S., Nagy G., and Mehle G., and Design, fabrication and characterization of an advanced graphite comosite structure for high speed rotating machines, *IEEE Trans. Mag.*, **35**, Part 1,

- 307-311 (1999).
31. Kasahara S., Method of manufacturing a plasma display panel, *U.S. Patent*, 5,860,843 (1999).
32. Schaller D.R. and Wirt M.W., Electrically conductive plastic light source, *U.S. Patent*, 5,685,632 (1997).
33. Kadomura S., Dry etching method using (SN).sub.x protective layer, *U.S. Patent*, 5,314,576 (1994).
34. Kadomura S., Dry etching method utilizing (SN).sub.x polymer mask, *U.S. Patent*, 5,326,431 (1994).
35. Stelens M.P., *Polymer Chemistry: An Introduction*, Oxford University, 425-446 (1990).
36. Manners I., Inorganic and organometallic polymers, *Ann. Rep. Prog. Chem., Sect. A*, 103-118(1993).
37. Zeldin M., Wynne K.J., and Allcock H.R., *Inorganomet. Polym.*, ACS Symp. Series, 360 ACS, 6-19 (1989).
38. Auner N. and Weis J., Organosilicon chemistry from molecules to materials, VCH, 317 (1994).
39. Matyjaszewski K., Cypryk M., Frey H., Hrkach J., Kim H.K., Moeller M., Ruehi K., and White M., Synthesis and characterization of polysilanes, *J. Macro. Sci. Chem.*, **A28**, 1151-1176 (1991).
40. Suzuki H., Hoshino S., Furukawa K., Ebata K., Yuan Chien-Hua, and Bleyl I., Polysilane light-emitting diodes, *Polym. Adv. Technol.*, **11**, 460-467 (2000).
41. Nagayama N., Maeda T., Sakurai Y., and Yokoyama M., Au colloid formation in polysilane/au layered film and its application as novel optical recording media, *Mole. Crys. and Liq. Crys. Sci. and Technol., Section A: Mole. Crystals and Liq. Crys.*, **316**, 411-414 (1998).
42. Nagayama N., Itagaki K., and Yokoyama M., Thermally induced colloid formation of au on a polysilane film pre-exposed to UV-light and its application to novel optical recording media, *Adv. Mat.*, **9**, 71-75 (1997).
43. Simmons-Potter K., Jamison G.M., Potter Jr. B.G., Thomes Jr. W.J., and Phifer C.C., Polysilane-based thin films with high photosensitivity, *Mat. Res. Soc. Symp. Proc.*, **726**, 401-407 (2002).
44. Yokoyama M., Polysilanes as imaging materials, *Proc. of the IS & T's Int. Con. on Adv. in Non-Impact Print. Technol.*, 507-511 (1995).
45. Miller R.D., Polysilanes. radiation sensitive materials for microlithography, *Polym. Pre., Div. Polym. Chem., Ame. Chem. Soc.*, **31**, 252-253 (1990).
46. Rahimi A., Inorganic Polymers, *Proc. of the 6th Iran. Int. Sem. on Polym. Sci. and Technol.*, (ISPST 2003), 75, Tehran, Iran, 12-15 (2003).
47. Rahimi A. and Shokrolahi P., Application of inorganic polymeric materials, I, polysiloxanes, *Int. J. Inorg. Mat.*, 843-847 (2001).
48. Rahimi A., Silicones, *Iran. Polym. Soc. News Letter (Persian)*, **9**, 8-11 (2001).
49. Faust C.B., Silicone rubbers, *Education in Chemistry*, **27**, 101-104 (1990).
50. Schubert U. and Hüssing N., *Synthesis of Inorganic Materials*, Wiley-VCH, 239-266 (2000).
51. Lanian S.Y., Gorshkov A.V., and Khazen L.Z., Medical-purpose elastic materials based on siloxane rubbers and items made from them, *Med. Prog. Through Technol.*, **18**, 95-100 (1992).
