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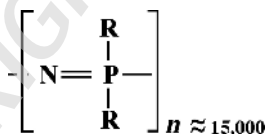
FLUORINATED POLYPHOSPHAZENES

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1.1 BACKGROUND

Polyphosphazenes (Structure 1.1) are a broad class of macromolecules with a backbone of alternating phosphorus and nitrogen atoms and with two side groups (R) attached to each phosphorus atom.



STRUCTURE 1.1

The skeletal architecture may be linear, branched, star, or dendritic, or it may be part of a di- or triblock copolymer in conjunction with organic macromolecules or poly(organosiloxanes) (silicones). However, it is in the wide variety of side groups that this system differs from many other polymer platforms. More than 250 different organic, organometallic, or inorganic side groups have been utilized in single-substituent arrays or in di-, tri-, or higher mixed-substituent patterns. Thus, hundreds of different polyphosphazenes are known with a corresponding diversity of properties

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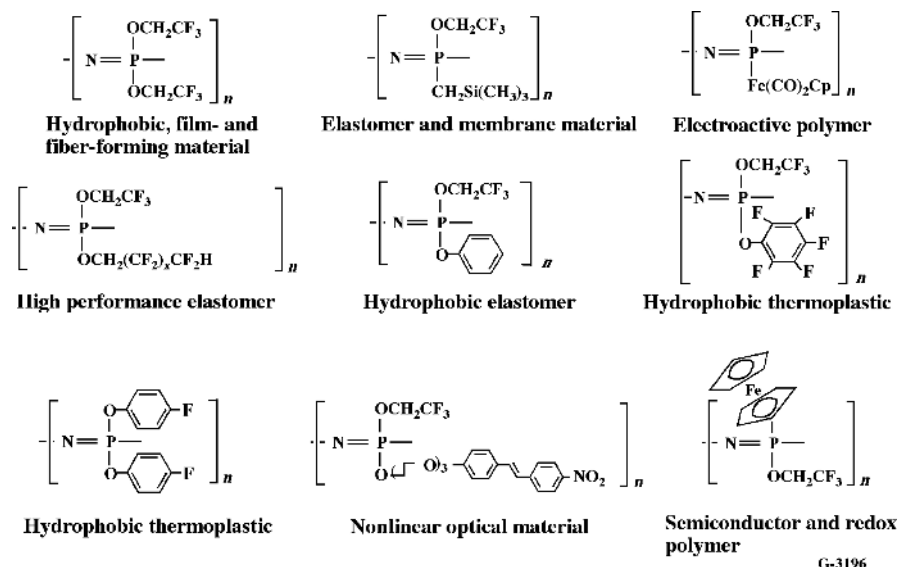


FIGURE 1.1 Examples of fluorinated organophosphazene polymers.

and potential uses [1]. These can be divided into different “families” of polymers such as inert biomaterials, bioerodible polymers, optical materials, membranes, ionic conductors, and so on. One of the most important and most interesting families consists of polyphosphazenes that bear fluorinated organic side groups. Examples of polymers within this group are shown in Figure 1.1.

1.2 SYNTHESIS METHODS AND PROPERTY DEVELOPMENT

A number of different access routes have been developed to poly (organophosphazenes) [1]. We have focused on a two-stage sequence that involves first the preparation of a linear polymeric reaction intermediate, poly(dichlorophosphazene), $(\text{NPCl}_2)_n$, followed in a second step by replacement of the chlorine atoms in this polymer by organic side groups (Figure 1.2) [2–4]. The reactive intermediate is accessible either by a ring-opening polymerization of a cyclic trimer, $(\text{NPCl}_2)_3$, or via a living cationic condensation polymerization of a phosphoranimine (Figure 1.2) [5–15]. Another route to poly(dichlorophosphazene) is via the condensation reactions of $\text{Cl}_3\text{P}=\text{N}-\text{POCl}_2$ [16], a method that yields lower molecular weight polymers than the ring-opening route. Replacement of the chlorine atoms in $(\text{NPCl}_2)_n$ is accomplished by reactions with nucleophiles such as alkoxides, aryloxides, amines, or organometallic reagents.

This is a very different protocol than that exists for most classical polymers, where the side groups destined for the final polymer must be in place on the monomer

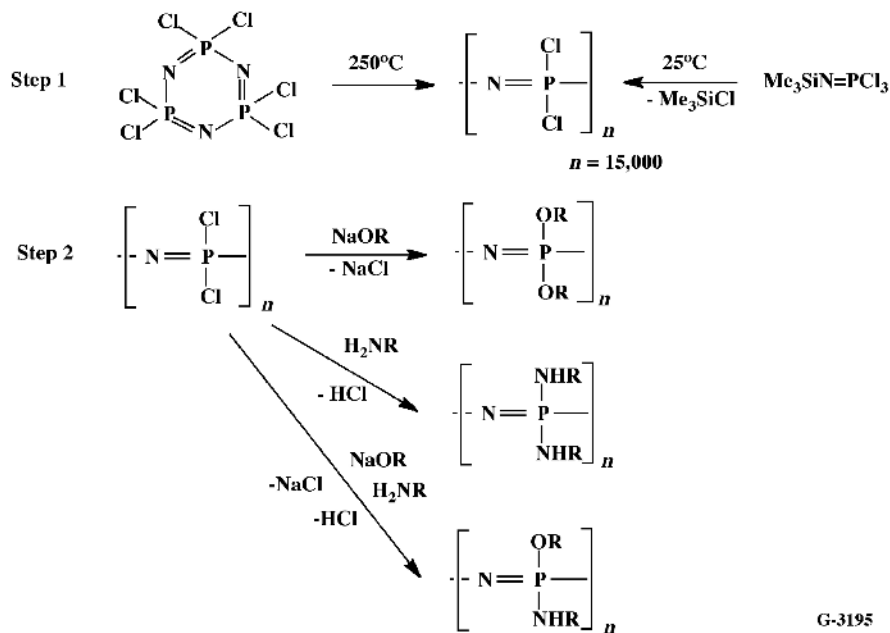


FIGURE 1.2 Two-stage synthesis of poly(organophosphazenes).

before polymerization [17]. Modification of the side groups in conventional macromolecules after polymerization is restricted to simple reactions such as hydrolysis of esters or partial sulfonation. It is the high reactivity of poly(dichlorophosphazene) that allows the broad diversity of structure and properties that are a characteristic of poly(organophosphazenes). Other valuable methods have been developed to prepare poly(organophosphazenes) that involve the condensation reactions of organic-substituted phosphoranimines [18–21], but the range of side groups used in that process is more restricted than in the macromolecular substitution method, and the molecular weights tend to be lower.

