Cross-Linking Reactions for the Conversion of Polyphosphazenes into Useful Materials

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The conversion of phosphazene high polymers to useful materials depends on the development of methods to cross-link the macromolecular chains. A number of crosslinking routes have been used including chemical, photochemical, and high-energy radiation techniques. The relationship of the cross-linking processes to electrochemical, electrooptical, elastomer, structural, membrane, surface, and biomedical properties is discussed.

A. Introduction

1. General Characteristics of Polymeric Materials. Polymers form one of the largest classes of materials.[1] Together with ceramics, metals, and a number of inorganic electronic and electrooptical solids, they constitute one of the main foundations of materials science. Polyphosphazenes are nonclassical macromolecules that, depending on the specific molecular structure, combine some of the properties of conventional organic petrochemical polymers with those of (the mainly inorganic) ceramics, semiconductors, metals, and electrooptical materials. As such, they provide access to combinations of properties that are not found in any of the classical materials areas.

Because the field of inorganic/organic materials is one of the most promising areas for the future evolution of materials science, polyphosphazenes provide numerous lessons that can assist in the development of other hybrid polymer systems.

Before considering some of the special properties of polyphosphazenes, it is worthwhile to remember a number of the important characteristics of polymers in general, and the ways in which these properties are utilized in materials science. Polymers have different properties depending on whether they are (a) in solution, (b) in the un-cross-linked solid state, or (c) part of a system in which the individual polymer chains are connected by cross-links.[2,3]

Polymers consist of long chains (often thousands of atoms in length) to which are attached side groups. The properties in solution and in the solid state depend on both the main chain structure and the nature of the side groups. For example, the flexibility of the main chain will determine the degree of either random coiling or "rigid rod" character in solution, while the side groups usually control the solubility in different solvents. Highly flexible, long-chain molecules become entangled in solution and markedly increase the viscosity of the solvent.

In the solid state, un-cross-linked polymer molecules interact strongly with their neighbors, either through complex entanglements or through the formation of ordered domains known as "microcrystallites". The macromolecular structure affects these interactions in several ways. For example, the presence of branched or dendritic structures will discourage microcrystallite formation, as will the random disposition of two or more different types of side groups along a linear chain. Any molecular feature that eliminates symmetry or linear order will be detrimental to the formation of lateral chain packing and, hence, to microcrystallite formation. Microcrystallites serve as thermally-labile cross-link sites by holding neighboring chains together by van der Waals forces. Hence, they have a profound influence on materials' properties.

The main structural differences between un-cross-linked polymers in the solid state become manifest in the glass transition temperature (T_g). This is the temperature above which an amorphous polymer is an elastomer, or a microcrystalline polymer is a thermoplastic and below which the material is a glass or a composite of glass and microcrystallites. The T_g is a feature of the amorphous state, and it depends on two molecular features. First, it represents the temperature below which the polymer chains lack the energy to undergo significant backbone motions. These motions mainly involve torsional modes of the skeletal bonds. Below the T_g, the randomly entangled chains can be visualized as being frozen in position. Above the T_g, the chains possess enough energy to allow the twisting motions that give rise to both molecular and materials' flexibility. At the molecular level, this can be translated into an influence by both the backbone and the side groups. Backbones that contain bonds with a high barrier to torsion or bulky side groups that incur steric interference as backbone bond twisting occurs will generate a high T_g (Figure 1).

Second, the size and shape of the side groups may create *free volume* between themselves and their counterparts on neighboring chains. The greater the free volume, the easier will it be for macromolecular motion to occur. Hence, systems with large free volumes are expected to have low T_g's.

Thus, the location of the T_g on the temperature scale will determine whether, at room temperature, for

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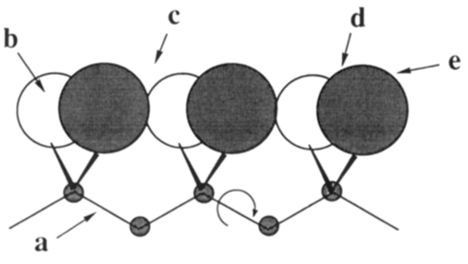


Figure 1. Factors that affect T_g and other physical properties of polymers: (a) elements and bond types in the main chain determine the intrinsic mobility of the chain via the torsional barrier; (b) shape and rigidity of the side groups affect chain flexibility via side group steric interference effects; (c) free volume between side groups on the same- or neighboring chains influences the T_g—the more free volume present, the easier it is for chain motion to occur; (d) side-group regularity and symmetry along the chain favor efficient chain-packing arrangements that lead to reduced free volume, formation of microcrystallites, and the generation of thermally labile, van der Waals "cross-links"; (e) side groups provide sites for the formation of covalent, ionic, or coordination cross-links.

example, the material is a glass, an elastomer, or a gum, and this in turn can often be rationalized or understood in terms of the details of the macromolecular structure.

The macromolecules in an amorphous un-cross-linked polymer at a temperature above its T_g have considerable freedom of motion, so much so that polymer molecules can move through the solid by the process of reptation.[4] The amorphous regions of a polymer are thus quasi-liquid. Amorphous polymers with low T_g's will flow slowly under the influence of applied pressure or gravity, a process known as "creep". Some polymers in this liquidlike state will act as solvents for salts, and the quasi-solid solutions can function as ionic electrical conduction media.[5,6] Moreover, the surfaces of many polymers that contain amorphous regions are constantly "turning over" as the liquidlike molecular motion first raises parts of a given chain to the surface and then subsequently buries them.

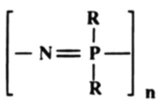
The formation of cross-links between polymer chains obviously places severe restrictions on these liquidlike solid-state molecular motions. Even an average of 1.5 cross-links per chain is sufficient to prevent broad-scale molecular migrations. Thus, cross-links prevent chains from sliding past each other when the material is placed under tension. This raises the tensile strength dramatically and generates rubber-elastic properties from materials that would otherwise be gums. Increased levels of cross-linking impart more and more rigidity to the system until, in the limit where a cross-link exists for every two or three chain atoms, the material becomes an inflexible, infusible ceramic.

Cross-linking affects solution properties also. Whereas an un-cross-linked amorphous polymer will usually dissolve in some solvent, cross-links will prevent the separation of polymer molecules and will prevent dissolution. The material may imbibe solvent to a degree that is limited by the density of cross-linking, but it will not completely dissolve. Such solvent-swelled "gels" are known as hydrogels if the solvent is water or organogels if an organic solvent is employed. Materials of this type may contain from, say, 50–95% of their weight as solvent, yet have definite size and shape. They constitute a state of matter between "solid" materials and traditional liquids. Many biological tissues and a few synthetic biomedical materials are hydrogels.

