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Metal-Containing Poly(Organophosphazenes)

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Summary: In this paper we highlighted the general situation of metal containing poly(organophosphazenes) and we presented the status of the art in this area in terms of interactions between phosphazene materials and different types of metals. Possible practical utilization of the polymers obtained is also envisaged.

Keywords: biomaterials; catalysts; Inorganic polymers; ionic conductors; poly(organophosphazenes); transition metals

Introduction

In recent times, the need of new materials showing outstanding properties in different applicative domains stimulated considerable research efforts in the field of inorganic[1] and organometallic[2] polymers, with particular concern in the case of poly(organophosphazenes)[3,4] (POPs).

Starting from the original synthesis of these materials disclosed by H.R. Allcock[5,6] in the middle of the sixties, the interest on POPs is rapidly increased over the time. Both their scientific and industrial applications are of importance. Thus, poly(organophosphazenes) rouse interest as flame-retardant[7] and thermally stable[8] macromolecules, low-temperature elastomers[9], biomaterials[10,11], photosensitive and/or photoinert substrates[12], solid state electrolytes[13], variable types of hybrids[14,15], membranes[16], solid state fuel cells[17], optical- and electrooptical-polymers[18], etc.

This is the result of the impressive series of valuable features showed by poly(organophosphazenes) that are not common in the scientific scenery of polymeric materials[19], *i.e.* very high synthetic versatility[20], elevate skeletal flexibility[21], controlled degradation of the phosphazene polymer chain[10], remarkable thermal[8] and/or fire stability[7], optical transparency of the polymeric backbone[12], that allowed the preparation and the characterization of more than 700 different phosphazene macromolecules[22] suitable to find practical exploitation in different industrial and technological domains.

Among the different types of poly(organophosphazenes)[19], in this paper we will focus our attention on a specific class of polymers that deserves particular consideration in view of the interesting series of possible practical applications, *i.e.* polyphosphazenes containing metals or ions. The intrinsic interest of these substrates will be accounted for in terms of property/structure relationships.

Property/Structure Relationships in Metal-containing Poly(organophosphazenes)

Two main categories of phosphazene features will be examined in order to account for the reason why these materials have been used as chemical support for metallic species, *i.e.*:

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1) synthetic versatility[19], including chemical functionalization[23], and the possibility of forming of P-Metal chemical bonds[22]; and
2) skeletal peculiarities, such as backbone mobility[21], chain degradability[10] and metal coordination to skeletal nitrogens[24–28].

These two points will be examined in detail.

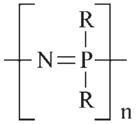
Synthetic Versatility

With the expression ''synthetic versatility'' is intended the possibility of synthesizing a great deal of poly(organophosphazenes) having different chemical structures by exploiting simple experimental procedures[19]. This can be seen easily by considering the basic structure of polyphosphazenes, as reported in Figure 1:

As formed by almost linear sequences of –P=N– monomeric units and substituent groups on the phosphorus, mostly (but not exclusively) formed by organic residues[4].

The versatility of the synthesis of these materials stands on the substitutive strategy used for their preparation[29]. This approach is described in Figure 2.

The Figure illustrates the general synthetic procedure adopted for the preparation of poly(organophosphazenes), based on the initial synthesis of poly(dichlorophosphazene) $(NPCl_2)_n$, by thermally-induced ring-opening polymerization process of hexachlorocyclophosphazene (H.R. Allcock, 1965[5,6]) and/or polycondensation reactions of dichlorophosphinoyliminotrichlorophosphorane (R.De Jaeger 1982[30]) or of trichlorotrimethylsilylphosphoranimine (I.Manners and H.R. Allcock, 1995[31]). Starting from this polymer, almost all the known poly(organophosphazenes) are prepared by nucleophilic substitution of the chlorine atoms with suitable nucleophiles, *e.g.* aliphatic[5,32,33] and aromatic[5,32,34] alcohols, aliphatic[6,35] and aromatic amines[36], alkyl or aryl groups[37,38], arylthiols[39], and dihydroxylated aromatic compounds[40], thus obtaining eight classes of phosphazene homopolymers[19].



$$\left[N{=}\overset{R}{\underset{R}{P}} \right]_n$$

Figure 1.

Looking at Figure 2, it appears quite clearly that the variation of the nucleophilic substituent to be reacted with poly(dichlorophosphazene) would automatically imply the property modification of the resulting macromolecules. This fact allows the preparation of POPs bearing substituent groups of different chemical structure, thus accounting for the high number[22] of polyphosphazenes known and the large diversity of their chemical and physical features.

Metal-containing phosphazene macromolecules could be obtained when the substituent groups attached to the phosphorus atoms of the polyphosphazene skeleton contain suitable coordination sites or functional groups that are able to interact with transition metals or ions. In fact, a series of coordinating substituents have been attached to poly(organophosphazenes), such as metallocenes[41–43], phosphines[44–48], arenes[49], pyridines[50–52], allyl derivatives[53], crown ethers[54–57], porphyrines[58,59], phthalocyanines[60], dicarboxylate ions[61–64], thio ethers[65], methylene carboranyl groups[45], 4-bromophenoxy groups[66] etc. which permit the synthesis of metal-containing phosphazene macromolecules, suitable to be used as electroconductive[60] and electroresponsive polymers[42,43,67], biomaterials[24,58,59,61–64,68,69], catalytic substrates[27,28,44,46,70,71], nonlinear optics materials[47], etc.. Furthermore, other types of substituents could be attached to the phosphazene skeleton able to interfere with ionic species in a weak way or to induce crosslinking processes in the presence of bi-valent salts, giving rise to polymeric electrolytes[13,19] or to biocompatible materials adapt to act as drug delivery systems[72–74] or as immunoadjuvants[75–77], respectively.

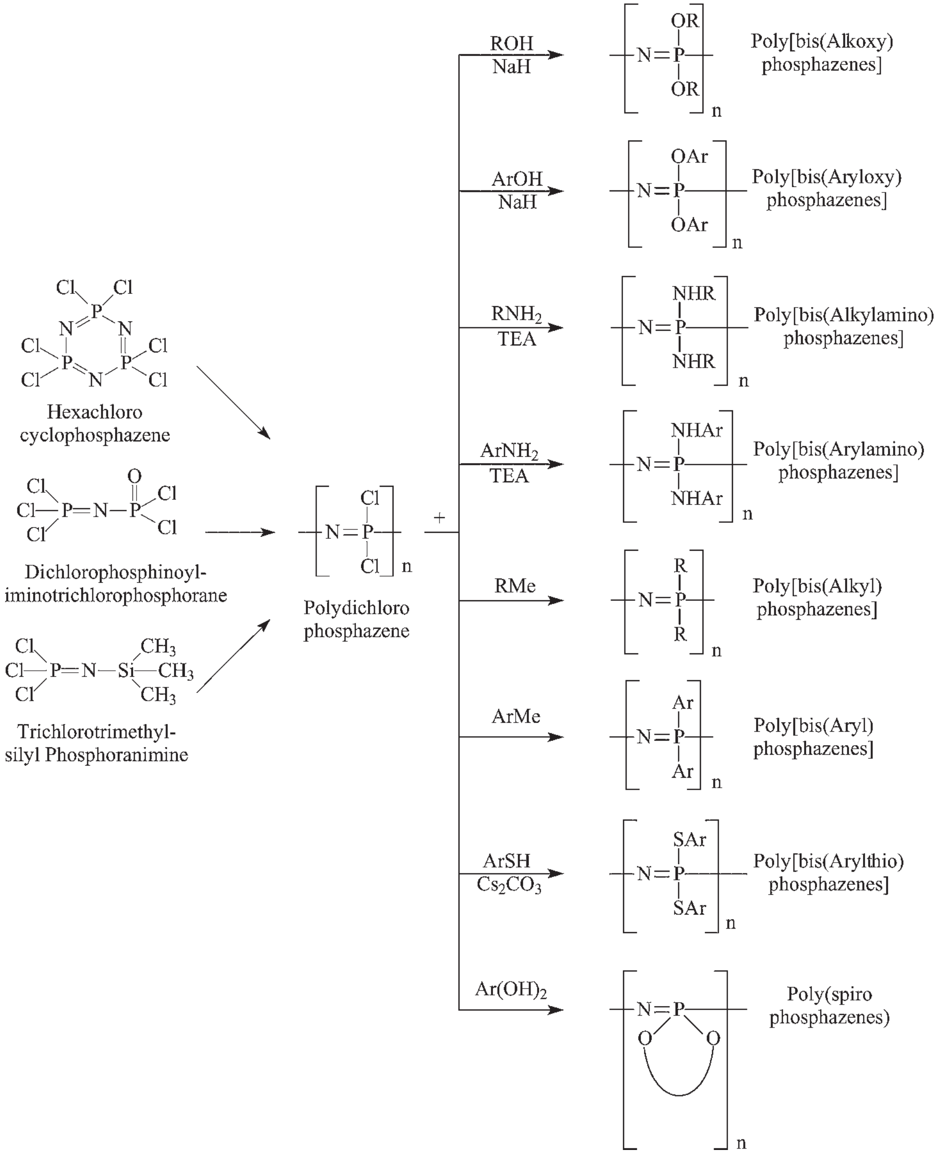


Figure 2.