Use of these synthetic techniques has led to the development of numerous different classes of phosphazene materials, many of which contain fluorine, but others that do not [1]. For example, a versatile class of hydrogel polyphosphazenes and ion conductive materials possesses nonfluorinated oligoethyleneoxy side chains. Nonfluorinated aryloxy substituents give fire-retardant polymers. Amino acid ester side groups or nonfluorinated alkoxy groups generate bioerodible properties that have been developed extensively for tissue engineering applications. Nevertheless, the presence of fluorine in the side group structure has led to some of the most intriguing developments, and this is the focus of the rest of this article. Using the two-step synthesis protocol, molecular diversity is accomplished in several different ways.

Method 1. Different nucleophiles give polymers with different side groups and diverse properties [1–4]. For example, oligoethyleneoxy side groups give

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water-soluble, water-stable polymers [22]. Aryloxy side units generate hydrophobic, water-insoluble polymers. Amino acid ester side groups or oligopeptide units linked to the polymer skeleton through the amino terminus generate bioerodible characteristics [23]. Fluoroalkoxy or fluoroaryloxy side groups generate hydrophobic, water- and radiation-stable polymers [24].

Method 2. A second method for structural and property tuning involves the introduction of two or more different side groups along the same polymer chain. For example, amphiphilic character is accessible by the use of fluoroalkoxy groups and oligoethyleneoxy side chains, with the exact properties being controlled by the ratios of the two. Two different fluoroalkoxy side groups on the same chain have a striking effect on the polymer morphology. A polyphosphazene with only trifluoroethoxy side groups is a film- or fiber-forming microcrystalline material, similar to poly(tetrafluoroethylene) in surface properties but, unlike Teflon, soluble in ordinary organic solvents such as acetone or methylethylketone. By contrast, the related polymer with both trifluoroethoxy and longer chain telomer fluoroalkoxy groups is an amorphous elastomer, prized for its low glass transition temperature (approximately -60°C), solvent and oil resistance, and impact-absorbing character.

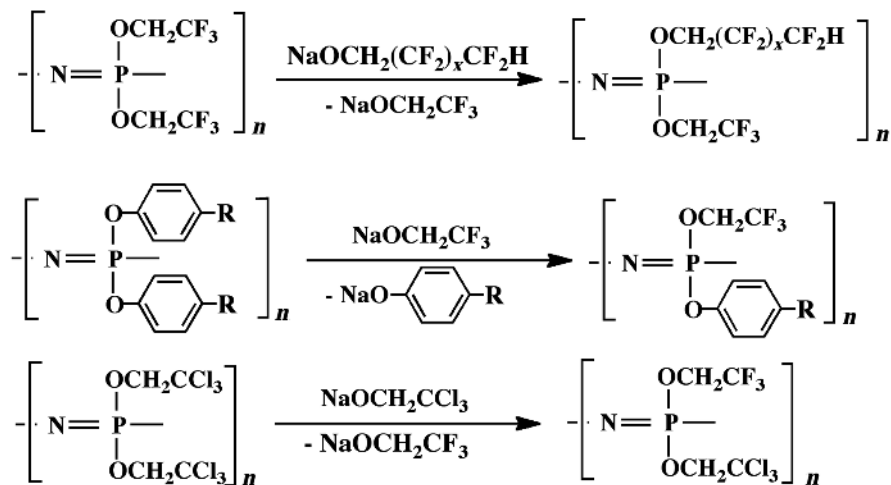
For polyphosphazene molecules that bear two or more different side groups, serious questions exist about the ratios and pattern of distribution of these groups along the polymer chains. These two factors have a significant influence on the properties of the final polymer. For example, a random distribution often precludes crystallinity and favors elastomeric character. Properties that result from a regular distribution may depend on whether the substituents are geminal or nongeminal, cis or trans, or if block structures are present (Figures 1.3 and 1.4). ^{31}P NMR spectra can sometimes provide clues about the distribution.

Note that the *order* of introduction of the side groups often plays a major role in controlling the distribution pattern and the properties. The distribution of the first substituent will control the positioning of the second substituent and, in turn, the precise combination will control the properties of the fully substituted polymer. *Simultaneous* addition of the two nucleophiles often yields results that depend on the electronic and steric characteristics of the reagents and also on the reaction conditions.

Method 3. The third opportunity for structural diversity arises through organic side group exchange chemistry (Figure 1.5). Thus, specific polyphosphazenes in solution can be modified by the replacement of one type of organic side group by exposure to another nucleophile. Fluoroalkoxide A will replace fluoroalkoxy group B. Aryloxy side groups with electron-withdrawing substituents may be replaced by trifluoroethoxy groups. Trichloroethoxy side groups can also be exchanged for trifluoroethoxy side units [25]. This is a useful way to fine-tune polymer properties such as solubility or morphology. It can also be used as a method for cross-linking polyphosphazene chains by the use of a difunctional nucleophile that can exchange with some of the organic side groups. Moreover, it provides an excellent method for modification of the *surface* of a solid polyphosphazene without affecting the composition of the interior [26, 27].