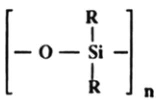
Thus, the cross-linking of macromolecules is one of the most important aspects of polymeric materials science. Polymers in their un-cross-linked state are easily fabricated but are prone to decompose at only moderately high temperatures. Cross-linking improves thermal stability. Moreover, the process of cross-linking is an essential part of photolithography, elastomer technology, biomedical materials research, and the conversion of polymers to ceramics. Indeed, one of the main challenges in the translation of fundamental polymer chemistry into useful materials research involves the development of cross-linking methods. This is especially obvious in the field of polyphosphazenes, as discussed in the following sections.

B. Synthesis of Polyphosphazenes

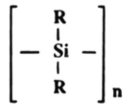
1. Perspective. Polyphosphazenes are linear or branched macromolecules with the general structure shown in **1**, where n, the degree of polymerization, may average 10 000–20 000 repeat units. Roughly 300


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

1


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

2


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

3

different types of polyphosphazenes are now known, with different organic, inorganic, or organometallic side groups linked to the phosphorus atoms in the skeleton. The molecular and materials' properties vary over a wide range as the side groups are changed, and it is this feature that provides valuable opportunities for fundamental investigation and for the design of useful materials.

Polyphosphazenes, together with poly(organosiloxanes) ("silicones", **2**) and poly(organosilanes) (**3**) form a trio of organic–inorganic polymer systems that is the current foundation of the hybrid polymers field.[7] Polysiloxanes have been developed technologically for the longest period of time (50 years), but a wider range of polyphosphazenes exists in spite of their relatively recent origins.

2. Synthesis of Polyphosphazenes. There are three basic approaches for the preparation of different polyphosphazenes. The first two were developed in our program[8–11] and use an unusual reaction sequence of a ring-opening polymerization, followed by macromolecular substitutions. The third approach includes several condensation-type polymerizations that were developed in other research groups.[12–15]

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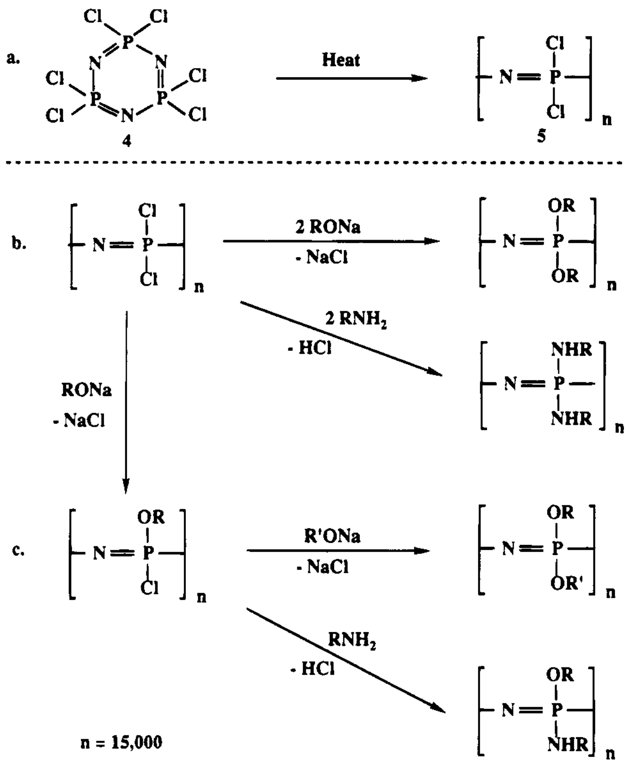
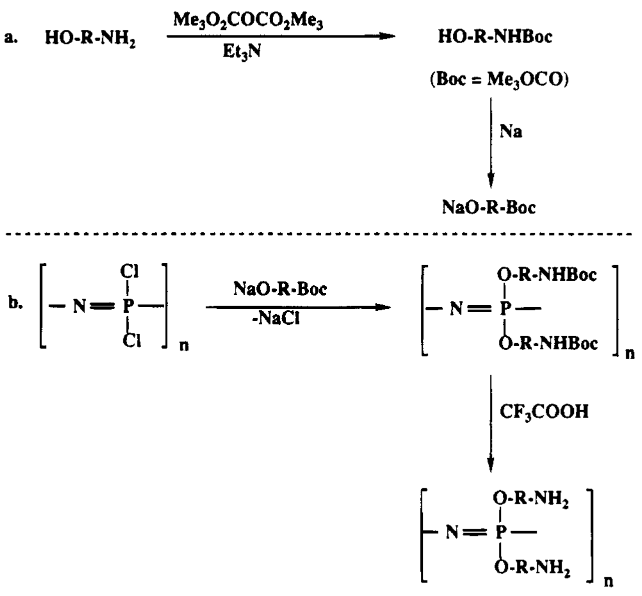
Scheme 1. Polyphosphazene Synthesis: Method 1



Scheme 2. Protection and Deprotection of Difunctional Reagents



(a) Method 1. Scheme 1 summarizes the most widely used synthesis approach.[8-10,16-20] It begins with the ring-opening polymerization of a cyclic "monomer" known as hexachlorocyclotriphosphazene (**4**), itself prepared in the laboratory or on an industrial scale from phosphorus pentachloride and ammonium chloride. The polymerization can be conducted in the molten state at 250 °C or at lower temperature in an organic solvent. Lewis acid catalysts are required for the solution-state polymerization.[21,22]

The resultant poly(dichlorophosphazene) high polymer (**5**) is a reactive, organic-solvent soluble macromolecule. The P–Cl bonds react with a wide variety of nucleophiles with replacement of the chlorine atoms by organic, inorganic, or organometallic groups. Perhaps the most surprising feature of this reaction is that it involves an average of 30 000 substitution reactions on each polymer molecule. With some active reagents, all the chlorine atoms are replaced within minutes of the start of the reaction. Failure to replace all or most of the chlorine atoms may yield a polymer that is sensitive to hydrolysis of the P–Cl bonds by atmospheric moisture with the resultant formation of P–O–P cross-links.

However, under controlled reaction conditions, a fraction of the total chlorine atoms can be replaced by the use of a deficiency of one reagent, and the remainder can then be removed by a second reagent (Scheme 1).[23] Alternatively, both reagents may be allowed to compete simultaneously for the available reaction sites.[24] In these ways, mixed-substituent polymers are accessible, and this provides a powerful means for fine-tuning materials' properties.

