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REVIEW

The Synthesis of Functional Polyphosphazenes and their Surfaces

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The macromolecular substitution approach for the synthesis of polyphosphazenes provides access to many different polymers. However, it precludes the use of reagents that contain two or more functional groups because such compounds would cause extensive crosslinking of the chains. This presents a problem because many of the uses for which polyphosphazenes seem ideally suited require the presence of -OH, -COOH, $-NH_2$, $-SO_3H$, $-PR_2$ and other functional units in the side-chain structure. We have developed two approaches to introduce such active sites: (1) protection–deprotection reactions; and (2) direct reactions of active reagents with the organic side-groups of non-functional poly(organophosphazenes). These methods have been applied both at the molecular level and in the form of reactions carried out only at polymer surfaces. The resultant polymers have special properties that are valuable in the microencapsulation of sensitive biological agents; in the formation of hydrophobic, hydrophilic, or adhesive surfaces; in crosslinking reactions; and in the development of solid polymer electrolytes, bio-erodible polymers, pH-triggered hydrogels, polymer blends and interpenetrating polymer networks. Overall, more than 700 different polyphosphazenes are now known, and a large number of these are functional macromolecules targeted for specific property combinations and uses. © **1998 John Wiley & Sons, Ltd.**

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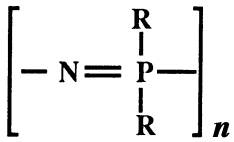
1 BACKGROUND

The term 'hybrid inorganic–organic polymers' covers a wide spectrum of materials that includes (1) macromolecules with inorganic elements in the backbone and organic side-groups,[1] (2) organic polymers with inorganic side-groups,[2] (3) polymers with both inorganic and organic units in the main chain[3] and (4) composite materials that contain mixtures of inorganic backbone and organic backbone polymers. Polyphosphazenes fall into the first category, although they have also been incorporated into composites with other types of polymers.[4–6]

The repeating unit in polyphosphazenes is shown in structure **1**, where the side-groups, R, can be organic, inorganic or organometallic units.



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This repeating unit can be part of a long linear chain, a branched arrangement, a crosslinked material or a dendritic structure. Most of the discussion in this review will be focused on polymers with a linear or lightly branched architecture and on the behavior of these polymers at the surface of a solid material. The emphasis will be on methods developed in our program for the introduction of functional sites on the side-groups both at the molecular level and at surfaces.

2 PRIMARY METHODS OF POLYPHOSPHAZENE SYNTHESIS

The methods described in this section have been optimized to produce polyphosphazenes that lack

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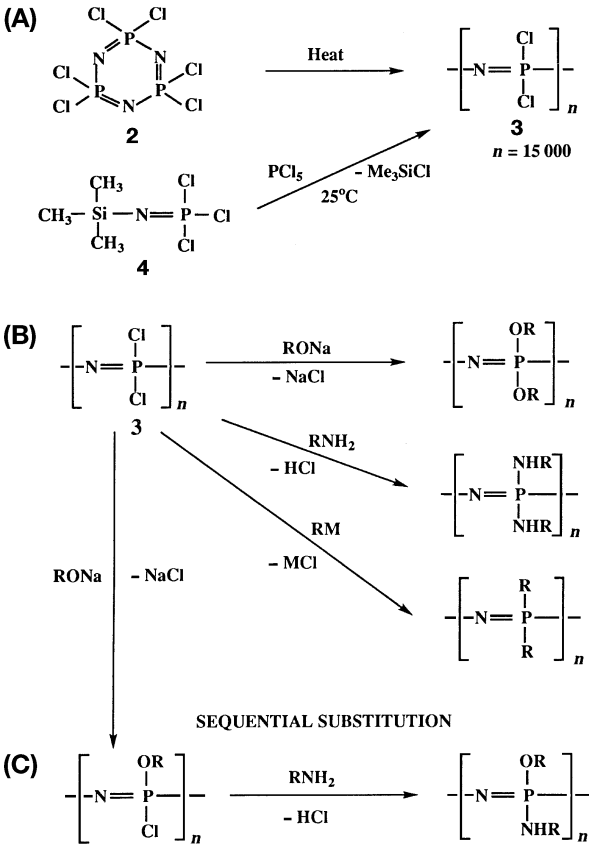
further reactivity. In other words, they are non-functional. Such polymers are valuable for their stability to heat and oxidation, biological environments, hydrolysis, organic solvents and γ- and ultraviolet radiation. Some of them are used as starting points for secondary reactions to introduce functionality, as described in Sections 3–6.

