Polyphosphazenes: New Polymers with Inorganic Backbone Atoms

A new class of macromolecules promises to solve many of the problems associated with synthetic high polymers.

Harry R. Allcock

High polymers are molecules that contain very long chains of skeletal atoms (linear polymers) or extensive sheets or three-dimensional arrays of atoms (cross-linked polymers). Linear polymers are important to modern technology because they are tough, flexible, or elastic, and are easily fabricated into fibers, films, or intricate shapes. These properties are a direct consequence of the presence of the long polymer chains.

The discovery of scores of synthetic polymers during the past 30 or 40 years has had a profound effect on the quality of civilized life. Synthetic fibers from nylon and polyesters are obvious examples, but synthetic polymers are now used in such a vast number of products from pocket electronic calculators and magnetic tape, to synthetic rubber, strong adhesives, and fiberglass boats that we take their presence very much for granted. Indeed, without high polymers many devices, such as artificial heart valves or portable artificial kidney machines, would not exist. Even if the older fabrication materials of wood, stone, metal, glass, and natural fibers could have been adapted to fulfill many of our modern needs, life would now be very much more expensive than it is.

Although few people outside polymer research and technology are aware of it, the last 5 to 10 years have seen a slackening of the pace with which new polymers have been introduced for fabrication and manufacture. Indeed, some polymer technologists believe that we may have reached the end of the first main expansive phase of polymer chemistry and that future developments will revolve around new fabrication techniques, novel reinforcement methods, and other ramifications of polymer engineering.

Although I do not subscribe to this view, the reasoning behind it should be examined. The argument is as follows. First, to a large degree, chemists have now synthesized most of the obvious organic polymers that were foreseen as logical developments from polyethylene, nylon, polyesters, and the like. This fact in itself is a tribute to the worldwide polymer synthesis attack that has been taking place since the 1940's. Second, it is reasoned that, with so many synthetic organic polymers now known, "blends" or "graft" combinations of them may solve many technological problems. Third, and perhaps more important, many chemists and technologists are concerned that we may now be demanding properties that synthetic organic polymers just cannot provide.

Deficiencies of Conventional High Polymers

Why do we need new polymers? What are the deficiencies and limitations of the available synthetic polymers? First, most of them are flammable—a natural consequence of the fact that they are made from organic materials. Second, they tend to melt or oxidize and char at high temperatures in the atmosphere—again a result of their organic composition. Only a few synthetic organic polymers remain flexible when cooled to low temperatures. Many of them soften, swell, or dissolve in gasoline, jet fuel, hot oil, or other hydrocarbons. Moreover, advances in biomedical engineering have been blocked by the fact that very few synthetic polymers can be used to fabricate artificial body components, such as artificial heart pumps, replacement blood vessels, and artificial kidneys. Many polymers either initiate a clotting reaction of blood, or they generate toxic, irritant, or even carcinogenic responses. The manufacturers of synthetic polymers are also aware of another problem: nearly all synthetic polymers are made from petrochemicals.

Inorganic Macromolecules

With these facts in mind, a number of research groups, including our own, have been attempting to develop entirely new classes of polymers that may eventually overcome the deficiencies described above and, at the same time, generate a second phase of polymer chemistry. The philosophy behind this approach is as follows. Nearly all polymers in common use today are organic polymers that contain long chains of carbon atoms in the backbone, or carbon atoms together with oxygen and nitrogen. The carbon atoms or the carbon-hydrogen bonds are believed to form weak links that are susceptible to oxidation or to decomposition catalyzed by ultraviolet light and are responsible for the flammability. Furthermore, because carbon has a relatively small covalent radius, the backbone bonds in organic polymers are quite short, and the torsional motions of the backbone linkages are inhibited. Hence, the elasticity or flexibility of many organic polymers is rather low. The "organic" nature of most high polymers is also believed to be responsible for the dissolution or swelling of many plastics and elastomers in hydrocarbon fuels and lubricants.

The new classes of polymers are those that contain inorganic elements such as silicon, phosphorus, sulfur, boron, or metal atoms in the backbone. Such atoms may impart flame-retardancy to a polymer, and they will undoubtedly alter the solubility and chain flexibility properties of a polymer. This new phase of polymer chemistry is still in its infancy; and, at the present time, only three systems have been developed to a commercial or precommercial stage. Two of these make use of silicon in the backbone, and the third has phosphorus in its backbone.