Two restrictions must be observed in the macromolecular substitution process. First, some reagents are too bulky or insufficiently nucleophilic to replace all the chlorine atoms under mild reaction conditions. In these circumstances, high temperatures and moderate pressures may be required to bring about complete substitution, or a second, more reactive, nucleophile is needed to replace the remaining chlorine.[25]

Second, difunctional reagents must be avoided because each reagent molecule could react with two separate chains and form covalent cross-links. Cross-link formation is often needed *in the later stages* of materials processing, but cross-linking during the primary synthesis process would bring the polymer out of solution before chlorine replacement was complete, thus yielding an insoluble material with residual P–Cl bonds and potential long-term hydrolytic sensitivity. Thus, difunctional reagents, such as diols, diamines, or amino alcohols, are usually used only after one reactive site in the reagent has been protected, and that site must then be deprotected after the unit has been linked to the chain and all chlorine atoms have been replaced (Scheme 2).[26]

The ring-opening polymerization/macromolecular substitution method has also been employed to prepare phosphazene-like polymers that bear phosphorus, nitrogen, and a third heteroelement in the chain, as shown in Schemes 3 and 4.[27-29]

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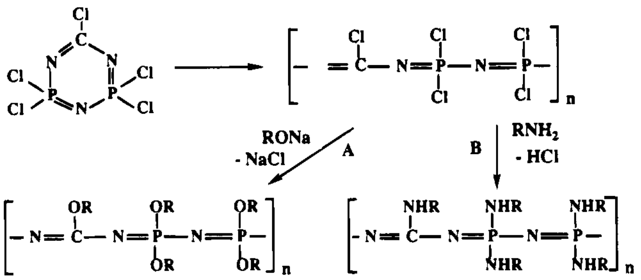
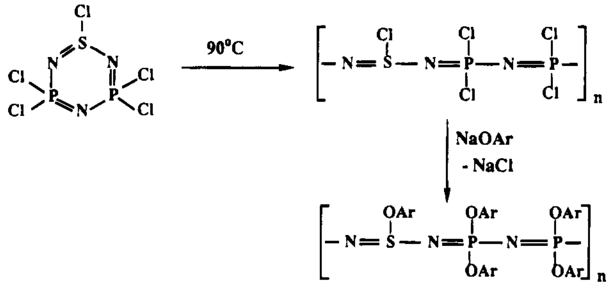
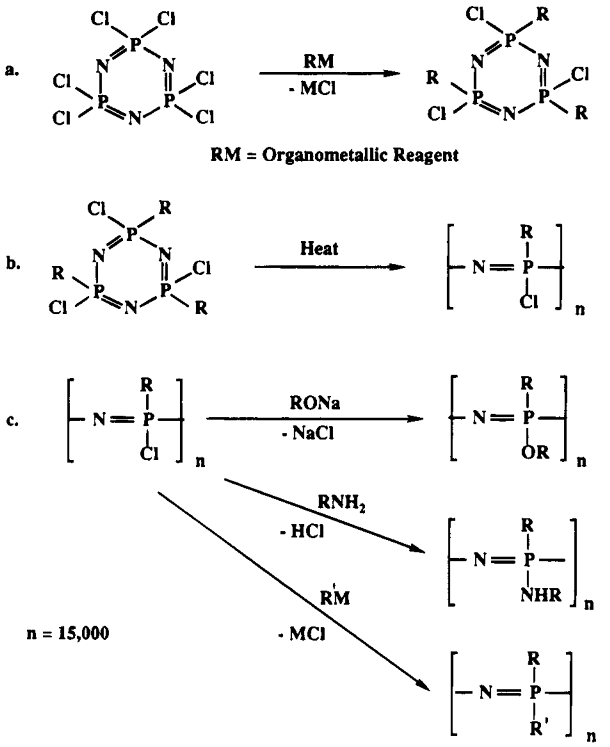
Scheme 3. Poly(carbophosphazenes)



Scheme 4. Poly(thiophosphazenes)



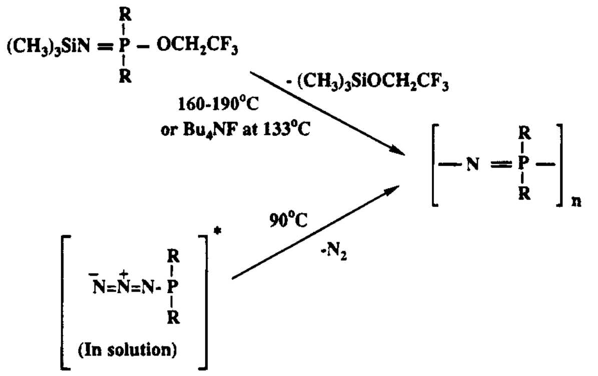
Scheme 5. Polyphosphazene Synthesis: Method 2



(b) Method 2. Scheme 5 illustrates the second synthesis approach, which is closely related to the first. Here, organic side groups are linked to the phosphorus atoms at the cyclic trimer stage, and these substituted rings are then polymerized. Polymerization is assisted (i) if some P–Cl (or P–F) groups remain, (ii) when the organic groups are small enough in size to minimize steric hindrance effects during chain propagation, and (iii) if the ring is strained as a result of the presence of a transannular structure or a third heteroelement in the ring.[30-35]

(c) Method 3. Different condensation approaches to phosphazene polymer synthesis are summarized in Scheme 6.[12-15,36,37] In general, these yield polymers with alkyl or aryl groups connected to phosphorus through C–P bonds, species that are available via the macromolecular substitution route but only with some difficulty. At least one of the condensation methods yields alkoxyphosphazene polymers, but with lower molecular weights than those obtained by the polymer substitution route.

Scheme 6



* This potentially explosive intermediate is not isolated, but is both prepared and decomposed in solution

C. Different Possibilities for Cross-Linking Polyphosphazenes

Three conceptually different approaches exist for the linking together of polyphosphazene chains. These are shown in Figure 2. Several variations on these methods, especially of route B, have been explored in a number of laboratories. Here, the emphasis is on methods developed in the author's laboratory and in association with collaborating groups.

1. Use of Microcrystallites. As discussed earlier, polymers that form microcrystalline domains behave in many ways as if they are cross-linked, as indeed they are through strong van der Waals forces. The difference from conventional covalent cross-linking lies in the fact that the linkage sites can be broken (melted) by heating, and that they re-form on cooling. Such thermally labile cross-link sites have many advantages from the viewpoint of materials' fabrication.

Two classes of microcrystalline polyphosphazenes have been studied in detail. These are single-substituent-type polymers with trifluoroethoxy or aryloxy side groups (**6**, **7**).[9,38-41] Both classes are tough, flexible films or fibers. The solid-state morphology of these polymers is quite complex with multiple transitions occurring above the T_g. However, the importance of the microc-

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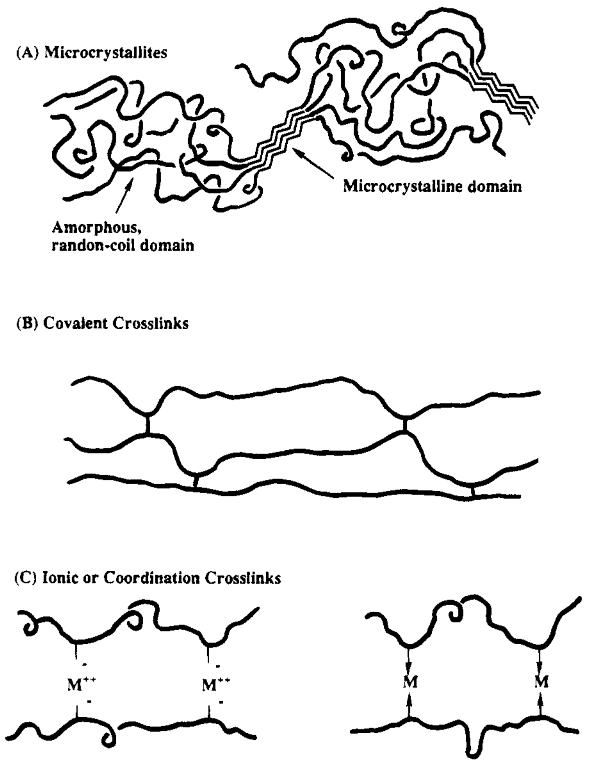
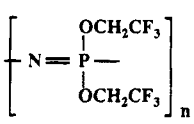
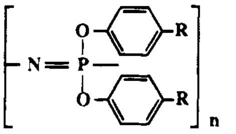


Figure 2. Different ways in which polyphosphazene chains can be linked together.



