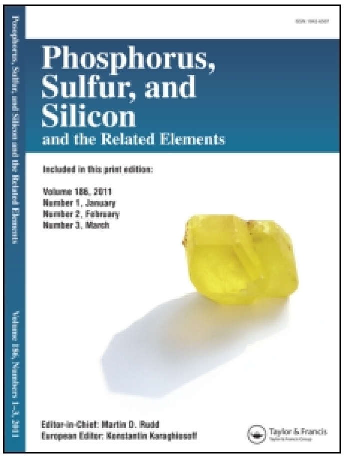

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Recent Advances in the Synthesis and Applications of Inorganic Polymer

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Polymers are ubiquitous in modern society. They are used in a variety of applications, ranging from sophisticated—such as electronics—to relatively simple ones like packaging. Inorganic polymers often have certain advantages over their organic counterparts—such as increased thermal stability and unique material properties—and have been an active area of research for many years. The potential technological applications that are imagined for some of these polymers, however, have mostly failed to be realized. This article aims to examine some of the advances in the general field of inorganic polymers, which have been made in the last three years. We also attempted to ascertain whether the promise of these materials will be realized in the near future, especially as advanced polymeric materials.

Keywords Inorganic; organometallic; polymer; silicones; synthesis; technology

INTRODUCTION

"Polymer is a term used to describe large molecules consisting of repeating structural units, or monomers, connected by covalent chemical bonds. The term is derived from the Greek words: polys meaning many, and meros meaning parts. A key feature that distinguishes

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polymers from other molecules is the repetition of many identical, similar, or complementary molecular subunits in these chains. These subunits, the monomers, are small molecules of low to moderate molecular weight, and are linked to each other during a chemical reaction called polymerization."[1] In simpler words, a polymer is a large molecule formed of repeated smaller molecules.

Polymers are everywhere you look in the world and can be classified as organic, biological, and inorganic. There are many definitions of what constitutes an inorganic polymer, and none are truly satisfactory. For the purposes of this article, we define an inorganic polymer as having inorganic repeating units in or on the backbone[2] and have concentrated on what scientists generally envisage when they picture a polymer, i.e., a soluble or elastomeric, fairly large molecular weight species. This definition therefore excludes materials like glasses and poly(vinyl chloride), which although has inorganic chlorine atoms on the polymer backbone, is generally considered, by most people, to be organic.

There are many reasons why polymers are such versatile materials, including cost and the tailorability of physical properties. Perhaps their primary asset is their processability, which means films, fibers, and shaped objects—with a range of final physical characteristics and properties—can be formed easily. The bulk of the polymers that we use in our daily lives are organic polymers, and there are problems associated with these substances, including: thermal instability, the release of toxic smoke upon ignition, degradation, softening or swelling at low temperatures, and so on.[2–4] They are also derived from petroleum, which as a natural resource is not in an inexhaustible supply.[5] Inorganic polymers avoid some or all of these problems, and the fact that they are not based on carbon means they might offer new properties not seen in or with organic polymers.

There has been renewed interest in the general field of inorganic polymers, in the last half decade, with three excellent books published.[2–4] The promise of these polymers, however, has often never been fulfilled. The aim of this article is to give a broad overview of some of the recent advances in the synthesis and applications of inorganic polymers, in the light of some exciting new developments in the last three years (a summary of which is shown in Figure 1), and to determine whether we might see these materials outside the laboratory in the near future, especially in advanced technological applications.

DISCUSSION

Polysiloxanes

Polysiloxanes (silicones) are easily the most common and familiar inorganic polymer, having been widely used in commercial products such as

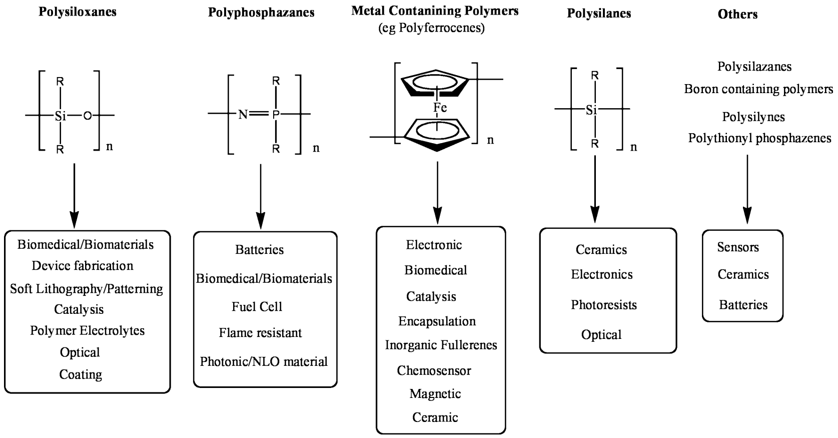


FIGURE 1 Types and applications of the inorganic polymers discussed in this article.

water repellants, adhesives, coatings, and so on for many years. They also find utility in medical applications—the best known of which is as silicone breast implants. Contention arose in the 1990s when it was claimed that these insertions were damaging women's health. However, since then, the overwhelming body of medical evidence has shown that this is not the case.[6] Polysiloxanes are also the subject of much current research interest, with perhaps the most exciting and fastest growing area of study being the field of soft lithography.