Up to now, the formation of direct P-Metal bonds on poly(organophosphazenes) could not be achieved and is limited only to the level of cyclophosphazenes[22].

Skeletal Characteristics of POPs.

Phosphazene skeleton is an interesting constituent of poly(organophosphazene) substrates that plays a very important role in determining the final properties of these materials.

–P=N– backbone, in fact, is very flexible[9], with reduced torsional energy barriers[78], in a way that polyphosphazenes show fairly low glass transition temperatures[79] (T_g values below −50 °C up to −105 °C are relatively common) and pronounced elastomeric properties[9]. As a consequence, polymers of this class bearing very flexible and mobile phosphorus substituents are expected to be amorphous materials, particularly suitable to be used for solid state ionic electric conductivity[13].

Furthermore, polyphosphazene chain exhibits an extraordinary versatile behavior in dependence of the nature of the substituent groups attached to the phosphorus atoms[20]. Functional substituents such as aryloxy-[5,34], fluoroalkoxy-[9], polyethyleneoxide-[80], aliphatic[6,35] or aromatic[36] amino- derivatives, etc, provide considerable chemical and hydrolytic stability to the polyphosphazene substrates, while nucleophiles such as simple aminoacids (*e.g.* glycine[81,82], alanine[81,83], etc.) or imidazole[84] are able to induce skeletal instability in the presence of water which brings about controlled polymer degradation and the delivery of phosphate and ammonia species as degradative products of the skeleton[3]. This makes polyphosphazenes very attractive, biocompatible, and bioerodible materials suitable to be used for the controlled delivery of drugs and of molecules of biological interest[10].

Finally, another important feature of the polyphosphazene skeleton is the unusual high basicity of the skeletal nitrogens, as measured by R.A.Shaw[85] for cyclophosphazene substrates between 1960 and 1980, that could be used successively for chain protonation reactions[25,86,87], coordination of metals[24] or reaction with Lewis acid molecules[88–90]. These aspects of the polyphosphazene chain behavior have important implications as far as the possibility of depositing Ru, Pd, Rh, and Pt metal nanoparticles on poly(organophosphazenes) for catalysis[28] is concerned.

Metal-Poly(organophosphazene) Interactions

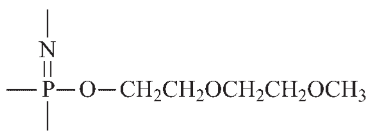
Interactions between poly(organophosphazenes) and metals or ions have been investigated over the time for several different phosphazene polymers and a variety of metals. For the sake of clarity in this paper we will classify different topics according to the metal sequence of the Periodic Table of Elements. Only the most important research concerning phosphazene and metals will be highlighted in this article, without pretending to be exhaustive.

Group-1. Lithium

Lithium salts have been investigated in combination with poly(organophosphazenes) especially for the preparation of ionic conductive polymeric materials[13].

This topic was originated by a paper published by H.R.Allcock in 1984[91] concerning the synthesis of poly[bis(methoxy-ethoxy-ethoxy)phosphazene], MEEP, (Figure 3) by reaction of poly(dichlorophosphazene) with the sodium salt of methoxy-ethoxy-ethanol. MEEP is an amorphous macromolecule[91], with a very low T_g (−83.5 °C), which bears Lewis Base sites in the side ethyleneoxide phosphorus substituents. Furthermore, this polymer is able to weakly coordinate Li^+ (and Ag^+) salts giving rise to homogeneous polymer salt complexes able to conduct electricity in an ionic way[92]. This electric conductivity[91] was found to be about 10^{-5} Scm^{-1}, *i.e.* a value that is two-three orders of magnitude higher than that measured for poly(ethylene oxide)-Li^+ complexes[13].

A variety of synthetic and functionalization strategies have been put forward over the time to improve mechanical and conductive performances of this polymer. Thus, the crosslinking of MEEP[93–99], together with its implication in blending[100,101] and in sol-gel[15] processes have been explored to enhance the dimensional stability of the macromolecule without depressing ionic conductivity. Moreover, different ethyleneoxide-containing alcohols of linear[102] or branched[103] structure



$$-\overset{\overset{|}{N}}{\overset{\|}{\underset{|}{P}}}-O-CH_2CH_2OCH_2CH_2OCH_3$$

Figure 3.

(see Figure 4) and free hydroxyl group-containing crown ethers[54–57] of different dimensions (Figure 5), have been exploited for the same purpose.

The products obtained showed an enhanced dimensional stability in the case of branched ethyleneoxide derivatives[103–105] without the need of reticulating the polymers, together with a conductivity which is one order of magnitude higher than that of MEEP[104]. At the same time, polyphosphazenes containing crown-ether residues exhibited a very poor conductivity, possibly due to the capture and immobilization of the alkaline ions inside the crown structure[57].

The mechanism of the ionic conductivity of these polyphosphazenes with lithium ions (and in same cases also of Ag^+ ions) was assigned to the weak coordination of the ionic species onto the Lewis Base sites of these materials[19,103–107] with the contribution of ion coordination on the nitrogen atoms[98,108,109] of the polyphosphazene skeleton.

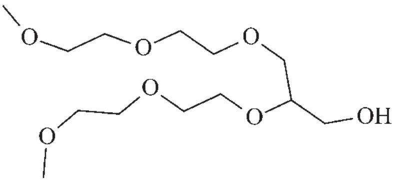


Figure 4.

Group-2. Calcium

The interaction between Ca^{2+} ions and poly(organophosphazenes) was explored in detail in the case of poly[bis(4-carboxylatophenoxy)phosphazenes], PBCPP, with the aim of preparing biocompatible hydrogels[72] suitable for trapping and successively delivering molecules of biomedical interest. PBCPP is a phosphazene polymer insoluble in acid or in neutral water but soluble in alkaline solutions[72,73]. When treated with bi- or tri- valent ions, such as Ca^{2+}, Cu^{2+} or Al^{3+}, the alkaline solutions of this macromolecule are able to reticulate forming soft, highly swollen hydrogels[72,74,110] according to the reaction mechanism reported in Figure 6.

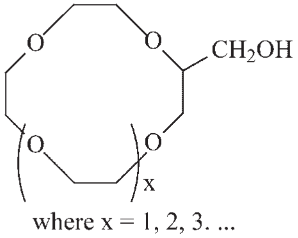


Figure 5.

Interestingly, the crosslinking process could be very easily reversed by simple contact with physiological solutions of NaCl, thus bringing back the polymer to its original form. This very simple reaction sequence stimulated a great deal of research on the utilization of PBCPP to microencapsulate[73,111–113] substrates of biological interest (*e.g.* proteins[73,74,110,112,114], cells[111] or antigens[75,115]), under very mild experimental conditions that are able to preserve the biological activity of the trapped species. At the same time, these species could be released[74,75,110,112,115] as soon as the gel is in the presence of NaCl solution. Additional attractive characteristics of phosphazene materials of this class are as immunoadjuvants[75,76] for antigens.

Group-6. Chromium, Tungstenum

Chromium

Chromium carbonyl complexes were coordinated to poly(organophosphazenes) using three different ligands, *i.e.* 2-phenoxyethoxy[49], pyridine[50], and cyano[116] groups.