$[N{=}P(OCH_2CF_3)_2]_n$

6



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rystallites becomes evident if similar but mixed-substituent polymers are studied. Here the lack of molecular symmetry prevents crystallite growth, and the polymers are amorphous elastomers rather than dimensionally stable materials.[24,42-44]

2. Formation of Covalent Cross-Links between Chains. Three main approaches exist to the linkage of polyphosphazene chains by covalent cross-links. These are as follows:

(a) Displacement Reactions at Phosphorus. The replacement of chlorine or fluorine at phosphorus by a diamine, diol, amino alcohol, or aminophenol has already been mentioned (Scheme 7). If this process could be carried out in the final stages of a macromolecular substitution, it would be an effective and useful cross-linking method. However, this is rarely possible, and in any case, it would generate problems of purification and fabrication. Similar objections apply to the use of unhindered primary amines, such as ammonia or methylamine as direct cross-linking reagents (Scheme 7, reaction 2, and Chart 1).

However, cross-linking by the displacement of *organic* side groups in a fully substituted polymer after it has been purified is a viable process. This option (known as metathetic exchange) is shown in Scheme 7, reaction 3. As an example of this process, the polymer [NP-

Scheme 7

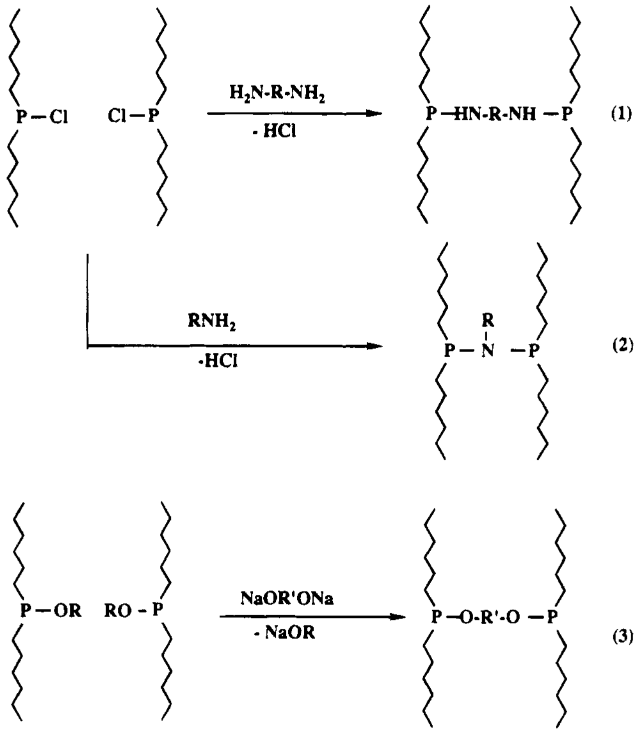
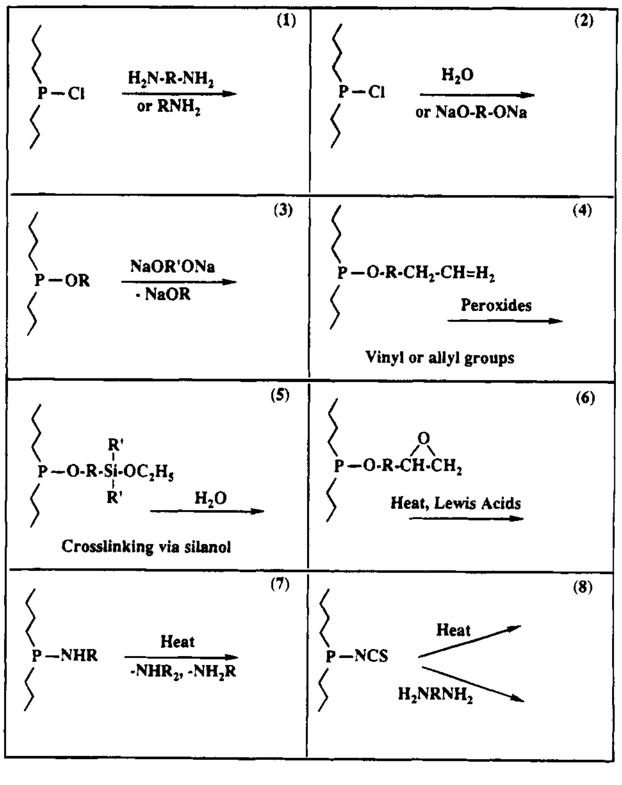


Chart 1. Covalent Cross-Linking Sites for Polyphosphazenes



$(OCH_2CF_3)_2]_n$ (**6**) can be cross-linked from solution by treatment with $NaOCH_2(CF_2)_xCH_2ONa$.[45]

(b) Chemical Cross-Linking via Reactive Sites on the Side Groups. A wide variety of options exist for this approach, a number of which are summarized in Chart 1. Of these, the peroxide-induced coupling of allyl groups (reaction 4) is used in a commercial process for producing phosphazene elastomers.[44] Reaction 7 is the

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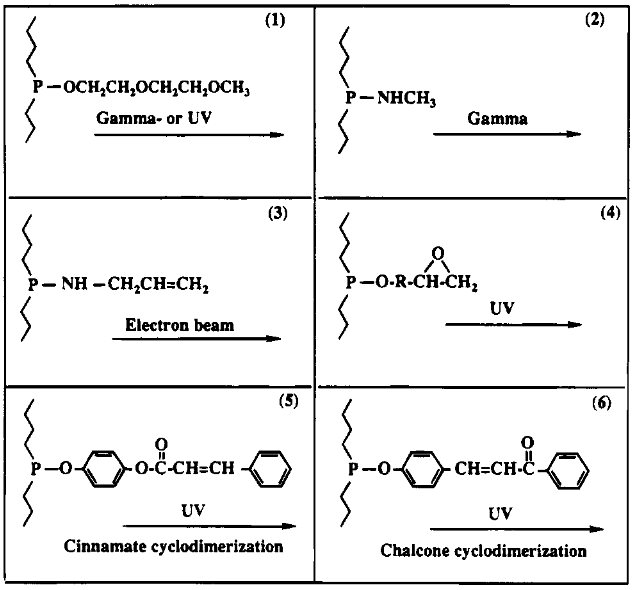
Chart 2. Side Groups for Radiation Cross-Linking



basis of an experimental process for the preparation of ceramics from polyphosphazenes.[46]