52. Nikolaev O.O., Urhanov V.B., Britov V.P., Babaev A.D., Bogdanov V.V., and Mirzadeh H., A thermoplastic rubber composition for medical purposes, *Iran. Polym. J.*, **10**, 9-14 (2001).
53. Sawyer A., Analysis of platelet responses to polyimide-siloxane polymers, *Trans. Ann. Meet. Soc. for Biomat. in Conjunction with the Int. Biomat. Symp.*, **14**, 42 (1991).
54. Lynch W., *Handbook of Silicone Rubber Fabrication*, Van Nostrand Reinhold, 221 (1978).
55. Anon, Silicone molding compounds for HV applications, *Wire*, **53**, 30-31 (2003).
56. Zhicheng G. and Zhidong J., The developments of room temperature vulcanized silicone rubber coating and its application in china, *Proc. of the IEEE Power Eng. Soc. Trans. and Dis. Conf.*, **3**, Asia Pacific, 2203-2206(2002).
57. Singler R.E., Schneider N.S., and Hagnauer G.L., Polyphosphazenes: synthesis-properties-applications, *Polym. Engi. Sci.*, **15**, 321-338 (1975).
58. Allen G., Lewis C.J., and Todd S.M., Polyphosphazenes: Part 1-Synthesis, *Polymer*, **11**, 31-43 (1970).
59. Allcock H.R., Connolly M.S., John T. Sisko, and Al-Shali S., Effects of organic side group structures on the properties of poly-(organophosphazenes), *Macromolecules*, **21**, 323-334 (1987).
60. Chen-Yang Y.W., Hwang J.J., and Chang F.H., Polyphosphazene electrolytes. 1. Preparation and conductivities of new polymer electrolytes based on

- poly[bis(amino)phosphazene] and lithium perchlorate, *Macromolecules*, **30**, 3825-3831 (1997).
61. Allcock H.R. and Austin P.E., Schiff base coupling of cyclic and high-polymeric phosphazenes to aldehydes and amines: chemotherapeutic models, *Macromolecules*, **14**, 1616-1622 (1981).
 62. Allcock H.R. and Fuller T.J., Phosphazene high polymers with steroidal side groups, *Macromolecules*, **13**, 1338-1345 (1980).
 63. Allcock H.R., Fuller T.J., Mack D.P., Matsumura K., and Smeltz K.M., Synthesis of poly[(amino acid alkyl ester) phosphazenes], *Macromolecules*, **10**, 824-830 (1977).
 64. Allcock H.R., Gebura M., Kwon S. and Neenan T.X., Amphiphilic polyphosphazenes as membrane materials: influence of side group on radiation cross-linking, *Biomaterials*, **9**, 500-508 (1988).
 65. Allcock H.R., Austin P.E., Neenan T.X., Sisko J.T., Blonsky P.M., and Shriver D.F., Polyphosphazenes with etheric side groups: prospective biomedical and solid electrolyte polymers, *Macromolecules*, **19**, 1508-1512 (1986).
 66. Veronese F.M., Marsilio F., Lora S., Caliceti P., Passi P., and Orsolini P., Polyphosphazene membranes and microspheres in periodontal diseases and implant surgery, *Biomaterials*, **20**, 91-98 (1999).
 67. Andrianov A.K., Cohen S., Visscher K.B., Payne L.G., Allcock H.R., and Langer R., Controlled release using ionotropic polyphosphazene hydrogels, *J. Con. Rel.*, **27**, 69-77 (1993).
 68. Rahimi, A., Properties and applications of polymers (in Persian) under review processes to be published by Iran Polym. and Petrochemical Institute (2003).
 69. Pittman C.U. Jr., Marlin G.V., and Rounsefell T.D., Organometallic polymers. XXIII. Free-radical-initiated, solution copolymerization of cyclopentadienyl-manganese tricarbonyl, *Macromolecules*, **6**, 1-8 (1973).