Soft lithography represents a non-photolithographic strategy based on self-assembly and replica molding for carrying out micro- and nanofabrication. It provides a convenient, effective, and low-cost method for the formation and manufacturing of micro- and nanostructures. The name "soft lithography" does not cover one specific method but rather a group of techniques with the common feature that at some stage of the process an elastomeric ("soft") material is used to create the chemical structures. These techniques use mostly poly(dimethylsiloxane) (PDMS) stamps with patterns on their surface in order to generate features with dimensions from tens of nanometers to hundreds of micrometers.[7] An example of a stamp making method is shown in Figure 2.

Traditional PDMS stamps have drawbacks, which have stimulated the search for new versions of stamp materials. Choi reports the synthesis and use of some alternative PDMS stamps for advanced soft lithography. They were produced from a new photocurable pre-polymer made from two commercially available PDMS pre-polymers: one is diglycidyl ether-terminated and the other bis(hydroxyalkyl)-terminated. The

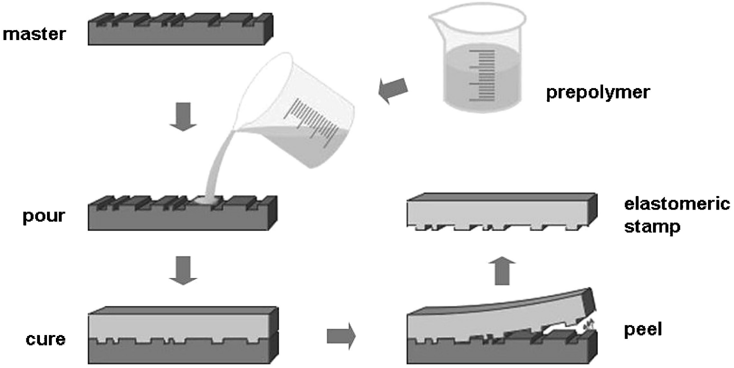


FIGURE 2 Representation of PDMS stamp replication process. Stamps are fabricated by casting a pre-polymer on a master with a negative of the desired pattern, curing it, and peeling the cured stamp off the master. Reprinted with permission from Dirk Burdinski© Dirk Burdinski http://www.research.philips.com/technologies/light_dev_microsys/softlitho.

stamps have adjustable toughness, and the new stiffer PDMS stamps that were made were shown to have advantages over the commercial PDMS stamps, including "photopatternability" and soft-lithographic resolution at the nanoscale.[8]

One of the principle aims of soft-lithography is to create functional materials. The ability to control hydrophobicity is of paramount importance in many such materials including drug delivery and microfluidic systems. Until recently, there was no way to locally control the wettability when fabricating substrates using any kind of printing method. Zheng et al. report a soft-lithographic method for the transference of PDMS patterns onto a variety of substrates.[9] The PDMS stamp is treated with oxygen plasma and sodium hydroxide and then placed on the surface—subsequent curing and peeling leaves PDMS features on the material. The method has many distinct advantages, including the ability to print on hard (silicon wafers, glass and gold) and soft (polymer) surfaces, as well as being able to control spatial wettability on non-planar surfaces.

Another important goal in soft-lithography is to fabricate complex two- or three-dimensional shapes and hopefully craft some useful appliances from these structures. Several interesting new devices have been manufactured in such a way. Kunnavakkam et al.[10] report a strategy to make low-loss microlens arrays, using PDMS, in a low-cost soft-lithographic process. Testing the physical and optical properties of the lenses reveals that their method may be suitable for a host of applications in micro- and integrated optics. They also note that the lenses, which were replicated from the master, have comparable performance in terms of focal length distribution and loss. In addition, they are found to be thermally stable in the region that would be required for any commercial applications. The authors believe that this approach might be used to fabricate other micro-optical components, such as grating and waveguides.[10]An easy non-lithographic approach for making microfluidic devices principally from PDMS is described by Vullev and co-workers using a LaserJet printer.[11] In their work, they fabricated a device that detects bacterial spores. Perhaps the real power of their study, however, is that their non-lithographic approach is both cheap and simple and would offer a research and development (R&D) alternative to the production of such devices, where specialized microfabrication facilities are not available.