Poly[bis(2-phenoxyethoxy-chromium-tricarbony)phosphazene] was prepared by

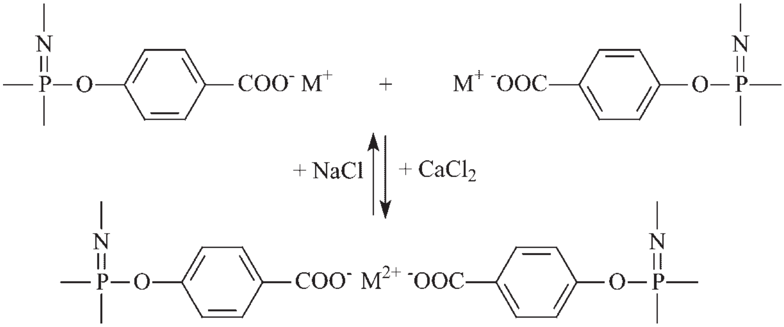


Figure 6.

reacting poly(dichlorophosphazene) with (η^6-2-phenoxyethoxy)-chromium tricarbonyl substrates[49] according to the reaction scheme reported in Figure 7:

The polymer obtained is a yellow macromolecule that turned to a green product upon standing, possibly due to the oxidation of the chromium (0) to chromium(III) derivatives. It was a sparingly soluble material, with a solubility which turned into insolubility, probably due to side group stacking phenomena in solid state with generation of microcrystalline domains of reduced solubility. It showed a T_g of +43 °C, which is much higher compared to that of the analogous polymer without chromium complexes (–8 °C), due to the chain rigidity introduced in the polymer skeleton by the chromium tricarbonyl complexes. Upon heating, it produces 40% of solid residue at 800 °C (by thermogravimetry) due to the incorporation in the solid material of chromium-containing species.

The second approach to coordinate chromium onto poly(organophosphazenes) was based on the exploitation of grafting reactions of bifunctional unsaturated monomers onto selected poly(organophosphazenes). Thus, the light-induced grafting reaction of 4-vinylpyridine onto poly[bis(4-methylphenoxy)phosphazene] in solid film could be achieved by irradiating benzophenone photoinitiator[50] in the presence of the monomer to produce poly[bis(4-methylphenoxy)phosphazene]-*g*-poly(4-vinylpyridine), PBMPP-*g*-P4VP copolymer. Chromium could be linked to these materials as $Cr(CO)_5$ complexes on the pyridine ligands, possibly for catalytic purposes. For the polymer obtained a T_g increase could be observed due to the enhanced stiffness of the phosphazene chain.

Finally, the incorporation of chromium pentacarbonyl complexes in phosphazene copolymers substituted with 2,2′-dihydroxybiphenyl (80%) and with 4-hydroxybenzylcyanide (20%) was achieved by C.Diaz[116] who succeeded in the preparation of an insoluble, green-colored poly (metalla phosphazene) having the structure reported in Figure 8 containing a loading of 14% in chromium complex.

The polymer showed an electric conductivity σ of 1.2×10^{-11} Scm^{-1}, a T_g value of 140 °C and almost 50% of solid residual material when heated at 800 °C.

Tungsten

Tungsten pentacarbonyl compounds $W(CO)_5$ attached to a phosphazene poly-

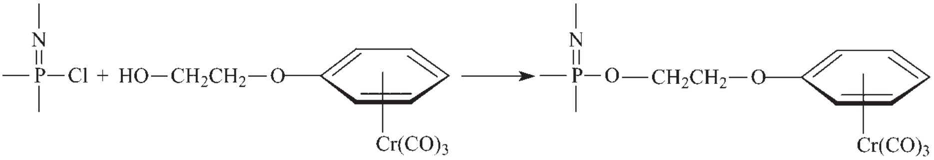


Figure 7.

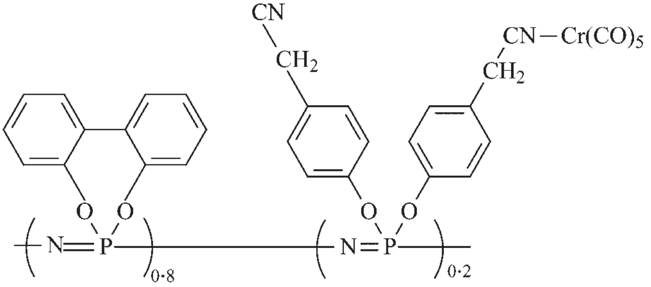


Figure 8.

mer were obtained by reacting a partially substituted polydichlorophosphazene with 2,2′-dihydroxybiphenyl (65%) with 4-hydroxytriphenylphosphine already complexed with the tungsten carbonyl complex $\{W(CO)_5[PPh_2(C_6H_4\text{–}OH)]\}$[47]. The phosphazene copolymer obtained has the structure shown in Figure 9:

The polymer obtained was fully characterized by conventional techniques.

Moreover, tungsten pentacarbonyl $W(CO)_5$ complexes with pyridine-functionalized polyphosphazenes could be obtained by Carriedo[51] by preparing a spirophosphazene copolymer containing 70% of 2,2′-dihydroxybiphenyl substituents and 30% of 4-hydroxy-pyridine ligands, and reacting it with $[W(OHMe)(CO)_5]$. The final material has the following structure (see Figure 10):

For this polymer no T_g could be detected in the range of −50 up to 250 °C. In addition the materials showed low thermal stability, starting decomposition at 75 °C, with a very high (70.8%) solid residue above 800 °C. A certain instability of the complex ligand was also measured with decrease in the metal content in the polymer over the time.

Group-7. Manganese

Manganese complexes were attached to polyphosphazene materials using three different types of ligands, *i.e.* phosphines[44,48], 4-cyanophenoxy[117] and 4-methylenecyanophenoxy[118] groups.

Thus, H.R.Allcock[44] succeeded in complexing $Mn(CO)_2(\eta^5\text{-}C_5H_5)THF$ with a phosphazene copolymer containing free pending phosphine groups, followed by G.A.Carriedo[48] who reacted $\{Mn(CO)_2(\eta^5\text{-}C_5H_4Me)[PPh_2(C_6H_4\text{–}OH)]\}$ with poly (dichlorophosphazene) partially substituted with 2,2′-dihydroxy-biphenyl substituents. The structures of the final polymers obtained are reported in Figure 11.

Polymer "A" showed tendency to crosslink[44] at room temperature, while polymer "B" exhibited a high T_g (+128 °C), moderate thermal stability[48] and the formation of 41% of solid residue at 800 °C.

Successive work in the area was carried out by G.A.Carriedo[117] and by C.Diaz[118]

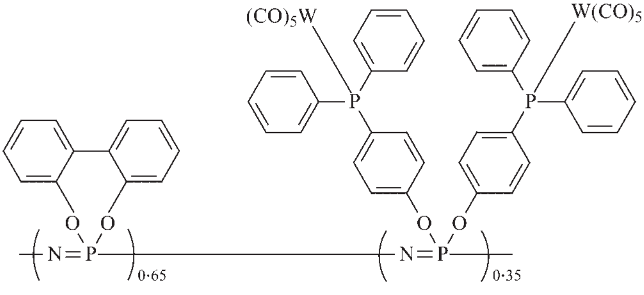


Figure 9.

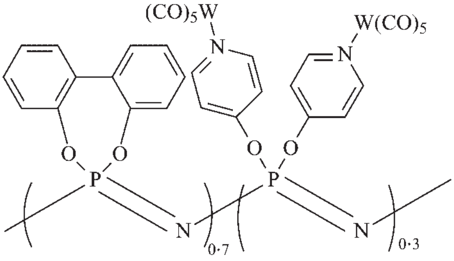


Figure 10.

who experienced the utilization of different cyano ligands to attach manganese complexes to polyphosphazenes. In fact, the reaction of *trans*-[BrMn(CO_2)(dppm)-{P(OPh_3)}] in the presence of Tl[PF_6] or of [(O_3ClO)Mn$(CO)_3$(dppe)] with a phosphazene copolymer containing variable amount of 4-cyanophenoxy moieties leads to the preparation of macromolecules having the structure shown in Figure 12 while the utilization of methylene cyanophenoxy phosphazene copolymers in combination with $HOC_6H_4CH_2CN$–$Mn(CO)_2(\eta^5\text{-}C_5H_4CH_3)$ produces the polymer of Figure 13

The materials have been characterized by usual techniques and their conductivity and thermal characteristics investigated.