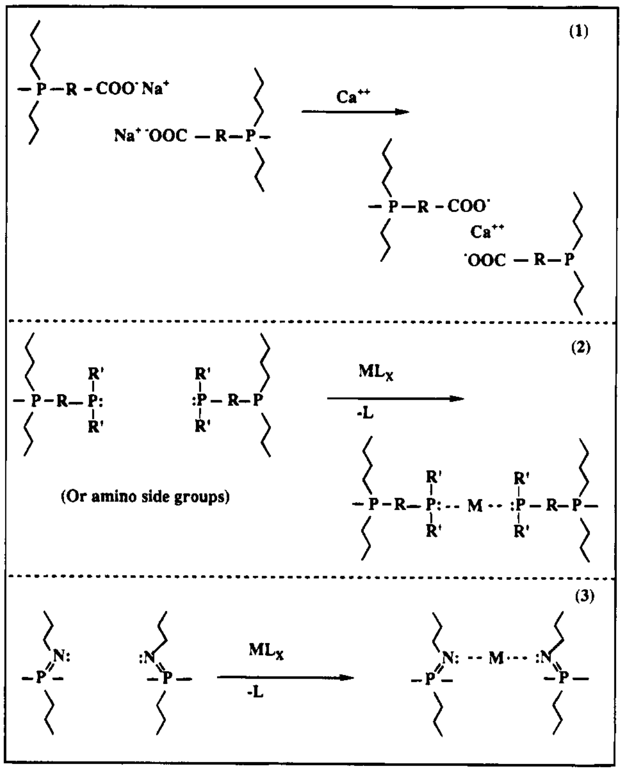
(c) Radiation-Induced Cross-Linking Reactions. The use of radiation for cross-linking polyphosphazenes has many advantages, mainly because the inorganic backbone is stable to irradiation by γ-rays or X-rays and is transparent to visible and near-UV light. Thus, the skeletal cleavage reactions that plague the radiation chemistry of many organic polymers are absent or insignificant for polyphosphazenes.[47]

Polyphosphazenes can be designed and prepared with side groups that are sensitive to γ-rays, X-rays, electron beams, and UV or visible radiation. Several examples are shown in Chart 2.

The γ-ray-induced cross-linking of polyphosphazenes that bear alkyl ether or other alkyl side units has proved to be important in the preparation of membranes, in the fabrication of solid polymeric battery electrolytes, and in the preparation of hydrogels, as will be discussed later. The underlying reaction is a radiation-induced C−H or C−C homolytic bond cleavage to give pendent carbon radicals. Cross-combination of these generates a covalent cross-link (see later). The advantages of this method are (i) the polymer before cross-linking does not bear chemically reactive side groups and can thus be handled without special precautions, (ii) the degree of cross-linking can be controlled within fine limits by the radiation dose (typically 1−5 Mrad of γ-rays), and (iii) no impurities other than hydrogen gas (formed by hydrogen radical combination) are introduced into the system. This last point is important when the cross-linked system forms part of a conductive material.

The use of allyl-substituted polyphosphazenes for electron-beam cross-linking is shown in Chart 2, reaction 3.[48] This process is of interest because of the high sensitivity and good resolution possible when these polymers are used in lithographic resists (see later).

Scheme 8



Allyl-substituted polyphosphazenes can also be cross-linked by γ-radiation.[49]

The use of ultraviolet light for cross-linking polyphosphazenes through photosensitive side groups has obvious advantages over the use of γ-rays. Reactions 1 and 4−6 in Chart 2 are examples of approaches that have been investigated in our program.[50−53] Cross-linking of alkyl-ether-substituted polyphosphazenes in the presence of benzophenone as a photosensitizer presumably occurs via radical-induced C−H bond cleavage and cross-combination in a way similar to that described for the γ-ray-induced reactions. Interestingly, cross-linking also occurs slowly in the absence of the photosensitizer perhaps as a consequence of skeletal absorption by short-wavelength UV and energy transfer to the side groups.

Side groups that bear terminal epoxy groups are also sensitive to UV irradiation and provide a facile route for cross-linking (Chart 2, reaction 4). Finally, side groups that bear cinnamate or chalcone units absorb UV radiation and undergo 2+2 cycloaddition reactions (Chart 2, reactions 5 and 6).[52,53] Coupling between groups on different chains generates cross-links. The chalcone system has proved to be the more sensitive of the two. Both systems are of interest for the stabilization of nonlinear optical (NLO) materials' properties and for photolithography.

3. Metal-Ion or Metal-Coordination Cross-Linking. These two processes are illustrated in Scheme 8. The first reaction shown in this scheme is an extremely useful method for cross-linking water-soluble phosphazene polymers in aqueous media. It is based on the

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(46) Allcock, H. R.; Welker, M. F.; Parvez, M. *Chem. Mater.* **1992**, *4*, 296.

(47) O'Brien, J. P.; Ferrar, W. T.; Allcock, H. R. *Macromolecules* **1979**, *12*, 108.

(48) Welker, M. F.; Allcock, H. R.; Grune, G. L.; Chern, R. T.; Stannett, V. T. In *Polymers for Microelectronics*; Thomson, L. F., Wilson, C. G., Tagawa, S., Eds.; ACS Symp. Series: 1994; Vol. 537, pp 293−303.

(49) Babic, D.; Souverain, D. M.; Stannett, V. T.; Squire, D. R.; Hagnauer, G. L.; Singler, R. E. *Radiat. Phys. Chem.* **1986**, *28*, 169.

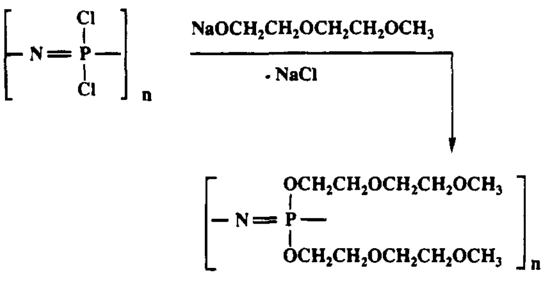
(50) Nelson, C. J.; Coggio, W. D.; Allcock, H. R. *Chem. Mater.* **1991**, *3*, 786.

(51) Nelson, C. J.; Coggio, W. D.; Allcock, H. R., unpublished results.

(52) Allcock, H. R.; Cameron, C. G. *Macromolecules* **1994**, *27*, 3125.

(53) Allcock, H. R.; Cameron, C. G. *Macromolecules* **1994**, *27*, 3131.