Silicone, or poly(organosiloxane) polymers have been known since the 1940's. Their structure is illustrated in **1**. They were first observed by Kipping (*1*) and were developed by the pioneering research work of Hyde (*2*), Rochow (*3*), and other investigators at the Corning Glass, Dow Corning, and General Electric research laboratories. Silicone rubber is now used in applications for which stability, flexibility, and biomedical compatibility are needed. A new class of thermally stable polymers based on alter-

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nating siloxane and carborane units have recently made their appearance (*4*).

The third class of inorganic polymers are the poly(organophosphazenes). In 1965 my co-workers and I synthesized the first examples of these (*5*), and more than 60 new polymers have been made since then (*5–15*). They now constitute a substantial class of new elastomers, thermoplastics, and fibers (*16*) that promise to solve many of the technological and biomedical problems mentioned above.

Phosphazene High Polymers

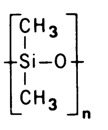
All linear, high polymeric polyphosphazenes have the general structure shown in **2**. The chemistry of small molecule phosphazenes can be traced back more than 100 years to the discoveries in Germany and Britain (*17*) that phosphorous pentachloride reacts with ammonia or ammonium chloride to yield a volatile, white solid, now known to have the ring structure shown in **3**. It was later noticed that strong heating of compound **3** caused it to melt and then form a transparent rubbery material. This process involves a ring-opening polymerization of the cyclic trimer **3** to poly(dichlorophosphazene) (**4**). This polymer remained a laboratory curiosity until the mid-1960's, mainly because it hydrolyzes slowly in contact with atmospheric moisture to yield a crusty conglomerate of ammonium phosphate and phosphoric acid.

When I first became interested in this subject in the early 1960's, it seemed clear that the hydrolytic instability of poly(dichlorophosphazene) was probably connected more with the chemical reactivity of the phosphorus-chlorine bonds than with any implied instability of the backbone bonds. Hence, it appeared that, if the chlorine atoms could be replaced by nonhydrolyzable organic units, the resultant polymers should be hydrolytically stable. Moreover, the unusual flexibility and elasticity of poly(dichlorophosphazene) held out a tantalizing promise that the organo-substituted phosphazene polymers might be elastomers, or at the very least, flexible thermoplastics.

The first approach tried was unsuccessful. We had reasoned, erroneously, that, if hexachlorocyclotriphosphazene (**3**) could be polymerized thermally, then perhaps organocyclophosphazenes, such as $[NP(OC_6H_5)_2]_3$ or $[NP(OCH_2CF_3)_2]_3$ would behave similarly. Such compounds do not polymerize and, as described later, we now know that ring-opening polymerizations of this type are inhibited by thermodynamic factors that result from the presence of the bulky organic substituents.

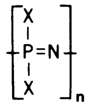
Fig. 1. Fibers of poly[bis(trifluoroethoxy)-phosphazene] prepared by solution extrusion into a nonsolvent.

The second strategy was the successful one. Because of the known high reactivity of phosphorus-chlorine bonds, it seemed possible that nucleophilic substitution reactions could be carried out on poly(dichlorophosphazene) to replace the chlorine atoms directly by organic residues. The initial experiments were disappointing because the poly(dichlorophosphazene) swelled in organic solvents, such as benzene or tetrahydrofuran, but it did not dissolve. The attempted nucleophilic substitutions were incomplete, and the resultant polymers were still hydrolytically unstable. However, a careful reinvestigation of the polymerization of **3** to **4** revealed that the reaction followed a two-step sequence. The polymer formed in the initial stages of the reaction was not cross-linked and was totally soluble in organic media. In the later stages, cross-linking occurred to give the insoluble material (*5, 6*).