Group-8. Iron, Ruthenium

Iron

The first class of iron-containing phosphazene materials developed deals with polymers of biological interest bearing imidazolyl groups as carrier molecules for Iron(II) and Iron(III) porphyrins[58,59], and with the investigation of the behavior of these materials in the presence of molecular

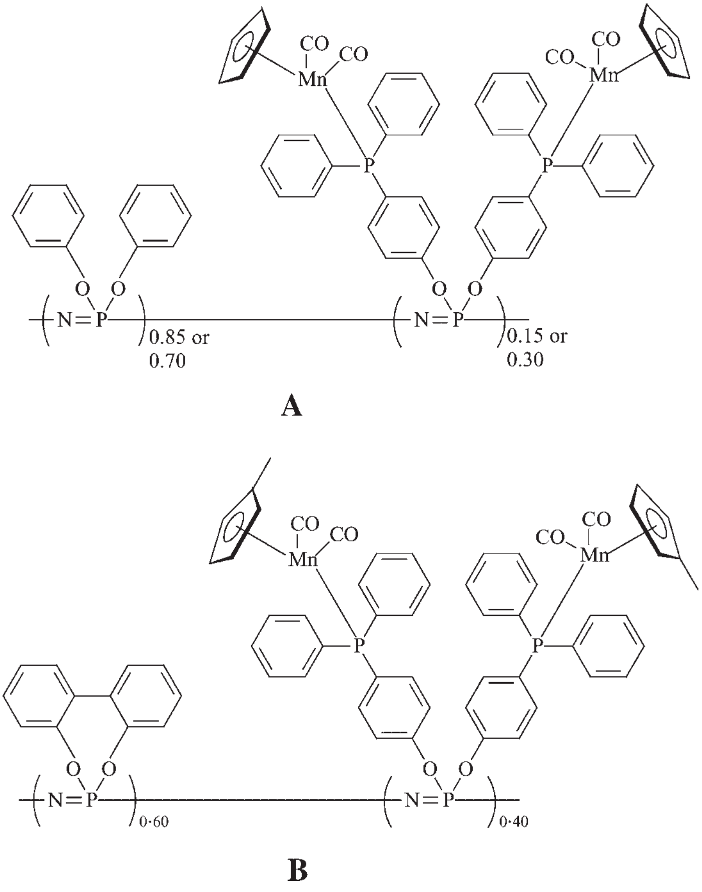


Figure 11.

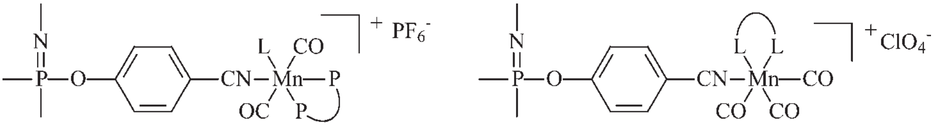


Figure 12.

oxygen and carbon monoxide both in solution and in solid state. The polymers have the structure shown in Figure 14 where the ellipse represents heme or hemine units. The principal aim of this research was to provide insight in the transport mechanism of molecular oxygen in living systems and to find possible hemoglobin substitutes.

This research was followed by the preparation of iron-containing polymers through functionalization of polyphosphazenes containing 4-bromophenoxy moieties[66,119], both in solution and in solid state. The covalent attachment through iron-carbon σ bonds of organo-iron compounds to aryloxy-substituted polyphosphazenes occurs according to the mechanism described in Figure 15 which implies the preliminary lithiation of the 4-bromophenoxy moieties of the polyphosphazenes to form lithiophenoxy derivatives, followed by reaction with cyclopentadienyliron dicarbonyl group. The resulting polymers were found to be paramagnetic in solid state, with a T_g of 41 °C (the pristine poly[bis(4-bromophenoxy)phosphazene] has a T_g of 10 °C), and able to form a higher solid residue at 900° (43% vs 10% of the original macromolecule) by TGA. Potential interest for these materials are in catalysis, electroresponsivity, and magnetism.

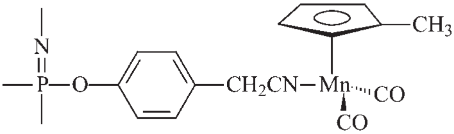


Figure 13.

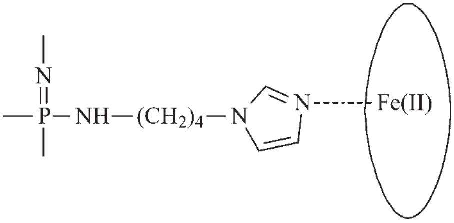
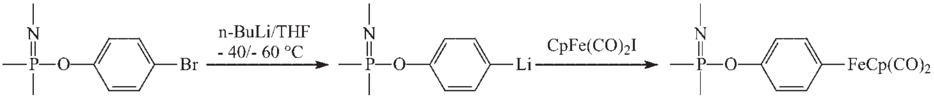


Figure 14.

Additional advances in the preparation of iron-containing poly(organophosphazenes) deal with the synthesis of polymers functionalized with ferrocenyl groups. The materials could be prepared principally by two different strategies, *i.e.* by thermally-induced ring-opening polymerization of cyclophosphazenes already containing ferrocenyl derivatives (H.R.Allcock[120–122], polymers "C" and "D") or by chemical modification of pre-synthesized poly(methyl/phenyl)phosphazene (P.Wisain-Neilson[41,42], polymer "E"). The resulting structures are reported in Figure 16:

The polymers prepared showed electroresponsivity due to the presence in their chemical structure of the ferrocenyl substituents, enhanced T_g values and dramatic changed in solubility.

Research on iron-containing poly(organophosphazenes) has been carried out also involving phosphazene polymers functionalized with phosphine ligands. Thus,



where: Cp stands for cyclopentadienyl

Figure 15.

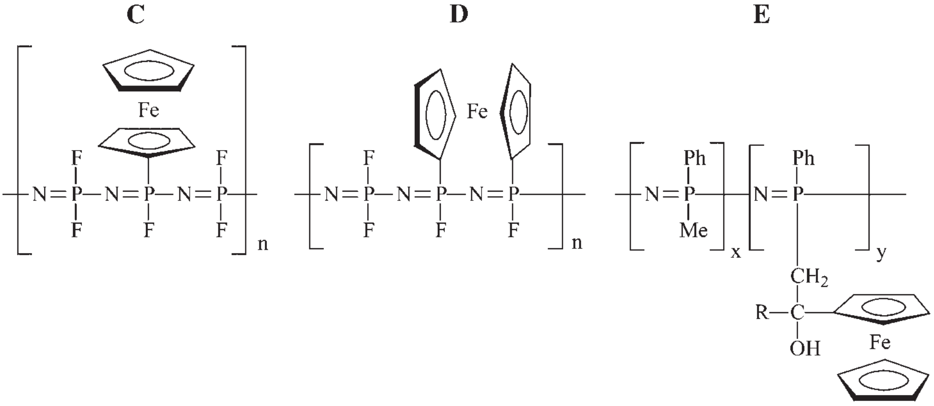


Figure 16.

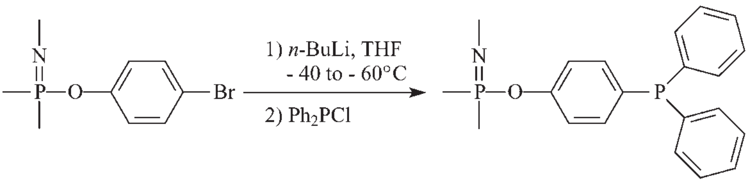


Figure 17.

phosphine-functionalized polyphosphazenes could be obtained by lithiation of 4-bromophenoxy substituted polyphosphazenes followed by the reaction of the lithium derivative with chlorodiphenylphoshine[119] (Figure 17)

The successive reaction of these materials with $Fe(CO)_3[PhCH{=}CHC(O)CH_3]$[44] formed polymers that are initially soluble, but immediately evolved to the crosslinked species. The interest on these iron complexes supported on polyphosphazenes is basically in catalysis.

More recent research on iron-containing poly(organophosphazenes) concerns phosphazene polymers functionalized with two different ligands both of them containing cyano groups[123,124]. According to Carriedo[123], in fact, the reaction of phosphazene copolymers substituted with phenoxy and 4-cyanophenoxy groups with iron cyclopentadienyl diphosphine complex $[Fe(CH_3CN)(dppe)Cp][PF_6]$ formed the phosphazene material of Figure 18

On the contrary, the reaction between 4-methylenecyanophenoxy polyphosphazenes (Figure 19) with cyclopentadienyl-bis(diphenylphosphino)ethane-iron complex led to the formation of reticulated materials possibly due to the deprotonation reaction of the methylene group of the bis(diphenylphosphino)ethane ligand[124].

Ruthenium

Ruthenium complexes have been exploited by H.R.Allcock in the middle of eighties[43,120] as ruthenocenyl compounds supported on cyclophosphazene derivatives,

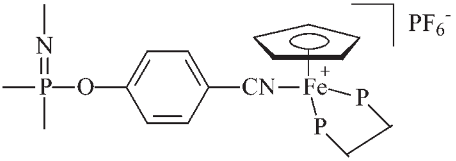


Figure 18.