Method 4. Finally, the preparation of polymers with multifunctional organic side groups raises a synthetic challenge. For example, if the objective is to produce a

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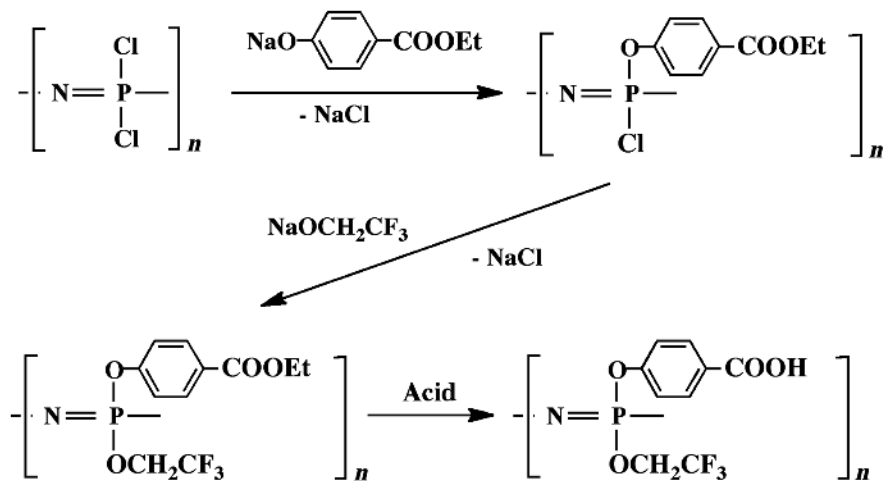
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FIGURE 1.5 Substituent exchange as an alternative route to the preparation of mixed-substituent polymers.

as the nucleophile to link the side group to the chain via the hydroxyl group, followed by hydrolysis of the ester function to generate the free carboxylic acid or carboxylate moiety (Figure 1.6). We have developed more complex protection–deprotection procedures to utilize numerous multifunctional biological side groups [23, 28].

In addition to the above methods, mixed side group systems have been synthesized through block copolymers with other polyphosphazenes, or with organic polymers or organosilicon polymers, and through the assembly of stars, or dendrimers, all by use of the living cationic polymerization route (Figure 1.2). These options further widen the opportunities for property development. As an example, amphiphilic diblock copolymers with one block bearing hydrophobic side groups and the second block being hydrophilic have been studied for micelle formation.

There is one additional experimental issue that is crucial for all this synthesis work. This is a consequence of the hydrolytic sensitivity of chlorophosphazenes. Both the cyclic trimer, $(\text{NPCI}_2)_3$, and the high polymer, $(\text{NPCI}_2)_n$, react with atmospheric moisture to produce P–OH units that can trigger ring or chain cleavage reactions or may undergo intermolecular condensation reactions to cross-link phosphazene molecules via P–O–P linkages. In the high polymer, this is a major source of unwanted cross-linking that can also restrict the extent of chlorine replacement by organic nucleophiles. Reports of difficulties with the preparation of polyphosphazenes by inexperienced investigators can almost always be traced to failure to purify commercial $(\text{NPCI}_2)_3$ or to protect the trimer or the polymer from atmospheric moisture before chlorine replacement. Moreover, dry reagents and solvents must be



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FIGURE 1.6 A variety of protection–deprotection strategies have been developed to prevent cross-linking when a polyphosphazene reacts with di- or tri-functional reagents. The simplest of these involves deprotection by the hydrolysis of an ester function.

used at every stage of the syntheses until all the chlorine atoms have been replaced by organic groups.

1.3 THE ROLE OF FLUORINE IN POLYPHOSPHAZENE SYNTHESIS CHEMISTRY

Polyphosphazenes with fluoro-organic side groups have played a major role in the development of this field. This is a consequence of the unique properties imparted to polyphosphazenes by fluorinated organic groups, but it also reflects the role played by fluorine in the synthesis chemistry as well. There are four ways in which fluorine plays an important role in the synthesis of polyphosphazenes.

1.3.1 Facilitation of Chlorine Replacement by Fluorinated Nucleophiles

In this first influence, fluorine as a component of various alkoxide, aryloxide, or amino nucleophiles accelerates the chlorine replacement reactions on which the syntheses of most poly(organophosphazenes) depend. This role is attributed to the strong electron-withdrawal associated with carbon–fluorine bonds, an effect that favors dissociation of, for example, the sodium–oxygen bond in sodium alkoxides or aryloxides and

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thus accelerates the substitution process. This effect supplements the driving force brought about by the precipitation of sodium chloride from organic media.

1.3.2 Enhancement of the Hydrolytic Stability and Resistance to Other Reagents When Fluorine Is Present in the Organic Side Groups

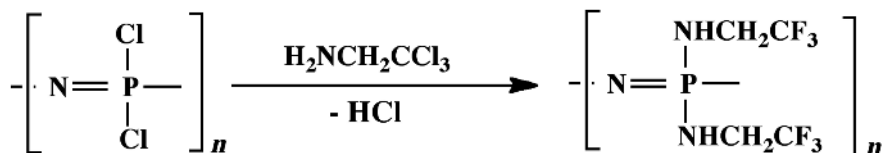
Carbon–fluorine bonds in the side groups withdraw electrons from the skeletal nitrogen atoms, thus retarding side reactions in which reagents such as water, acids, or bases attack and cleave the skeletal linkages. Fluorine in the organic side groups also imparts other useful properties such as hydrophobicity, low glass transition temperatures, resistance to oil, and general chemical resistance. These attributes become evident when, for example, poly[diethoxyphosphazene], $[\text{NP}(\text{OEt})_2]_n$, is compared with poly[bis(trifluoroethoxy)phosphazene], $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$. The nonfluorinated ethoxy derivative is hydrolytically unstable whereas the trifluoroethoxy counterpart is resistant to hydrolysis.

1.3.3 Influence by the Structure of the Fluorinated Alkoxide Nucleophile

Although polyphosphazenes with trifluoroethoxy side groups are among the most interesting and useful polymers, deviations from this structure lead to synthetic challenges. Thus, the preparation of sodium fluoroalkoxides by the treatment of $\text{HOCH}_2(\text{CF}_2)_x\text{CF}_2\text{H}$ with metallic sodium or sodium hydride is a facile reaction provided two criteria are met. First, mild conditions must be ensured to avoid elimination of HF from the $-\text{CF}_2\text{H}$ terminus [29]. However, the formation of terminal unsaturation can be utilized for cross-linking processes. Second, fluoroalkoxy nucleophiles with two adjacent methylene units, such as $-\text{O}(\text{CH}_2)_2(\text{CF}_2)_x\text{CF}_3$ are especially prone to HF elimination in the presence of sodium metal or sodium hydride [30] and this ultimately leads to the formation of colored, insoluble products rather than chlorine replacement. Both small molecule model reactions and polymer syntheses have been used to study these side reactions.

