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The design and synthesis of new materials are two of the key steps in the advancement of technology. Significant advances in nearly all fields of advanced technology depend almost completely on the rate at which useful new materials can be devised and synthesized. One of the most promising approaches to the development of new materials that combine the advantages of organic polymers with those of inorganic solids is to devise polymers that have a backbone of inorganic atoms to which are attached organic or organometallic groups. Some inorganic-organic polymer systems are discussed.

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INORGANIC-ORGANIC POLYMERS AND THEIR ROLE IN MATERIALS SCIENCE

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INORGANIC-ORGANIC POLYMERS AND THEIR ROLE IN MATERIALS SCIENCE

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Introduction

The design and synthesis of new materials are two of the key steps in the advancement of technology. For example, the bottleneck in fields as diverse as electro-optics, biomedical materials, or energy storage is not the visualization of new devices, but a lack of materials that can live up to the requirements of advanced designs. Thus, significant advances in nearly all fields of advanced technology depend almost completely on the rate at which useful new materials can be devised and synthesized.

Polymer chemistry is one of the four main classical areas that together comprise the field of materials science. The other three, shown in Figure 1, are based almost entirely on inorganic substances, whereas most classical polymers are derived from organic starting materials (mainly petroleum). Each of the four main areas of materials science deals with classes of materials that have distinct property advantages and equally distinct limitations. For example, organic polymers are lightweight, tough, and easy to fabricate, but in general they cannot withstand exposure to severe thermal stress, challenging oxidation conditions, or high energy radiation. On the other hand, most ceramics have the opposite set of characteristics.

An answer to this dilemma is to design, synthesize, and develop entirely new materials that have properties that are some combination of those of different classical materials, such as toughness combined with thermo-oxidative stability, or ease of fabrication plus semiconduction or non-linear optical behavior. Conceptually, such materials should be accessible via research carried out in the central region that connects the classical areas, as shown in Figure 1.

Perhaps the most important point to be stressed is that the four areas shown in Figure 1 are not distinct fields, each with its own special set of principles, but rather that common principles exist which apply to all of the areas, especially with respect to the influence on properties of linear, branched, or crosslinked solid state structures. For example, most of the attributes of polymers are a direct consequence of the very long chain structure which favors molecular entanglements and shock-absorbing character in the solid state, and which results in low volatility and ease of fabrication. If these "geometrical" factors are taken into account, most of the differences between the various classes of materials can be ascribed to the presence of different elements in the backbone and different structural groupings in the side units.

One of the most promising approaches to the development of new materials that combine the advantages of organic polymers with those of inorganic solids is to devise polymers that have a backbone of inorganic atoms to which are attached organic or organometallic side groups.[1-5] The inorganic backbone elements can provide heat-, fire-, or radiation-resistance, or electrical conductivity, as well as materials' flexibility and ease of fabrication. The side groups control properties such as solubility or resistance to solvents; liquid crystallinty or non-linear optical behavior; refractive index; and surface properties such as hydrophobicity, hydrophilicity, adhesion, and biological compatibility. They also provide the means for generating crosslinks between chains. Such polymers are known as "inorganic-organic polymers", often abbreviated to "inorganic polymers." A related class of polymers that contain an organic backbone with inorganic elements in the side groups ("organic-inorganic" systems) will not be discused here, but a comprehensive review article on this subject has recently been published.[6]

Polymers of these types serve as a critically important bridge between the organic and inorganic materials areas. From the viewpoint of properties, they span the gap between classical biological and petrochemical polymers on the one hand, and mineralogical materials and synthesized ceramics on the other. Figure 2 illustrates this author's visualization of where inorganic-organic polymers lie in the broad spectrum of macromolecular materials. The "exotic organic polymer" category includes a number of carbon-backbone polymers that also serve as a bridge to classical inorganic materials because of their electronic conductivity and electro-optical properties.

Within the category of inorganic-organic polymers are several systems that have received widespread attention in recent years. Some of these are listed as structures 1-14. Of these, the poly(organosiloxanes) (silicones) (1) are one of the oldest and most extensively developed systems, whereas polysilanes (2) and carbosilanes (4) are among the newest.[2] The polyphosphazenes (6) include by far the largest number of different side group structures and the widest diversity of properties.[7,8] Thus, they will be used here as one of the main means for illustrating general principles. Polyphosphazenes have reached an intermediate stage of commercial development between those of the polysiloxanes and polysilanes.

These four types of polymers, together with others such as polysilynes (3),[9] polysilazanes (5), [10] polycarbo-, thio-, and thionylphosphazenes(7-9), [11-15] polymeric sulfur (10) and poly(sulfur nitride) (11), [16] poly(organooxothiazenes) (12),[17] and several metal-containing carbon backbone polymers (13, 14)[18,19] have combinations of properties that are quite distinct from those of classical organic macromolecules. Polymers with exclusively silicon-oxygen or phosphorus-nitrogen units in the backbone are generally more thermo-oxidatively stable than their totally organic counterparts. Inorganic-organic polymers are often more flexible and more easily fabricated than totally inorganic species such as polysilicates or polyphosphates. This increased flexibility usually arises because of the absence of ionic crosslinks or three-dimensional covalent matrices. Moreover, polymers with an inorganic backbone but with organic side groups are usually more hydrolytically stable than polyphosphates or linear polysilicates because the organic side units protect the backbone against hydrolytic attack.

Finally, at the bottom right of Figure 2, are the non-oxide ceramics such as silicon carbide, silicon nitride, boron nitride, etc., materials that are renowned for their hardness, thermal stability, and high softening temperatures. These properties are a consequence of the three-dimensional, covalently crosslinked structure of these materials. Several of the polymers found in the inorganic-organic polymer category, including polysilanes, polysilazanes, and boron-nitrogen polymers, are used as reaction intermediates for pyrolysis to non-oxide ceramics.[20]

It should also be noted that an intermediate type of polymer structure exists between that of linear polymers and three-dimensionally crosslinked systems. These are polymers that have a highly branched or dendritic structure. Polysilynes (3) fall into this category, with their radiating, branched network of silicon atoms which generate a roughly spherical overall structure.[9]

Influence of the Backbone Elements

The properties of any linear polymer can be understood in terms of the influence by the backbone system, on which is superimposed the effect of the side groups. The backbone elements affect the properties in the following ways.

Polymer Chain Flexibility. The torsional mobility of the bonds in a polymer chain are responsible for the overall chain flexibility, and ultimately for the materials' flexibility and its uses in different applications. A measure of chain and materials' flexibility is provided by the glass transition temperature, T_g, the temperature below which the material is a glass because of severely restricted macromolecular motions, and above which the chains possess sufficient bond torsional energy to generate flexible or rubbery properties.

The chains of alternating silicon and oxygen atoms in poly(organosiloxanes) are among the most flexible units known. Poly(dimethylsiloxane) (15) has a T_g of -130°C, one of the lowest of all polymers This can be attributed to (a) the inherently low barrier to torsion of the Si-O bonds, (b) the ability of the Si-O-Si bond angle to widen under moderate tension, a result that reduces intramolecular interactions, and (c) the fact that, unlike many organic polymers, the skeleton supports side groups on *every other* chain atom rather than every single skeletal atom. This also reduces intramolecular interactions.

A similar situation exists for polyphosphazenes. For example, polymer 16 has a T_g of -105°C.[21] Again, the absence of side groups on the nitrogen atoms and the angular flexibility of the P-N-P segments is thought to underlie this property. However, the inherently low barrier to twisting of the -P=N- bonds (estimated to be roughly 0.1 Kcal) is surprising by comparison with the situation found in carbon-carbon double bonds. It can be rationalized that the P=N double bonding is not of the "organic" p_π -p_π double bond type, but involves the phosphorus 3d-orbitals in a d_π -p_π overlap arrangement. Twisting of the bond brings each of the alternative 3d orbitals into an overlap position during 360° torsion. Hence the barrier is low. Introduction of carbon atoms into the skeleton in poly(carbophosphazenes) (7) raises the T_g by approximately 20°C, and this is consistent with the argument made above.[12] The introduction of sulfur-IV, as in poly(thiophosphazenes) (8), apparently has little effect,[14] whereas preliminary results with sulfur-VI systems (9) suggests that S(Halogen)(O) units in the chain reduce flexibility, provided that the halogeno or organic groups attached to phosphorus are small units.[15] Similarly, the -S(R)(O)=N- repeating unit in poly(organo-oxo-thiazene (12) is reported to stiffen the chain compared to polyphosphazenes.[17]

Thermo-Oxidative Stability. The main defect of organic polymer backbones, especially those with aliphatic -C-C- or -C=C- skeletal units, is their sensitivity to oxidation and chain cleavage at temperatures above 100°C. It can be argued that this sensitivity reflects the tendency for carbon to follow reaction pathways that lead to hydroperoxides, peroxides, and carbon dioxide.

Polysiloxanes have a very high thermo-oxidative stability.[22] A strong tendency exists for silicon to combine with oxygen: however, two of the bonds to each silicon are already linked to oxygen. Hence, there is no oxidative driving force for skeletal cleavage.

This is not necessarily true for the backbones in polysilanes, polysilynes, or carbosilanes, which are reported to be sensitive to oxidation.