2.1 The macromolecular substitution process

The most widely used method for the synthesis of stable poly(organophosphazenes) is a two-step reaction sequence. The first step involves the preparation of poly(dichlorophosphazene) (**3**), and the second requires the replacement of the chlorine atoms in **3** by reactions with organic or organometallic nucleophiles.[5–13] The overall sequence is shown in Scheme 1.



Scheme 1 Synthesis of poly (organophosphazenes) in two steps: (A) synthesis of poly (dichlorophosphazene) (**3**), followed by (B) simultaneous replacement of chlorine atoms (C) sequential substitution of chlorine.

The reactive polymer intermediate (**3**) can be produced by several different methods. The most effective route to high-molecular-weight poly(dichlorophosphazene) is via the ring-opening polymerization of the cyclic trimer (**2**), either in the molten state or in solution.[5,6,14–16] This gives a polymer with a broad molecular-weight distribution, but with an M_w near 2 000 000, which corresponds to approximately 15 000 repeating units per chain Lower-molecular-weight polymers can be produced by condensation reactions between PCl_5 and NH_3,[17] or by the condensation polymerization of $Cl_3P{=}NP(O)Cl_2$.[18] These polymers, too, have broad molecular-weight distributions. A new method recently developed through a collaboration between our group and the team of I. Manners in Toronto is shown in Scheme 1.[19–22] It is a room-temperature, cationically catalyzed, living condensation polymerization of $Me_3SiN{=}PCl_3$, which yields narrow molecular-weight distributions and control over the chain length through variations in the ratios of monomer to PCl_5 catalyst. This approach also provides access to block copolymers and star geometries.

The second step in the synthesis of non-reactive polyphosphazene involves the replacement of the chlorine atoms in **3** by reactions with metal alkoxides or aryloxides, amines or organometallic reagents. Typically, an average of 30 000 chlorine atoms per molecule must be replaced at this stage, and the fact that this is possible is an indication of the high reactivity of the P–Cl bond. Inherent in this macromolecular substitution process is the opportunity to introduce two or more different types of side-groups by sequential or simultaneous chlorine replacement reactions. Several hundred different poly(organophosphazenes) have been synthesized by this method. Different side-groups or side-group combinations yield low-T_g elastomers, high-T_g glasses, microcrystalline fibers and films, and a range of bioinert materials. Most of the current industrially important polyphosphazenes are made by this method.[23,24]

2.2 Other synthesis routes

Three other synthesis routes to poly(organophosphazenes) exist that are useful for the production of polymers with direct P–C bonds between the skeleton and the side-groups: (1) the ring-opening polymerization of phosphazene cyclic trimers that have alkyl or aryl units linked to the ring;[15] (2)

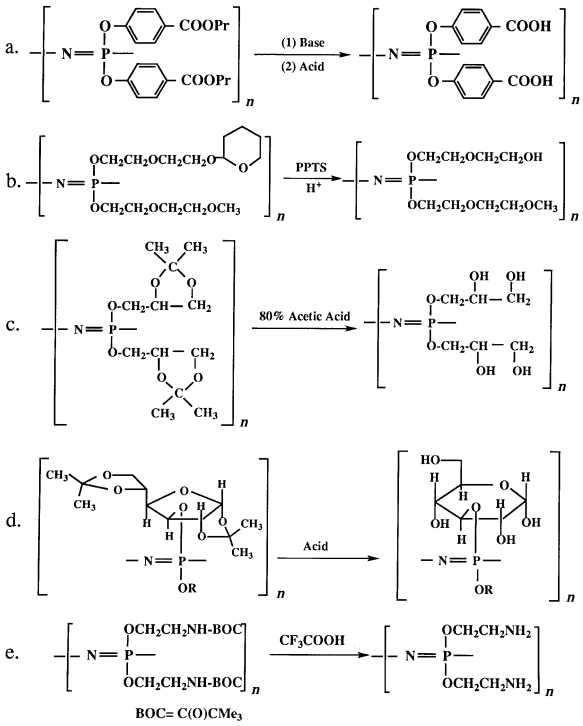
condensation reactions of organophosphoranimines;[25,26] and (3) denitrogenation reactions of organophosphorus azides.[27]