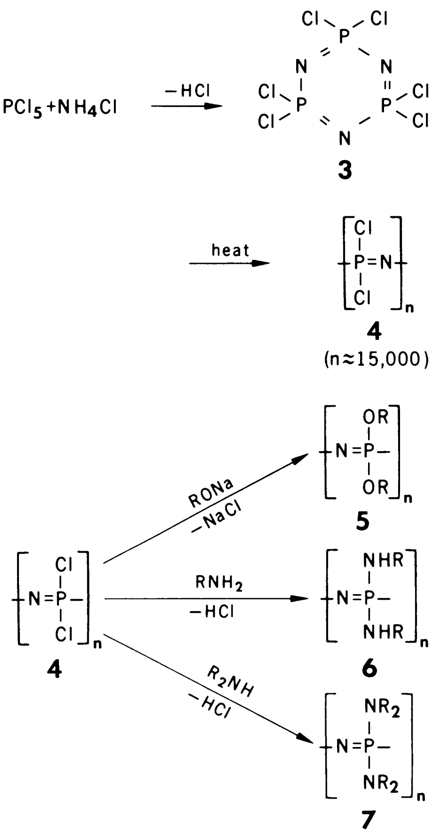
$$\left[\begin{array}{c}\mathrm{CH_3}\\ | \\ -\mathrm{Si}-\mathrm{O}- \\ | \\ \mathrm{CH_3}\end{array}\right]_n$$

1



$$\left[\begin{array}{c}\mathrm{X}\\ | \\ -\mathrm{P}=\mathrm{N}- \\ | \\ \mathrm{X}\end{array}\right]_n$$

2



Nucleophilic substitution reactions carried out on this soluble high polymer resulted in complete replacement of the halogen and the formation of a highly unusual series of hydrolytically stable new polymers (*5–7*). The overall nucleophilic substitution processes are illustrated in the formation of **5**, **6**, and **7**.

The polymers formed have molecular weights up to and sometimes exceeding 3 to 4 million, which indicates that the degree of polymerization is often in excess of 15,000. Immediately after the first successful experiments, it was clear that the introduction of different substituent groups had a marked effect on the properties of the polymers. Some substituents (methoxy and ethoxy) gave rise to low-temperature elastomeric properties. Others, such as phenylamino or dimethylamino, generated glassy polymers. Many substituents, such as phenoxy or trifluoroethoxy, yielded polymers that were flexible, film-forming materials. All were stable to water, base, or aqueous acid. A quick consideration of the vast choice of different alcohols, phenols, and primary or secondary amines that are available to chemists illustrates that the unique advantage of polyphosphazenes is the ease with which a large variety of polymers, all with different properties, can be made from one precursor.

The first polymers made in our laboratory were homopolymers—that is, they contained only one type of substituent group in each chain. Most of these materials were flexible or rigid thermoplastics. They could be readily fabricated into fibers, woven fabrics, flexible films, or tubes (Figs. 1 and 2). Because they do not burn, many of them function as flame retardants for organic polymers. Indeed, cotton fabrics can be impregnated with

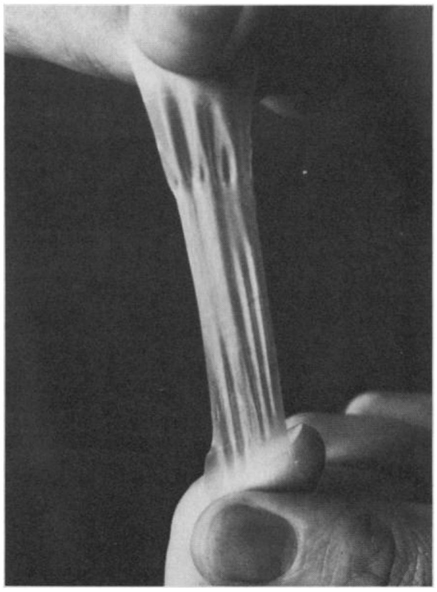


Fig. 2. An oriented film of an alkoxyphosphazene high polymer.

phosphazene polymers to induce waterproofing and flame retardance (Fig. 3). Certain polyphosphazenes, particularly those that contain fluoroalkoxy substituent groups, such as $[NP(OCH_2CF_3)_2]_n$ ($OR = OCH_2CF_3$ in structure **5**), are so water repellent that they do not interact with living tissues. Hence, these materials can be considered as promising candidates for the fabrication of replacement blood vessels and other artificial organ devices. Several organophosphazene polymers remain flexible at temperatures as low as −80° to −90°C.