Two interesting—new—all PDMS devices have been reported. In the first, a complete miniature hydrogen air proton exchange membrane (PEM) was built and tested—the first of its kind.[12] The design is simple and compact ,and the feasibility of building such a device from cheap materials like PDMS is demonstrated. The authors' note that the performance is not competitive compared to standard PEM approaches. In the second, the first example of electrochemical detection in an all PDMS device is presented, thus extending the capabilities of lab-on-a-chip devices.[13] A particularly stunning example of a novel 3-D microfabrication technique for PDMS is reported by Ober and Coenjarts (Figure 3).[14] They introduce a two-photon strategy that could be viewed as an alternative or complementary method to existing microfabrication techniques.

As we were writing this article, two other articles that were recently published caught our attention, and we felt they were worthy of discussing. In one, Crosby and Chan report an alternative way of fabricating an array of microlenses using PDMS.[15] By "wrinkling" the PDMS surface, they were able to not only form a microlens, but this particularly clever method enables patterning on both planar and nonplanar surfaces. The authors also believe that this methodology could be extended to the nanoscale if the right materials are used. In the other article, Choi et al. show the use of siloxane co-polymers as practical nanoimprint lithography (NIL) materials; the first such report.[16] NIL is considered a low, cost alternative for patterning with ultrahigh resolution; a technology that could "change the world." Generally researchers use organic polymers for this process, which are not particularly suitable for the job. In this work a range of PDMS co-polymers were produced which were shown to have superior performance, compared to the organic polymers, allowing feature sizes of 50 nm or less to be imprinted.

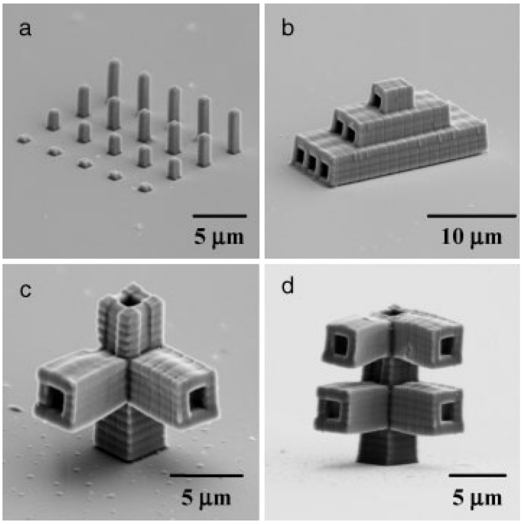


FIGURE 3 PDMS microstructures formed from a "Two-Photon Three-Dimensional Microfabrication of Poly(Dimethylsiloxane) Elastomers." Reprinted with permission from Coenjarts and C.K. Ober,[14]© 2004 American Chemical Society.

In spite of the recent scare with silicone, one of the major uses and important research areas of polysiloxanes is in biological and medical applications, often due to either their biocompatibility or bioactivity. The range of potential applications is large and extends from bone reconstruction to prevention of human immunodeficiency virus (HIV) infection.

Because bioactive materials have the ability to induce direct bonding to living bone these materials are of interest as bone tissue regenerators. Vallet-Regi and co-workers recently prepared hydrolytically stable and flexible polyorganosiloxanes from N-(2-aminoethyl)-3 aminopropyltrimethoxysilane (DAMO) and γ-methacryloxypropyltrimethoxysilane (MPS); bioactivity was promoted by adding a calcium salt during synthesis.[17] The DAMO:MPS molar ratio gives tailored performance in simulated body fluid indicating that it could be a promising alternative for bone regeneration.

Another bone regeneration approach is guided bone regeneration (GBR). This is a well-established method where a membrane is used to protect the bone defect from invasion by other tissues. Poly(tetrafluoroethylene) has to date been the most widely used material in these applications; however, the polymer has to be removed in a secondary operation after the bone has healed. There is therefore great interest in other materials which are biodegradable, but maintain their biocompatibility. Maeda et al. have synthesized a new hybrid membrane containing a polysiloxane which seems to satisfy these requirements and is a promising new candidate for GBR.[18]

The hydrophobic nature of polysiloxanes means that when placed in a biological environment they tend to interact strongly with surrounding proteins; this fact is sometimes beneficial in biomedical applications, especially in uses like drug delivery. More often than not this property is, generally, undesirable when its imagined use is as a biomaterial. Therefore controlling protein adsorption is of paramount importance. Liu et al. prepared siloxane microspheres with a poly(methylmethacrylate)(PMMA)/poly(3-methacryloxypropyltrimethoxysilane) (PMPS) core-shell structure and studied their behavior with bovine serum albumin.[19] The presence of PMPS was found to a key factor in determining the adsorption/interaction between the polymer and the protein.