3 CHALLENGES IN THE SYNTHESIS OF FUNCTIONAL POLY(ORGANOPHOSPHAZENES)

Although unreactive ('non-functional') polyphosphazenes, such as species with fluoroalkoxy or phenoxy side-groups, are important materials for science and technology,[28–30] an increasing need exists for polymers with functional units in the side-group structure. These functional sites include -OH, $-NH_2$, -COOH, -COONa, $-CH{=}CH_2$, $-CH_2CH_2{=}CH_2$, $-SO_3H$, oxirane and a range of metal-coordinating groups such as ether, thioether, sulfoxide, sulfone, pyridinyl or imidazolyl units etc. Photosensitive crosslinking groups are also needed. Such functional sites are required to generate water solubility, crosslinking processes, polyelectrolyte behavior or compatibility with other polymers in blends, or for the linkage of proteins, drugs, catalysts and liquid-crystalline, NLO or other optical units to the polymer. Such functional polyphosphazenes can be viewed as 'second-generation' materials.

The most obvious way to introduce functional sites is the use of difunctional nucelophiles in the chlorine-replacement process. For example, in theory, a pendant carboxylate or amino functionality might be introduced by the reactions of $(NPCl_2)n$ with $NaOC_6H_4COOH$ or $NaOC_6H_4NH_2$. Unfortunately, the use of such difunctional reagents brings about the crosslinking of $(NPCl_2)n$ in the early stages of the reaction. Once such crosslinking has occurred, the remaining chlorine atoms will be inaccessible to the organic reagents and an insoluble, partly substituted material will be obtained. Such products are of little scientific interest and of no technological value because of their long-range hydrolytic instability due to the presence of residual P–Cl bonds.

Thus, functionality must be introduced *after* all the chlorine atoms in **3** have been replaced by organic units. Several strategies that have been developed in our program to accomplish this are mentioned in the following sections. They have been carried out at two levels—first by reactions carried out on the macromolecules in solution, and secondly by processes restricted to the surface regions of solid polymer films.



Scheme 2 Molecular-level deprotection reactions.

4 PROTECTION–DEPROTECTION REACTIONS

This approach has been widely used in our program to generate pendant-COOH, -OH and $-NH_2$ units at the termini of organic side-groups linked to a polyphosphazene chain. Several examples are described below and are shown in Scheme 2.

(1) Protection of a carboxylic acid function by means of an ester group, as in the reaction of $(NPCl_2)n$ with $NaOC_6H_4COOC_3H_7$ to give $[NP(OC_6H4COOC_3H_7)_2]_n$. Treatment of this polymer with base yields $[NPOC_6H_4COO^-M^+)_2]_n$ or $[NP(OC_6H_4\text{-}COOH)_2]_n$ (Scheme 2a).[31] This polymer has been developed as a calcium-crosslinked material for use in biological micro-encapsulation[32] and as an adjuvant in vaccines.[33]