 70. Pittman C.U. Jr., Carraher C.E. Jr., Sheaus J.E., Timken M.D., and Zeldin M., *Inorganic and Metal-Containing Polymers. an Overview*, J.E., Sheats, Carraher C.E. Jr., Pittman C.U. Jr., Zeldin X., and Currell B., Eds., Plenum, New York, 1-27 (1990).
 71. Kolinsky P.V., Hall S.R., Venner M.R.W., Croxall D.F., Welford K., and Swatton S., Development of solid state non-linear absorbers-dyes in polymer hosts, *Mat. Res. Soc. Symp. Proc.*, **374**, Materials for Optical Limiting, 195-199 (1995).
 72. Bao Z., Chen Y., and Yu L., New metalloporphyrine containing polymers from the heck coupling reaction, *Macromolecules*, **27**, 4629-4631 (1994).
 73. Lee J.C., Nishio A., Tomita I., and Endo T., Synthesis of organometallic polymers containing cobalt-cyclopentadiene moieties in the main chain. synthesis of organocobalt polymers from various diynes, *Macromolecules*, **30**, 5205-5212(1997).
 74. Gaudiello J.G., Kellogg G.E., Tetrick S.M., and Marks T.J., Molecular metals with widely tunable band filling structure/stoichiometry/counterion relationships in the electrochemistry of a cofacially joined polymeric phthalocyanine metal, *J. Am. Chem. Soc.*, 5259-5271 (1989).
 75. Raithby P.R., Rigid-Rod organometallic polymers, *Polym. Prep.*, **41**, 435 (2000).
 76. Venkatachalam S. and Prabhakaran P.V., Electrically conducting polymer based on polymeric phthalocyanine containing polyamide units, *Eur. Polym. J.*, **29**, 711-714(1993).
 77. Wright M.E. and Toplikar E.G., Organometallic nonlinear optical polymers-4-organometallic main-chain, side-chain, and guest-host polymers: A study of their orientation and relaxation using second harmonic generation, *Macromolecules*, **27**, 3016-3022 (1994).
 78. Caruso U., Matola A.D., Panunzi B., Roviello Z., and Sirigu A., Side chain organometallic polymers containing cyclopalladated potentially second order nonlinear optical active fragments as pendants, *Polymer*, **42**, 3973-3980 (2001).
 79. Pittman C.U.Jr. and Smith Larry R., Selective, high-yield, linear dimerization of 1,3-butadiene catalyzed by $(PPh_3)_2 NiBr_2$ and $NaBH_4$ and its polymer-bound Ni(O) analog, *J. Amer. Chem. Soc.*, **97**, 341-349 (1975).
 80. Pittman C.U, Jr., and Smith Larry R., Sequential multistep reactions catalyzed by polymer-anchored homogeneous catalysts, *J. Amer. Chem. Soc.*, **97**, 1749-1754 (1975).
 81. Pittman C.U., Jr., Smith L.R., and Hanes Ronnie M., Catalytic reactions using polymer-bound vs. homogeneous complexes of nickel, rhodium, and ruthenium, *J. Amer. Chem. Soc.*, **97**, 1742-1748 (1975).
 82. Tatarsky D., Kohn D.H., and Cais M. Organometallic polymers. VI. Anchoring of arenechromium car-

- bonyl complexes to macromolecular polymers, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 1387-1397 (1980).
83. Yamamoto T., π -conjugated polymers with electronic and optical functionalities: preparation by organometallic polycondensation, properties and applications, *Macromol. Rapid Commun*, **23**, 583-606 (2002).
84. Kickelbick G., Concepts for the incorporation of inorganic building blocks into organic polymers on a nanoscale, *Prog. Polym. Sci.*, **28**, 83-114(2003).
85. Schmidt H., Sol-Gel derived nanoparticles as inorganic phase in polymer type Matrices, *Macromol. Symp.*, **159**, 43-55 (2000).
86. Kasemann R. and Schmidt H., Coatings for mechanical and chemical protection based on organic-inorganic sol-gel nanocomposites, 1st. Euro. Workshop on Hybrid Organic-Inorganic Materials, France, 8-10 (1993).