1.3.4 Fluoroaryloxy Side Groups

Replacement of chlorine atoms in poly(dichlorophosphazene) occurs readily with fluorine-substituted aryloxides such as 4-fluorophenoxide, 4-trifluoromethylphenoxide, or 3,5-bis(trifluoromethyl)phenoxide; although, for steric reasons the preparation of mixed-substituent polymers with both fluoroaryloxy and trifluoroethoxy groups is easier than the introduction of single-substituent fluoroaryloxy derivatives [31, 32]. However, attempts to synthesize polymers that bear *only* pentafluorophenoxy groups have proved problematic due to the high crystallinity and insolubility of the polymer as it approaches 100% chlorine replacement. On the other hand, mixed-substituent polymers with both pentafluorophenoxy and trifluoroethoxy substituents are relatively easy to produce. Like the other reactions, these fluoro-aryloxide substitutions can be modeled fairly well by the reactions of the cyclic trimer, $(\text{NPCI}_2)_3$ before expending effort on the polymer syntheses.



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FIGURE 1.7 Fluoroalkylamino groups can be linked to the polyphosphazene chain. These reactions are facilitated by the presence of nonfluorinated tertiary amines as hydrochloride acceptors.

1.3.5 Fluorinated Alkylamino Side Groups

Although fluorinated alkoxy and aryloxy polyphosphazenes have been investigated in some detail, fluorinated *aminophosphazene* polymers have received less attention. A possible reason is the lower reactivity of these amines compared to the fluoroalkoxides. However, an example of this class has been investigated recently with the synthesis of 2,2,2-trifluoroethylamino derivatives (Figure 1.7) [33].

1.3.6 Poly(difluorophosphazene) and Derivatives as Alternatives to Poly(dichlorophosphazene)

Reactions of organometallic reagents with phosphazenes are facilitated if the macromolecular intermediate bears P–F rather than P–Cl bonds. Reactions of poly(dichlorophosphazene) with organometallic reagents such as Grignard, organolithium or organocopper compounds are often accompanied by coordination of the organometallic species to the lone pair electrons of the skeletal nitrogen atoms, a process that can eventually lead to insolubilization or phosphorus–nitrogen bond cleavage.

However, when phosphorus–fluorine rather than phosphorus–chlorine bonds are present in the macromolecular intermediate, the chemistry favors halogen replacement by organometallic reagents [34]. The nitrogen lone pair electron density is reduced by the direct electron-withdrawal by the proximal P–F bonds, thus favoring fluorine replacement over nitrogen coordination. The use of poly(difluorophosphazene) as a macromolecular intermediate is complicated by its insolubility in nearly all solvents [35]. However, polymerization of monophenylpentaf luorocyclotriphosphazene, $\text{N}_3\text{P}_3\text{F}_5\text{Ph}$ [36], yields a linear polymer with one phenyl group on every third phosphorus atom [37]. This polymer is sufficiently soluble in common organic solvents that it can be used for the replacement of the fluorine atoms using organometallic reagents. Polymers with phenyl, trimethylsilyl, and trifluoroethoxy side groups have been prepared by this route (Figure 1.8) [38].

An alternative source of a fluorophosphazene macromolecular intermediate is via the living cationic polymerization of $\text{Me}_3\text{SiN}=\text{PF}_2\text{Ph}$, a counterpart of the reaction shown in Figure 1.2 [39]. The overall polymerization reaction is shown in Figure 1.9.

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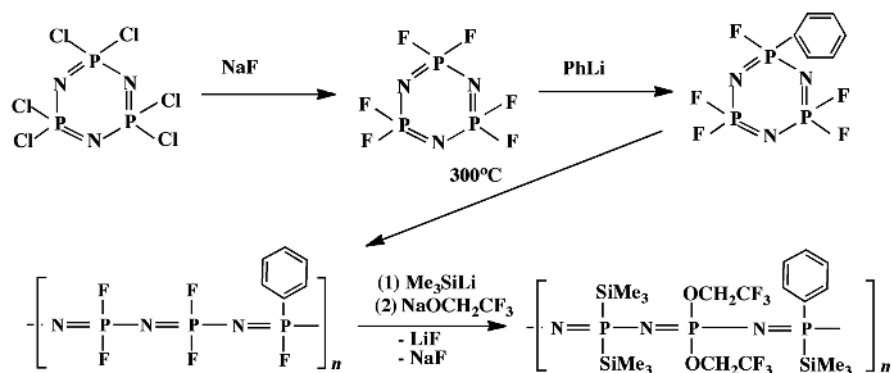
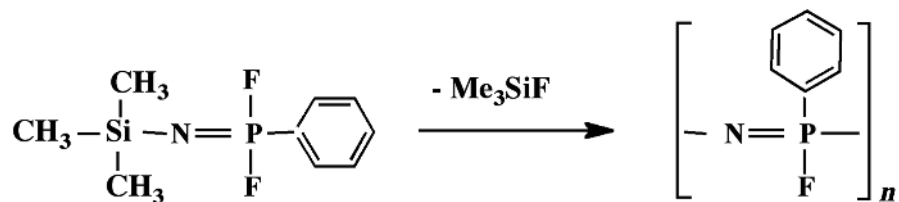


FIGURE 1.8 The presence of phenyl groups along a poly(fluorophosphazene) chain generates solubility in common organic solvents, and this allows the fluorine atoms to be replaced by the use of organometallic reagents.