Further examples of advances in the use of silicones in medical/biological applications include: the facile formation of bioactive hydroxyapatite coatings on metals; [20] the improvement of mechanical properties in implantable devices;[21] the development of a new material for cardiovascular applications;[22] the synthesis of a titania/silicone composite, which has good cell adhesion and antibacterial properties;[23] the use of silicone in the tissue engineering of skeletal muscle;[24] the demonstration of using a silicone elastomer as a vaginal ring, which offers the protection against heterosexual HIV transmission;[25] and the continued use in personal care.[26]

A particularly novel use of PDMS in the field microfluidics is demonstrated by Thorslund et al.[27] They fabricated a PDMS microfluidic device for separating plasma from whole human blood. The lost-cost and processability of using PDMS in such devices has already been mentioned. The constant drive to miniaturization, however, adds a further complication for this particular invention—an increase in interaction between the blood and channel walls causes coagulation and stops the device from working. With the addition of heparin, which acts as an anti-coagulant and prevents the blood from clotting, it adds long-term stability to the device. The authors believe such a methodology will enable the use of PDMS when working with similar biological samples.[27]

The interest in polysiloxanes is not limited to just soft lithography and biological applications, and there have been many other advances in the field, both in synthesis and their uses. A new, highly efficient and facile synthesis between dihydrosilanes and dialkoxysilanes has lead to the preparation of polysiloxane co-polymers.[28] The reaction requires tris(pentafluorophenyl) borane, $B(C_6F_5)_3$, as a catalyst and takes places under ambient conditions. The demonstrated generality of the process means it could serve as a very useful method for producing novel siloxane polymers and copolymers. Another reaction where $B(C_6F_5)_3$ was found to be an effective catalyst was in the synthesis of optically pure and completely diisotactic phenyl and naphthyl-substituted polysiloxanes.[29] The reaction—again—takes place under mild conditions and the stereochemically controlled polymers offer improved properties such as increased thermal stability. They are also expected to exhibit novel properties compared to ordinary polysiloxanes.

One of the great advantages of polymers like polysiloxanes and in particular PDMS is the ability to functionalize the polymer with various non-reactive and reactive groups. Recent work.[30] has shown that PDMS ionomers (polymers with ions covalently bound to the backbone) can be synthesized which have different rheological and morphological properties compared to organic analogues.[30] The hydrogen bonding of a polyhedral oligomeric silsesquioxane (cluster structures related to the polysiloxanes) to a modified PDMS polymer has been studied.[31] The polymer's monolayers spread at the air/water interface have potential applications as optical devices and biomimetic surfaces. Hydrogen bonding is also postulated as the reason for the interaction between a modified PDMS and functionalized fullerene (C_{60}), which has been prepared by supramolecular assembly.[32] The resultant nanocomposite has superior thermal and mechanical properties and unique dielectric properties. There is also the possibility that these types of materials could also access some of the properties of fullerenes such as superconducting, optical, catalytic, and medicinal.

Another nanocomposite in which polysiloxanes plays a key role is in the formation of recyclable chemoselective hydrogenation catalysts,[33] which are of importance in the petroleum and other industries. They have been synthesized under mild conditions and in high yield by the reduction of a palladium (Pd) salt and poly(methylhydrosiloxane). The polymer serves multiple roles in the Pd-polysiloxane nanocomposite from stabilization to facilitating self assembly.

One of the most unusual uses of the polysiloxanes has been found out by accident. Silicone grease, as most inert atmosphere organometallic chemists know, is used for sealing glassware joints and is generally regarded as being chemically inactive. However, it seems that the grease is not as inert as had once been thought. With highly polar organometallic reagents, both unusual and unexpected products are serendipitously formed, including supramolecular ones.[34]

Polysiloxanes have also been used to prepare polymer electrolytes[35] that can be used in solid-state devices such as batteries, capacitors, and anti-fouling agents,[36] which have been shown to be minimally adhesive to marine organisms and protect steel from corroding and novel fluoropolymers which are being investigated as release agents for coating applications.[37] This by no means covers the entire spectrum of uses of polysiloxanes but does indicate the wide variety of possible applications for these polymers.

Polyphosphazenes

Perhaps the second most important class of inorganic polymer and certainly the focus of much research attention are the polyphosphazenes. Polyphosphazenes are a novel class of polymer primarily developed by Harry Allcock during the 1960s. Their unique structure and the simple macromolecular substitution of side groups with other groups, which leads to tailorable properties, has lead to them being considered in a broad range of applications, including flame resistant and as biomaterials.[38]

Often the road to commercialization of inorganic polymers, including polyphosphazenes, is hampered by a suitable simple and industrially viable synthetic route. In 2004, was developed reaction strategy that may have solved this problem.[39] In this work, he polymerizes phosphoranimine ($Cl_3P{=}NSiMe_3$) to produce poly(dichlorophosphazene). The author readily admits that it is likely that the synthesis will have to be modified for large scale, industrial applications. However, the one-pot method developed has several distinct advantages over previous approaches; these include: the reaction being performed under ambient conditions; and the fact that the very reactive monomer does not have to be vacuum distilled. All of these factors contribute to ease-of-synthesis and potential cost savings.