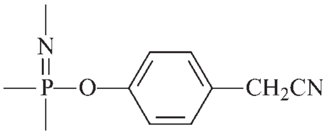


Figure 19.

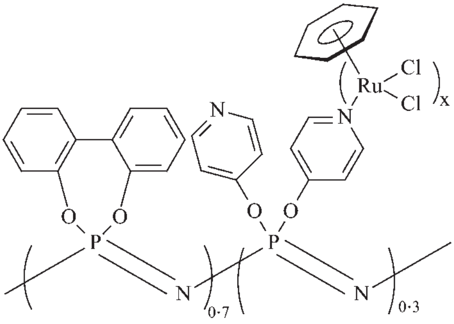


Figure 20.

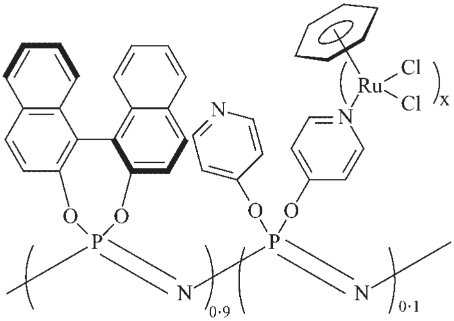


Figure 21.

that have been successively polymerized by thermally-induced ring-opening polymerization processes. This argument has been already treated in the case of ferrocenyl complexes reported above (*vide supra*).

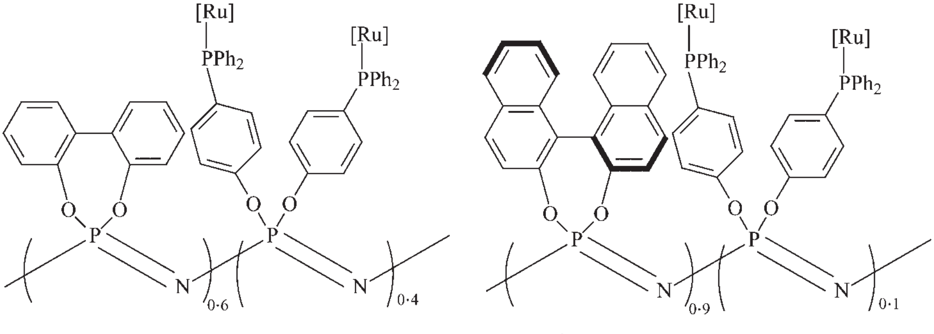
Moreover, the coordination of Ru(II) (η^6-*p*-cymene) complexes have been investigated by Carriedo[52] for the coordination on pyridine-functionalized spirophosphazene copolymers, to obtain a material having the chemical structure described in Figure 20

In this material the Ru(II)(η^6-*p*-cymene) is inserted in an achiral polymer. Following the same strategy, however, it could be possible to insert the same Ru(II) complex in a chiral phosphazene copolymer bearing (R)-2,2′-dioxy-1,1′-binaphthyl units. The structure of the resulting materials is reported in Figure 21

When this reaction is carried out in acetone the crosslinking reaction of the polymer takes place with formation of a reticulated material in which a chlorine atom in the coordinative sphere of the ruthenium complex is replaced by the pyridine ligand belonging to another phosphazene chain. The potential interest of this new substrate stands on the observation that the Ru(II) complex is inserted in a rigid, crosslinked and chiral structure, thus showing potential application for enantiomeric catalysis.

Extending this approach to phosphine ligands, G.A. Carriedo[71] recently reported the synthesis of triphenylphosphine-containing spirophosphazene copolymers partially substituted with 2,2′-dihydroxybiphenyl and with (R)-2,2′-dioxy-binaphthyl residues, respectively, having the following structure (Figure 22) bearing Ru(II) complexes. A crosslinked form of the chiral polymer was also prepared.

These materials were tested for catalytic activity and enantioselectivity by investigating the reduction reaction of acetophenone by isopropanol, because of the



where [Ru] stands for $RuCl_2(\eta^6$-*p*-cymene)

Figure 22.

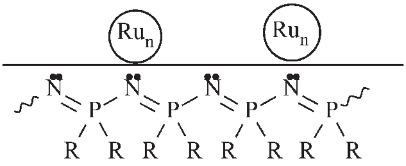


Figure 23.

possibility of orienting the steric selectivity of this reaction by inserting the catalyzing complexes inside "chiral pockets" along the polyphosphazene chain. Unfortunately, no enantiomeric excess of the reaction products could be detected in spite of the high conversion reached of acetophenone to the corresponding alcohol.

Finally it was recently reported by Pertici and Vitulli[27,28] that ruthenium nanoparticles homogeneously distributed on the surface of poly(dimethylphosphazene) and of a variety of other aryloxy-substituted polyphosphazenes (see Figure 23), have been exploited as hydrogenation catalysts for unsaturated compounds, such as olefins, carbonyls and aromatic compounds. The nanoparticles have been prepared by hydrogen-induced decomposition of the Ru(η^6-cycloocta-1,3,5-triene)(η^4-cycloocta-1,5-diene) complex in the presence of poly(dimethylphosphazene) (PDMP) and of other different aryloxy-substituted phosphazene homopolymers.

Group-9: Rhodium

Similarly to the procedure already illustrated in the case of ruthenium catalysts (*vide supra*), rhodium nanoaggregates have been deposited on polyphosphazene materials in an homogeneous way through Metal Vapor Synthesis (MVS) technique, to form catalysts that are valuable for the selective hydrogenation of α,β-unsaturated aldehydes and ketones to the corresponding saturated carbonyl derivatives[28,125]. Thus the catalyzed hydrogenation of cinnamaldehyde as test reagent for this kind of reactions was investigated, as reported in Figure 24 The reaction proceeds efficiently with a chemoselectivity toward the reduction of the cinnamaldehyde insaturation of the 91%. Interestingly, it is possible to operate in heterogeneous phase (toluene, THF) as well as in homogeneous phase (alcohol) depending on the solubility of polyphosphazene in the dispersing liquid. In the case of homogeneous catalysis, the reaction is fast and the catalytic system can be recovered by precipitation with a non-solvent (pentane, diethylether) and reused without loss of activity.

Group-10. Palladium, Platinum

Palladium

This research has been carried out with the aim of modifying the physical properties of a phosphazene elastomer of the following structure (Figure 25) through palladium-induced intermolecular complexation at the allyl residue present in the phenoxy phosphazene substituents[53]. These species, although present in very low percentage (5% mol), are sufficient to induce the crosslinking of the phosphazene copolymers in the presence of bis(acetonitrile)dichloropalladium(ii), forming complexes whose structure is represented in Figure 26.

The resulting polymers show elastic modulus and T_g that increase with the increase in the content of Pd(II) complex in the phosphazene matrix, as proved by stress-stain and DSC tests, respectively. As expected, the solubility of the materials obtained was also drastically changed.

Palladium nanoparticles[28,125] dispersed on polydimethylphosphazene, obtained as described above in the case of rhodium derivatives (*vide supra*), have been exploited in the vinylation reaction of aryl halides (Heck Reaction). Thus iodobenzene has been reacted with methylacrylate

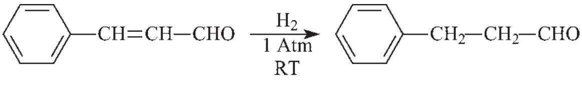


Figure 24.

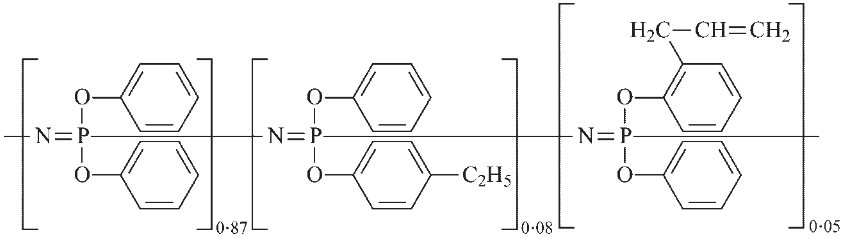


Figure 25.

in N-methylpyrrolidone (NMP) to obtain *trans*-methylcinnamate, according to the following reaction sequence (see Figure 27)

The conversion obtained for this reaction is quantitative in 5 hours. As the poly(dimethylphosphazene) dissolves in the solvent used for the catalytic process, palladium nanoparticles substantially operate in homogeneous solution. The catalyst can be recovered by precipitation with a non-solvent (diethylether, THF) and reused with the same catalytic activity. No leaching of palladium was observed. This catalyst was found to be considerably more active than homogeneous and heterogeneous commercially available palladium catalysts.