(2) Protection of one hydroxyl group of a diol with a tetrahydropyranyl unit to give $HO(CH_2)xO\text{-}C_5H_9O$, conversion of the remaining hydroxyl group to the sodium salt, and use of this to replace the chlorine atoms in $(NPCl_2)n$. Treat-

ment of the resultant polymer with pyridinium *p*-toluenesulfonate (PPTS) (in the presence of H^+) then deprotects the terminal units to give $[NP(O(CH_2)_xOH)_2]_n$ (Scheme 2b).[34] All but one of the hydroxyl groups of glycerol and glucose have been protected by formation of the isopropylidene derivative before linkage to the phosphazene skeleton through the remaining hydroxyl group, and subsequent deprotection using acetic or trifluoroacetic acid (Schemes 2c and d).[35–37] Other research groups have used arylmethoxy units as protected hydroxyl sites with deprotection by boron tribromide, benzyloxy–aryloxy units for deprotection by catalytic hydrogenation[38] or alkylmethoxy units in which the methoxy groups are replaced by trimethylsiloxy moieties which are subsequently hydrolyzed to hydroxy functions.[39]

(3) Protection of the amino terminus of $HOCH_2CH_2NH_2$ with di(t-butyl) dicarbonate to yield a 'BOC' (t-butoxycarbonyl) unit. The sodium salt of this alcohol then reacts with $(NPCl_2)_n$ to produce $[NP(OCH_2CH_2NH\text{-}BOC)_2]_n$, which can then be deprotected by treatment with trifluoroacetic acid to yield $[NP(OCH_2CH_2CH_2NH_2)_2]_n$ (Scheme 2e).[40]

All of these protection–deprotection processes are, of course, well known in small-molecule organic synthesis. The difference here is that an average of 30 000 of these reactions are carried out on each molecule.

5 DIRECT FUNCTIONALIZATION OF NORMALLY UNREACTIVE POLY(ORGANOPHOSPHAZENES)

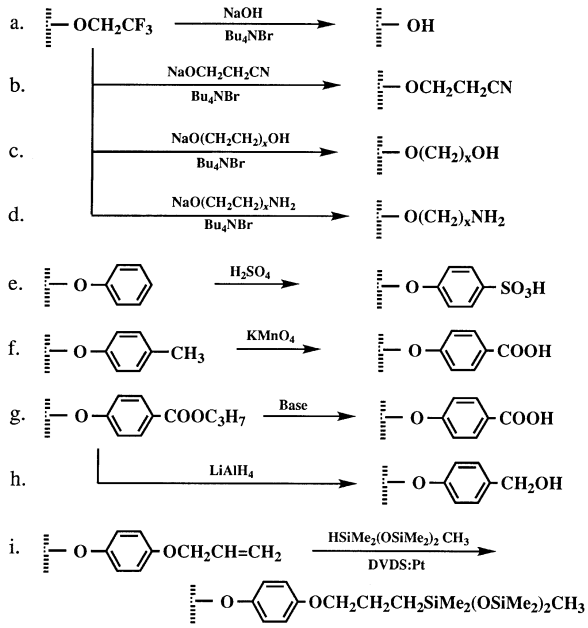
Although polymers such as $[NP(OC_6H_5)_2]_n$ or $[NP(OC_6H_4CH_3)_2]_n$ are normally considered to be unreactive, they can be induced to interact with strong acids such as H_2SO_4/SO_3 or with oxidizing agents. For instance, a variety of aryloxyphosphazene polymers have been sulfonated to give, for example, water-soluble $[NP(OC_6H_4\text{-}SO_3H)_2]_n$.[41,42] The *p*-methyl groups of $NP(OC_6H_4CH_3)_2]n$ can be oxidized to COOH groups with permanganate.[43] Bromoaryloxyphosphazene polymers such as $[NP(OC_6H_4Br)_2]_n$ undergo metal–halogen exchange with n-butyllithium to give $[NP(OC_6H_4Li)_2]_n$, a reactive species that can be used to form linkages to phosphines or organometallic units.[44] The phosphine-bound polymers are macromolecular ligands for transition-metal catalysts. Similar processes are possible starting from $[NP(CH_3)C_6H_5]_n$ and $[NP(CH_2Li)(C_6H_5)_n$.[45] The challenge with reactions of this type is to complete the functionalization without inducing cleavage of the inorganic backbone. An additional type of functionalization at the molecular level has involved the linkage of *B*-chloroborazine units to a polyphosphazene chain via P-NH_2 side-group units.[46] The resultant polymers have additional functionality in the sense that, on pyrolysis, they undergo crosslinking and condensation reactions to give ceramic materials, and ultimately hexagonal boron nitride.