1.3.7 Block Copolymers and Micelles

Access to the room temperature cationic condensation polymerization, shown in Figure 1.2, has provided a method for precise control of the chain length of poly(dichlorophosphazene) and synthesis of block copolymers via reactions of the living chain termini. One aspect involves the formation of block copolymers with two phosphazene blocks that bear different side groups [39]. A polyphosphazene chain can also be coupled to organic polymers or poly(organosiloxanes) via the use of terminal reactivity in both polymers [40]. Some examples are shown in Figures 1.10 and 1.11. In diblock copolymers, if one block bears hydrophilic side groups and the other block contains fluorinated hydrophobic groups (or *vice versa*) then access is gained to micelles. We have explored micelle formation and its consequences in some detail [41–43], especially when the hydrophobic blocks bear fluoroalkoxy side groups. These micelles are of interest as nanoscale carriers for hydrophobic guest molecules in aqueous media.



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FIGURE 1.9 Preparation of a polyphosphazene with one fluorine and one phenyl group on every phosphorus atom using the living cationic polymerization technique.

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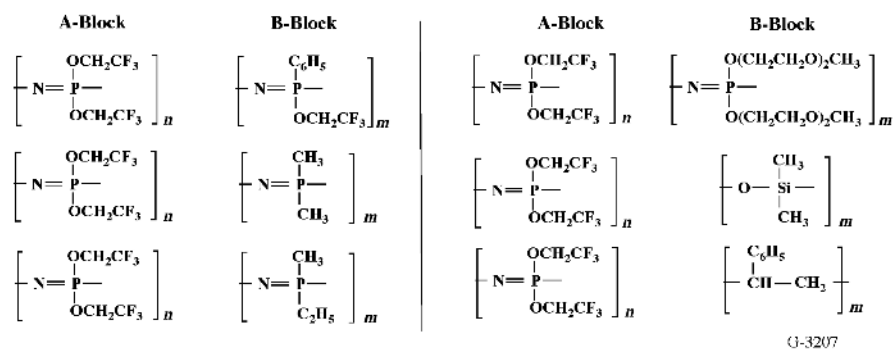


FIGURE 1.10 Diblock polymers containing polyphosphazene units, produced via the living cationic polymerization technique.

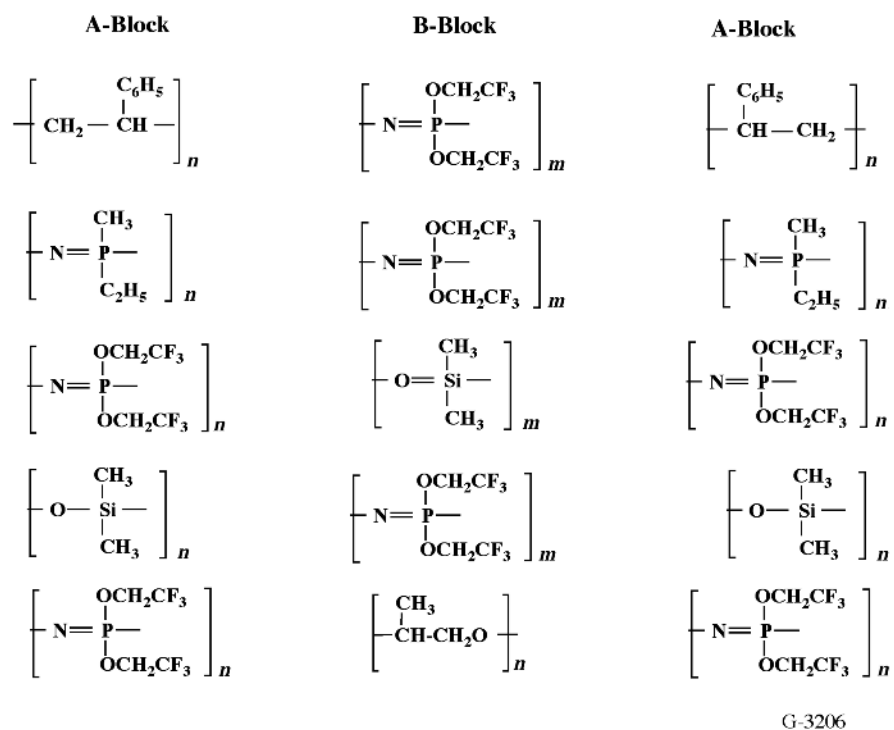


FIGURE 1.11 Triblock copolymers containing polyphosphazene units, accessed via the living cationic polymerization method.

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1.4 PROPERTIES OF FLUORINATED POLYPHOSPHAZENES

Fluorinated poly(organophosphazenes) have distinctly different properties from their nonfluorinated counterparts. This is due to the stabilizing effect of the fluorinated side groups on the backbone, the hydrophobicity or super-hydrophobicity of films or fibers, and the general biomedical stability and compatibility of polymers with fluorocarbon units in the side group structure. The following examples illustrate some of the main properties.

1.4.1 Solubility as a Function of Side Group Structure

The solubility of a polymer in different solvents holds the key to its use in many fabrication techniques such as solution fiber spinning, electrospinning, film fabrication, and spin coating. The lack of solubility in hydrocarbon fuels and lubricants and aggressive hydraulic fluids is important for many engineering applications. Fluoroalkoxy groups linked to a polyphosphazene chain control solubility in organic solvents in the following ways. Trifluoroethoxy side groups confer solubility in solvents such as tetrahydrofuran (THF), acetone, or methylethylketone. Co-substituent side groups of the type $-\text{OCH}_2(\text{CF}_2)_x\text{CF}_2\text{H}$ permit solubility in the same solvents but with the solubility decreasing as the number of CF_2 groups increases. With the exception of trifluoroethoxy side groups, fluoroalkoxy units of type $\text{OCH}_2(\text{CF}_2)_x\text{CF}_3$ with CF_3 terminal units yield polymers that are less soluble in the same solvents. Fluorinated *aryloxy* side groups give rise to polymers that are less soluble than their alkoxy counterparts in nearly all solvents.