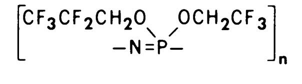
Mixed Substituent Polymers

High polymers are useful because, unlike small molecules, they can exist in the solid state as glasses, tough and flexible solids, or rubbery solids. They do not, in general, form single crystals. This is not to say that crystalline character cannot exist in a polymer, but rather that *whole* polymer molecules can only rarely fit together in a regular crystalline lattice. However, short segments of adjacent polymer chains can and do pack together in a regular fashion to form microcrystalline domains buried in an amorphous matrix. These crystalline domains function as temporary cross-link sites and serve to toughen a polymer and limit the degree to which it can be stretched. In contrast, destruction of the crystallinity increases the flexibility and may even generate rubbery or elastomeric properties.

This effect is illustrated in a number of organophosphazene high polymers. Many of the homopolymers are microcrystalline because the symmetry of the molecules allows adjacent chains to pack together. However, if the symmetry is destroyed by the random introduction of two or more substituent groups along each chain, the polymers are rubbery elastomers. These materials are among the most technologically useful phosphazene macomolecules.

Three ways have been developed to achieve mixed substitution. First, the poly(dichlorophosphazene) precursor (**4**) can be allowed to react simultaneously with two different nucleophilic reagents—for example, with a mixture of sodium trifluoroethoxide and sodium pentafluoropropoxide. This is illustrated in Eq. 1. Such mixed-substituent polymers are rubbery elastomers (*11*, *12*). A number of such materials (with a variety of different OR groups) are being developed commercially (by the Firestone Tire and Rubber Company) for use in O-rings, gaskets, hydrocarbon fuel hoses, and fire-resistant foam rubber devices (Fig. 4). The advantages of the phosphazene elastomers over organic elastomers or silicone rubber are their unusual resistance to oils, gasoline, jet fuel, and hydraulic fluid, as well as their low-temperature flexibility. The flexibility of a polymer is usually defined by its glass transition temperature (T_g), the temperature below which the polymer is a glass, but above which it is an elastomer or a flexible thermoplastic. For a material to be a useful elastomer it must have a T_g below about −40°C and resist crystallization at low temperatures. Polyphosphazene elastomers have T_g values as low as −80°C and they show a low tendency for crystallization (Figs. 1 to 4).

$$(NPCl_2)_n \xrightarrow[-NaCl]{NaOCH_2CF_2CF_3+\ NaOCH_2CF_3}$$



$$\left[\overset{CF_3CF_2CH_2O\quad OCH_2CF_3}{-N{=}P-}\right]_n \qquad (1)$$

A second route to the preparation of mixed substituent elastomers is illustrated in Eq. 2. It involves a partial exchange of one organic ligand by another (*9*).

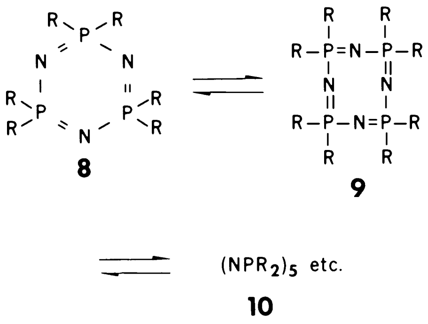
$$(NPCl_2)_n \xrightarrow[-NaCl]{NaOR} [NP(OR)_2]_n$$

$$\xrightarrow[-NaOR]{NaOR'} [NP(OR)(OR')]_n \qquad (2)$$

A third method involves the partial replacement of halogen in $(NPCl_2)_n$ by a bulky substituent group, such as $-N(C_2H_5)_2$, followed by replacement of the remaining chlorine atoms by a second substituent (Eq. 3) (*8*). Once again, it will be obvious that the variety of different polymers accessible by these methods distinguishes phosphazenes from all other polymer systems.

$$(NPCl_2)_n \xrightarrow[-HCl]{(C_2H_5)_2NH} [NP(Cl)N(C_2H_5)_2]_n$$

$$\xrightarrow[-NaCl]{RONa} [NP(OR)N(C_2H_5)_2]_n \qquad (3)$$



Direct Polymerization of Organophosphazene Trimers

The synthesis routes described above are indirect. It is usually more convenient to perform substitution reactions on phosphazene trimers, such as **3**, than it is on the high polymer **4**. However, as was mentioned earlier, all attempts to polymerize organic-substituted trimers have, so far, proved unsuccessful. Nevertheless, it is worthwhile to explore the reasons why such trimers cannot be polymerized directly, in the hope that such information may suggest ways in which the problem may eventually be overcome.

