CHEMISTRY AND APPLICATIONS OF POLYPHOSPHAZENES pdf

1: Polyphosphazenes for Biomedical Applications :: Book :: ChemistryViews

Harry Allcock's Chemistry and Applications of Polyphosphazenes provides the only published compilation of material on polyphosphazenes, detailing synthetic methodologies and physical properties for each substance.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited. This article has been cited by other articles in PMC. The degradation profiles of the polyphosphazenes prepared are analyzed by GPC, 31P NMR spectroscopy, and UVâ€”Vis spectroscopy in aqueous media and show tunable degradation rates ranging from days to months, adjusted by subtle changes to the chemical structure of the polyphosphazene. Furthermore, it is observed that these polymers demonstrate a pH-promoted hydrolytic degradation behavior, with a remarkably faster rate of degradation at lower pH values. These degradable, water soluble polymers with controlled molecular weights and structures could be of significant interest for use in aqueous biomedical applications, such as polymer therapeutics, in which biological clearance is a requirement and in this context cell viability tests are described which show the non-toxic nature of the polymers as well as their degradation intermediates and products. The incorporation of various specific substituents remarkably affects the hydrolytic degradability of the polymer. There are several different pathways suggested for the degradation process of polyphosphazenes including the hydrolysis and thus release of the substituted side groups, followed by the attack of water on the phosphazene backbone, leading to the formation of hydroxyphosphazenes and phosphazanes. It is well-established that the rate of degradation of polyphosphazenes can be tailored through the addition of amino acid ester side groups. Thus, with the aim to extend their applicability to aqueous applications, we sought to prepare water-soluble variants with similarly good control of degradability. Although a mixed substitution with both amino acid esters and hydrophilic groups is also possible, 14 this route clearly has its upper incorporation limits and thereby degradation limit , with increasing hydrophobic portion also leading to amphiphilic polymers and furthermore aggregation. Furthermore, we describe how decreases in pH-value lead to rapid acceleration of the degradation profile as well as preliminary cell viability tests showing the biocompatibility of the polymers and the benign nature of their degradation products. Solvents were dried using standard laboratory methods. PCl5 was purified by sublimation and stored in the glovebox under argon. NEt3 was dried over molecular sieves and distilled prior to use. All other chemicals were purchased from Sigmaâ€”Aldrich and used without further purification. The molecular weights were calculated relative to polystyrene standards from PSS using a conventional calibration of the refractive index detector. The samples were filtered through a nylon microfilter 0. The reaction was then filtered through celite and the volatiles were removed under vacuum. Synthesis of Poly dichlorophosphazene The polymers were synthesized according to the procedure for the living cationic polymerization of trichlorophosphoranimine. After 12 h, the solvent was removed under vacuum. The obtained poly dichlorophosphazene was used for macromolecular substitution without further purification. In a second flask, 1. The mixture was allowed to warm to room temperature and stirred overnight. The formed precipitate was then removed by filtration. The filtrate was added to a solution of 7. The solvent was removed under vacuum and the product further dried under high vacuum to yield MValine-Boc as a white wax-like product. The organic phase was dried over MgSO4 and removed under vacuum. The product was further dried by co-evaporation with toluene and chloroform to obtain MValine. In the glovebox, poly dichlorophosphazene 0. A solution of MValine 1. The suspension was filtered to remove the formed ammonium chloride and the solvent was concentrated under vacuum. The polymer was purified by several precipitations into chilled diethyl ether from THF and dried under high vacuum.

CHEMISTRY AND APPLICATIONS OF POLYPHOSPHAZENES pdf

2: Chemistry and Applications of Polyphosphazenes, Cat# Â« www.enganchecubano.com

Polyphosphazenes are polymers containing nitrogen as part of their backbone; they are commonly used in O-rings, pipelines, and seals in oil, fuel delivery, and storage systems. New polyphosphazene derivatives have been proven biocompatible, biodegradable, and bioactive, and some of them are being investigated for possible medical applications.