6 SURFACE FUNCTIONALIZATION

Materials science revolves around two different sets of properties—(1)bulk properties such as strength, toughness, elasticity, transparency and refractive index and (2) surface properties such as hydrophilicity or hydrophobicity, biological activity and adhesion. Often these two sets of properties are mutually exclusive, e.g. when a material is needed that has a hydrophobic interior but a hydrophilic surface. This presents one of the major problems in materials science because materials that are optimized for a particular set of bulk properties often have the wrong surface characteristics, and vice versa.

An answer to this problem lies in the development of surface reaction chemistry. A material is designed primarily to optimize its bulk properties and then, after fabrication into films, fibers or molded objects, the surface is subjected to chemical reactions which improve the surface characteristics. For this approach to be successful, two requirements must be met. First, the chemical reaction must not penetrate deeply into the bulk phase; secondly, once modified, the altered surface must remain in the interfacial region without being buried over time by molecular motions.

Polyphosphazenes are ideal materials for surface reactions because many types of side-groups and different side-group ratios can be designed into the polymer at the macromolecular substitution stage. The following examples, illustrated in Schemes 3 and 4, show how this approach has been developed in our program.



Scheme 3 Functional groups formed by surface reactions on polyphosphazenes. DVDS, tetramethyl-1,3-divinyl-disiloxane.

6.1 Surface hydrolysis of fluoroalkoxyphosphazene polymers

Poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$, is a hydrophobic, non-adhesive, film- and fiber-forming polymer. Immersion of films of this material in aqueous sodium hydroxide/Bu_4NBr solutions for short periods of time induces replacement of the surface P-OCH_2CF_3 groups by hydrophilic and adhesive P-OH or P-O-NBu_4^+ groups[47] (Scheme 3a). This change can be monitored by a contact angle decrease from 108° to 90°, by anionic dye absorption, ATR IR spectroscopy and X-ray photoelectron spectroscopy. The relatively high contact angle after surface hydrolysis indicates that some hydrophobic units remain and that the surface is amphiphilic.

In addition, surface trifluoroethoxy groups can be exchanged for -OCH_2CH_2CN, -$O(CH_2)x$OH, -$O(CH_2xNH_2$, and other groups by exposure to solutions that contain the appropriate sodium alkoxide[29,48] (Schemes 3b–d)

6.2 Surface sulfonation of aryloxyphosphazene polymers

The molecular level sulfonation of poly(aryloxyphosphazenes) is facilitated by the solubility of these polymers in concentrated sulfuric acid.[42] However, this is a severe disadvantage for surface transformations. This problem was circumvented by the use of mixed-substituent polymers with phenoxy, biphenyleneoxy or naphthaleneoxy groups and *m*-ethylphenoxy co-substituent groups.[42] The polymer films were crosslinked by radiation through the ethyl units to prevent dissolution and to slow the penetration of sulfuric acid into the bulk materials. The changes in surface structure were again followed by contact angle measurements, dye absorption, ATR IR and XPS methods. Surface sulfonation converts a hydrophobic material (contact angle 70–90° to water) to a hydrophilic product (contact angle 5–40°). Under certain reaction conditions, the sulfonation penetrates deep enough to form a hydrogel outer layer bonded to the hydrophobic interior.