First, we have found that cyclic trimers **8**, such as $[NP(CH_3)_2]_3$, $[NP(C_6H_5)_2]_3$, or $[NP(OCH_2CF_3)_2]_3$, equilibrate at high temperatures to yield cyclic tetramers **9**, cyclic pentamers **10**, and traces of higher cyclics; but high polymers are not formed. Nevertheless it is known that, if R is fluorine, chlorine, or bromine, high polymers are formed.

Why does replacement of a halogen atom by an organic residue prevent polymerization? The reason cannot be entirely mechanistic because, clearly, a mechanism of trimer-, tetramer-, pentamer-equilibration is accessible to the organic derivatives, and this mechanism may be the same as that required for polymerization.

We believe that an additional reason

involves the size of the substituent groups. Molecular models (and nonbonding intramolecular calculations) show that the act of opening a ring to form a chain forces the organic substituent groups closer together or closer to the nearby chain atoms. Hence, the enthalpy of the polymer is higher than that of the trimer. Thus, organo-substituted trimer polymerization is inhibited because of thermodynamic factors. Confirmation of this is provided by the fact that those high polymers which contain the bulkiest organic substituents [prepared by substitution reactions on $(NPCl_2)_n$] will depolymerize to the appropriate cyclic trimers or tetramers if heated above 200°C (*18*).

If this explanation is correct, it should be possible to prepare organophosphazene polymers directly from the trimers if the trimer contains both organic and small halogen substituents. In this way the enthalpy increase on polymerization should be minimal. We have been able to show that polymerization occurs if one substituent group on **8** is phenyl or trifluoroethoxy, and the other five are chloro or fluoro (*9, 19*). Increasing the number of organic groups lowers the tendency for polymerization. The presence of more than one organic group on each phosphorus totally inhibits polymerization.

Undoubtedly, the ability of a particular cyclic trimer (or tetramer) to polymerize depends on a subtle combination of mechanistic and steric factors. Steric factors alone cannot explain all the observations. For example, when R is bromo, trimer **8** does polymerize, but, when R is methyl, polymerization does not occur. This is in spite of the fact that bromo and methyl groups are believed to have similar steric dimensions. This aspect of the subject provides a serious challenge for the application of fundamental ideas to an important practical problem.

Biomedical Developments

The important role that synthetic polymers could play in medicine has not been widely recognized until quite recently. Three medical areas are of special importance. First, polymers are needed for the fabrication of replacement body parts, such as heart valves, blood vessels, temporary skin, and replacement bone. Second, a need exists for the discovery of polymers that will fulfill a temporary function (such as suture material) and then degrade to harmless products. Third, polymers promise to play an ever-increasing role in the slow, controlled release of chemotherapeutic agents. These aspects are considered below.

Most common synthetic organic polymers are unsuitable for use in replacement body parts because they initiate blood clotting reactions or are actually toxic to living tissues. Some of the best synthetic organic polymers in this respect are those that are highly water-repellent, such as Teflon. Marlex polyethylene or polypropylene mesh can be used as an implanted reinforcement material. Silicone rubber is widely used for a variety of implant applications, partly because it is very hydrophobic, but also because it is a flexible, rubbery material. As was mentioned earlier, some poly(organophosphazenes), especially those with fluorinated alkoxy side groups, are exceedingly hydrophobic, more so in fact than Teflon or silicone rubber. In vitro blood clotting tests performed in our laboratory indicate that the blood compatibility of these is equal or superior to that of silicone rubber. Hence, a strong possibility exists that the polyphosphazenes may be used to fabricate replacement body components. In vivo animal testing of a number of our polymers is now under way at several laboratories.