1.4.2 Solid State Properties

A comparison of polyphosphazenes that bear fluorinated or nonfluorinated side groups reveals that the nonfluorinated species are usually amorphous whereas the fluorinated examples are microcrystalline. For example, the polyphosphazene with ethoxy side groups is an amorphous gum. Its counterpart with 2,2,2-trifluoroethoxy side groups is a microcrystalline film- and fiber-former. However, polymers with two or more fluorinated side chains of different length have lower crystallinity or are amorphous presumably due to the lack of molecular order. The presence of fluorine in the side chains increases the glass transition temperature compared to nonfluorinated analogs but, even so, T_g values as low as -66°C have been recorded for trifluoroethoxy-substituted derivatives. This value can be compared with the -84°C T_g for ethoxy-substituted polyphosphazenes. The presence of crystallinity in the trifluoroethoxy-substituted species can be attributed to the polarity generated by the fluorine atoms and possibly to a lower torsional mobility of the fluorinated groups compared to ethoxy substituents.

The crystallinity of the fluorinated derivatives (particularly the trifluoroethoxy-single-substituent polymer) is responsible for the formation of flexible films, fibers, and nanofibers by solution casting, solution-precipitation spinning, or by

electrospinning. Orientation of films and fibers by stretching can yield highly crystalline, tough, and strong materials. As mentioned above, mixed-substituent phosphazene polymers tend to be elastomers. This applies to polymers with two different fluoroalkoxy side groups or to those with both fluoroalkoxy and nonfluorinated alkoxy or aryloxy side units, although the exact properties depend on the ratios of the two (or more) different substituents. A recent example is the elastomer that bears both trifluoroethoxy and trichloroethoxy side groups [33].

1.4.3 Surface Properties

It is no surprise that polyphosphazenes with fluorinated alkoxy or aryloxy side groups are hydrophobic. Contact angles to water in the range of 100° are found routinely [32, 43]. Superhydrophobicity, with contact angles in the range of 160° are generated by nanofiber mats produced by electrospinning (Figure 1.12) [43]. The surface hydrophobicity can be converted to hydrophilicity if the interface is treated with, for example, a hydrophilic nucleophile such as the sodium salt of p-hydroxybenzoic acid. Fluoroalkoxyphosphazene polymer films also respond well to environmental plasma processing. For example, films of poly[bis(trifluoroethoxy)phosphazene] can be patterned via masking to generate films with hydrophilic images by the use of

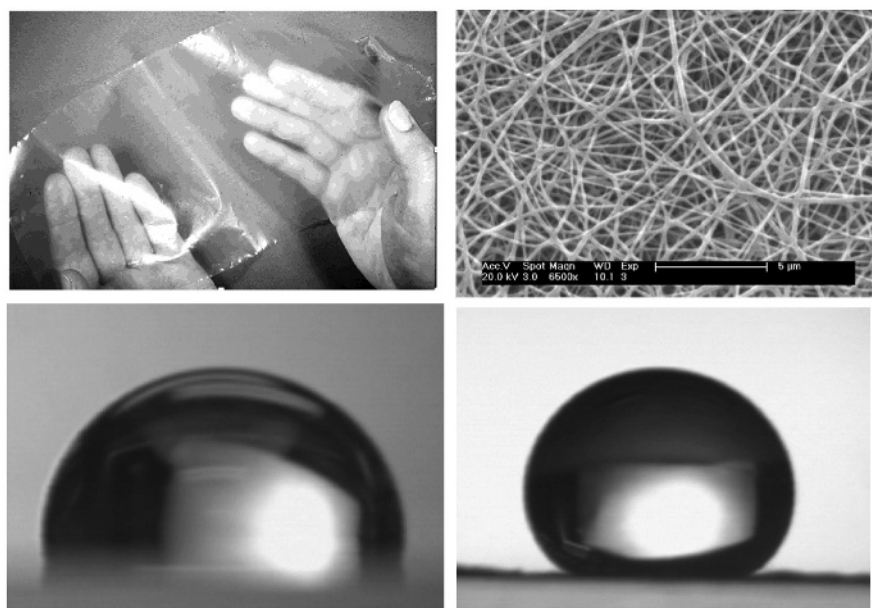


FIGURE 1.12 Poly[bis(trifluoroethoxy)phosphazene] surfaces. Top left: a solvent cast film. Top right: solvent-electrospun ~ 80 nm nanofibers. Bottom left: water droplet on film surface with advancing contact angle of 104° . Bottom right: water droplet on nanofiber mat with advancing contact angle of 155° .

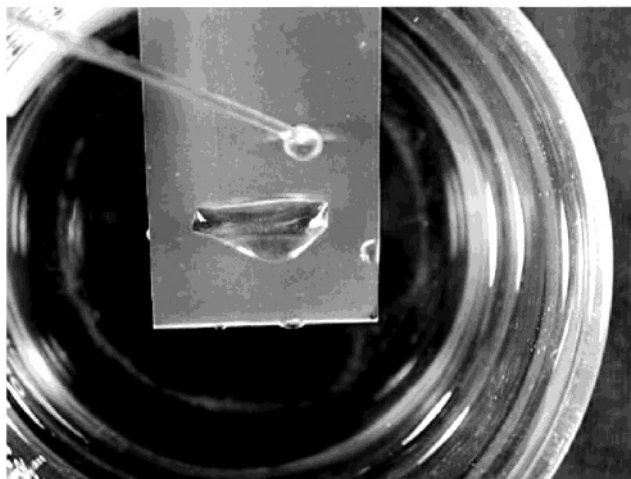
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FIGURE 1.13 Film of poly[bis(trifluoroethoxy)phosphazene] masked and exposed to an environmental plasma to convert a region of the surface interface to hydrophilic.

oxygen, nitrogen, or ammonia plasmas (Figure 1.13) [44]. The same polymer surface exposed to a CF_4 plasma generates a superhydrophobic interface with a contact angle to water of 150° .