6.3 Surface carboxylic acid and benzylic alcohol groups by two different methods

Carboxylic acid groups can be produced on polyphosphazene surfaces either by the oxidation of alkyl groups on aryloxy side-groups[49] or by the hydrolysis of arylcarboxylic esters.[50] The oxidation process is illustrated in Scheme 3(f). With permanganate as the oxidant, the depth of reaction can be varied from *ca*25 to 1000 nm. The concentration of carboxylic acid units at the surface can be controlled by the use of a polymer that bears both phenoxy and *p*-methylphenoxy side-groups, since the phenoxy groups are unreactive under these conditions.[50] The changes are detectable from contact angle measurements (a decrease from 92° to 25°), XPS, ATR IR and salt formation. The carboxylic acid groups could be reduced by $LiAlH_4$ to benzylic alcohol units, and these were used to bind antibiotic molecules through an ester linkage.[49]

The alternative method for generating carboxylate surface groups begins with films cast from the ester polymer, $[NP(OC_6H_4COOC_3H_7)_2]_n$[50] (Scheme 3g). Exposure of these films to aqueous base at 50 or 80°C reduces the contact angle from 90° to 40°. The existence of carboxylic acid units was confirmed by the further decrease to 15° after conversion to the sodium carboxylate salt, and by XPS, SEM and ATR IR techniques. Reduction of the surface of the ester polymer by $LiAlH_4$ yielded benzylic alcohol units.

6.4 Dimethylsiloxane surface grafts

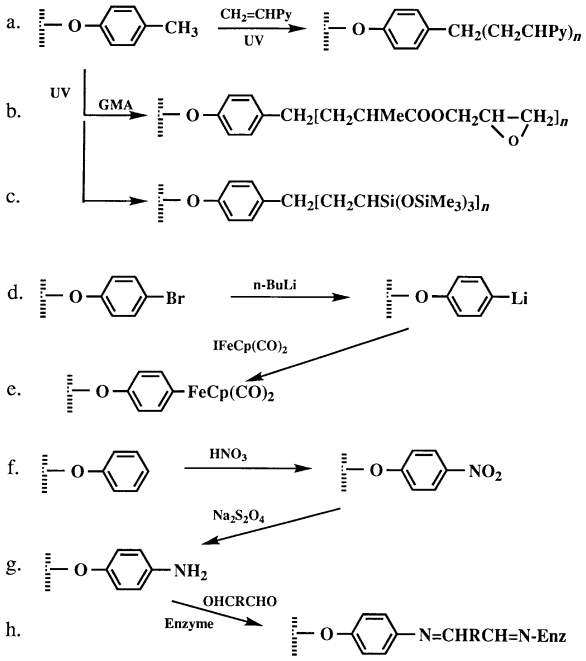
A number of hybrid phosphazene–siloxane polymer systems have been synthesized in our program. The most recent example involves the addition of silicon–hydrogen bonds across the double bond of pendant allyl groups at both the molecular and surface levels.[51] This surface reaction is illustrated in Scheme 3(i). In this process a solvent for the heptamethyltrisiloxane (hexane or 2-propanol) was chosen, which is also a non-solvent for the phosphazene. The depth of grafting varied from 25 to 60 μm depending on reaction conditions, but the efficiency of the silylation reaction under these conditions was only moderate.

6.5 Surface grafting of MEEP

The surface behavior of both organic and phosphazene polymers can be altered dramatically by the surface grafting of poly[bis(methoxyethoxyethoxy) phosphazene (MEEP).[52] MEEP is a water-soluble, water-stable polymer that is sensitive to γ-ray or ultraviolet crosslinking to form materials that swell in water to form hydrogels. The crosslinking mechanism is believed to involve aliphatic C–H and C–C homolytic cleavage, and free-radical cross-combination. If a film of MEEP is spread on the surface of a second polymer that contains surface aliphatic-C–H, C–C or C–halogen sites, free-radical grafting of MEEP to the substrate polymer will occur during irradiation. Exposure of the laminate to water results in swelling of the MEEP layer to form a hydrogel that is covalently bonded to the solid polymer beneath. The biomedical potential of such a system is quite high, since hydrogels are known to display high biocompatibility and to favor tissue overgrowth and adhesion.