In a preferred embodiment for random mixed substituent polyphosphazene compounds of Formula A: Specific embodiments synthesised by the applicants have given rise to values of x from 0. The skilled man will appreciate that values of x, y and z varying independently from 0. In specific embodiments random mixed substituent polyphosphazene compounds of Formula A have been prepared, consisting of: This synthetic pathway comprises the use of novel polymeric alkoxy substituted precursors that enable energetic linear polyphosphazenes to be synthesised rather than through the use of direct attachment of energetically substituted pendant side groups. Accordingly there is provided a method for the synthesis of random mixed substituent energetic polyphosphazenes of Formula A comprising the steps of: Wuts, Wiley Interscience Employing Step l [b], Step 2 , Step 3 [b] such that all the chloro groups are replaced by the C2-C2O pendant groups of the precursor described in Step 2 and Step 4 will result in poly phosphazene homopolymers of the Formula B. Accordingly there is provided a method for the synthesis of energetic polyphosphazene homopolymers of Formula B. In a further preferred embodiment the pendant fluoroalkoxy group referred to at Step l [a] comprises a lH,lH-perfluoropentan-l-oxy group. In a preferred embodiment the replaceable group in Step l [b] comprises chlorine. In a preferred embodiment the attachment of Step 3 is undertaken via random mxcleophilic substitution of trifluoroethoxy groups. In a specific embodiment the attachment of Step 3 is undertaken via displacement of chloro groups. Accordingly there is provided random mixed substitutent energetic polyphosphazenes of Formula A obtainable by the above method where: Preferably the substitutable polyphosphazene precursor used in Step l [a] comprises poly[bis trifluoroethoxy phosphazene]. Where the polyphosphazene precursor used in Step l [a] comprises poly [bis trifluoroethoxy phosphazene]: Preferably the substitutable pendant group precursor used in Step 2 comprises 2,2- dimethyl-[l,3]-dioxolanyl -ethanol. Preferably the substitutable pendant group precursor used in Step 2 comprises 2,2- dimethyl-[1 ,3]-dioxolanyl -butanol. Preferably the substitutable pendant group precursor used in Step 2 comprises 2- pyranyloxy ethanol. Preferably the substitutable pendant group precursor used in Step 2 comprises 3- methyl-oxetanyl -methanol. Preferably the substitutable pendant group precursor used in Step 2 comprises 6- azidohexanol. Preferably the substitutable pendant group precursor used in Step 2 comprises 5,6- diazidohexan- 1 -ol. Where the polyphosphazene precursor used in Step l [b] comprises poly dichlorophosphazene: Preferably the substitutable pendant group precursors used in Step 2 comprise 2,2-dimethyl-[l,3]-dioxolanyl -methanol and followed by IH5IH- perfluoropentanol. Accordingly there is provided polyphosphazene homopolymers of Formula B obtainable by the above method where: Preferably the substitutable poly phosphazene precursor used in Step 1 comprises poly dichlorophosphazene. Preferably the substitutable pendant group precursor used in Step 2 comprises 2,2- dimethyl-[1 ,3]-dioxolanyl -methanol. Preferably the substitutable pendant group precursor used in Step 2 comprises 2,2- dimethyl-[1 ,3]-dioxolanyl -ethanol. Preferably the substitutable pendant group precursor used in Step 2 comprises 3- azidopropanol. By varying the degree of substitution of the polymer chain by energetic side groups it is possible to modify the energy content of the polyphosphazene and through the judicious selection of different chain lengths and substitution patterns, other parameters such as density and glass transition temperature can be manipulated. The disclosed synthetic method therefore makes it possible to optimise the desired characteristics of a particular polyphosphazene for a given application. The degree of substitution of energetic side groups can be modified by increasing the degree of subsitution a of the alkoxide precursor prior to nitration and b of the azidated side chains. Accordingly there is provided a method for varying the degree of substitution i. Variation can be effected by one or more of the following: It is found that by increasing the relative proportion of alkoxide to polymer precursor as above increases the relative degree of substitution. It is found that increasing the reaction time increases the relative degree of substitution of the fluoroalkoxy groups in the precursor and the chloro groups in the precursor, by