A quite remarkable one-pot synthesis of a polyphosphazene nanotube has been reported.[40] The synthesis is very simple—they are prepared simply by mixing hexachlorocyclotriphosphazene and 4,4′-sulfonyldiphenol in the presence of triethylamine. The resulting structures might find use in a variety of applications ranging from biomedical to electronic. The authors also suggest that the synthesis might also be applied to other polymerizations, which in turn might provide access to polymer nanotubes with controlled dimensions.

In terms of the possible applications of polyphosphazenes, there is undoubtedly interest in two key areas: the first is in the production of ion-conducting membranes; and the second is as a biomaterial or in biomedical research.

In the near future, fuel cells will surely become a key energy conversion technology. A vital component of any fuel cell is the PEM.

Polyphosphazenes are excellent candidates for these due to the ease with which the side groups can be modified.[41] Metal sea water batteries can be considered as a (semi-) fuel cell. Allcock and coworkers demonstrated the use of cyclic phosphazene substituted polynorbornenes/polyoxanorbornenes in this type of device.[42] These polymers offer the unusual combination of lithium ion conduction and water repellency which protects the metal anode from water. The authors found that lithium ion conduction was adequate but noted that the hydrophobicity of the polymer needs to be improved.[42] A new synthetic strategy for synthesizing similar kinds of polymers is presented by the same research group and the researchers also believe that these polymers may also be used as novel photonic materials.[43] There are other reports of polyphosphazenes used in composite polymer electrolytes[44] and as PEMs in hydrogen[45] and direct methanol fuel cells.[46] Again, the tailorability of the chemical and physical properties of the polyphosphazenes is paramount in the improvement of certain desirable properties in these devices.

These factors also play a key role in the use of polyphosphazenes in biological applications as well as their bio-"neutrality." Nair et al. have synthesized polyphosphazene nanofibers (Figure 4).[47]

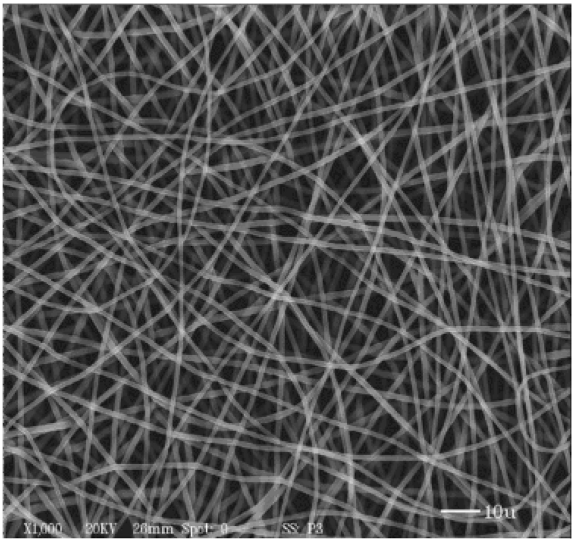


FIGURE 4 Scanning electron micrograph of electrospun polyphosphazene fibers. Reprinted in part with permission from Nair et al., [47]© 2004 American Chemical Society.

The formation of electrospun mats from these nanofibers has been shown to promote adhesion of endothelial cells and adhesion and proliferation of osteoblast-like cells, indicating that they could be used in such areas as wound dressing and prosthetic organs. The same author also reports that polyphosphazenes can be used as a component of "self-setting bone cements."[48] A range of novel polyphosphazenes has been prepared featuring biodegradability[49,50] and hydrophobic and super-hydrophobic surfaces[52,53]—all important factors in a range of biomedical and other applications.

Metal-Containing Polymers

The last major group of structurally classified inorganic polymers is the metal-containing ones. The incorporation of metals either directly into or onto a polymer backbone or through coordination of the metal species to the polymer provides the opportunity of accessing unique structures with novel properties.[54] One of the key goals is to combine the electrical properties of metals with the processability, strength, and flexibility of polymers. One of the most important types of the metal containing polymers are the polyferrocenes and co-polymers. Cazacu et al. synthesized some new condensation polymers from siloxane and ferrocene derivatives.[55] The ferrocene units add redox activity to the polymers and the electrochemical behavior of the polymers, when studied, suggests possible uses in the chemical modification of electrodes. Much of the most exciting work done on polyferrocene polymers and their derivatives/relatives, is done by Abd-El-Aziz and Manners,[56] and the reader is encouraged to access these numerous papers and a brand new book (Frontiers in Transition Metal-Containing Polymers) themselves.[56] There are, however, two papers that we feel warrant discussion in further detail.[57,58]