Polyphosphazenes also are resistant to skeletal oxidative cleavage at elevated temperatures. Although phosphorus, like silicon, has a strong tendency to combine with oxygen, the phosphorus atoms in phosphazenes are already in one of the highest oxidation states accessible for the element (+V). Hence, the thermodynamic driving force for oxidative skeletal cleavage may be weak. The influence of the carbon or sulfur atoms in carbo- or thiophosphazenes such as 7-9 is not yet known.

General Chemical Stability. It is often difficult to separate the role of the skeletal atoms from the influence of the side groups with respect to resistance to heat, water, acids, bases, halogenating agents, etc.

At high temperatures, in the absence of oxygen, all linear or branched polymers are thermodynamically unstable to depolymerization to small molecule rings or monomers or to random fragmentation. The breakdown to small molecules represents an attempt by the system to maximize the entropy as represented by the $T\Delta S$ term in the usual free energy relationship. This is the reason why many polysiloxanes and polyphosphazenes depolymerize to small-molecule cyclic analogues when heated at temperatures above 200-250°C. Virtually the only way to prevent this process is to crosslink the chains through the side groups, an aspect that will be discussed later. Poly(methylsilane) undergoes an interesting thermal rearrangement.[23,24] At elevated temperatures (450°C) carbon atoms from the methyl side groups migrate into the skeleton to generate a carbosilane structure (4). This is a preliminary step *en route* to the formation of silicon carbide.

The stability of a polymer to aqueous media is usually one of the primary requirements for technological applications. Hydrolytic stability is sometimes difficult to predict on the basis of the chain structure. The silicon-oxygen bonds in poly(organosiloxanes) are in principle almost as sensitive to hydrolytic cleavage as are their counterparts in linear silicates. The fact that most poly(*organo*siloxanes) are stable to aqueous media reflects the protective function of the hydrophobic organic side groups. The same is true of polyphosphazenes. Most polyphosphazenes are stable to water and aqueous acid or base. But, if an organic side group (such as amino acid ester side unit) can be hydrolyzed and replaced by an -OH side unit linked to phosphorus, a rearrangement occurs in which the proton migrates from oxygen to skeletal phosphorus, saturating the skeleton and rendering the resultant phosphazane susceptible to hydrolytic sketelal cleavage. This is an example of a system in which hydrolytic sensitivity is actually a useful property since it underlies the design of polyphosphazenes for bioerodible medical uses.[25] Polysilanes are reported to be insensitive to hydrolysis especially when the backbone is well protected by hydrophobic side groups. Polysilynes are also stable, possibly because the dendritic arrangement generates a more sterically crowded structure.

Electronic Conductivity. The "exotic organic" polymers (Figure 2) are of interest mainly for their backbone electronic conductivity after doping with oxidizing or reducing agents. Polysiloxane and polyphosphazene backbones lack this property, but polysilane chains and silyne dendritic structures are semiconductors after they have been doped.

This semiconduction arises from sigma-electron delocalization, as distinct from the pi-electron delocalization found in the organic conductors.[26-29] The sigma (single) bonds in polysilanes have bonding (σ) and antibonding (σ^*) orbital components. As in solid elemental silicon, the more silicon atoms present in the system and the larger the number of sigma-orbitals, the greater will be the tendency for the bonding and antibonding levels to coalesce into bands, and the smaller will be the band gap. Treatment of a polysilane with an oxidizing agent such as AsF_5 removes an electron from the silicon chain to leave a hole (radical cation). These are believed to be the current carriers.

Optical Properties Associated with the Backbone. The polysiloxane backbone has a broad window of transparency (as measured for poly(dimethylsiloxane)) from the 250 nm region in the ultraviolet to the near infrared. The polyphosphazene skeleton (perhaps surprisingly, in view of the formally unsaturated bonding) has a similar, broad window from the 220 nm region in the ultraviolet to the near infrared. By contrast, polysilanes with their sigma-conjugation and relatively easy $\sigma \rightarrow \sigma^*$ electron transitions have an intense electronic absorption in the 300-400 nm region of the near ultraviolet. The specific absorption wavelength depends on the temperature and the types of side groups present in ways that suggest that the conformation of the backbone has a marked influence on the absoption characteristics. Properties such as photoconductivity and piezochromic behavior are also associated with these phenomena. In addition, because of the strong photo-absorption characteristics of the backbone, polysilanes undergo facile chain scission when irradiated with ultraviolet light, a property that underlies their investigation as microlithographic resists. [23,30,31] Polysilynes behave in a similar fashion. [32]

The transparency of the backbone in species such as polyphosphazenes or polysiloxanes is an advantage for applications where stability to visible- or ultraviolet radiation is important (space applications or terrestrial exposure to intense sunlight), or where radiation-induced reactions of the side groups are required without affecting the polymer backbone.

Resistance to High Energy Radiation. One of the most important advantages of polymers that contain no carbon in the backbone is their resistance to chain cleavage when exposed to X-rays or γ-radiation. This is especially important for medical materials that must be sterilized by radiation techniques or for polymers that must be radiation crosslinked through the side groups without cleavage of the main chain. Unlike -C-C- units, backbones that consist of -P=N- or -Si-O- units are resistant to free-radical cleavage processes. Hence, these inorganic polymers have important advantages for uses in all areas of radiation technology.

Influence of the Side Groups

As mentioned earlier, the properties generated by a polymer are a composite of those imposed by the backbone structure and those that result from the presence of different side groups. In practice, fine-tuning of the properties is accomplished most easily by changes in the side group structures. For example, solubility or insolubility in different solvents depends critically on the types of organic side groups attached to the main chain. So too do a variety of other properties from materials flexibility to optical and surface properties.

Influence of Side Groups on Polymer and Materials Flexibility. The flexibility and toughness of a polymer depend not only on the backbone structure but also on the size, shape, flexibility, and polarity of the side groups. Even though the backbone may be highly flexible, that flexibility may be reduced by the presence of side groups that interact strongly with each other via van der Waals or polar forces. Such strong interactions will raise the barrier to torsion of individual repeating units, reduce the overall chain flexibility, and raise the glass transition temperature. This relationship has been studied in greatest detail for the polyphosphazenes. However, the principles involved are quite general and are believed to apply to other systems also.

In polyphosphazenes, the Tg can be tuned over a range of more than 200°C by side group changes. The larger, more rigid side units, or those that can associate by hydrogen bonding, give rise to the highest T_g values. For example, the following progression of T_g's in $(NPR_2)_n$ reflects these changes: R = $OCH_2CH_2CH_2CH_3$ (16) (-105°C), $-OCH_2CH_2OCH_2CH_2OCH_3$ (21) (-84°C), OCH_2CF_3 (17) (-66°C), O-Phenyl (19) (-8°C), compound 27 (+68°C), and the polymer where R = NH-Phenyl (+91°C). Even greater subtlety is possible by the incorporation of two or more different types of groups into the same polymer molecule.

Influence on Crystallinity. The materials' properties of polymers depend not only on the elements and side groups present but also on the ways in which the polymer chains interact with each other in the solid state. Ordered packing of the chains gives rise to microcrystalline domains. These serve as meltable crosslinks that provide strength and toughness. The side groups attached to an inorganic polymer chain play the major role in microcrystallite formation since it is the side groups that usually dominate in intramolecular interactions. Again, illustrations from phosphazene polymer chemistry will make this clear.

Polymer 17, poly[bis(trifluoroethoxy)phosphazene], forms microcrystalline fibers and films.[33] So too does polymer 19, poly(diphenoxyphosphazene).[33] However, the counterpart polymers that contain two similar but different types of side groups, 18 and 20, are amorphous.[34,35] This is because the lack of molecular symmetry in 18 and 20 prevents an ordered packing of the chains. Moreover, polymers 16 and 21 are amorphous even though only one type of side group is linked to each chain.[21] Here, the high flexibility and conformational disorder of the side groups prevents ordered packing in the solid state. Thus, it will be clear that multiple opportunities exist for tailoring the physical properties by the rational introduction of different side groups.

Optical Properties. Five different types of optical properties can be designed into an inorganic polymer by the incorporation of specific side groups. These are: optical absorption in the UV or visible over and above that imposed by the backbone, tailored refractive index, side chain liquid crystallinity, non-linear optical behavior, and photochromism.

If the backbone is transparent in a particular region of the spectrum, the optical absorption can be controlled by the spectral characteristics of the side groups. Thus, for polyphosphazenes, which are transparent throughout the visible and near ultraviolet, side groups can be incorporated that absorb in specific regions within this window.[36] This is useful for the preparation of optical filters and for the design of photosensitive films for use in photography or photolithography.

The ability to tune the refractive index of a polymeric material is important in the design of polymers for lightweight lenses, prisms, and optical waveguides. Because the refractive index of an organic compond varies with the number of pi-electrons in the molecule, the refractive index of a polymer can be adjusted by the replacement of one type of side group by another that has a different number of pi-electrons.[37] Polyphosphazenes are particularly appropriate for this type of property tuning because the side groups can be changed so easily (see later). Polymer 22 forms a glass that has a refractive index of 1.686 at 623 nm.