Scheme 9



"MEEP"

8

exchange of monovalent for di- or trivalent cations along a polyelectrolyte chain. This process is important for the cross-linking of biomedical polymers and especially for the microencapsulation of biologically active species, as discussed later.

The second approach makes use of metal coordination between phosphine or amino groups on different chains in aqueous or nonaqueous media. This is a method with broad possibilities, not only for the preparation of cross-linked polymers but also for the simultaneous immobilization of transition-metal catalysts.[54] In some cases, the cross-linking is reversible if the system is treated with a nonpolymeric phosphine or amine. A variant of this approach is to use the phosphazene skeletal nitrogen atoms as coordinative ligands (Scheme 8, reaction 3).[55] A wide range of metals can be used for all these reactions, and the processes can be used to recover metals from solution or separate one type of metal ion from another.

D. Use of the Cross-Linking Processes in Specific Applications

As discussed earlier, the cross-linking of polyphosphazene chains is often a critical step in the conversion of a polymer to a useful material. Each of the cross-linking methods described above has advantages for the development of specific materials' properties. This is illustrated by the selected examples discussed in the sections that follow.

1. Cross-Linking of Solid Polymeric Ionic Conductors. The polymer known as "MEEP" {poly[bis((methoxyethoxy)ethoxyphosphazene]} (**8**) was first synthesized in our laboratory as part of a collaborative project with the group of D. F. Shriver at Northwestern University.[56−59] The synthesis pathway is shown in Scheme 9. The objective was to design a polymer specificially optimized to function as a solid polymeric ionic conduction medium. Polymers such as poly(ethylene oxide) had been studied for many years as a solid solvent for salts such as lithium triflate,[5,6] but that polymer is microcrystalline and gives good ionic conductivities only above the crystallite melting temperature near 80 °C. Solid polymeric electrolytes have attracted wide attention as possible electrolytes for large area, robust, lightweight rechargeable lithium batteries which, ideally, would function efficiently at room temperature and below.[60] Poly(ethylene oxide), because of its crystalline morphology, is clearly inappropriate for this application and, moreover, has only a limited solvation and ion-pair separation capacity since it possesses only one donor oxygen atom per repeat unit.

MEEP is completely amorphous, and each repeating unit bears six oxygen atoms for coordination to lithium cations, thus favoring ion-pair separation. Furthermore, the polymer chains and side groups have a high degree of flexibility which assists cation migration as the lithium ions are passed from one side group to another. In practice, conductivities that are 2−3 orders of magnitude higher than that of poly(ethylene oxide) at 25 °C have been measured.

However, MEEP has one drawback. Because its T_g is low (−86 °C) and because it is noncrystalline, the polymer is a viscous gum at room temperature. As such, it lacks dimensional stability and is slowly extruded from batteries when subjected to pressure. A cross-linking reaction was therefore needed that would provide dimensional stability without impairing ion transport and without introducing conductive impurities.

As mentioned earlier, MEEP can be cross-linked by exposure to 1−5 Mrads of γ-radiation[61−63] or by ultraviolet irradiation.[50] This converts the gum into a nonflowing rubbery elastomer. If the salt is incorporated into the polymer before cross-linking, the final cross-linked material has a conductivity similar to that of the un-cross-linked counterpart. Because only few cross-links per chain are needed to prevent materials' flow, the segmental motions of the intervening repeating units are not affected by the cross-link sites.

Experimental thin-film rechargeable lithium batteries based on this electrolyte have been prepared in our laboratory (Figure 3),[64] and these have proved to be excellent prototypes for further development.

2. Electron-Beam Lithographic Resists. Polyphosphazenes offer several advantages for use as resists in lithography. These include (i) the ease with which electron-sensitive side groups can be linked to the polymer chain, (ii) the facility with which the T_g can be tuned by the introduction of different side groups (high T_g's are preferred for resist applications), (iii) the stability of the polymer backbone to electron beams, hence, no complications from depolymerization or random fragmentation are anticipated, and (iv) in principle, a negative-type resist could be baked to give a ceramic coating.

On the basis of these requirements, several polyphosphazenes were synthesized in our laboratory and examined as e-beam resist materials in the laboratory of V. T. Stannett at North Carolina State University.[48] The

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(54) Allcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* **1983**, *2*, 267.

(55) Allcock, H. R.; Allen, R. W.; O'Brien, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 3984.

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

(57) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.

(58) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *Solid State Ionics* **1986**, *19*, 258.

(59) Tonge, J. S.; Blonsky, P. M.; Shriver, D. F.; Allcock, H. R.; Austin, P. E.; Neenan, T. X.; Sisko, J. T. *Proc. Electrochem. Soc.* **1987**, *1*, 533.

(60) Shriver, D. F.; Farrington, G. C. *Chem. Eng. News* **1985**, *63* (20), 20.

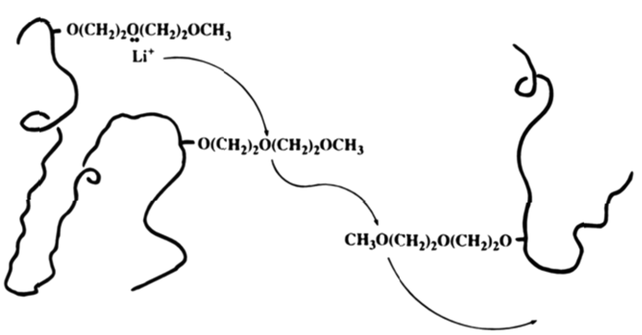
(61) Allcock, H. R.; Gebura, M.; Kwon, S.; Neenan, T. X. *Biomaterials* **1988**, *9*, 500.

(62) Allcock, H. R.; Kwon, S.; Riding, G. H.; Fitzpatrick, R. J.; Bennett, J. L. *Biomaterials* **1988**, *9*, 509.

(63) Bennett, J. L.; Dembek, A. A.; Allcock, H. R.; Heyen, B. J.; Shriver, D. F. *Chem. Mater.* **1989**, *1*, 14.

(64) Napierala, M.; O'Connor, S.; MacDonald, D.; Allcock, H. R., work carried out at the Pennsylvania State University in the Department of Chemistry and the Advanced Materials Laboratory, 1994.

(a) Cation Transport Through Solid MEEP



(b) MEEP-Based Rechargeable Lithium Battery

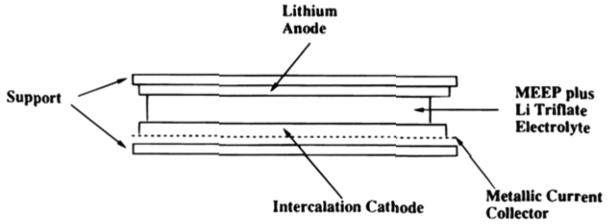


Figure 3. (a) Cations such as Li$^+$ can migrate through the matrix of a polymer such as MEEP as they are passed in a hand-to-hand fashion from one loosely coordinating side group to another, even when the polymer is cross-linked. This solid ionic conductivity is the basis of experimental rechargeable lithium batteries. (b) Cross section of a rechargeable battery that makes use of MEEP/lithium triflate as the electrolyte.