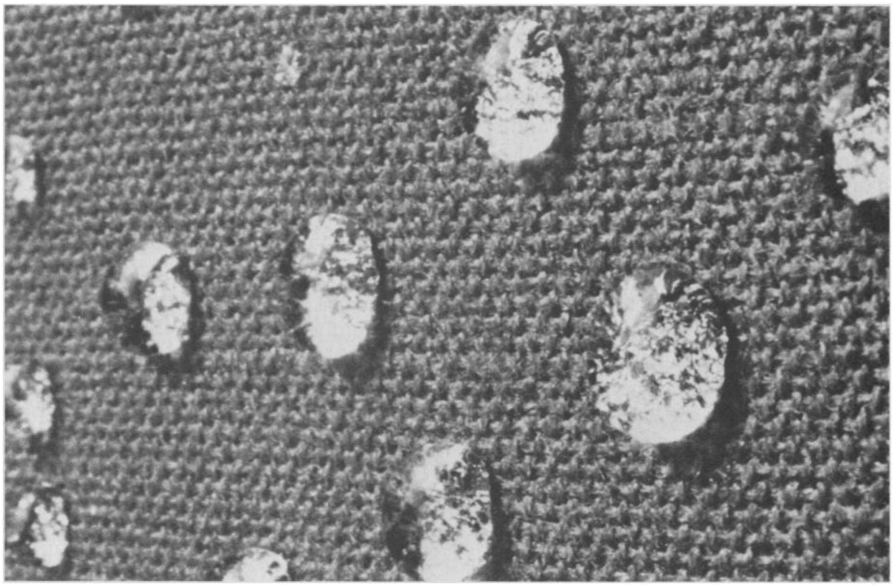


Fig. 3. Cotton fabrics impregnated with fluoroalkoxyphosphazene polymers are highly water repellent.

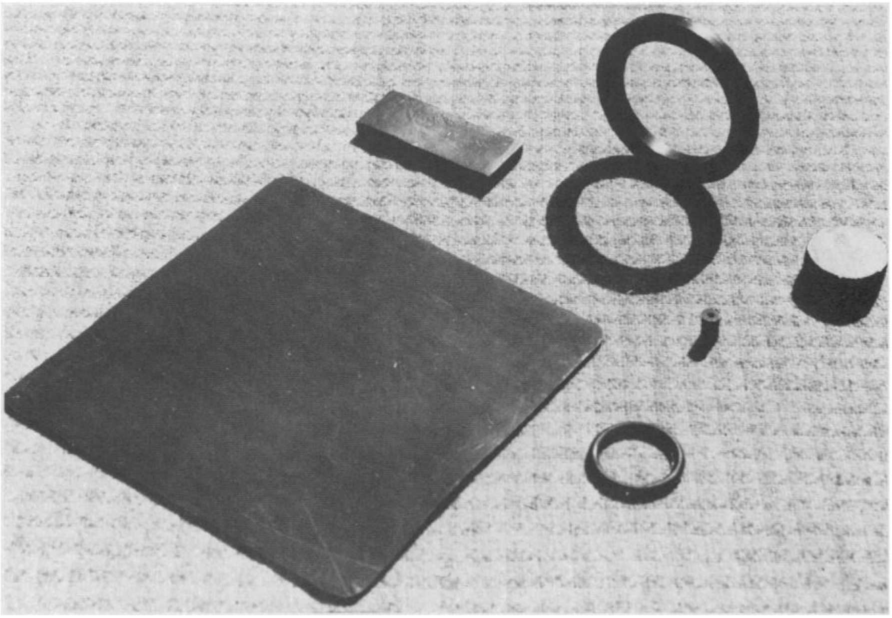


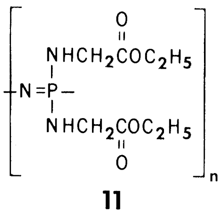
Fig. 4. Gaskets, O-rings, and sheet elastomer fabricated from mixed-substituent phosphazene elastomers at the Firestone Tire and Rubber Company laboratories.

Polyphosphazenes also appear to have a role to play in the field of biodegradable polymers. The need for a synthetic surgical suture material to degrade slowly to innocuous products is obvious. However, equally important is the search for polymers that can be used to replace body parts, but which will degrade and disappear slowly as new cell growth takes place. In our laboratory, we have focused particular attention on this problem and have synthesized a class of polyphosphazenes that bear amino acid ester residues as substituent groups on the chain (*20*). A typical example is poly[bis(ethylglycinato)phosphazene], shown in **11**. This polymer is a tough leathery material, which degrades slowly under aqueous conditions to an amino acid, phosphate, and ammonia. By the introduction of bulkier amino acid residues, such as alanine or leucine esters, the polymer can be designed to undergo molecular weight decline and dissolution spontaneously at body temperature over a period of several weeks, although it can be stored indefinitely at low temperatures.