Platinum

The first attempt of synthesizing platinum-containing anticancer agents based on polyphosphazenes was carried out by H.R.Allcock in the middle of seventies[24,68], by supporting $PtCl_2$ units onto poly[bis(methylamino)phosphazene]. For these species, the coordination of the platinum salt at the skeletal nitrogens could be demonstrated. For the product obtained the structure proposed is reported in Figure 28.

For this compound a noticeable anticancer activity was detected in initial screening tests.

Additional platinum-containing polyphosphazene anticancers were prepared in more recent time by Korean scientists, using dicarboxylate side groups attached to the polyphosphazene skeleton[61–63,69,126].

For the synthesis of these materials was used a low molecular weight poly(dichlorophosphazene) ($M_w = 10^4$ dalton) substituted with hydrolyzed ethylglycinate or

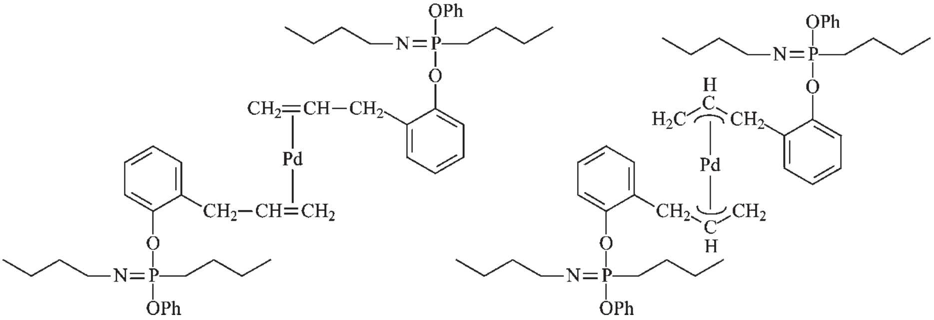


Figure 26.

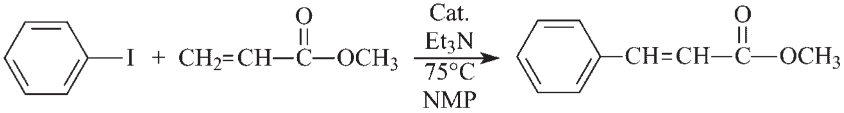


Figure 27.

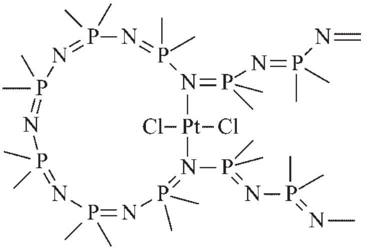


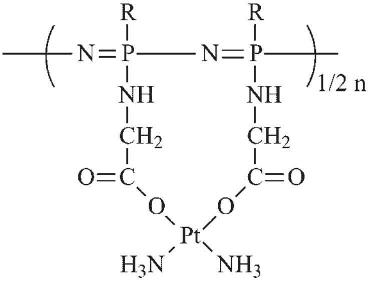
Figure 28.

glycinemethylamido derivatives, in combination with diamine platinum(II) iodide complex[61]. The resulting materials are showed in Figure 29 This research has been successively extended to polyphosphazenes having the general structure of Figure 30, containing one Pt(II) anticancer complex[62–64], a new anticancer substrate (*i.e.* doxorubicin[126]), or both of them coupled in the same polymeric structure[69]. OH, OCH_3, $NHCH_3$, $N(CH_3)_2$[62] or poly(ethylene oxide)[64] residues have been used as solubilizing groups. Dicarboxylate spacers based on glutamate and/or aspartate[62–64,126] substituents could be exploited. *β*-Galactosyl liver targeting groups[63,126] have been also inserted in the phosphazene anticancer materials.

As far as the catalytic activity of platinum is concerned, the activity of Pt nanoparticles dispersed on PDMP has been exploited in the catalytic reduction of cinnamaldehyde[28,125] as reported above in the case of rhodium catalysts (*vide supra*). Differently from Rh/PDMP catalyst, however, which reduces cinnamaldehyde mostly to the corresponding 3-phenylpropanal (*vide supra*), the Pt/PDMP system hydrogenates prevalently the carbonyl group, leading to the unsaturated *trans*-cinnamyl alcohol in high yield (chemoselectivity = 96%), according to the reaction of Figure 31,

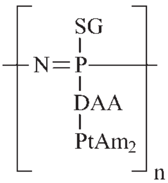
with an activity and a selectivity much higher than that of commercial catalysts.

As observed for Rh/PDMP catalyst, also in this case it is possible to operate in heterogeneous (toluene, THF) as well as in homogeneous phase (alcohol). In this last



where R can be:
1) $NH-CH_2-COOH$; or
2) $NH-CH_2-CONHCH_3$ or
3) $NHCH_3$

Figure 29.



where: SG stands for a Solubilizing Group
DAA stands for Di-Carboxylic Amino Acid Groups
Am stands fo Diamines

Figure 30.

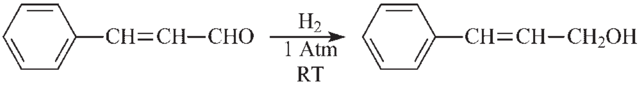


Figure 31.

case, the reaction is very fast and the catalytic system can be easily recuperated by precipitation in pentane or diethylether and reused. No loss of activity was observed after this treatment.

Conclusions

In this paper we highlighted the interactions that can take place between phosphazene polymers and copolymers and metallic atoms. Thus the formation of direct phosphorus-metal linkages could not be achieved at polymeric level, this kind of interaction being demonstrated only for cyclophosphazene substrates. The formation of transition metal complexes between side phosphorus substituents in polyphosphazenes and suitable metals could be obtained using a variety of different coordinating sites on the polyphosphazene substituent groups and exploiting different metals. Furthermore, interactions between ionic species and side phosphorus substituents in polyphosphazenes have also been explored. Eventually, it could be demonstrated the possibility of direct coordination of transition metal complexes to the skeletal nitrogens of the polyphosphazene skeleton. A series of examples of polyphosphazene/metal complexes have been described, together with their potential utilization as catalysts, electroresponsive substrates, biomaterials, etc., without pretending to be exhaustive.

[1] R. D. Archer *Inorganic and Organometallic Polymers*; Wiley-VCH: New York, 2001.

[2] *Macromolecule-Metal Complexes*; F. Ciardelli; E. Tsuchida; D. Wöhrle, Eds.; Springer: Berlin, 1996.

[3] H. R. Allcock *Chemistry and Applications of Polyphosphazenes*; Wiley: Hoboken, N.J., 2003.

[4] *Phosphazenes. A Worldwide Insight*; M. Gleria; R. De Jaeger, Eds.; NOVA Science Publishers: Hauppauge, 2004.

[5] H. R. Allcock; R. L. Kugel; K. J. Valan, *Inorg. Chem.* **1966**, *5*, 1709.

[6] H. R. Allcock; R. L. Kugel, *Inorg. Chem.* **1966**, *5*, 1716.

[7] C. W. Allen; D. Hernandez-Rubio in reference 4, 2004; Chapt. 20, p 485.

[8] J. P. Critchley; G. J. Knight; M. M. Wright *Heat-Resistant Polymers*; Plenum Press: New York, 1983, Chapt. 8, p 389.

[9] M. Gleria; R. Bertani; R. De Jaeger, *J. Inorg. Organomet. Polym.* **2004**, *14*, 1.

[10] M. Heyde; E. Schacht in reference 4, 2004; Chapt. 15, p 367.

[11] L. Gettleman in reference 4, 2004; Chapt. 16, p 399.

[12] M. Gleria; P. Bortolus; F. Minto in reference 4, 2004; Chapt. 17, p 415.

[13] K. Inoue in reference 4, 2004; Chapt. 22, p 535.

[14] H. R. Allcock; S. E. Kuharcik, *J. Inorg. Organomet. Polym.* **1995**, *5*, 307 and **1996**, *6*, 1.

[15] G. Brusatin; M. Gleria; S. Dirè; G. Facchin; M. Guglielmi in reference 4, 2004; Chapt. 19, p 467.

[16] G. Golemme; E. Drioli in reference 4, 2004; Chapt. 23, p 555.

[17] P. N. Pintauro; R. Wycisk in reference 4, 2004; Chapt. 25, p 591.