87. Voevodin N.N., Grebasch N.T., Soto W.S., Arnold F.E., and Donley M.S., Potentiodynamic evaluation of sol-gel coatings with inorganic inhibitors, *Surf. Coat. Technol.*, **140**, 24-28 (2001).
88. He J. and Schoenug J.M., Nanostructured coatings: Review, *Materials Science and Engineering*, A336, 274-319 (2002).
89. Ershad Langroudi A. and Rahimi A., DGEBA-TEOS ormosil coatings for metal surfaces, *Proc. 6th Iran. Semi. on Polym. Sci. and Technol.*, (ISPST 2003) Tehran, Iran, 331, 12-15 May (2003).
90. Chiang C.-L. and Mac.-C.M., Synthesis, characterization and thermal properties of novel epoxy containing silicon and phosphorus nanocomposites by sol-gel method, *Eur. Polym. J.*, **38**, 2219-2224 (2002).
91. Metroke T.L., Kachurina O., and Knobbe E.T., Spectroscopic and corrosion resistance characterization of GLYMO-TEOS ormosil coatings for aluminum alloy corrosion inhibition, *Prog. Org. Coat.*, **44**, 295-305 (2002).
92. Du Y.J., Damron M., Tang G., Zheng H., Chu C.J., and Osborne J.H., Inorganic/Organic hybrid coatings for aircraft aluminium alloy substrates, *Prog. Org. Coat.*, **41**, 226-232(2001).
93. Keijman J.M., Ameron BV, and Kennedylan J.F., Properties and use of inorganic polysiloxane hybrid for the protective coatings industry, 2^{as} Jornadas Da Revista Corrosão E Protecção de Materiais Lisboa, 1-13, 22 de Nov. de (2000).
94. Meth S. and Sukenik C.N., Siloxane-anchored thin films on silicon dioxide-modified stainless steel, *Thin Sol. Films*, **425**, 49-58(2003).
95. Winkler R.-P., Arpac E., Schirra H., Sepeur S., Wegner I., and Schmidt H., Aqueous wet coatings for transparent plastic glazing *Thin Sol. Films*, **351**, 209-211 (1999).
96. Dumont B., Thiery R., Welter J.-M., and Duterne J.P., Hybrid sol-gel clear coatings for decoration brass profiles, *Surf. Eng.*, **17**, 254-258 (2001).
97. Pilz M., Romich H., sol-gel derived coatings for outdoor bronze conservation, *J. Sol-Gel Sci. Technol.*, **8**, 1071-1075 (1997).
98. Callardo J., Galliano P., and Duran A., Bioactive and protective sol-gel coatings on metals for orthopaedic prostheses, *J. Sol-Gel Sci. Technol.*, **21**, 65-74 (2001).
99. Guglielmi M., Sol-gel coatings on metals, *J. Sol-Gel Sci. Technol.*, **8**, 443-449 (1997).
100. Wagner G.W., Sepeur S., Kasemann R., and Schmidt H., Novel corrosion resistant hard-coatings for metal surfaces, *Key Eng. Mat.*, **150**, 193-198 (1998).
101. Lee S.Y., Lee J.D. and Yang S.M., Preparation of silica-based hybrid materials coated on polypropylene film, *J. Mat. Sci.*, **34**, 1233-1241 (1999).
102. Frings S., Meinema H.A., Van Nostrum C.F., and Van der Linde R., Organic-inorganic hybrid coatings for coil coating application based on polyesters and tetraethoxysilane, *Prog. Org. Coat.*, **33**, 126-130 (1998).
103. Schottner S., Kron J., and Deichmann A., Industrial application of hybrid sol-gel coatings for the decoration of crystal glassware, *J. Sol-Gel Sci. Technol.*, **13**, 183-187 (1998).
104. Ershad Langroudi A., Mai C., Vigier G., and Rene V., Hydrophobic hybrid inorganic-organic thin film prepared by sol-gel process for glass protection and strengthening applications, *J. Appl. Polym. Sci.*, **65**, 2387-2393 (1997).