the first alkoxide or free alcohol , in Steps 3 [a] and 3 [b] respectively. That is the sodium cation is more effective than the lithium cation. It is found that by increasing the reaction temperature this also has the effect of increasing the relative degree of substitution of the fluoroalkoxy groups in the precursor. The degree of substitution of the polymer and the nature of the substituting pendant side groups themselves modify the physical properties of the polymer. Accordingly there is provided a method for varying the physical properties of the polyphosphazene products of Formula A and Formula B. Variation of the physical properties of the polymer can be effected by variation of one or more of the following: As to ii the energy, density, energy density and glass transition temperature can be varied by varying the length of the carbon chain of the substitutable pendant side- groups. As to iii the energy and energy density can be increased by increasing the number of energetic functionalities attached to the substituted pendant side-groups; the glass transition temperature and density can be varied by varying the number of energetic functionalities attached to the substituted pendant side groups. As to iv the energy, density, energy density, glass transition temperature and thermal stability can be varied by attaching more than one type of substituted pendant side-group to the polymer backbone. As to v the energy, density, energy density, glass transition temperature and thermal stability can be varied by varying the type of energetic functionality attached to the substituted pendant side-group. Physical data of selected polyphosphazene products of Formula A and Formula B are summarised in Table 1, along with data for commercially available energetic polymers for comparison. The data of Table 1 demonstrate that high energy densities are achievable for the energetic polyphosphazenes of Formula A and Formula B and in some cases these exceed those of commercially available energetic polymers. In addition, some of the listed values approximate to those of some current explosives. This promotes improved detonation performance over other known polymeric binders. The polyphosphazene compounds of Formula A and Formula B offer a range of glass transition temperatures including desirable low glass transition temperatures, whilst at the same time retaining high relative energy-density. The possession of low glass transition temperatures minimises or negates the need to add either plasticisers or energetic plasticisers to a formulation for low temperature use. This is an advantage because, over time plasticisers can migrate out of formulations, potentially compromising the mechanical properties of a formulation, particularly at low temperature. Thus, the use of unplasticised or marginally plasticized polyphosphazene binders will lead to enhanced ageing performance of the bound explosive. The possession of a low glass transition temperature Tg coupled with high energy density confers the significant advantage that when these compounds are used as binders, the bound explosive may be shaped and used over a wide temperature range, whilst the whole material retains its high explosive power. As described in the examples, the energetic polyphosphazenes of the present invention unexpectedly act as very effective binders for energetic materials using a solvent paste process; however, they are not chemically curable. Nevertheless, we have established that some of the polyphosphazenes described herein are miscible with certain commercial energetic polymers such as polyGLYN and polyNIMMO, which are curable in their own right using standard isocyanate technology and that the mixed binder may itself be isocyanate cured. In the case of polyGLYN the mixed binder has a glass transition temperature intermediate between that of the two individual binders, dependent upon the proportions. Thus, polyphosphazenes of the present invention, when employed as co- binders, can be valuable not only for enhancing the energy-density of the complementary binder, but also for depressing its glass transition temperature. The term co-binder refers to use of these polyphosphazenes as binders in conjunction with other binder materials. This is evident from the observed hissing and effervescent nature of the combustion of these compounds. Embodiments of the invention will now be described with reference to the figures and examples below and wherein: The mixture was heated to reflux ca. After all phosphite had been consumed after approx. The pure phosphoranimine product was isolated from the crude mixture via vacuum distillation, to yield a colourless liquid. The crude mixture was decanted into a flask containing chloroform ml , cooled to ca. The polyphosphazene product appeared immediately as a white solid precipitate. This was filtered and washed thoroughly with portions of chloroform and hexane, before drying in vacuo for several hours. Method 2 Step 1 - Freshly sublimed hexachlorocyclotriphosphazene 17g was placed in a dry pyrex tube and sealed under vacuum. The tube was allowed to cool to room temperature, broken open inside an inert atmosphere glovebox and the contents