6.6 Functional sites for metal coordination to surfaces

Several different surface chemistry reactions have been developed based on the polymer $[NP(OC_6H_4CH_3\text{-}p)_2]_n$ (Schemes 4a–c). For example, UV irradiation of this polymer in the presence of benzophenone (as a photosensitizer) generated free-radical sites at the methyl groups which initiated grafting and polymerization of vinylpyridine to give $[NP(OC_6H_4CH_3)OC_6H_4CH_2(CH_2CH\text{-pyridine})_x]_n$.[53] Films of this polymer bind metal carbonyls such as $Cr(CO)_5$, $(Mo(CO)_5$ and $W(CO)_5$ to the surfaces or within the bulk material. Surface



Scheme 4 Additional surface functionalization methods for polyphosphazenes. Py, pyridine; GMA, glycidyl methacrylate.

coordination of metal carbonyls offers a route to the fabrication of very thin conductive metallic films on a polymer surface.

A second approach to binding metallo species to the surface of polyphosphazenes is via aryl-lithium intermediates (Schemes 4d and 4e).[54] For example, films of $[NP(OC_6H_5Br)_2]_n$ were first crosslinked by -irradiation to reduce their ability to swell in organic solvents. Exposure of the films at $-78°C$ to n-butyl-lithium, followed by $CpFe(CO)_2I$ (Cp = cyclopentadienyl), yielded surface structures of the type $[NP(OC_6H_4FeCp(CO)_2)_x(OC_6H_4Br)_y]_n$. This demonstrates a way in which catalytic species can be immobilized on a polyphosphazene surface.

6.7 Protein binding to surface functional sites

The photolytic reactions of $[NP(OC_6H_4CH_3\text{-}p)_n$ have also been used to bind proteins to polyphosphazene surfaces.[53] Photo-grafting of glycidyl methacrylate gave $[NP(OC_6H_4CH_2(CH_2C(CH_3)\text{-}COOCH_2\text{-oxirane})_x)_2]_n$. The epoxide functionality was then employed to bind a number of amines to the surface of polymer films, including Protein A. The removal of immunoglobulin from phosphate buffer saline solutions and its release from the

surface in citrate buffer allowed this system to be evaluated as a device for controlling immunoglobulin concentrations in medical applications. The advantage in using polyphosphazenes for this type of synthesis is that the backbone is stable to the UV irradiation conditions needed for the grafting process.

Enzymes have been linked to polyphosphazene surfaces by another reaction sequence (Schemes 4f–h).[55] In this, poly(diphenoxyphosphazene), $[NP(OC_6H_5)_2]_n$, was first coated onto the surface of porous alumina particles, and then surface-nitrated. The nitro groups were reduced to the amine by dithionite, and the surface amino groups were then coupled to enzymes such as trypsin or glucose 6-phosphate dehydrogenase by means of glutaric dialdehyde. The immobilized enzyme particles were used in experimental continuous flow reactors. Immobilization considerably enhanced the useful lifetime of the enzymes.

6.8 Immobilized dopamine

Finally, although this is not specifically a surface synthesis, it was demonstrated earlier in our program[56] that diazo coupling reactions can be used to immobilize dopamine at the molecular level, and that the surfaces of films of this polymer interact with mammalian cell membrane receptors to elicit a biological response.

7 USES OF SURFACE-FUNCTIONALIZED POLYPHOSPHAZENES

The immobilization of biologically active molecules on polymer surfaces has obvious utility in medical sensors, biological separations and biotechnological processes. The formation of hydrophilic or hydrogel surfaces on hydrophobic polymers has broad implications for adhesion, for mammalian cell growth on artificial organs and in tissue engineering. Acidic groups on surfaces also open up opportunities for adhesion research, membrane design and the preparation of materials that resist bacterial or fungal colonization or which deter colonization by marine organisms.

Surface chemical modification is clearly a major aspect of modern materials science. Polymers such as polyphosphazenes that possess a stable inorganic backbone to which are attached organic side-groups provide access to the wide range of organic functionalization reactions. Moreover, when used as coatings on metals or ceramics they provide an effective connector between the totally inorganic materials and the diverse functionalities of modern organic chemistry. This promises to be true also for the formation of blends (alloys) formed between functionalized inorganic–organic polymers and totally inorganic or totally organic polymers. As the field of inorganic–organic polymers and materials continues to develop, the use of functionalized species may prove to be the most important aspect of all.

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