1.4.4 Thermal and Thermo-Oxidative Stability

The thermal stability of all polymers can be understood in terms of three different factors—resistance to fragmentation, depolymerization, and combustion. The upper thermal stability limits of polymers are set by the onset temperature of thermal cleavage of the backbone and the bonds in the side groups. This theoretical limit is rarely reached for fluorinated alkoxy or aryloxy polyphosphazenes due to their propensity to depolymerize to cyclic small molecules at elevated temperatures. Thus, poly[bis(trifluoroethoxy)phosphazene] depolymerizes to a mixture of cyclic trimeric, tetrameric, and higher ring systems with the same repeating structure as the high polymer at temperatures above 300°C . This is a consequence of an entropy-driven process in which the ΔS term in the Gibbs equation exceeds the ΔH term at a “ceiling temperature,” so that many small molecules constitute a more stable system than a few high polymer molecules. This is the same reason why poly(organosiloxanes) (silicones) depolymerize at moderately high temperatures. However, the resistance to depolymerization of polymers can often be enhanced by cross-linking, and this is possible for polyphosphazenes. In general, the smaller the dimensions of the side groups, the higher will be the ceiling temperature.

Resistance to combustion is an aspect where nearly all polyphosphazenes are superior to their all-organic counterparts or poly(organosiloxanes). Small molecule phosphorus compounds have long been employed as fire-retardant additives for other

polymers because of the ability of phosphorus to interrupt the chain reactions that are responsible for fire and also their ability to generate an intumescent char that isolates the polymer from oxygen. Nitrogen, along with phosphorus, is especially useful in this regard. Thus, the backbone of polyphosphazenes is an inherent fire retardant which enhances the combustion resistance of these polymers. This effect is present in both the fluorinated and nonfluorinated species and also in the aryloxy counterparts.

1.5 EXISTING AND EMERGING APPLICATIONS FOR FLUORINATED POLYPHOSPHAZENES

The fundamental science of polyphosphazenes has far outstripped the commercial development of this field. To a large extent this is a consequence of the novelty in the industrial preparation of the starting materials and the unusual synthesis procedures compared to the main methods used for the manufacture of conventional organic polymers. Nevertheless, commercial interest in these polymers continues to grow, an interest that is driven by the recognition that unique combinations of properties are accessible. A large part of the recent research in our program has involved the development of an understanding of structure–property relationships in this field as a prelude to identifying potential applications. Recent structure–property work for nonfluorinated polyphosphazenes has been focused on bioabsorbable biomedical applications, optical materials, fire-resistant polymers, membranes, gels, and polymer electrolytes. However, the fluorinated derivatives are in several cases closer to widespread utilization, especially in the following fields mentioned here.

1.5.1 Fibers and Nanofibers

As mentioned earlier, poly[bis(trifluoroethoxy)phosphazene] is a fiber-forming, microcrystalline polymer that can be fabricated into microfibers by solution extrusion from THF into a nonsolvent such as heptane. Alternatively, it can be electrospun to nanofibers from a solution in THF. The structure–property relationships for this polymer are fairly well understood, and these provide a basis for expanding the understanding to polymers with other side groups.

1.5.2 Impact-Absorbing Elastomers

As described above, the presence of two different fluoroalkoxy side groups generates low temperature elasticity (T_g approximately -60°C) (Figure 1.14) coupled with hydrophobicity, solvent and oil resistance, and resistance to combustion. These properties were the reason for the development of so-called PNF elastomers for military applications in the Cold War era [45–48]. Interest in these polymers for biomedical applications continues at the present time, with applications in dentistry [49] and cardiovascular devices being prominent. Research carried out in our program in recent years has provided tools for expanding the range of properties and potential uses for these elastomers and for optimizing the synthesis procedures.

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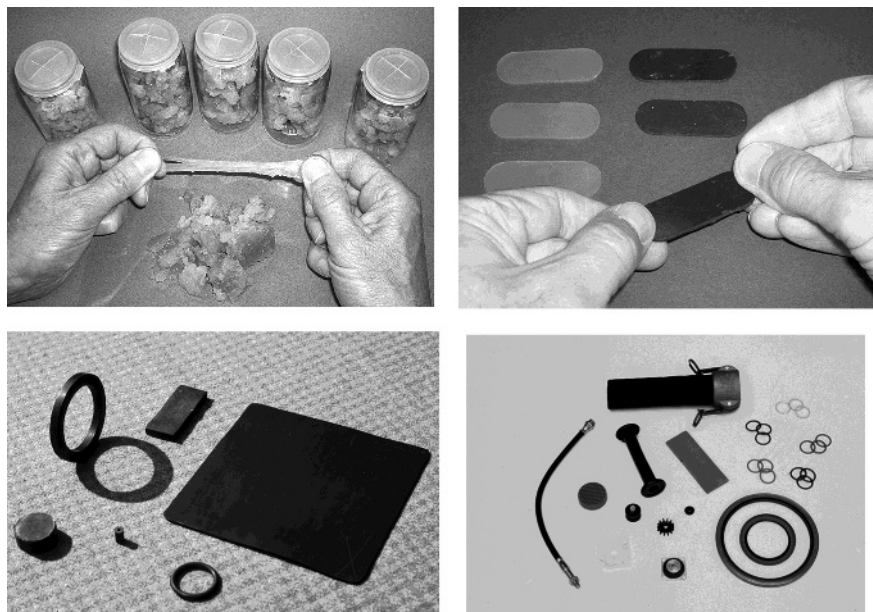


FIGURE 1.14 PNF-type elastomers. Top left: raw gum-stock after synthesis and purification. Top right: the same polymer after cross-linking, with and without carbon reinforcement. Bottom left: fabricated seals and O-rings. Courtesy of Ethyl Corporation and used with permission. Bottom right: aerospace components. Courtesy of Firestone Tire Company and used with permission.

1.5.3 Surface Coatings

The high hydrophobicity of soluble fluorinated polyphosphazenes has drawn attention to their possible use as surface coatings in applications where insoluble fluoropolymers like Teflon cannot be used. This also applies to PNF-type elastomers that, in the uncross-linked state, are highly adhesive. One application that has shown promise is as ice-phobic coatings on helicopter rotor blades. Another reported application is the use of trifluoroethoxy-substituted polyphosphazenes for coating biomedical devices.