[18] H. R. Allcock in reference 3, 2003, Chapt. 18, p 633.

[19] M. Gleria; R. De Jaeger, *Top. Curr. Chem.* **2005**, *250*, 165.

[20] R. De Jaeger; M. Gleria, *Prog. Polym. Sci.* **1998**, *23*, 179.

[21] H. R. Allcock, *Contemp. Top. Polym. Chem.* **1979**, *3*, 55.

[22] H. R. Allcock in reference 4, 2004; Chapt. 1, p 1.

[23] M. Gleria; F. Minto; R. Bertani; G. Facchin; E. Tondello, *Gazz. Chim. Ital.* **1997**, *127*, 343.

[24] H. R. Allcock; R. W. Allen; J. P. O'Brien, *J. Am. Chem. Soc.* **1977**, *99*, 3984.

[25] P. Wisian-Neilson; F. J. Garcia-Alonso, *Macromolecules* **1993**, *26*, 7156.

[26] A. J. Hill; T. J. Bastow; P. Meakin; T. W. Turney; M. Hoang; N. Scalera; P. Pertici; G. Vitulli, *Desalination* **2002**, *144*, 61.

[27] A. Spitaleri; P. Pertici; N. Scalera; G. Vitulli; M. Hoang; T. W. Turney; M. Gleria, *Inorg. Chim. Acta* **2003**, *352*, 61.

[28] P. Pertici; G. Vitulli; P. Salvadori; E. Pitzalis; M. Gleria in reference 4, 2004; Chapt. 26, p 621.

[29] H. R. Allcock *Phosphorus-Nitrogen Compounds. Cyclic, Linear, and High Polymeric Systems*; Academic Press: New York, USA, 1972.

[30] R. De Jaeger; P. P. in reference 4, 2004; Chapt. 2, p 25.

[31] H. R. Allcock in reference 4, 2004; Chapt. 3, p 49.

[32] H. R. Allcock; R. L. Kugel, *J. Am. Chem. Soc.* **1965**, *87*, 4216.

[33] H. R. Allcock; M. S. Connolly; J. T. Sisko; S. Al-Shali, *Macromolecules* **1988**, *21*, 323.

[34] R. E. Singler; G. L. Hagnauer; N. S. Schneider; B. R. LaLiberte; R. E. Sacher; R. W. Matton, *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 433.

[35] H. R. Allcock; W. J. Cook; D. P. Mark, *Inorg. Chem.* **1972**, *11*, 2584.

[36] J. E. White; R. E. Singler; S. A. Leone, *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2531.

[37] H. R. Allcock; J. L. Desorcie; G. H. Riding, *Polyhedron* **1987**, *6*, 119.

[38] P. Wisian-Neilson in reference 4, 2004; Chapt. 5, p 109.

[39] G. A. Carriedo; J. Jimenez; P. Gomez-Elipe; F. J. G. Alonso, *Macromol. Rapid Commun.* **2001**, *22*, 444.

[40] G. A. Carriedo; F. J. Garcia Alonso in reference 4, 2004; Chapt. 8, p 171.

[41] P. Wisian-Neilson; R. R. Ford, *Organometallics* **1987**, *6*, 2258.

[42] A. L. Crumbliss; D. Cooke; J. Castillo; P. Wisian-Neilson, *Inorg. Chem.* **1993**, *32*, 6088.

[43] H. R. Allcock, *J. Inorg. Organomet. Polym.* **2005**, *15*, 57.

[44] H. R. Allcock; K. D. Lavin; N. M. Tollefson; T. L. Evans, *Organometallics* **1983**, *2*, 267.

[45] H. R. Allcock, In *Rings, Clusters and Polymers of the Main Group Elements*; A. H. Cowley, Ed.; American Chemical Society: Washington, USA, **1983**; Chap. 3; Vol. *232;* p 49.

[46] R. A. Dubois; P. E. Garrou; K. D. Lavin; H. R. Allcock, *Organometallics* **1986**, *5*, 460.

[47] G. A. Carriedo; F. J. Garcia Alonso; P. A. Gonzalez; P. Gomez-Elipe, *Polyhedron* **1999**, *18*, 2853.

[48] G. A. Carriedo; F. J. G. Alonso; P. A. Gonzalez; C. D. Valenzuela; N. Y. Saez, *Polyhedron* **2002**, *21*, 2579.

[49] H. R. Allcock; A. A. Dembek; E. H. Klingenberg, *Macromolecules* **1991**, *24*, 5208.

[50] H. R. Allcock; C. J. Nelson; W. D. Coggio, *Chem. Mater.* **1994**, *6*, 516.

[51] G. A. Carriedo; F. J. G. Alonso; J. L. G. Alvarez; C. D. Valenzuela; N. Y. Saez, *Polyhedron* **2002**, *21*, 2587.

[52] G. A. Carriedo; F. J. G. Alonso; A. Presa, *J. Inorg. Organomet. Polym.* **2004**, *14*, 29.

[53] P. Das; E. M. Indra; L. A. Belfiore, *Polym. Eng. Sci.* **1997**, *37*, 1909.

[54] J. M. G. Cowie; N. Sadaghianizadeh, *Makromol. Chem., Rapid Commun.* **1988**, *9*, 387.

[55] J. M. G. Cowie; K. Sadaghianizadeh, *Polym. Commun.* **1988**, *29*, 126.

[56] J. E. Denness; D. Parker; H. S. A. Hubbard, *J. Chem. Soc., Perkin Trans.* 2 1994, 1445.

[57] H. R. Allcock; D. L. Olmeijer; J. M. O'Connor, *Macromolecules* **1998**, *31*, 753.

[58] H. R. Allcock; P. P. Greigger; J. E. Gardner; J. L. Schmutz, *J. Am. Chem. Soc.* **1979**, *101*, 606.

[59] H. R. Allcock; T. X. Neenan; B. Boso, *Inorg. Chem.* **1985**, *24*, 2656.

[60] H. R. Allcock; X. T. Neenan, *Macromolecules* **1986**, *19*, 1495.

[61] H. G. Baik; O. S. Jung; Y. K. Sung; Y. S. Sohn, *Bull. Korean Chem. Soc.* **1995**, *16*, 1074.

[62] Y. S. Sohn; H. Baek; Y. H. Cho; Y. A. Lee; O. S. Jung; C. O. Lee; Y. S. Kim, *Int. J. Pharm.* **1997**, *153*, 79.

[63] S. C. Song; S. Y. Soo, *J. Controlled Release* **1998**, *55*, 161.

[64] S. B. Lee; S. C. Song; J. L. Jin; Y. S. Sohn, *Polym. J. (Tokyo)* **1999**, *31*, 1247.

[65] U. Diefenbach; A. M. Cannon; B. E. Stromburg; D. L. Olmeijer; H. R. Allcock, *J. Appl. Polym. Sci.* **2000**, *78*, 650.

[66] H. R. Allcock; E. N. Silverberg; C. J. Nelson; W. D. Coggio, *Chem. Mater.* **1993**, *5*, 1307.

[67] R. A. Saraceno; G. H. Riding; H. R. Allcock; A. G. Ewing, *J. Am. Chem. Soc.* **1988**, *110*, 7254.

[68] H. R. Allcock; R. W. Allen; J. P. O'Brien, *J. Chem. Soc. Chem. Commun.* 1976, 717.

[69] S. C. Song; C. O. Lee; Y. S. Sohn, *Polymer International* **1999**, *48*, 627.

[70] R. A. Dubois; P. E. Garrou; K. D. Lavin; H. R. Allcock, *Organometallics* **1984**, *3*, 649.

[71] G. A. Carriedo; P. Crochet; F. J. Garcia Alonso; J. Gimeno; A. Presa-Soto, *Eur. J. Inorg. Chem.* **2004**, 3668.

[72] H. R. Allcock; S. Kwon, *Macromolecules* **1989**, *22*, 75.

[73] S. Cohen; M. C. Bano; K. B. Visscher; M. Chow; H. R. Allcock; R. Langer, *J. Am. Chem. Soc.* **1990**, *112*, 7832.

[74] A. K. Andrianov; S. Cohen; K. B. Visscher; L. G. Payne; H. R. Allcock; R. Langer, *J. Controlled Release* **1993**, *27*, 69.

[75] L. G. Payne; S. A. Jenkins; A. Andrianov; B. E. Roberts In *Vaccine Design: The Subunit and Adjuvant Approach*; M. F. Powell, M. J. Newman, Eds.; Plenum Press: New York, 1995; Chapt. 20, p 473.