dissolved in a minimum amount of anhydrous toluene. The product, consisting of poly dichlorophosphazene , was isolated as a colourless rubbery material upon precipitation into an excess of anhydrous hexane. Step 2 - Sodium trifmoroethoxide was prepared by adding a solution of rrifluoroethanol 5. The reaction mixture was heated to reflux for 6 hours before adding to water, resulting in precipitation of a white solid consisting of poly[bis-trifluoroethoxy phosphazene]. The product was purified by precipitation as an acetone solution into toluene. Stirring was continued at ambient temperature for a further hours. The product was isolated in pure form via vacuum distillation. Stirring was maintained at ambient temperature for hours or until the reaction was complete, as indicated by 31P 1H NMR spectroscopy. Dichloromethane was removed in vacuo to yield the product as a colourless, tacky viscous liquid. Poly dichlorophosphazene may also be prepared via Method 2 Step 1 of process A2 above]. A41 Synthesis of r2. The mixture was allowed to stir at ambient temperature for 24 hours. The organic solution was then dried over anhydrous MgSO4, filtered and solvent removed in vacuo, to yield the product as a colourless liquid. AS Synthesis of 2. The product was isolated as a colourless liquid. Water ca, cm3 was then added, resulting in a biphasic mixture. The organic phase containing the desired product was collected and the aqueous phase containing excess ethylene glycol extracted with further portions of dichloromethane 3 x 50 cm3. The combined organic phase and washings were dried over anhydrous magnesium sulphate, filtered and solvent removed in vacuo to yield the crude product containing, almost exclusively, the mono-protected alcohol. The desired product was isolated via flash column chromatography using silica gel 60 and a 3: B General procedure for synthesis of Li salts of 2,2-dimethyl-[1. During addition, warming of the reaction flask was noticeable. The solution was left to stir at ambient temperature for hours, yielding a pale yellow solution of the Li salt in THF quantitative conversion. C General procedure for synthesis of Na salts 2. An equimolar amount of the appropriate alcohol, as a solution in THF, was added dropwise at ambient temperature. The mixture was allowed to stir for several hours at ambient, yielding the Na-salt as a suspension in THF quantitative conversion. The mixture was heated to reflux and stirred for 18 hours. The aqueous mixture was then acidified to ca. The aqueous solution was decanted and the polymer redissolved in dichloromethane ca 50ml if soluble otherwise dried in vacuo at 5O0C for several hours. The organic solution was then extracted with saturated sodium chloride solution 2 x 30ml and finally with water 1 x 30ml before drying over anhydrous MgSO4 alternatively multiple precipitations into water can be used followed by disolution in dichloromethane and drying over MgSO4. After filtration and removal of solvent in vacuo, the product was dissolved in a minimum quantity of acetone and precipitated into hexane ca ml. The hexane was decanted and the product dried in vacuo precipitation into hexane was repeated until the product was pure, via 1H NMR. The polymeric product was isolated as a pale yellow viscous liquid.

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3: Polyphosphazenes by Maddie Demming on Prezi

Hypervalent Iodine Chemistry is the first comprehensivetext covering all of the main aspects of the chemistry of organicand inorganic polyvalent iodine compounds, including applicationsin chemical research, medicine, and www.enganchecubano.coming a comprehensive overview of the preparation,properties, and synthetic.