Side groups that form liquid crystalline domains can be linked to flexible polymer chains, such as polysiloxanes or polyphosphazenes to generate liquid crystalline polymers such as 23.[38,39] Similarly, polarizable organic side groups, as in 24, can be poled at temperatures above the polymer Tg to generate second order NLO activity.[40] Polymer 24 has a high initial d_{33} coefficient of 34-45 pm/V, which is similar to that of lithium niobate. Finally, polymer 25 is an example of a photochromic material.[41]

In all of these examples the inorganic polymer chain serves as a stable and optically transparent platform for the photoactive side groups. This is also true for polymers that bear side groups that react under the influence of radiation, as discussed in the following section.

Side Groups that are Sensitive to UV and Higher Energy Radiation. Polymer 26 has a high sensitivity to crosslinking through the side groups when exposed to an electron beam.[42] This polymer has been studied as a resist material for electron beam microlithography. Polyphosphazenes that bear alkyl ether side groups, such as 21, undergo facile crosslinking when exposed to γ-rays, a reaction which involves free radical C-H and C-C bond cleavage, followed by cross combination between different chains.[43,44] This crosslinking process has been studied as a route to biomedical hydrogels, dimensionally stable solid polymeric electrolytes, and for grafting biomedically compatible surfaces onto other polymers. The same side groups can be crosslinked by ultraviolet radiation. As mentioned in an earlier section, it is the radiation stability of the inorganic backbone that favors the use of these polymers in this type of process.

Electronic Conductivity via the Side Groups. A number of systems exist in which the inorganic backbone serves as an electrically inert platform for side groups that favor electronic conduction in the solid state. Perhaps the most dramatic of these are the siloxane-phthalocyanine polymers [45] which, when doped with an oxidizing agent, show metal-level conductivity. The conduction pathway is via the phthalocyanine side groups, perhaps assisted by the counter anions present in the lattice.

Polyphosphazenes with ferrocene side groups (27) can be oxidized chemically or electrochemically to yield semiconducting solids. [46] The electroactivity arises from the metallocene side groups and not from the backbone. Furthermore, polyphosphazenes with pyrrole, thiophene, or furan side groups undergo limited side group polymerization and become conductive when oxidized chemically.[48]

Ionic Conductivity Arising From Side Group Structure. One of the most promising solid polymeric ionic conductors for use as the electrolyte in solid rechargeable lithium batteries was discovered as a result of a collaboration between members of the author's synthesis group at The Pennsylvania State University and the electrochemistry group of D. F. Shriver at Northwestern University.[49-53] The objective of the research was to design, find pathways for the synthesis, and evaluate the electrochemistry of a new polymer that would be an improvement over poly(ethylene oxide)/lithium triflate, the normal standard in this area.

The macromolecule known as MEEP (21) was the outcome of this work, a polymer designed to utilize the high chain mobility of polyphosphazenes and the flexibility, cation complexation-, and ion-pair separation-properties of oligo-alkyl ethers. Unlike poly(ethylene oxide), MEEP is completely amorphous, and has a low T_g of -80°C. Solid solutions of lithium triflate in this polymer show room temperature conductivities nearly three orders of magnitude higher than in poly(ethylene oxide). The investigation of this system as an electrolyte in lightweight, large surface area, lithium batteries is continuing, with special emphasis on electrolytes that are crosslinked by radiation techniques. A similar system to MEEP, but based on a siloxane backbone, has also been reported. [54,55]

Influence of the Side Groups on Thermal Behavior. The types of side groups linked to an inorganic polymer chain have a striking influence on the response of the polymer to elevated temperatures. If the side group is itself relatively unreactive at high temperatures, as in the examples shown in 15, 17, 19, or 28, the main reaction will be the depolymerization of the polymer to small molecules, probably cyclic species with the same repeating structure as the high polymer. In this case, as mentioned earlier, large side groups that generate intermolecular steric repulsions will lower the temperature at which depolymerization occurs, because depolymerization relieves the steric constraints.[56] On the other hand, if the side groups react with other side groups at high temperatures, especially by condensation or free radical cross-combination reactions, then crosslinks will be formed. Extensive crosslinking will generate ceramics.[57]

The now-classical examples of this crosslinking process involve the conversion of polysilanes, carbosilanes, and silazanes to silicon carbide or silicon nitride.[10,24] The alkyl side group condensation process involves volatilization of alkanes or hydrogen, and eventually leads to a total loss of the organic components.[20,58] Similar processes occur during the formation of boron nitride[59-61] and phosphorus nitrides[62] from the corresponding inorganic-organic polymers. The advantages of the preceramic polymer processes are that the material can be shaped at the linear or branched polymer level before crosslinking occurs. The onset of crosslinking stabilizes the shape of the object under conditions where liquefaction of a linear polymer would normally occur.

Side Groups for Biomedical Properties. Polymeric materials are becoming increasingly important as biomedical materials - as inert replacements for living tissues, as membranes, microencapsulants, and bioerodible materials for controlled drug delivery or temporary tissue reinforcement. Two classes of inorganic polymers - polysiloxanes and polyphosphazenes are at the forefront of these developments. Poly(dimethylsiloxane) is widely used in biomedicine as an inert elastomer and as a matrix for the diffusion release of birth control drugs, mainly because of its elasticity and hydrophobic character, which discourage biological rejection mechanisms. As mentioned earlier, it is the $Si-CH_3$ side units that define the hydrophobic character.

The potential for biomedical uses are far greater for polyphosphazenes because (a) the side groups can be varied to generate elasticity, water solubility, hydrogel formation, hydrophobicity, antibacterial character, bioerodibility, membrane formation, and microcapsule formation, and (b) the choice of appropriate side groups allows the possibility of hydrolytic degradation to harmless small molecules that can be metabolized or excreted.[25] Perhaps the most striking recent biomedical development is the use of polymer 29, crosslinked by calcium cations, as a microencapsulation hydrogel for mammalian cells, proteins, and microorganisms. [63,64] Other biomedical polymers that depend for their properties on the side groups attached to a polyphosphazene chain have been described in a recent review chapter.[25]

It could be argued that all of these side group variations can be used to tune the properties of *organic* backbone polymers, and this is partially true. However, the inorganic backbone systems provide a special advantage with respect to conversion of polymers to ceramics, optical transparency, and biomedical attrributes. Moreover, at least in the polyphosphazene series, the method of synthesis allows a far wider range of side groups to be linked to the backbone than in organic polymer systems and favors higher loadings of "active" side groups. This fact is illustrated below.

Methods of Synthesis

Ring-Opening Polymerization.. The primary method for the assembly of long chain inorganic polymer backbones is the ring-opening polymerization of small-molecule cyclic species. Three examples are shown in Scheme 1, and these are the main access routes to polysiloxanes, polyphosphazenes, and polysilanes. A novel variation is shown in the fourth reaction.[18] The polymer obtained by the phosphazene polymerization shown in the third reaction is not a final product, but rather is a macromolecular intermediate for use in polymer substitution reactions. This was the basis of our discovery of poly(organophosphazenes) [33] and it underlies the present broad diversity of this system.

Macromolecular Substitution. One of the most important advantages of phosphazene polymer 30 is its high reactivity to replacement of the chlorine atoms by organic groups, as illustrated in Scheme II. This high reactivity is virtually unique in polymer chemistry, and it results from the presence of the inorganic backbone and the ease of replacement of chlorine (or fluorine) atoms linked to phosphorus. The significance of this process is that a very wide range of different organic or organometallic side groups can be linked to the backbone *without the need to assemble a new polymer chain for each new example.* From a polymer design and synthesis viewpoint this is an enormous advantage that has so far allowed access to more that 300 different types of phosphazene polymers each with a different set of properties.[8]

Condensation. The linkage of small, difunctional molecules via the elimination of small molecules such as water is the main method for the synthesis of organic polymer [illegible] as polyamides and polyesters, and of totally inorganic polymers such as polysilicates and polyphosphates. Condensations of a different kind are employed for the synthesis of polysilanes and silynes, in which chlorine atoms are removed by treatment with a molten alkali metal such as sodium (Scheme III).[23] Also, Scheme III shows condensation routes to polyphosphazenes, which allow the synthesis of polymers not accessible via the reactions of intermediate **30**.[65-69]

Addition Polymerization. Unlike the situation in organic polymer chemistry, addition reactions play a relatively insignificant role in inorganic polymer synthesis. The main exception is where the inorganic component is the side group unit and the backbone is an organic chain. [6]

Surface Reactions. At the materials' rather than the molecular level, it is possible to synthesize special surfaces by chemistry carried out in the surface region of an inorganic-organic polymer. Again, the largest number of examples have been reported for polyphosphazenes,[70,71] but the principles are applicable to other inorganic polymer systems as well.

Composites. Finally, a hybridization of linear inorganic polymer chemistry with sol-gel ceramic processes has been achieved by the preparation of composites that involve MEEP (**21**) and silicon, titanium, zirconium, or aluminum oxide crosslinked gels.[72,73] These composites have improved mechanical, optical, and ionic conductivity properties compared to the individual components.

Future Developments

The field of inorganic polymers is still in its infancy. Apart from polysiloxane technology, which is well-advanced, most other areas are still at the stage of development of synthesis methods, molecular and materials characterization, and structure-property correlations. Specific polyphosphazene elastomers are manufactured for use as broad temperature range, non-burning oil-, heat-, and chemically resistant applications, but the emerging biomedical, surface, electrolytic, and electro-optical uses may well dominate the future. The future of polysilanes and polysilynes will undoubtedly revolve around their role in synthesized ceramics and their uses in the electronics industry.