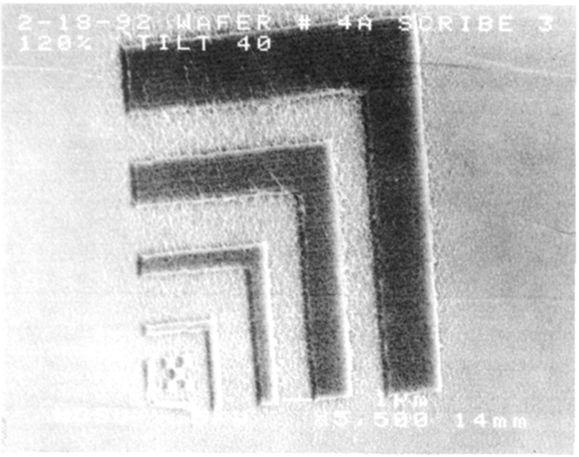


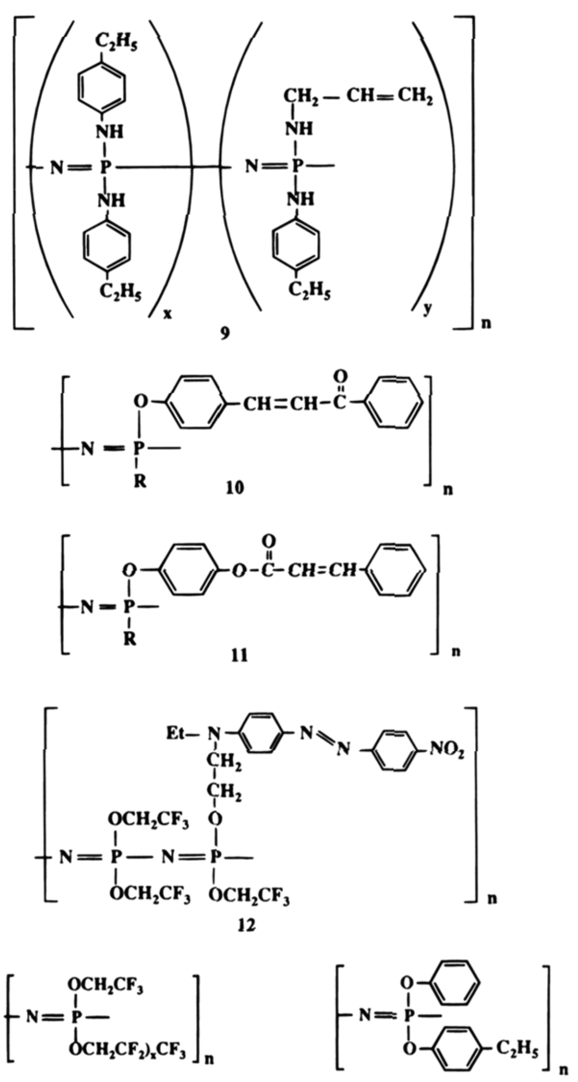
Figure 4. Test pattern for electron-beam microlithography using polymer 9 (M. F. Welker, H. R. Allcock, G. L. Grune, R. T. Chern, and V. T. Stannett, ref 48). Lithographic pattern obtained by G. L. Grune, courtesy of IBM Laboratories, Research Triangle Park, NC.

need for a high T_g was satisfied by the use of arylamino side groups, and the required sensitivity to electrons by the incorporation of allyl cross-linker groups. A typical polymer studied in this work is shown in Chart 3, structure **9**. Figure 4 illustrates the resolution obtained for a test pattern.

3. Ultraviolet-Induced Cross-Linking for Resists and Nonlinear Optical Stabilization. The 2+2 cycloaddition reactions mentioned earlier for cross-linking via cinnamate or chalcone side groups have a number of potential uses. Two examples include the formation of negative tone resists and the stabilization of NLO activity in a polyphosphazene.

The polymers shown as **10** and **11** in Chart 3 are typical of the phosphazene-based photosensitive species prepared in recent work.[52,53] Because the chalcone system (**11**) has a higher photosensitivity than the cinnamate derivative, the behavior of the chalcone-bearing polymer will be described here.

Chart 3



9

10

11

12

13

14

First, the cross-linking for polymer **11** can be followed from changes in the UV–visible spectrum, as shown in Figure 5. Cross-linking was confirmed by the insolubility of the polymer in all solvents following irradiation at 260–380 nm. An indication of the photosensitivity of polymer **11** is provided by the onset of cross-linking after 30 s exposure to a 450 W mercury vapor lamp. The UV transparency of the backbone in these polymers allows maximum photon interactions with the chalcone units and avoids reactions that might lead to concurrent skeletal cleavage.

Recent work on the synthesis of polyphosphazenes with side groups that possess χ^2 NLO activity has been carried out in our program.[65,66] For example, polymer **12** can be poled at temperatures above its T_g (44 °C) to generate χ^2 coefficients of 34–46 pm/V, which is in the same range as that of lithium niobate, the classical standard in this field. However, the nonlinearity is lost rapidly after the poling voltage is discontinued, even when the polymer is cooled below its T_g. Incorporation

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(65) Dembek, A. A.; Kim, C.; Allcock, H. R.; Devine, R. L. S.; Steier, W. H.; Spangler, C. W. *Chem. Mater.* **1990**, *2*, 97.

(66) Allcock, H. R.; Dembek, A. A.; Kim, C.; Devine, R. L. S.; Shi, Y.; Steier, W. H.; Spangler, C. W. *Macromolecules* **1991**, *24*, 1000.

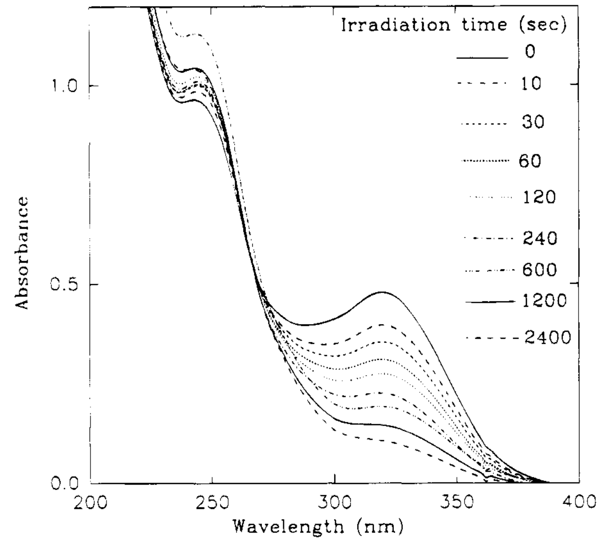


Figure 5. Ultraviolet–visible spectral changes of polyphosphazene–chalcone derivative **11** during irradiation with 260–380 nm ultraviolet light. The changes reflect loss of unsaturation that accompanies cyclodimerization-type cross-linking of the polymer.

of the cinnamate or chalcone side groups as cosubstituents in this type of polymer is expected to stabilize the effect over a long period of time.