1.5.4 Radiation Resistant Polymers

Poor resistance to high energy radiation is a characteristic of many classical organic polymers. The polyphosphazene backbone provides enhanced resistance to both free-radical damage and ionization decomposition when exposed to wavelengths from the mid-ultraviolet through to the X-ray and γ -ray regions. The energy transmission window of the backbone extends throughout the visible wavelengths and to the 220 nm region in the ultraviolet, and the lack of absorptions within this window avoids the sensitivity to photochemical decomposition. Specific transparency windows also exist in the infrared region. In this sense, the skeleton has characteristics more typical of inorganic compounds than carbon-containing backbones. Thus, the organic side groups

are the most sensitive sites to photo-decomposition in phosphazene polymers, and this can be exploited for cross-linking purposes. Nevertheless, preliminary evidence suggests that fluorinated side groups are among the least vulnerable substituents, and such polymers show impressive resistance to visible and ultraviolet radiation. Polymers with both fluorinated and nonfluorinated side groups allow tailoring of the properties to favor radiation cross-linking without causing general decomposition.

1.5.5 Membranes

The ease of changing side groups and the film-forming properties of many polyphosphazenes have attracted attention for their possible use as membranes for gas- and liquid-phase separations. Their promise for these applications was recognized by studies in the 1990s [50] and by later engineering evaluations [51].

1.5.6 Micelles

Amphiphilic block copolymers are well-known starting points for the preparation of micelles—either organized structures in the solid state or individual spherical or worm-like micelles suspended in a liquid medium. In polyphosphazene science, it is relatively easy to prepare diblock copolymers. As discussed above, both blocks can be phosphazenes or one can be a phosphazene and the other an organic polymer block or a poly(organosiloxane). Provided one block is hydrophilic and the other hydrophobic, micellar characteristics (Figure 1.15) are accessible. One example

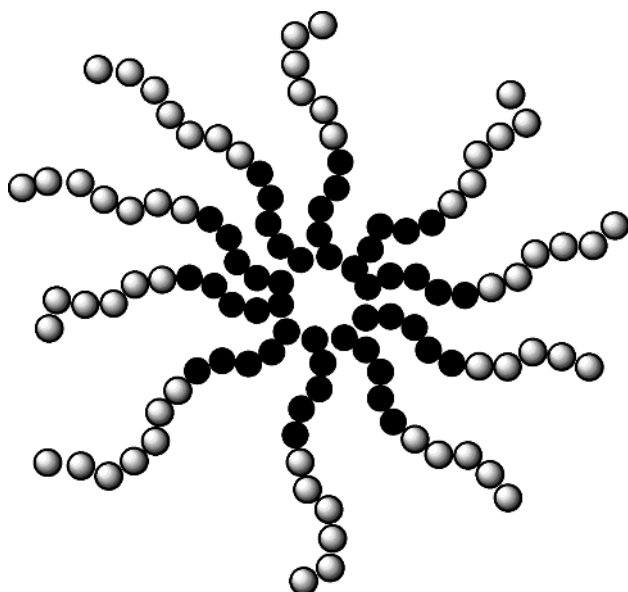
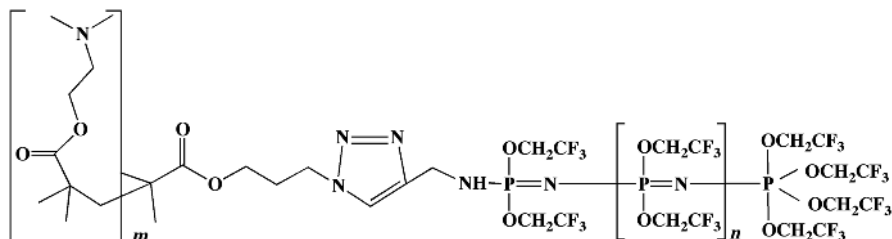


FIGURE 1.15 Schematic illustration of a micelle generated in water. The black circles represent hydrophobic repeating units; the lighter circles, the hydrophilic components.

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prepared recently in our program that readily generates spherical micelles in aqueous media is an amphiphilic block copolymer constructed from a hydrophobic poly[bis(trifluoroethoxy)phosphazene] and a hydrophilic poly[dimethylamino]ethyl methacrylate] block (Structure 1.2) [52]. The fluorinated hydrophobic core can be used to “solubilize” hydrophobic drug molecules or nanoparticles in aqueous media.



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STRUCTURE 1.2

1.5.7 Uses for Fluorophosphazene Oligomers

Although this review is about fluorophosphazene high polymers, it is worthwhile to note that a few of the cyclic oligomers have been developed for commercial uses. For example, liquid cyclic trimers with both trifluoroethoxy and aryloxy side groups on the same ring were developed as advanced hydraulic fluids, presumably because of their thermal stability and their general inertness in contact with gaskets and O-rings. Similar compounds are reported to be lubricants for use in machinery and hard disk drives [53]. In principle, there are many other potential applications for the oligomeric derivatives now that the cyclic trimer, $(\text{NPCl}_2)_3$, is readily available on a large scale.

Discussion about the applications of any evolving polymer system inevitably raises inquiries about the feasibility of scale-up of the syntheses to the manufacturing level. For polyphosphazenes, this question has intrigued many observers. Scale-up of the fluorinated PNF-type polyphosphazene elastomers has already been demonstrated by several organizations including the Firestone Tire and Rubber Company (now Bridgestone), Ethyl Corporation, the US military, and by smaller companies in the United States, as well as organizations in the former Soviet Union. Perhaps the greatest impediment to wider commercialization is the difference in chemistry compared to that used in conventional petrochemical polymer manufacturing. In this sense, the novel chemistry that was needed for the commercial development of the poly(organosiloxanes) (silicones) following World War II is an example of what can be accomplished if the incentive is strong enough. Thus, the technical requirements for the commercial development of polyphosphazenes are high quality inorganic-organic chemistry, with meticulous purification of starting materials, and protection of starting materials and intermediates from atmospheric moisture. Polyphosphazenes may never be as widely available as their conventional

fluorocarbon counterparts or even silicone polymers, but they have properties that make them ideal for many high performance applications in engineering and medicine for which there are no current alternatives.

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