Synthesis[edit] The method of synthesis depends on the type of polyphosphazene. The most widely used method for linear polymers is based on a two-step process. In the second step the chlorine atoms linked to phosphorus in the polymer are replaced by organic groups through reactions with alkoxides , aryloxides , amines or organometallic reagents. Because many different reagents can participate in this macromolecular substitution reaction , and because two or more different reagents may be used, a large number of different polymers can be produced, each with a different combination of properties. Variations to this process are possible using poly dichlorophosphazene made by condensation reactions. Properties and uses[edit] The linear high polymers have the geometry shown in the picture. More than different macromolecules that correspond to this structure are known with different side groups or combinations of different side groups. In these polymers the properties are defined by the high flexibility of the backbone. Other potentially attractive properties include radiation resistance, high refractive index , ultraviolet and visible transparency, and its fire resistance. The side groups exert an equal or even greater influence on the properties since they impart properties such as hydrophobicity , hydrophilicity , color , useful biological properties such as bioerodibility , or ion transport properties to the polymers. Representative examples of these polymers are shown below. Thermoplastics[edit] The first stable thermoplastic poly organophosphazenes , isolated in the mid s by Allcock , Kugel, and Valan, were macromolecules with trifluoroethoxy, phenoxy , methoxy , ethoxy , or various amino side groups. It has also been a substrate for various surface reactions to immobilize biological agents. The polymers with phenoxy or amino side groups have also been studied in detail. Phosphazene elastomers[edit] The first large-scale commercial uses for linear polyphosphazenes were in the field of high technology elastomers , with a typical example containing a combination of trifluoroethoxy and longer chain fluoroalkoxy groups. They have also been used in biostable biomedical devices. Polymer electrolytes[edit] Linear polyphosphazenes with oligo - ethyleneoxy side chains are gums that are good solvents for salts such as lithium triflate. These solutions function as electrolytes for lithium ion transport, and they were incorporated into fire-resistant rechargeable lithium-ion polymer battery. The cross-linked polymers absorb water to form hydrogels , which are responsive to temperature changes, expanding to a limit defined by the cross-link density below a critical solution temperature , but contracting above that temperature. This is the basis of controlled permeability membranes. Other polymers with both oligo-ethyleneoxy and carboxyphenoxy side groups expand in the presence of monovalent cations but contract in the presence of di- or tri-valent cations, which form ionic cross-links. Different polymers have been studied as macromolecular drug carriers , as membranes for the controlled delivery of drugs , as biostable elastomers , and especially as tailored bioerodible materials for the regeneration of living bone. These polymers hydrolyze slowly to a near-neutral, pH- buffered solution of the amino acid, ethanol, phosphate, and ammonium ion. The speed of hydrolysis depends on the amino acid ester, with half-lives that vary from weeks to months depending on the structure of the amino acid ester. Nanofibers and porous constructs of these polymers assist osteoblast replication and accelerate the repair of bone in animal model studies. Commercial aspects[edit] No applications are commercialized for polyphosphazenes. The cyclic trimer hexachlorophosphazene NPCl2 3 is commercially available. It is the starting point for most commercial developments. An aryloxy-substituted polymer has also been developed as a fire resistant expanded foam for thermal and sound insulation. The patent literature contains many references to cyclomatrix polymers derived from cyclic trimeric phosphazenes incorporated into cross-linked resins for fire resistant circuit boards and related applications.

CHEMISTRY AND APPLICATIONS OF POLYPHOSPHAZENES pdf

4: OhioLINK ETD: Kroger, Jessica

Polyphosphazenes are polymers containing nitrogen as part of their backbone; they are commonly used in O-rings, pipelines, and seals in oil, fuel delivery, and storage systems. New polyphosphazene derivatives have been proven biocompatible, biodegradable, and bioactive, and some of them are being.