[76] L. G. Payne; S. A. Jenkins; A. I. Woods; E. M. Grund; W. E. Geribo; J. R. Loebelenz; A. K. Andrianov; B. E. Roberts, *Vaccine* **1998**, *16*, 92.

[77] A. K. Andrianov; J. R. Sargent; S. S. Sule; M. P. Le Golvan; A. Woods; S. A. Jenkins; L. G. Payne, *J. Bioactiv. Compatible Polym.* **1998**, *13*, 243.

[78] H. R. Allcock in reference 3, 2003, Chapt. 12, p 400.

[79] L. Fambri; A. Pegoretti; M. Gleria in reference 4, 2004; Chapt. 12, p 257.

[80] H. R. Allcock; P. E. Austin; T. X. Neenan; J. T. Sisko; P. M. Blonsky; D. F. Shriver, *Macromolecules* **1986**, *19*, 1508.

[81] H. R. Allcock; T. J. Fuller; D. P. Mack; K. Matsumura; K. M. Smeltz, *Macromolecules* **1977**, *10*, 824.

[82] H. R. Allcock; S. R. Pucher; A. G. Scopelianos, *Biomaterials* **1994**, *15*, 563.

[83] Y. Lemmouchi; E. Schacht; S. Dejardin, *J. Bioactiv. Compatible Polym.* **1998**, *13*, 4.

[84] C. T. Laurencin; H. J. Koh; T. X. Neenan; H. R. Allcock; R. Langer, *J. Biomed. Mater. Res.* **1987**, *21*, 1231.

[85] N. Gunduz; T. Gunduz; E. Kilic; S. G. Oztas; M. Tuzum; L. S. Shaw; R. A. Shaw, *J. Chem. Soc. Dalton Trans.* 1987, 925, and references therein.

[86] P. Wisian-Neilson; M. S. Islam; S. Ganapathiappan; D. L. Scott; K. S. Raghuveer; R. R. Ford, *Macromolecules* **1989**, *22*, 4382.

[87] M. C. Gallazzi; G. Freddi; G. Sanvito; G. Viscardi, *J. Inorg. Organomet. Polym.* **1996**, *6*, 277.

[88] E. Montoneri; M. Gleria; G. Ricca; G. C. Pappalardo, *Makromol. Chem.* **1989**, *190*, 191.

[89] E. Montoneri; M. Gleria; G. Ricca; G. C. Pappalardo, *J. Macromol. Sci., Chem.* **1989**, *A26*, 645.

[90] E. Montoneri; P. Savarino; G. Viscardi; M. C. Gallazzi; M. Gleria; F. Minto, *J. Inorg. Organomet. Polym.* **1992**, *2*, 421.

[91] P. M. Blonsky; D. F. Shriver; P. E. Austin; H. R. Allcock, *J. Am. Chem. Soc.* **1984**, *106*, 6854.

[92] P. M. Blonsky; D. F. Shriver; P. E. Austin; H. R. Allcock, *Polym. Mater. Sci. Eng.* **1985**, *53*, 118.

[93] K. M. Tonge; D. F. Shriver, *J. Electrochem. Soc.* **1987**, *134*, 269.

[94] J. L. Bennett; A. A. Dembek; H. R. Allcock; B. J. Heyen; D. F. Shriver, *Chem. Mater.* **1989**, *1*, 14.

[95] G. A. Nazri; S. G. Meibuhr, *J. Electrochem. Soc.* **1989**, *136*, 2450.

[96] C. J. Nelson; W. D. Coggio; H. R. Allcock, *Chem. Mater.* **1991**, *3*, 786.

[97] Y. Tada; M. Sato; N. Takeno; T. Kameshima; Y. Nakacho; K. Shigehara, *Macromol. Chem. Phys.* **1994**, *195*, 571.

[98] F. F. Stewart; R. E. Singler; M. K. Harrup; E. S. Peterson; R. P. Lash, *J. Appl. Polym. Sci.* **2000**, *76*, 55.

[99] F. Minto; M. Gleria; A. Pegoretti; L. Fambri, *Macromolecules* **2000**, *33*, 1173.

[100] K. M. Abraham; M. Alamgir; S. J. Perrotti, *J. Electrochem. Soc.* **1988**, *135*, 535.

[101] K. M. Abraham; M. Alamgir; R. K. Reynolds, *J. Electrochem. Soc.* **1989**, *136*, 3576.

[102] H. R. Allcock; S. E. Kuharcik; C. S. Reed; M. E. Napierala, *Macromolecules* **1996**, *29*, 3384.

[103] H. R. Allcock; M. E. Napierala; D. L. Olmeijer; C. G. Cameron; S. E. Kuharcik; C. S. Reed; S. J. M. O'Connors, *Electrochim. Acta* **1998**, *43*, 1145.

[104] H. R. Allcock; S. J. M. O'Connor; D. L. Olmeijer; M. E. Napierala; C. G. Cameron, *Macromolecules* **1996**, *29*, 7544.

[105] H. R. Allcock; N. J. Sunderland; R. Ravikiran; J. M. Nelson, *Macromolecules* **1998**, *31*, 8026.

[106] M. A. Ratner; D. F. Shriver, *Chem. Rev.* **1988**, *88*, 109.

[107] H. R. Allcock; M. E. Napierala; D. L. Olmeijer; S. A. Best; K. M. Merz, *Macromolecules* **1999**, *32*, 732.

[108] T. A. Luther; F. F. Stewart; J. L. Budzien; R. A. LaViolette; W. F. Bauer; M. K. Harrup; N. S. Allen; A. Elayan, *J. Phys. Chem. B* **2003**, *107*, 3168.

[109] Y. Wang; P. B. Balbuena, *J. Phys. Chem. B* **2004**, *108*, 40.

[110] A. K. Andrianov; L. G. Payne; K. B. Visscher; H. R. Allcock; R. Langer, *J. Appl. Polym. Sci.* **1994**, *53*, 1573.

[111] M. C. Bano; S. Cohen; K. B. Visscher; H. R. Allcock; R. S. Langer, *Bio/Technology* **1991**, *9*, 468.

[112] A. K. Andrianov; L. G. Payne In *Microparticulate Systems for the Delivery of Proteins and Vaccines*; S. Cohen, H. Bernstein, Eds.; Marcel Dekker, Inc.: New York, USA, 1996; Chapt. 4, p 127.

[113] A. K. Andrianov; J. Chen; S. S. Sule; B. E. Roberts, In *Controlled Drug Delivery*; ACS Symp. Ser: Washington, USA, **2000**; Chap. 37; Vol. *752;* p 395.

[114] A. K. Andrianov; L. A. Payne, *Advances in Drug Delivery Review* **1998**, *31*, 185.

[115] L. G. Payne; S. A. Jenkins; A. Andrianov; R. Langer; B. E. Roberts In *Advances in Mucose Immunology*; J. Mestecky, et al., Eds.; Plenum Press: New York, USA, 1995, p 1475.

[116] C. Diaz; P. Castillo, *J. Inorg. Organomet. Polym.* **2001**, *11*, 183.

[117] G. A. Carriedo; L. Fernandez-Catuxo; F. Garcia-Alonso; P. Gomez-Elipe, *J. Organometallic Chem.* **1995**, *503*, 59.

[118] C. Diaz; P. Castillo; G. A. Carriedo; P. Gomez-Elipe; F. J. Garcia-Alonso, *Macromol. Chem. Phys.* **2002**, *203*, 1912.

[119] H. R. Allcock; T. J. Fuller; T. L. Evans, *Macromolecules* **1980**, *13*, 1325.

[120] H. R. Allcock; K. D. Lavin; G. H. Riding, *Macromolecules* **1985**, *18*, 1340.

[121] H. R. Allcock; G. H. Riding; K. D. Lavin, *Macromolecules* **1987**, *20*, 6.

[122] H. R. Allcock; J. A. Dodge; I. Manners; G. H. Riding, *J. Am. Chem. Soc.* **1991**, *113*, 9596.

[123] G. A. Carriedo; F. J. G. Alonso; P. Gomez-Elipe; C. D. Valenzuela; N. Y. Saez, *J. Chil. Chem. Soc.* **2003**, *48*, 25.

[124] C. Diaz; M. L. Valenzuela; M. Barbosa, *Materials Research Bulletin* **2004**, *39*, 9.

[125] L. Barazzone, *Thesis*, University of Pisa, Italy, (2004).

[126] S. C. Song; C. O. Lee; Y. S. Sohn, *Bull. Korean Chem. Soc.* **1999**, *20*, 250.