But the best clues to the future of the field of inorganic polymers are to be found in the materials properties that *cannot* be achieved using commercial organic polymers. This includes the wide range of properties that are now taken for granted for totally inorganic materials, as summarized in Figure 1. From a research point of view, the need for the future is to use the principles summarized in this article to devise and prepare polymers that contain elements other than or in addition to silicon, phosphorus, sulfur, and carbon, and to understand the special advantages that each new element confers on the polymer and on the materials properties. In this way, new materials can be designed that will play a key role in the future development of materials science and technology.

References

[1] H. R. Allcock, *Heteroatom Ring Systems and Polymers*, Academic Press, New York 1967.

[2] J. E. Mark, H. R. Allcock, R. West, *Inorganic Polymers*, Prentice Hall, Englewood Cliffs, N. J. 1992.

[3] M. Zeldin,, K. J. Wynne, H. R. Allcock (eds.), *Inorganic and Organometallic Polymers*, ACS Symp. Ser. 360, American Chemical Society, Washington, D.C. 1988.

[4] H. R. Allcock, F. W. Lampe, *Contemporary Polymer Chemistry*, Academic Press, 2nd. ed., 1990, Ch. 9.

[5] R. M. Laine, ed., *Inorganic and Organometallic Polymers with Special Properties* (NATO ASI Ser., Applied Sciences, Vol. 206), Kluwer, Dordrecht, 1992.

[6] L. McNally, C. W. Allen, *Heteroatom Chem.* 1993, 4, 159.

[7] H. R. Allcock, *Phosphorus-Nitrogen Compounds*, Academic Press, New York 1972.

[8] J. E. Mark, H. R. Allcock, R. West, *Inorganic Polymers*, Prentice Hall, Englewood Cliffs, N. J. 1992, Ch. 3.

[9] P. A. Bianconi, F. C. Schilling, T. W. Weidman, *Macromolecules* 1989, 22, 1697.

[10] D. Seyferth, G. H. Wiseman, J. M. Schwark, Y.-F. Yu, C. A. Poutasse in *Inorganic and Organometallic Polymers* (Eds: M. Zeldin, K. J. Wynne, H. R. Allcock), ACS Symp. Ser. 360, American Chemical Society, Washington, D.C. 1987, p. 262.

[11] I. Manners, G. Renner, O. Nuyken, H. R. Allcock, *J. Am. Chem. Soc.* 1989, 111, 5478.

[12] H. R. Allcock, S. M. Coley, I. Manners, G. Renner, O. Nuyken, *Macromolecules* 1991, 24, 2024.

[13] J. A. Dodge, I. Manners, H. R. Allcock, G. Renner, O. Nuyken, *J. Am. Chem. Soc.* 1990, 112, 1268.

[14] H. R. Allcock, J. A. Dodge, I. Manners, *Macromolecules* 1993, 26, 11.

[15] M. Liang, I. Manners, *J. Am. Chem. Soc.* 1991, 113, 4044; *Polym Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1993, 34, 324.

[16] M. M. Labes, P. Love, L. F. Nichols, *Chem. Rev.* 1979, 79, 1.

[17] A. K. Roy, *J. Am. Chem. Soc.* 1992, 114, 1530; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1993, 34, 332.

[18] D. A. Foucher, B. Z. Tang, I. Manners, *J. Am. Chem. Soc.* 1992, 114, 6246.

[19] H. W. Roesky, M. Lucke, *J. Chem. Soc., Chem. Commun.* 1989, 748.

[20] L. L. Hench, J. K. West, eds. *Chemical Processing of Advanced Materials*, Wiley, New York 1992, Ch. 49, 53, 62, 68, 69, 70.

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

[22] J. E. Mark, H. R. Allcock, R. West, *Inorganic Polymers*, Prentice Hall, Englewood Cliffs, N. J. 1992, Ch. 4.

[23] *ibid* Ch. 5

[24] S. Yajima, J. Hayashi, M. Omori, *Chem. Lett.* 1975, 931; S. Yajima, K. Okamura, J. Hayashi, *Chem. Lett.* 1975, 1209.

[25] H. R. Allcock in *Biodegradable Polymers as Drug Delivery Systems* (Eds: R. Langer, M. Chasin), Marcel Dekker, New York 1990, p.163.

[26] J. Michl, *Acct. Chem. Res.* 1990, 23, 127.

[27] K. Takeda, H. Teramae, N. Matsumoto, *J. Am. Chem. Soc.* 1986, 108, 8166.

[28] P. Trefonas, R. West, R. D. Miller, D. Hofer, *Polym. Lett. Ed.* 1983, 21, 832.

[29] K. Klingensmith, J. Michl, *J. Am. Chem. Soc.* 1986, 108, 7438.

[30] T. Karatsu, R. D. Miller, R. Sooriyakumaran, J. Michl, *J. Am. Chem. Soc.* 1989, 111, 1140.

[31] R. D. Miller, J. Rabolt, R. Sooriyakumaran, W. Fleming, G. N. Fickes, B. L. Farmer, H. Kuzmany in *Inorganic and Organometallic Polymers* (Eds. M. Zeldin, K. J. Wynne, H. R. Allcock), ACS Symp. Ser. 360, American Chemical Society, Washington, D. C. 1988, p.43.

[32] R. R. Kunz, M. W. Horn, R. B. Goodman, P. A. Bianconi, D. A. Smith, C. A. Freed, *J. Vac. Sci. Technol.* 1990, B8(6), 1820.

[33] H. R. Allcock, R. L. Kugel, *J. Am. Chem. Soc.* 1965, 87, 4216; H. R. Allcock, R. L. Kugel, K. J. Valan, *Inorg. Chem.* 1966, 5, 1709.

[34] S. H. Rose, *J. Polymer Sci. B.* 1968, 6, 837.

[35] R. E. Singler, N. S. Schneider, G. L. Hagnauer, *Polymer Sci. Eng.* 1975, 15, 321.

[36] H. R. Allcock, S. D. Wright, K. M. Kosydar, *Macromolecules* 1978, 11, 357.

[37] H. R. Allcock, M. N. Mang, A. A. Dembek, K. J. Wynne, *Macromolecules* 1989, 22, 4179.

[38] R. E. Singler, R. A. Willingham, R. W. Lenz, A. Furakawa, H. Finkelman, *Macromolecules*, 1987, 20, 1727.

[39] C. Kim, H. R. Allcock, *Macromolecules* 1987, 20, 1726.

[40] H. R. Allcock, A. A. Dembek, C. Kim, R. L. S. Devine, Y. Shi, W. H. Steier, C. W. Spangler, *Macromolecules* 1991, 24, 1000.

[41] H. R. Allcock, C. Kim, *Macromolecules* 1991, 24, 2846.

[42] M. F. Welker, H. R. Allcock, G. L. Grune, R. T. Chern, V. T. Stannett, *Polym. Prepr.* 1992.

[43] H. R. Allcock, S. Kwon, G. H. Riding, R. J. Fitzpatrick, J. L. Bennett, *Biomaterials* 1988, 19, 509.

[44] J. L. Bennett, A. A. Dembek, H. R. Allcock, B. J. Heyen, D. F. Shriver, *Chemistry of Materials* 1989, 1, 14.

[45] T. J. Marks, Science, 1985, *227*, 881. T. J. Marks, J. G. Gaudiello, G. E. Kellogg, S. M. Tetrick in *Inorganic and Organometallic Polymers* (Eds. M. Zeldin, K. J. Wynne, H. R. Allcock), ACS Symp. Ser. 360 , American Chemical Society, Washington, D. C. 1988, p. 224.

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

[47] R. A. Saraceno, G. H. Riding, H. R. Allcock, A. G. Ewing, *J. Am. Chem. Soc.* 1988, 110, 980.

[48] H. R. Allcock, J. A. Dodge, L. S. Van Duyke, C. R. Martin, *Chemistry of Materials* 1992, 4, 780.

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

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

[51] P. M. Blonsky, D. F. Shriver, P. E. Austin, H. R. Allcock, *Solid State Ionics* **1986**, 18 & 19, 258.

[52] J. L. Bennett, A. A. Dembek, H. R. Allcock, B., J. Heyen, D. F. Shriver, *Chemistry of Materials* **1989**, 1, 14.

[53] C. J. Nelson, W. D. Coggio, H. R. Allcock *Chemistry of Materials* **1991**, 3, 786.

[54] P. G. Hall, G. R. Davies, J. E. McIntyre, I. M. Ward, D. J. Bannister, K. M. F. Le Brocq, *Polym. Commun.* **1986**, 27, 98.

[55] D. Fisk, I. M. Khan, J. Smid, *Makromol. Chem., Rapid Commun.* **1986**, 7, 115.

[56] H. R. Allcock, *J. Macromol. Sci. - Revs. Macro. Chem.* **1970**, C4, 149.

[57] H. R. Allcock in *Chemical Processing of Advanced Materials* (Eds: L. K. Hench, J. K. West), Wiley, New York **1992**, p. 699.

[58] *Inorganic and Organometallic Polymers* (Eds: M. Zeldin, K. J. Wynne, H. R. Allcock), ACS Symp. Ser. 360, American Chemical Society, Washington, D.C. **1988**, Ch. 10-13, 30-32.