Progress has also been made in the application of polyphosphazenes to a third area of biomedicine—the synthesis of polymers that function as carrier molecules for biologically active units. Two examples suffice to illustrate the approaches that we are pursuing.

It has been shown by Rosenberg (*21*) that square planar platinum complexes are powerful anticancer drugs. Unfortunately, because they are small molecules, they are excreted rapidly through the kidneys and can cause kidney damage. It occurred to us that the rate of excretion can probably be reduced by binding the platinum complex to a water-soluble polymer. Several poly(aminophosphazenes) are water soluble. One in particular—poly[bis(methylamino)phosphazene]—is also an excellent ligand for transition metals. Thus, square planar complexes have been prepared between this polymer and platinum-containing residues. Preliminary cancer chemotherapy screening indicates that this complex has appreciable anticancer activity (*22*). Incidentally, the pure polymer itself functions as a powerful anticoagulant in in vitro blood tests.

We are also exploring a second area in which polyphosphazenes may have biological utility. It is well known that in many metal-containing globular proteins, the role played by the protein is obscure. In nearly all cases, the metal atom is the active component in processes such as oxygen transport and electron transfer. However, it seems clear that one elementary function of the protein is to bind the metal atom in order to prevent its excretion and also, in some cases, to prevent the close approach of two or more metal atoms. The function of the protein is undoubtedly more complicated than this. Nevertheless, water-soluble polyphosphazenes provide an almost unique model with which to test the elementary influence of the protein as a "simple" macromolecule.



$$\left[-N=\overset{NHCH_2\overset{O}{\overset{\|}{C}}OC_2H_5}{\underset{NHCH_2\underset{O}{\underset{\|}{C}}OC_2H_5}{P}}- \right]_n$$

11

For example, the iron(II)-porphyrin residues in hemoglobin and myoglobin are coordinatively bound to imidazole residues on the globin chains. In the absence of the protein, the iron(II) units are rapidly and irreversibly oxidized to iron(III), which is not an O_2 carrier. A number of different theories have been formulated to explain the function of the protein component. The role of a sterically hindered, hydrophobic site at the porphyrin has received wide attention (*23*). However, a second function of the globin molecule is undoubtedly to keep the iron-porphyrin residues apart, since oxidation of iron(II) to iron(III) occurs rapidly when iron-porphyrin residues can approach closely. Two clear illustrations of this have been reported (*24*). Can a synthetic water-soluble polymer mimic the behavior of globin and prevent oxidation of iron(II) to iron(III)?

Again, poly[bis(methylamino)phosphazene] is an excellent model. It is water soluble, it possesses coordinative binding sites, and it is basic. We have shown (*25*) that hemin forms strong water-soluble complexes with this polymer. Reduction of the iron(III) to iron(II) in the complex can be accomplished with dithionite ion. Exposure of concentrated solutions or films to oxygen results in reversible binding of the oxygen without oxidation of the iron. In dilute solutions, oxidation is the preferred reaction, presumably because no hydrophobic pocket is present and because the polymer chains become more extended at higher dilutions. We are in the process of modifying our polymer substrate in an attempt to overcome this problem.

Structure of Polyphosphazenes

Finally, with the recognition that polyphosphazenes possess a versatility that is unusual in synthetic polymer chemistry, the question must be asked, "Why are they so different?" One answer, of course, is that their method of synthesis allows an unprecedented versatility not found in any other polymer system. But a more profound answer must take into account the fundamental structure of these compounds and the correlation of structure with chemical and physical behavior.

Members of my research group have attacked this problem with the use of x-ray diffraction and theoretical techniques (*26*). At present it appears that many polyphosphazenes are extremely flexible because the substituent groups are attached only to every other chain atom. Thus, when the polymer chains coil and uncoil by torsion of the backbone bonds, the side groups either do not approach close enough to inhibit these torsional motions, or the side groups themselves can undergo subtle avoidance motions. Thus, the barriers to backbone bond torsion are low and the molecules can assume a broad range of different conformations without incurring an energy penalty.