Specifically, we design and find ways to synthesize ion-conductive polymers for use as electrolytes in rechargeable lithium batteries, polymer electrolyte fuel cells, and dye-based solar cells. Work on supercapacitors is just beginning. Secondary Lithium Batteries A severe need exists for new lithium battery energy storage science especially in automotive technology. The development of new polymer electrolyte systems to replace the flammable organic electrolytes currently used in lithium batteries has become a major challenge. These gum-like polymers are capable of solubilizing lithium salts and facilitating ion-pair separation by coordination to the cations. In addition, low volatility small molecule counterparts such as 2, have also been studied as electrolytes. Of special interest is the mechanism of ion conduction in these systems. Recent work has provided evidence that, contrary to previous interpretations, both anion and cation transport is important in these electrolytes. Polymer Electrolyte Fuel Cells Proton-conductive polymers based on the polyphosphazene platform are being synthesized and studied for uses in polymer electrolyte fuel cells. The phosphazene polymers have aryloxy side groups functionalized with sulfonic acid, phosphonic acid, or sulfonimide groups. These polymers appear to be especially useful for incorporation into direct methanol or ethanol fuel cells because they are resistant to alcohol crossover- which is a serious problem with classical polymers like Nafion. We are also studying the mechanism of proton transport in these membranes using solid state NMR spectroscopy and are finding evidence for the existence of organized, ice-like water associated with the acidic side groups as well as the normal liquid water in the hydrophilic domains. Dye-based Solar Cells The use of volatile organic solvents in the electrolytes of dye-based solar cells is a factor that lowers the lifetime of these devices. We are investigating polymeric and oligomeric phosphazenes, similar to those used in the lithium battery work, as electrolytes in Gratzel cells. A major challenge is to facilitate penetration of the electrolyte into the nanostructured TiO2 electrodes. Advances have been made using TiO2 nanosphere-type electrodes and those with nanowires or nano-columns as part of the surface structure. General Principles The ability to tune the properties of polyphosphazenes by the use of different skeletal architectures and by the introduction of different side groups makes them particularly attractive materials for uses in biomedicine. Polyphosphazenes as Bioerodible Materials a For tissue engineering. As part of a long-term NIH-supported collaborative program with the group of Dr. Cato Laurencin, now at the University of Connecticut Medical Center, we have developed more than 20 different polymers that are platforms for colonization by osteoblasts for the regeneration of bone. The most useful materials are polyphosphazenes with amino acid esters or dipeptide esters as side groups linked to the main chain through the amino terminus of the side group. Three methods are being explored to optimize this system. First, the rates of hydrolysis are controlled by the types of side groups on the polyphosphazene, and by their disposition along the chains. Second, the sensitivity to hydrolysis is being modified via composites produced between bioerodible polyphosphazenes and poly lactic-glycolic acid PLGA a long-existing commercial bioerodible polymer that suffers from some limitations. The phosphazene modifies the physical properties of the PLGA and reduces the acidity of the hydrolysis medium. Third, the physical form of the polymer affects the biomedical behavior - whether the polymer is in the form of films, porous constructs, or micro- or nano-fiber mats. Fifth, the eroding polymer systems must also provide a means for the controlled release of growth factors to encourage osteoblast replication. Understanding how to balance these factors and enhance the compatibility with osteoblasts and their rate of colonization is the major challenge that we are attempting to solve. In general terms, our group at Penn State focuses on the polymer design, synthesis, and characterization aspects, while our colleagues at the University of Connecticut concentrate on the materials science and biological evaluations. Hydrolysis prod b For controlled drug or vaccine delivery. Bioerodible polyphosphazenes are useful not only for growth factor release but also for the controlled release of vaccines and drugs. One aspect of controlled release that has