[59] Y. Kimura, Y. Kubo, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1993**, 34(1), 337.

[60] K. Su, E. E. Remsen, G. A. Zank, L. G. Sneddon, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem)*. **1993**, 34(1), 334.

[61] R. T. Paine, M. Fan, A. Hanprasopwattana, A. K. Datye, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1993**, 34(1), 336.

[62] H. R. Allcock, G. S. McDonnell, G. H. Riding, I. Manners, *Chemistry of Materials,* **1990**, 2, 425.

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

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

[65] R. H. Neilson, P. Wisian-Neilson, *Chem. Rev.* **1988**, 88, 541.

[66] P. Wisian-Neilson, R. H. Neilson, *J. Am. Chem. Soc.* **1980**, 102, 2848.

[67] R. H. Neilson, R. Hani, P. Wisian-Neilson, A. K. Roy, G. L. Hagnauer, *Macromolecules*, 1987, 20, 910.

[68] E. P. Flindt, H. Rose, Z. *Anorg. Allg. Chem.* 1977, 428, 204.

[69] R. A. Montague, K. Matyjasjewski, *J. Am. Chem. Soc.*, 112, 6721.

[70] H. R. Allcock, R. J. Fitzpatrick, *Chemistry of Materials* 1991, 3, 450.

[71] H. R. Allcock, S. Kwon, *Macromolecules* 1986, 19, 1502.

[72] B. K. Coltrain, W. T. Ferrar, C. J. T. Landry, T. R. Molaire, N. Zumbulyadis, *Chemistry of Materials* 1992, 4, 358.

[73] B. K. Coltrain, W. T. Ferrar, C. J. T. Landry, T. R. Molaire, D. E. Schildkraut, V. T. Smith, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* 1993, 34(1), 266.

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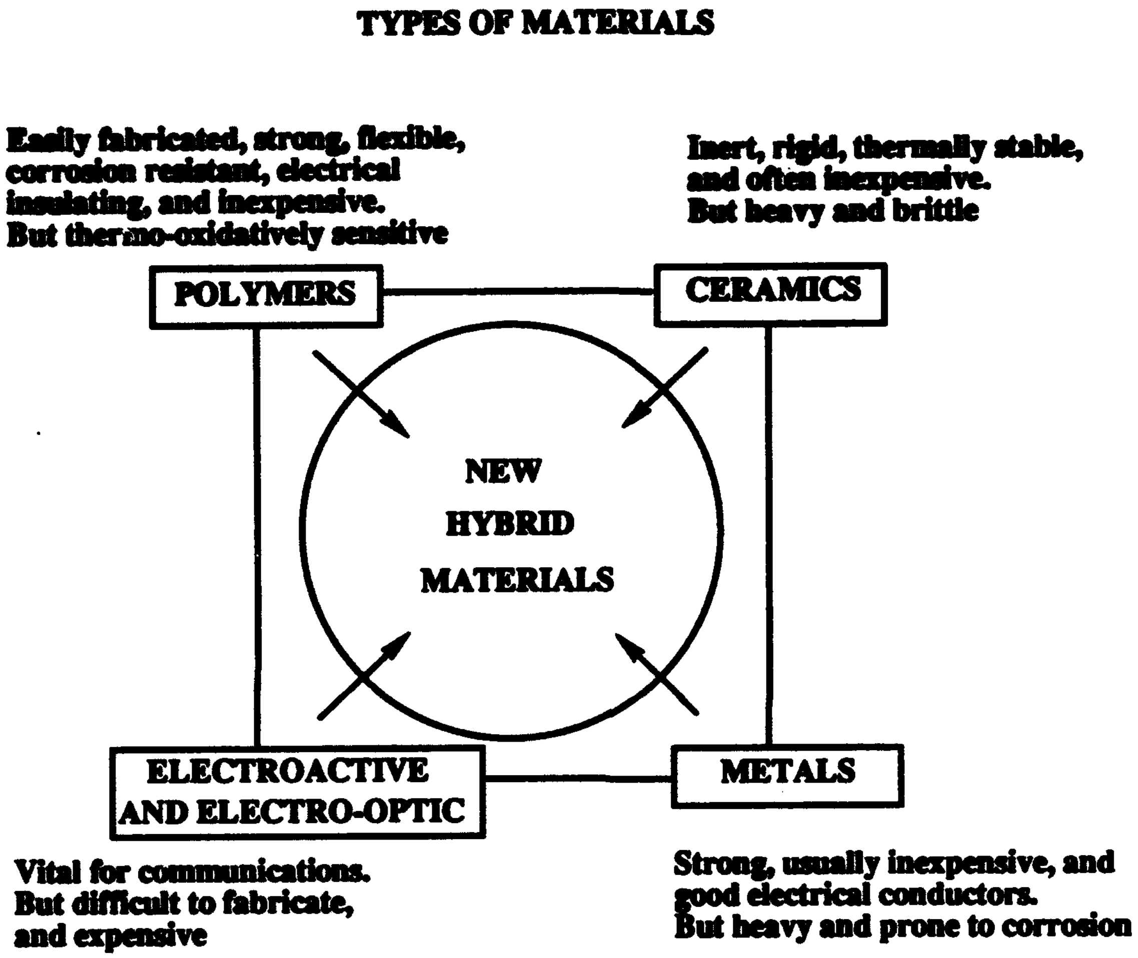
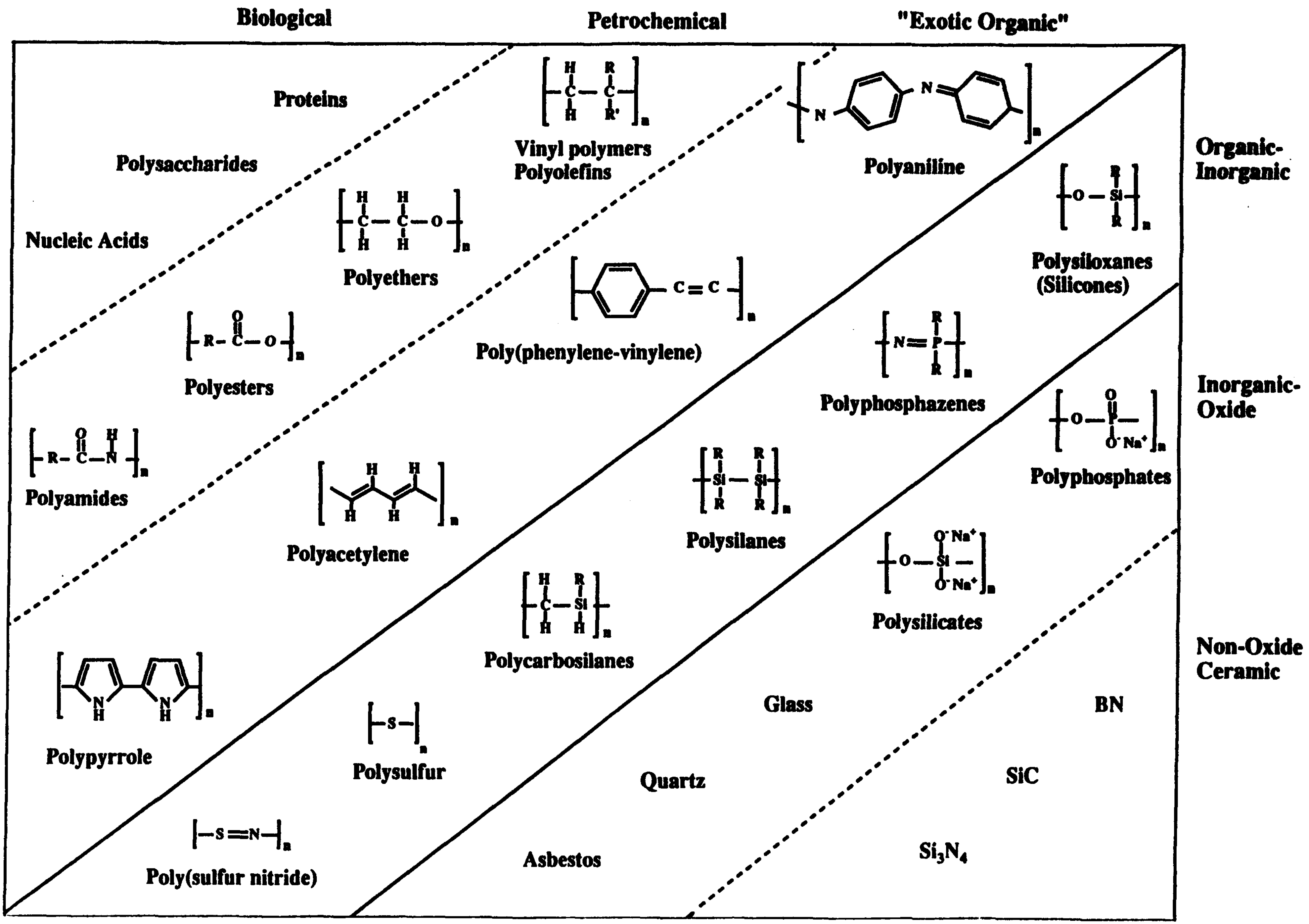
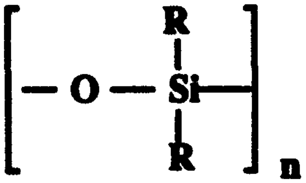


Figure 1. The four classical types of materials and their relationship to new hybrid materials that combine the strengths and minimize the weaknesses of existing substances.