Summary

Polyphosphazenes are emerging as a new class of macromolecules that have an obvious future as technological elastomers, films, fibers, and textile treatment agents. However, they also possess almost unique attributes for use in biomedicine as reconstructive plastics or as drug-carrier molecules. Moreover, their possible value as "pseudo-protein" model polymers is an exciting prospect.

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NEWS AND COMMENT

Auto Safety: Coleman to Act on Controversial Air Bag Issue

> *I had dozed for a moment after a hard day in the office, but awakened in time to see that I was driving into a large city metro bus. . . . I never saw the air bag inflate or deflate, nor did I feel or hear it, it was so fast. My glasses were not broken. I felt stunned and amazed to be uninjured and alive.*——ARNOLD V. ARMS, a Kansas City physician, testifying on 3 August at a hearing conducted by the Secretary of Transportation on possible amendments to standards issued under the National Traffic and Motor Vehicle Safety Act of 1966.

Since crashing head-on into that city bus in October 1975, Arnold Arms has been trying to get air bags for his new car, but without success. Neither General Motors—which for a few years offered air bag systems as a $315 option on some of its luxury cars—nor any other automobile manufacturer is now offering these protective devices, either as standard or optional equipment. "I decry the lack of human interest [by the auto manufacturers] in the death and mutilation on the highways," Arms said.

As an answer to societal problems, the "technological fix" has often been oversold. But many advocates of highway safety have been convinced for nearly a decade now that the air bag system—a relatively simple system consisting of a deceleration sensor and inflatable bags that cushion the driver and front seat passengers in frontal collisions—is one very real answer to the carnage on the highways.

Highway smashups are such a common, everyday phenomenon that there are probably few adults living in America today who, even if they have escaped involvement in a serious accident themselves, have not known a relative or friend either to die in one or suffer cruel and perhaps crippling injuries. Although highway deaths and injuries have been reduced in number by the 55-mile-per-hour speed limit and the vehicle safety improvements mandated in recent years by federal law, the annual toll remains high, with more than 45,000 persons killed and several million injured.

The National Highway Traffic Safety Administration (NHTSA) estimates that about a third of the some 27,000 fatalities suffered by drivers and passengers in automobile accidents in 1975 could have been prevented had air bags and automatic safety belts—another "passive restraint" system that does not have to be buckled up by front seat occupants—been in general use.* The 400,000 serious injuries that occurred could also have been greatly reduced.

The automobile industry's unwillingness to put passive restraint systems into all their cars forthwith, and the fact that the federal government has not yet required them to do this, has been regarded as an outrage by some public health epidemiologists and insurance underwriters, as well as by activists such as Ralph Nader and Clarence M. Ditlow III, executive director of the Nader-founded Center for Auto Safety.

Secretary of Transportation William T. Coleman, Jr., has now promised to act on this issue before the year is out. But, while a ruling directing the automobile industry to begin installing passive restraint systems by the 1980-model year is a real possibility, it is by no means a foregone conclusion. The automobile industry strongly opposes issuance of such a ruling and its leaders carry plenty of political weight at the White House.

The first air bag system was patented in 1952, and, since then, this system's technical feasibility seems to have been established. Air bags have been installed in some 12,000 cars—about 10,000 of them sold by General Motors—and the experience to date, while limited, indicates that they are dependable and effective in frontal and front-angle crashes, which are the only kind for which they are designed to cope.

Why Detroit is opposing issuance of a safety standard requiring air bags is not altogether clear, for the industry's stand may stem as much from an aversion to regulation as from any real or alleged disadvantages associated with the devices. A major disadvantage cited by the industry is that the air bag does not constitute a truly passive restraint system requiring nothing of the driver or front seat passenger to be effective.

All agree that lap belts should be used with this system for the protection of front seat occupants in side-impact and rollover crashes and in those frontal crashes occurring at speeds too low to trigger the bag's deployment. Indeed, a safety standard making air bags standard equipment on new cars would be coupled with one retaining lap belts.

Industry spokesmen argue, therefore, that the air bag system demands as much of drivers and passengers as the lap and

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*The automatic belt, which plays in and out on an inertial reel and locks in place when the driver or passenger closes the door, is now offered as standard equipment on the deluxe model of the Volkswagen Rabbit; this system is adaptable, however, only to cars with bucket seats.