In the first,[57] a range of dendronized polyferrocenylsilanes were synthesized. Dendronized polymers are those that have dendron side groups in every repeat unit on a linear polymer. By increasing the size of the Dendron, it is possible to eventually turn the polymer backbone into a cylindrical shape (which might be a useful nanoscale moiety for the development of novel nanodevices/materials) or into a sphere. After synthesis they also tried to directly visualize the polymers using atomic force microscopy (AFM). These studies show that single polymer chains have a spherical shape. They hypothesize that at the core of these particles are the redox active iron atoms surrounded by the dendrons; suggesting possible applications in such fields as catalysis and encapsulation. In the second article,[58] the synthesis of diblock inorganic/ organic co-polymers of polystyrene-block-poly(ferrocenylethylmethylsilane) is reported. Block co-polymers are of interest across a spectrum of applications, from membranes (porous) to photonic. The formation of an inorganic/organic co-polymer, particularly if the inorganic part contains a transition metal, means the possibility of using these polymers as ceramic precursors, conductive materials, and so on. Preliminary data from their research indicates that these polymers self-assemble into thin films which permits patterning; again opening up a host of "nanochemical" possibilities for these materials.[59]

A rather unique class of metal containing polymer has been synthesized.[60] The arsenic-containing polymers, called the poly(vinylene-arsine)s ($-[\mathrm{AsMe\text{-}CH{=}CPh}]_n-$), are not claimed to have any interesting properties for high-tech applications (but that is because this has not been investigated), but their synthesis does have general ramifications for the synthesis of some inorganic polymers. The researchers polymerized a cyclic arsenic compound with phenylacetylene in the absence of a radical initiator or catalyst, to give a 1:1 alternating co-polymer. The authors are continuing their studies by looking at expanding the scope of this synthetic method, which they believe will be appropriate in the synthesis of other inorganic polymers—ones that have silicon, germanium, phosphorus, and so on in the backbone.[60] Such an approach may well yield novel polymers with novel properties.

A hybrid organic-inorganic polymer, containing sulfur and coordinated to Cu^{2+}, has been synthesized and has been shown to be highly sensitive and selective towards iron cations.[61] In this elegant work, the system acts as a fluorescence "turn-on" chemosensor. This differs from most sensors which use a fluorescence quenching mechanism as the measured response. By using such an approach, sensitivity is increased, and the likelihood of getting a false positive response decreased. The authors believe that this unique polymer could be modified for the detection of other metal ions which would be incredibly useful in biological systems and environmental monitoring applications.

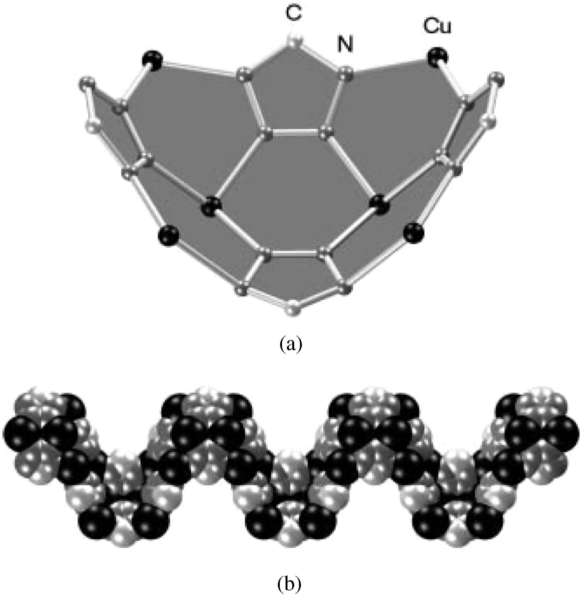
Other novel coordination polymers have been synthesized, which may have, as yet undetermined, unique properties. The synthesis of some novel polymers formed from triazole containing ligands and silver (I) salts has been reported.[62] Sijbesma and co-workers present a general strategy for the synthesis of palladium and platinum polymers using phosphorous ligands.[63] Zhai et al. have designed a unique three-dimensional coordination polymer based on copper,[64] and Ghosh et al. synthesized two new cadmium (II) coordination polymers,[65] which have a supramolecular structure formed through hydrogen bonding and/or Se-Se interactions. These articles are just a small amount of the work published in a large and active field; but, they are an indication of the novel synthetic strategies, which are being developed and/or unusual polymer structures which are being accessed.