Classification of Different Types of Polymer Systems

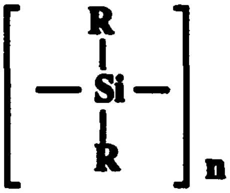


The Silicon Series



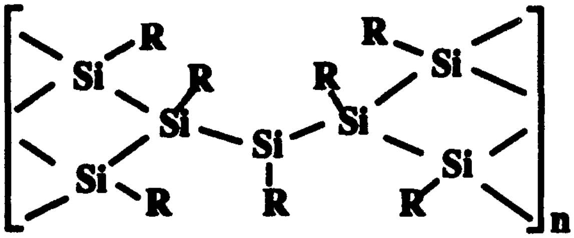
$\left[-\mathrm{O}-\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{Si}}}-\right]_n$

1

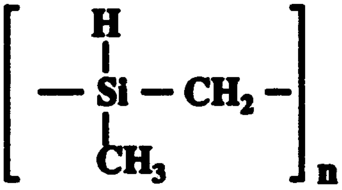


$\left[-\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{Si}}}-\right]_n$

2

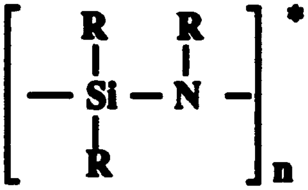


3



$\left[-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_2}-\right]_n$

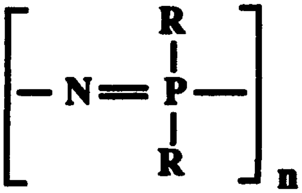
4



$\left[-\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{Si}}}-\overset{\mathrm{R}}{\mathrm{N}}-\right]_n^{*}$

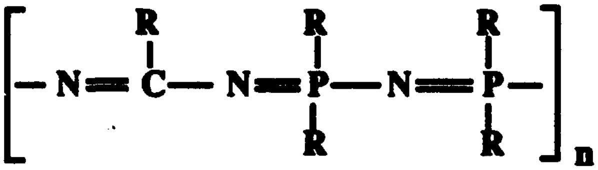
5

The Phosphorus Series



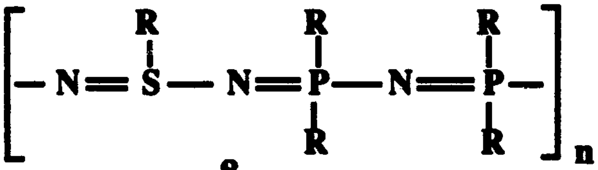
$\left[-\mathrm{N}=\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{P}}}-\right]_n$

6



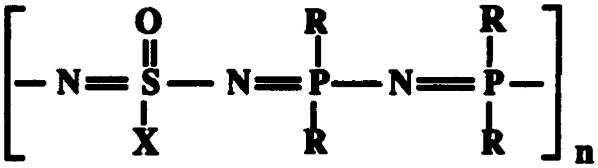
$\left[-\mathrm{N}=\overset{\mathrm{R}}{\mathrm{C}}-\mathrm{N}=\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{P}}}-\mathrm{N}=\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{P}}}-\right]_n$

7



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

8



$\left[-\mathrm{N}=\overset{\mathrm{O}}{\underset{\mathrm{X}}{\overset{\|}{\mathrm{S}}}}-\mathrm{N}=\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{P}}}-\mathrm{N}=\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{P}}}-\right]_n$

9

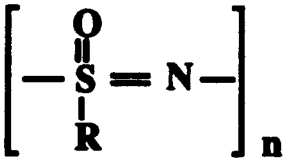
The Sulfur Series

$\left[-\mathrm{S}-\right]_n$

10

$\left[-\mathrm{S}=\mathrm{N}-\right]_n$

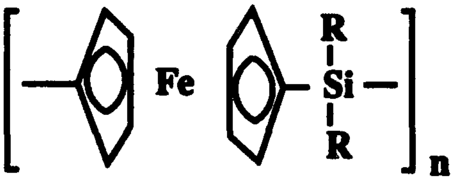
11



$\left[-\overset{\mathrm{O}}{\underset{\mathrm{R}}{\overset{\|}{\mathrm{S}}}}=\mathrm{N}-\right]_n$

12

The Metallo Series



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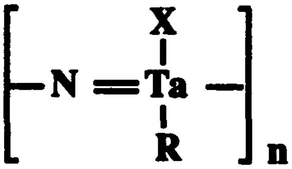
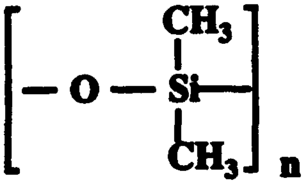


$\left[-\mathrm{N}=\overset{\mathrm{X}}{\underset{\mathrm{R}}{\mathrm{Ta}}}-\right]_n$

14

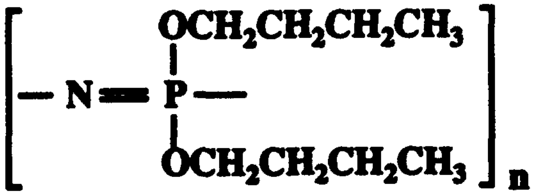
R = an organic group, X = a halogen atom

***Polysilazanes probably contain a high proportion of linked *cyclic* units**



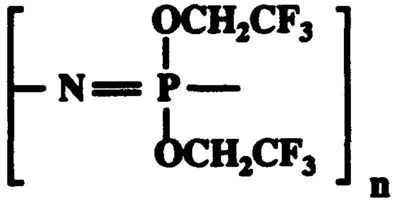
$$\left[-O-\overset{CH_3}{\underset{CH_3}{Si}}-\right]_n$$

15



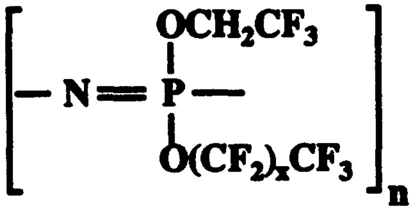
$$\left[-N{=}\overset{OCH_2CH_2CH_2CH_3}{\underset{OCH_2CH_2CH_2CH_3}{P}}-\right]_n$$

16



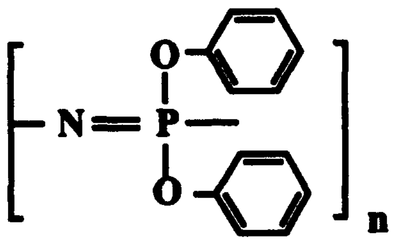
$$\left[-N{=}\overset{OCH_2CF_3}{\underset{OCH_2CF_3}{P}}-\right]_n$$

17



$$\left[-N{=}\overset{OCH_2CF_3}{\underset{O(CF_2)_xCF_3}{P}}-\right]_n$$

18



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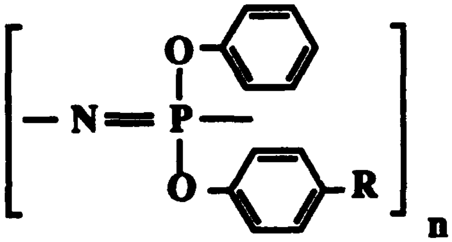

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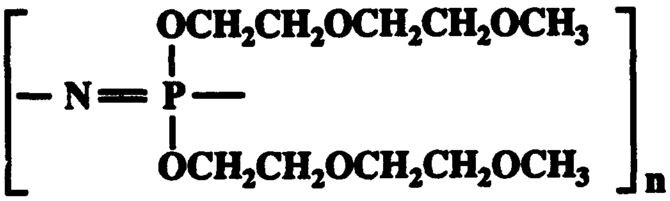
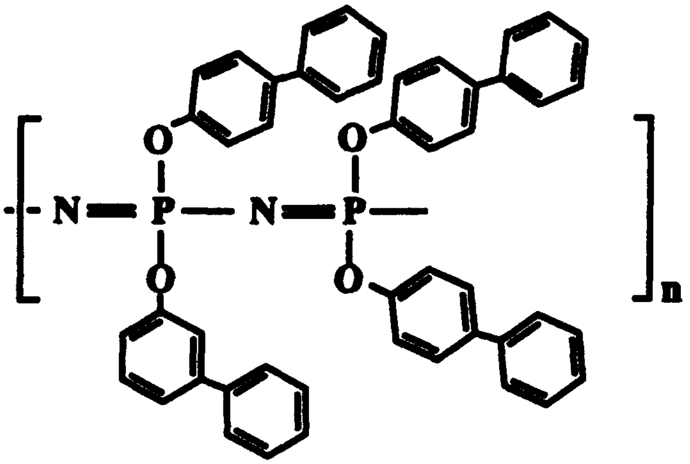