received considerable attention is the use of polyphosphazene microspheres for the oral delivery of vaccines. The decrosslinking step in the small intestine releases the trapped vaccine molecules and immunizes the patient. Currently our group is also exploring the use of micelles derived from amphiphilic polyphosphazene block copolymers for the delivery of chemotherapeutic drugs. We have recently shown that specific bioerodible polyphosphazenes have shape-memory characteristics. The materials can be physically programmed to return to a predetermined shape when warmed to a certain temperature see photograph. Potential uses as stents or other tissue reinforcement materials may be possible. Biostable Polymers a Possible cardiovascular materials. A number of investigators worldwide have examined the use of fluoroalkoxyphosphazene polymers as replacements for polyurethanes or silicone rubber in cardiovascular devices. The phosphazenes have surfaces that are less prone to induce thrombus formation than most polymers. This is an application that holds strong potential for future developments, and some of our surface science work see later is targeted to further developments in this area. Other elastomers that are emerging from our program, such as hybrids of phosphazenes and silicones, are also of interest for this application. The use of biostable membranes for the controlled release of drugs or for hemodialysis is of ongoing interest in the biomedical community. Our recent research has focused on the use of polyphosphazene hydrogels and nanoporous films as responsive membranes for biomedical uses. Hydrogels are derived from water-soluble, water-stable polyphosphazenes that have been lightly crosslinked. Specific gel membranes have been produced that open or close to the passage of drug molecules following changes in pH, ion strength, or the replacement of monovalent by multivalent cations. In addition, hydrogels produced from polyphosphazene polyelectrolytes crosslinked by di- or trivalent cations can be induced to expand or contract by the application of an electric current that electrochemically reduces or oxidizes the cation. This is the basis of variable permeability membranes and simple muscle-like devices that bend and unbend when an electric current is applied. Recent work in our laboratories has examined the use of polyphosphazene hydrogels as surfaces for the cultivation of nerve cells. Devices constructed by our collaborators can detect and amplify the weak electrical signals generated by the cells when they are exposed to the vapor of specific compounds. The advantage of the polyphosphazene system is that its molecular structure can be fine-tuned to favor the growth of specific cell lines for the detection of different compounds in different regions of the device. Collaborative work on the use of polyphosphazenes for stem cell cultivation is just beginning. Background Phosphazene rings and polymers provide an almost unique platform for the development of optical materials. The high electron density in the skeleton and the broad window of transparency from the near ultraviolet to the near infrared provides an excellent starting point for the design and synthesis of a variety of optical and photonic materials. Basically, beyond the properties provided by the backbone, optical properties can be generated and tuned by the choice of different organic side groups or different skeletal architectures, as illustrated by the following examples. Controlled Refractive Index Materials Organic side groups with high electron densities, such as aryl, halogenoaryl, or sulfur-containing groups allow the refractive index values of phosphazene oligomers and polymers to be as high as 1. Low refractive index values can be generated via the use of fluorinated organic side groups. Thus, combinations of different side groups allow fine-tuning of the refractive index. The polymers may be in the form of transparent glasses, or ring systems can be incorporated into cyclolinear or clear cyclomatrix resins. Coupled with refractive index tuning is the need to minimize chromatic dispersion, which typically rises with high refractive index materials that have absorptions in the near ultraviolet. Recent progress toward low chromatic dispersion materials has been made with the use of sulfur-containing side groups. Linkage of spiropyrans to a polyphosphazene chain has been accomplished as a means to control the response time. Electroluminescent Polymers Polymers that emit light of specific wavelengths of light when stimulated with an electric current are the basis of a growing number of devices, including flat panel computer and television screens. We have synthesized the first phosphazene-based polymers that are electroluminescent. These have a cyclolinear architecture see example structure below , in which conjugated unsaturated organic oligomeric chains link cyclotriphosphazene units. The cyclophosphazene units interrupt the electron delocalization in the organic regions and define the emission wavelength. Other organic side groups on the phosphazene rings provide solubility in organic solvents, a