As mentioned earlier, the marriage of an inorganic polymer to a fullerene opens up the possibility of an alliance of desirable properties. There is also a great deal of interest in creating all inorganic, fullerene-like molecules; such molecules are likely to have novel properties. Synthetically this is a great challenge to inorganic chemists; mainly dealing with problems in controlling the curvature. Therefore, even the synthesis of a part of an inorganic fullerene (a buckybowl) would be a great achievement. Recently, Wu et al. synthesized a coordination polymer containing inorganic buckybowl analogues (Figure 5).[66]

The Mtta ligand (Mtta = 5-methyltetrazolate) seems useful in synthesizing these types of structures, and the work opens up an avenue of exploration for synthesizing other fullerene fragments or perhaps even an entire inorganic fullerene.

Pre-ceramic Polymers

There are some polymers that avoid rigid classification by account of their structure but are classified, more commonly, according to their



(a)

(b)

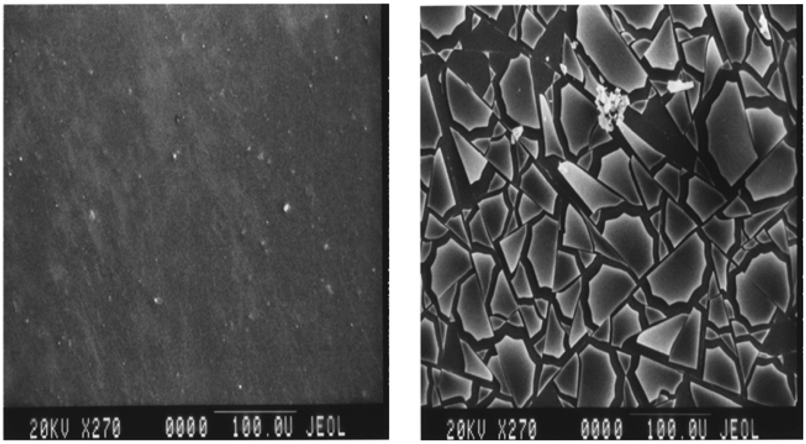
FIGURE 5 (a) View of the buckybowl composed of Cu_6 $(Mtta)_4$ with four five-membered rings and five six-membered rings. (b) 1-D wavy ribbon constructed by alternating convex and concave buckybowls. Reprinted with permission from Wu et al.,[66]© 2006 Wiley-VCH.

use. Possibly, the most important of these are the pre-ceramic polymers, which includes one of the few, relatively well-known, inorganic polymer products to reach the marketplace; Nicalon$^{\mathrm{TM}}$ [silicon carbide (SiC) fibers formed from the pyrolysis of polycarbosilane (a polysilane with a carbon atom incorporated into the inorganic backbone)]. An excellent summary of the field of pre-ceramic polymers was published by Seyferth in 1995.[67] Generally, the most sought after polymers are ones that produce superhard materials like SiC and silicon nitride, this means that the starting materials tend to be organosilicon polymers.[68] The three basic methods for transforming the polymeric precursors into ceramic materials are pyrolysis (heating in the absence of oxygen), chemical vapor deposition (CVD) (if the precursors are volatile), and chemical liquid deposition, which has increasingly been shown to be feasible in microstructure fabrication.[69]

One of the most exciting developments in the last three years has been the work of Bianconi and co-workers.[70] They synthesized a new polymeric precursor to SiC called poly(methylsilyne). The unique network structure of the polymer means that no cross-linking is required to obtain high ceramic yields, which is contrary to popular thought in the field of pre-ceramic polymer chemistry.[3] High-quality polymer films can be spun from solution and then heated to form smooth continuous films of stoichiometric silicon carbide—the first of its kind. Figure 6 shows the advantage of using this polymer compared to another related polymer, poly(n-hexylsilyne), which has high mass loss during heating and therefore low ceramic yields.

The incredible smoothness of the films might open up the use of this polymer in electronic applications. The only drawback with this work is that the polymer is synthesized from the sonochemical reduction of liquid sodium-potassium alloy (NaK—explosive and pyrophoric) using high intensity ultrasound and then further refluxing with methyllithium in highly flammable organic solvents. Such a process is unlikely to be scaled up industrially. However, these polymers can be synthesized electrochemically which would provide a commercially viable route to these types of polymers.[71,72]

Pyrolysis conditions have been shown to be very important in the microstructure of the final ceramic material. Ma et al. have shown that the microstructure and mechanical properties, including porosity, density and strength of silicon oxycarbide (produced from a polysiloxane precursor) depends on heating rate, temperature, number of cycles, and hot pressing.[73] In some cases, a porous ceramic is not a defect but rather a desired property, especially in such applications as filters, catalytic supports, and so on. Recently, a low temperature route to porous SiC ceramics has been developed from the heat treatment



(a) (b)

FIGURE 6 Scanning electron micrograph images of SiC films obtained by pyrolysis of polysilynes: (a) SiC film from poly(methylsilyne); and (b) SiC film from poly(n-hexylsilyne). Reprinted with permission from Pitcher et al.,[70]© 2004 Wiley-VCH.