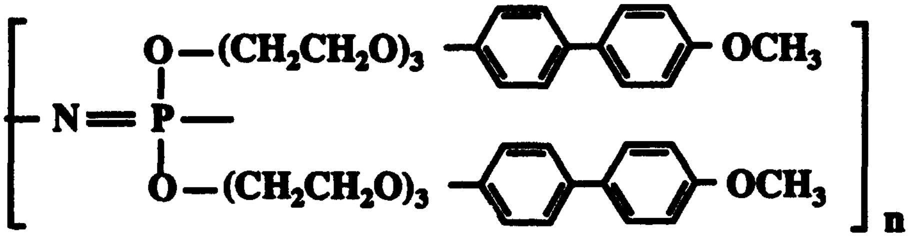
$$\left[-N{=}\overset{OCH_2CH_2OCH_2CH_2OCH_3}{\underset{OCH_2CH_2OCH_2CH_2OCH_3}{P}}-\right]_n$$

21



22

$T_g = +64_oC$. $n_{623\,nm} = 1.686$



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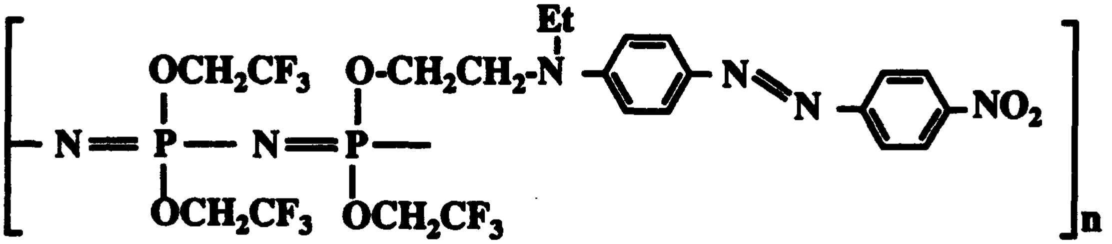
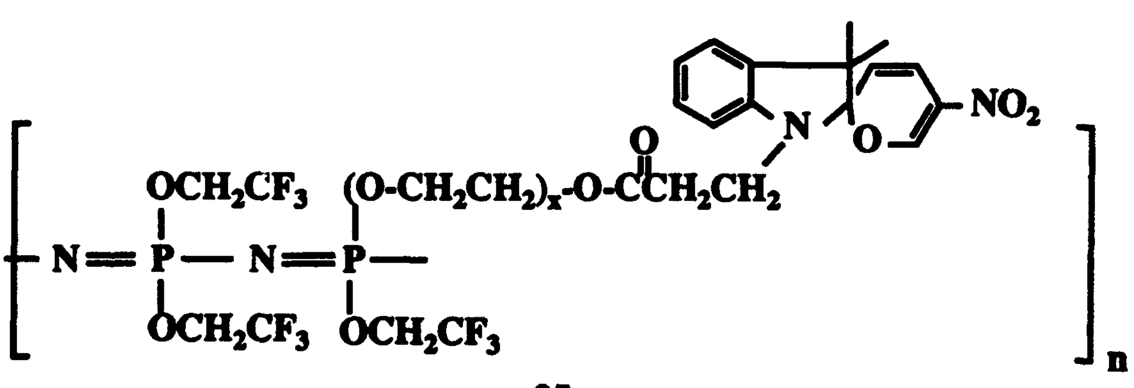


24

T_g = 19-44°C. d_{33} = 34-45 pm/V



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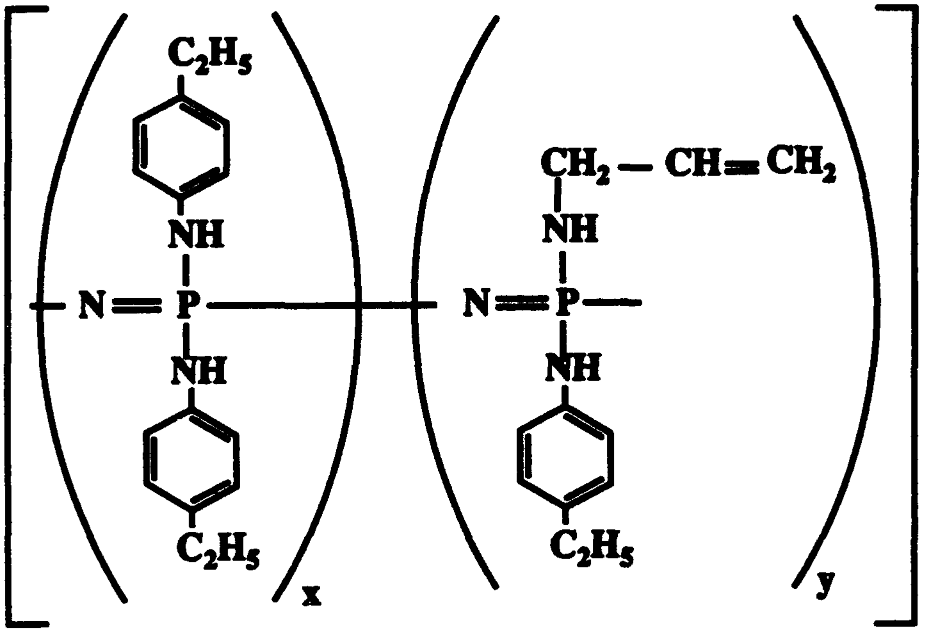

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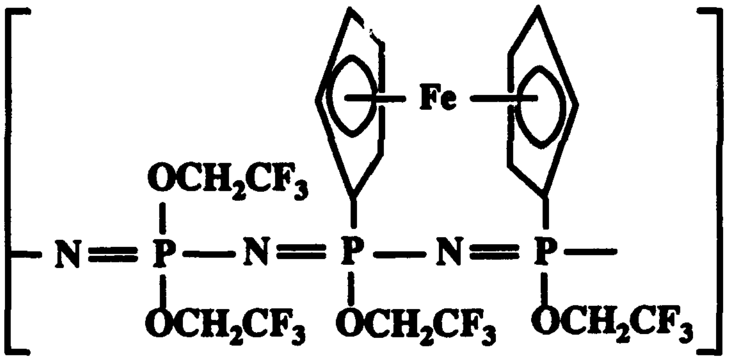

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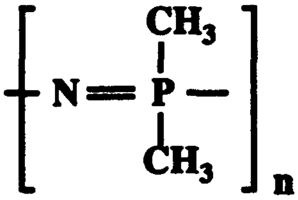
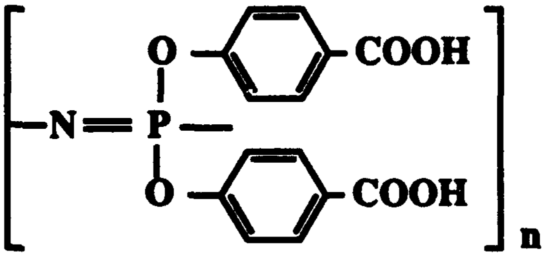


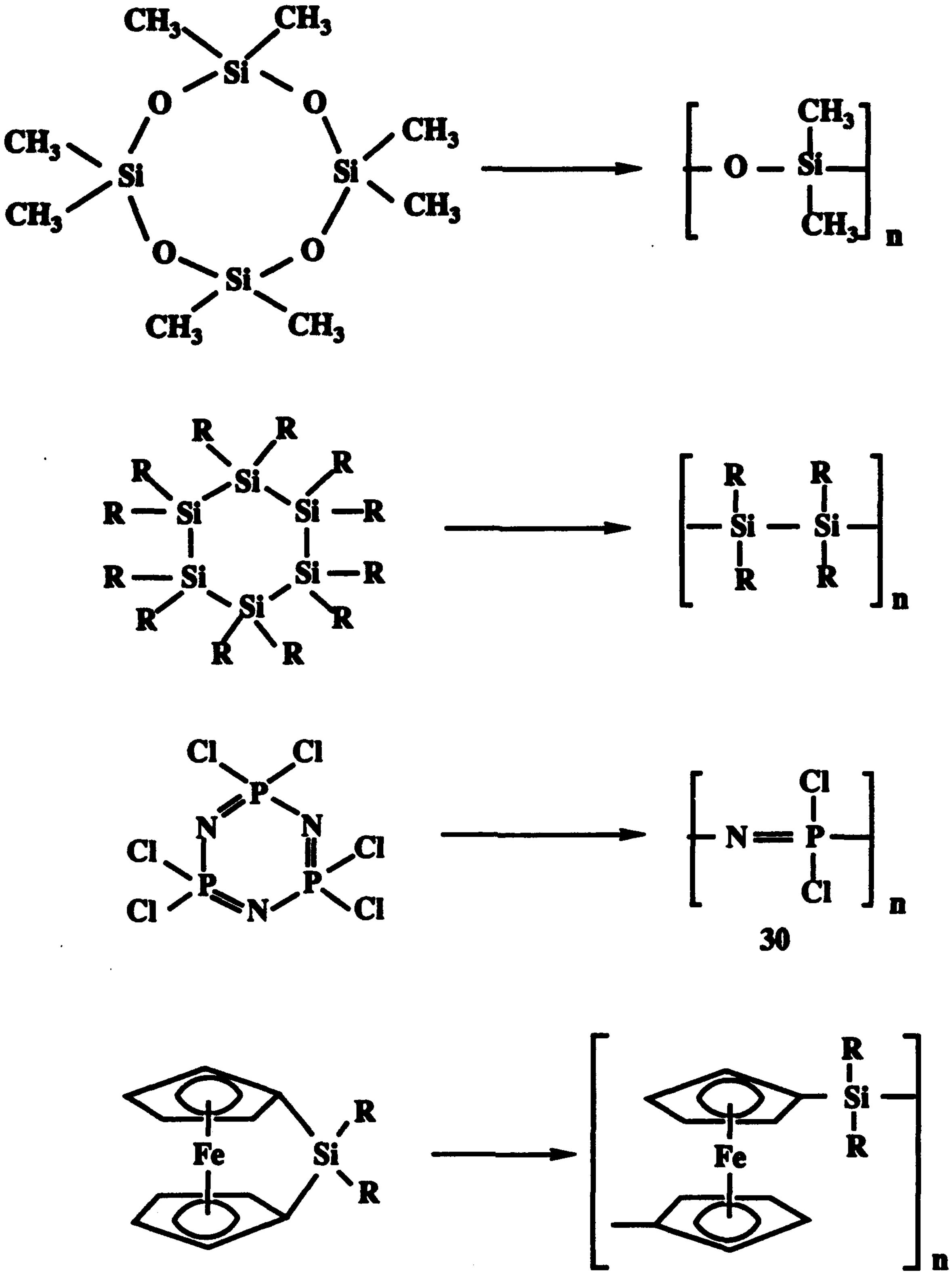
$$\left[\!-N{=}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{P}}-\right]_n$$