prime requirement for the fabrication of flat panel devices. These properties include low temperature flexibility and elasticity; resistance to hydrocarbon fuels, oils, and hydraulic fluids; fire resistance, radiation resistance, and ultraviolet stability. The specific applications fall into four main categories based on 1 elastomeric properties, and 2 fire-resistant composite materials and foams. Phosphazene Elastomers This is one of the most established uses for polyphosphazenes. They are used to fabricate O-rings, seals, and shock-absorbing devices for low temperature uses. The presence of two or more different types of side groups in these polymers ensures a lack of crystallinity and provides the molecular free volume needed for elasticity. The fluoroalkoxy derivatives are also noted for their ability to absorb and dampen impact energy, a valuable property for certain applications. Illustrations of components manufactured from phosphazene elastomers are shown in the following photographs This aspect of the field evolved in industry directly from our earliest fundamental discoveries. Our current work is designed to investigate different side groups and skeletal architectures that give rise to elastomeric character, and to cooperate with engineering specialists to identify advanced uses. Polyphosphazenes in Fire-resistant Composite Materials and Foams Considerable work has been done in our group and elsewhere to examine the chemistry that underlies the formation of composites formed between polyphosphazenes and organic polymers, or between polyphosphazenes and sol-gel silicates. This is also related to the formation of block copolymers derived from polyphosphazenes and organic polymers or silicones. Compatibility between two polymers usually depends on the existence of weak attractive forces such as hydrogen bonding. Thus, polyesters and several other organic macromolecules form compatible blends with phosphazenes that bear etheric, acidic, or amino side groups. The main technological interest in such composites is based on the ability of the phosphazene to serve as a non-volatile fire retardant or impact absorber for the organic polymer. For example, polyphosphazenes with arylcarboxylic acid side groups react with and are excellent fire retardants for polyurethanes, including those used in aircraft construction. Lightweight polyphosphazene foams have been produced in industry as non-flammable thermal and electrical insulation. Recently we have shown that fluorinated polyphosphazenes are soluble in supercritical carbon dioxide, and that expanded foams are formed when the pressure is released. Non-flammable hydrophobic foams produced from fluoroalkoxy phosphazenes have a density less than one, and are thus of interest in flotation devices. Fire-resistant polymers are needed for advanced aerospace, automotive, and housing applications. The phosphorus-nitrogen skeleton in polyphosphazenes is inherently fire resistant and fire retardant, and this property, combined with elasticity, adhesion, hydrophobicity or superhydrophobicity, is an attractive motivation for engineering researchers to utilize these materials and for us to design and find ways to synthesize new polymers based on this skeleton. Importance of Surface Character Many engineering and biomedical applications depend on the surface character of a polymeric material as well as on the internal characteristics. It follows that the surface properties of phosphazene elastomers and thermoplastics control several areas of application. Properties such as hydrophobicity or hydrophilicity, adhesion, biological compatibility, or corrosion protection are important. In polyphosphazene science and technology the materials surface may depend on the "native" surface character of the pristine material, which often depends on the structure of the polymer side groups, or it may depend on post-synthesis modification methods. Treatment of a surface with chemical reagents or by means of an atmospheric plasma are methods being used in our program to produce different surfaces. Added to these factors is the ability of a polymer surface to change in response to the medium with which it is in contact. Contact with water may cause hydrophilic units of the polymer to migrate to the surface, while contact with a hydrophobic organic solvent will bring the hydrophobic components to the interface. The picture below illustrates the behavior of a droplet of water on a hydrophilic and a hydrophobic or superhydrophobic phosphazene interface. Chemical Surface Modification In earlier work we showed that certain side groups attached to a polyphosphazene chain can undergo facile surface reactions when the solid polymer is treated with aqueous solutions of various reagents. For example, surface trifluoroethoxy side groups can be replaced by exposure to solutions of a variety of sodium alkoxides including those that have functional groups at the opposite end of the reagent from the alkoxide unit. In this way pendent amino units at a surface are available for coupling to biologically useful molecules. Aryloxy side groups can be surface-sulfonated to convert a hydrophobic interface to a

hydrophilic one. The use of these surface "wet chemistry" reactions is an ongoing part of both our biomedical work and investigations of adhesive interfaces.

5: Polyphosphazene - Wikipedia

Polyphosphazenes are polymers containing nitrogen as part of their backbone; they are commonly used in O-rings, pipelines, and seals in oil, fuel delivery, and storage systems. This work deals with the chemistry and applications of Polyphosphazenes.

6: Chemistry and Applications of Polyphosphazenes : Harry R. Allcock :

Harry Allcock s Chemistry and Applications of Polyphosphazenes provides the only published compilation of material on polyphosphazenes, detailing synthetic methodologies and physical properties for each substance.

7: Harry Allcock | Penn State Department of Materials Science and Engineering

Polyphosphazenes are polymers containing nitrogen as part of their backbone; they are commonly used in O-rings, pipelines, and seals in oil, fuel delivery, and storage systems.

8: Table of contents for Library of Congress control number

Previous article in issue: Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products. Herausgegeben von Albert Padwa und William H. Pearson.

9: Chemistry and Applications of Polyphosphazenes: Harry R. Allcock: www.enganchecubano.com: Books

Polyphosphazenes are Polymers containing nitrogen as part of their backbone; they are commonly used in O-rings, pipelines, and seals in oil, fuel delivery, and storage systems. New polyphosphazene derivatives have been proven biocompatible, biodegradable, and bioactive, and some of them are being investigated for possible medical applications.

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