of a polycarbosilane, where the pore size can be easily controlled.[74] In other work, highly uniform and tailored SiC and silicon carbonitride porous ceramics were derived from a polysilazane (a nitrogen containing polysilane relative) or polycarbosilane derivative and incorporated into devices for the catalytic reforming of hydrocarbons[75] (an attractive route to producing hydrogen for fuel cells). Initial tests indicate the promise of these materials and incidentally PDMS molds were also used in the fabrication of this device. Silicon nitride produced from a polysilazane precursor has also shown to be effective in reinforcing silica fibers.[76]

Of particular interest in recent years has been the study and production of quaternary Si/B/C/N ceramics. Their high temperature durability and low densities make them highly desirable for demanding applications such as turbines. Two recent reports have shown that these materials can be formed from boron containing polymeric precursors and that the Si:B:C:N ratios can be controlled leading to tunable properties.[77,78] In the second paper,[78] a layered composite material was synthesized with aluminum foil; the authors believe that the homogeneous incorporation of different metals into the ceramic material may lead to the production of novel functional materials. This effect is seen in the work of Dumitru et al.—they synthesized ceramics from copolymers of a polysilane and polyferrocene using plasma assisted CVD.[79] They found that the synthesis parameters could be altered to give ceramic materials with tunable magnetic properties.

Miscellaneous Polymers

Boron containing polymers can be used in a variety of applications, one of which has already been mentioned; in the production of advanced ceramic materials, but they are also of interest in a variety of other high-tech applications. They can be synthesized by a variety of methods. A particularly intriguing new approach has been developed by Jäkle and co-workers.[80] They have found an efficient way to introduce electron deficient boron centers into the side chains of organic polymers. One of the key advantages presented by this procedure is the ability to take advantage of the easy and reversible co-ordination chemistry available to these centers, which in turn provide further avenues for the functionalization and manipulation of the polymers. In other work, a poly(lithiumorganoborate) was directly synthesized.[81] The ionic conductivity of the polymer was better than those synthesized by other methods and starting materials and so may find applications in such devices where this property is important' i.e., sensors, conductive materials, and so on.

Two sulfur-containing polymers related to the polyphosphazenes have also been reported. Xu et al. have synthesized a new inorganic polymer poly(phosphazene disulfide).[82] It is made simply by refluxing linear poly(phosphazene dichloride) with Na_2S_2. The unique composition and crosslinked structure of the polymer has led to initial trials as a cathode material for the next generation of lithium batteries, with great success. The good chemical, thermal, and electrochemical stabilities and outstanding capacity density are just some of the advantages of using this polymer. Wang and Manners,[83] have synthesized a new range of polythionylphosphazene polyelectrolytes—the stable cationic and anionic water soluble polymers and a luminescent cationic version. These may find use in a variety of applications including use as an oxygen sensor. In addition, some novel optical polyphosphazenes have been created,[84] the polyphosphazenes were functionalized with a sulfonyl based chromophore. The polymers are soluble in common organic solvents, and the synthesis and purification are easy. The non-linear optical (NLO) activity measurements are encouraging; the authors believe that many other similar polymers could be prepared by this new and simple method, for NLO applications.

Interest in the polysilanes is primarily focused around their use as polymeric precursors for silicon carbide ceramics; however, they are also candidates for other applications such as photoresists and certain electronic devices due to their unique optical and electronic properties. Joshi and Shankar have synthesized a range of new unsymmetrical polysilanes, their studies suggest that the electronic properties of these polymers are tunable by altering the pendant groups on the silicon backbone.[85] Manners and co-workers also demonstrate the ability to control the optical and electronic properties of polysilanes, but by using a polyferrocenylsilane instead.[86] A room-temperature synthesis, which again might open up simpler and/or cheaper routes for industrial methods of production of the polysilanes, is reported.[87] The method is a Wurtz-coupling type, which is often used in the synthesis of these and related polymers By using tetrahydrofuran as the solvent instead of toluene, however, the need for heating (110°C) is removed, and the polymers are produced in higher yields. The method has been used to synthesize three different polysilanes, so it seems to be a general method for these types of polymers.

CONCLUSION

It is impossible in this short review to cover every advance in the synthesis and applications of inorganic polymers in the last three years.[88] Any omissions are the responsibility of the authors, not a reflection of the importance of the work. The future for inorganic polymers is, however, auspicious. The breadth of their uses is especially noteworthy. Further improvements in the synthesis and even more imaginative uses will be found—work for chemists, biologists, and indeed scientists from all disciplines for years to come. It is surely only a matter of time before some of these polymers, or products that are produced from them, follow Nicalon,™and a range of silicones into the marketplace.

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