28



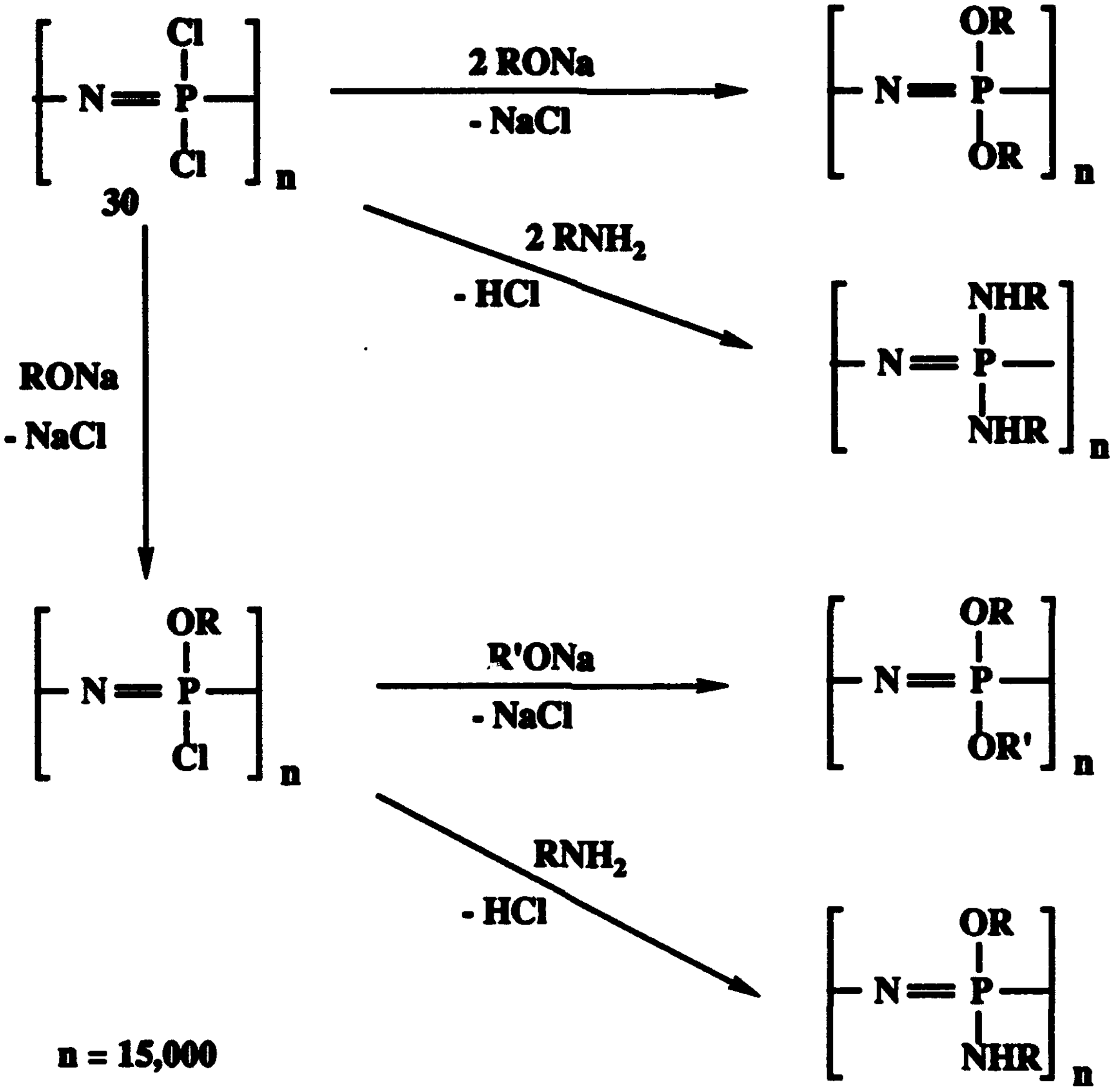
29

Scheme I



30

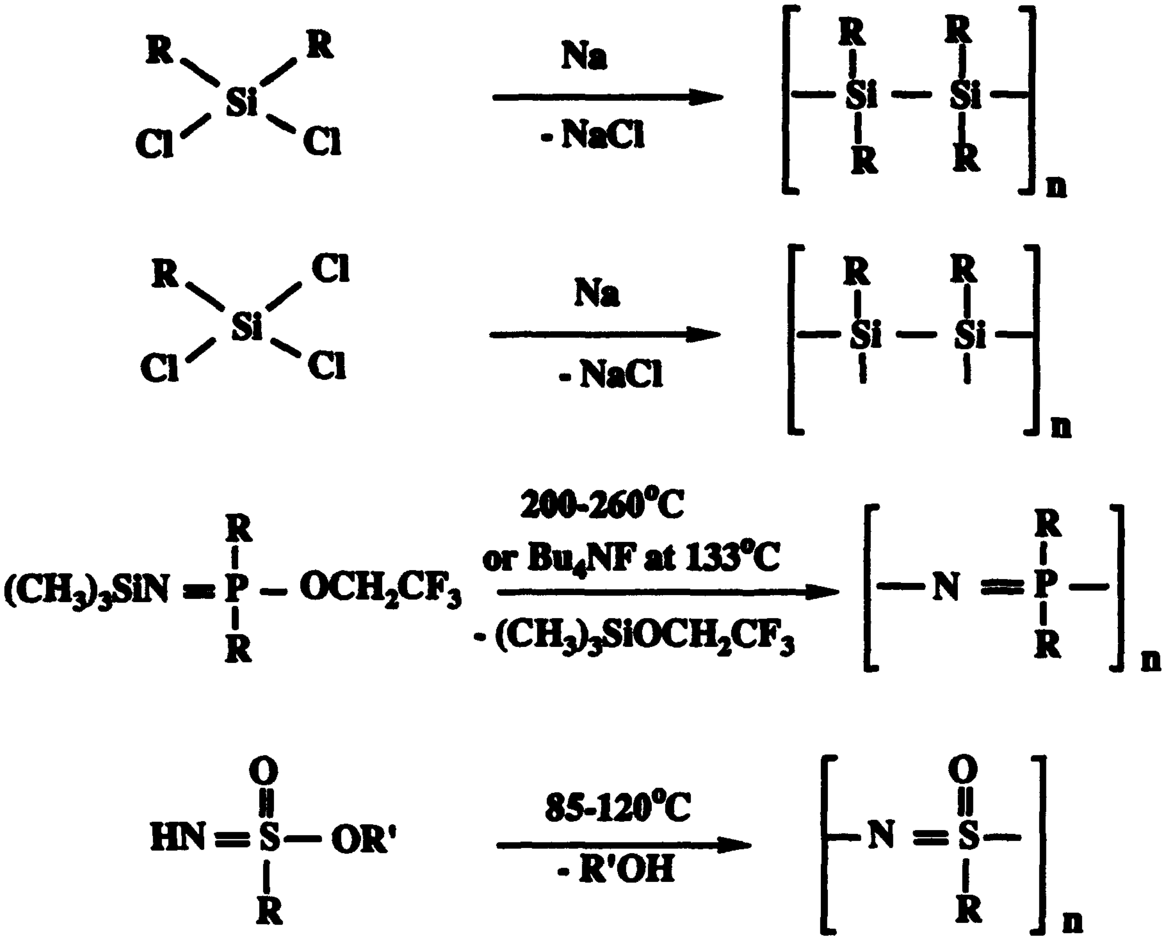
Scheme II



n = 15,000

R = an organic group

Scheme III


R
R
Si
Cl
Cl
Na
- NaCl
R
R
Si
Si
R
R
n
R
Cl
Si
Cl
Cl
Na
- NaCl
R
R
Si
Si
n
R
(CH3)3SiN = P - OCH2CF3
R
200-260°C
or Bu4NF at 133°C
- (CH3)3SiOCH2CF3
R
N = P
R
n
O
HN = S - OR'
R
85-120°C
- R'OH
O
N = S
R
n

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