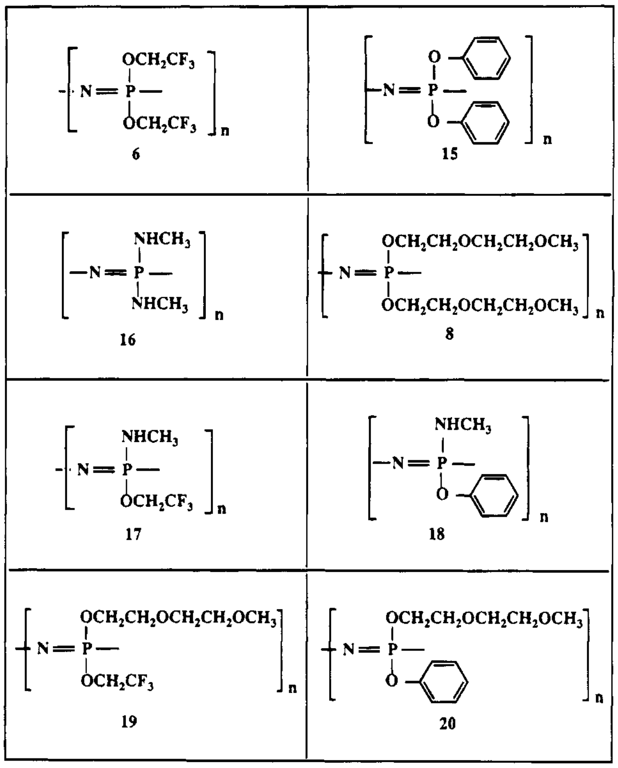
4. Cross-Linking in Phosphazene Elastomer Technology. The production of high-performance phosphazene elastomers is one of the most advanced aspects of phosphazene technology. These elastomers have been used in aerospace applications, military hardware, seals, gaskets, tubes, pipes, and in nonflammable heat, sound, and electrical insulation.[24,42-44] Uses in dentistry have also been commercialized.[67]

Polymers of this type fall into two different categories—those based on mixed-substituent fluoroalkoxyphosphazene structures (**13**) and those that bear two or more types of aryloxy side groups (**14**). In the uncross-linked state, polymer **13** is a gum which flows slowly under the influence of gravity. Cross-linking converts it to a rubbery elastomer. Both polymers can be cross-linked via the heat- and peroxide-induced intermolecular coupling of pendent allyl groups. In practice, this must be accomplished during or after the fabrication of the final shaped object. Because the aryloxyphosphazene elastomers are usually employed in the form of foam rubber, the cross-linking process must be synchronized with the generation of gas bubbles by the decomposition of proprietary additives.

The utility of the fluoroalkoxy-substituted elastomers (**13**) stems from their low glass transition temperature (−60 °C), their solvent resistance and hydrophobic surface character, and their resistance to burning. The aryloxy derivatives have higher T_g's (−30 to −20 °C) but are less expensive and also resist burning. Both polymers are excellent impact-absorbing materials, a property that can be attributed to the flexibility of the backbone, which transposes impact energy into bond torsion and conformational changes rather than bond cleavage.

Both polymers can also be cross-linked by γ-irradiation.[49] Although this is not yet a commercial process, it has interesting ramifications for the use of these polymers in nuclear power plant technology.

Chart 4. Hydrophobic, Hydrophilic, and Amphiphilic Polymers[a]



[a] Note that, in structures **17–20**, the two sets of side groups may be geminal or nongeminal, or be part of random or block arrangements.

5. Polyphosphazene Membranes. The use of synthetic polymers in membrane research and technology is an expanding area of interest that encompasses uses that range from gas-separation devices to hemodialysis equipment. Polyphosphazenes are particularly useful in membrane studies because of the ease with which the molecular flexiblity, hydrophobicity, and guest transport properties can be altered by changes in the side groups. However, in nearly every case studied so far, the physical properties of the membrane must be enhanced by the formation of cross-links. This has been accomplished mainly by radiation cross-linking techniques, as described below.

(a) Semipermeable Membranes for Liquid-Phase Separations. The separation of solutes in solution via the use of semipermeable membranes depends both on the internal and surface characteristics of the membrane. The polyphosphazenes shown in Chart 4 differ markedly in their hydrophobic and hydrophilic surface and bulk characteristics. For example, species **6** and **15** are highly hydrophobic, whereas **16** and **8** are soluble in water. Each of these species could function as membranes (the water-soluble species would need to be cross-linked for dialysis of aqueous media), but greater subtlety in membrane behavior can be achieved through the synthesis of mixed-substitutent, amphiphilic polymers such as **17–20**. Moreover, by changing the ratios of hydrophobic to hydrophilic side groups, the membrane can be "tuned" to optimize its solute transmission behavior.[61]

Cross-linking is necessary to prevent disintegration of the membrane in aqueous media at high ratios of the

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(67) Gettleman, L.; Ross, L. M. *Polym. Mater. Sci. Eng.* **1985**, *53*, 770.

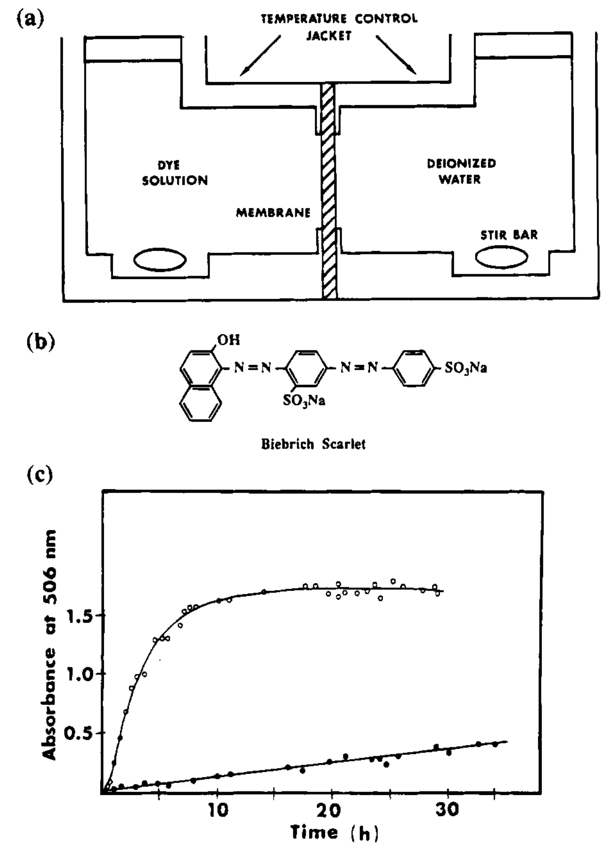
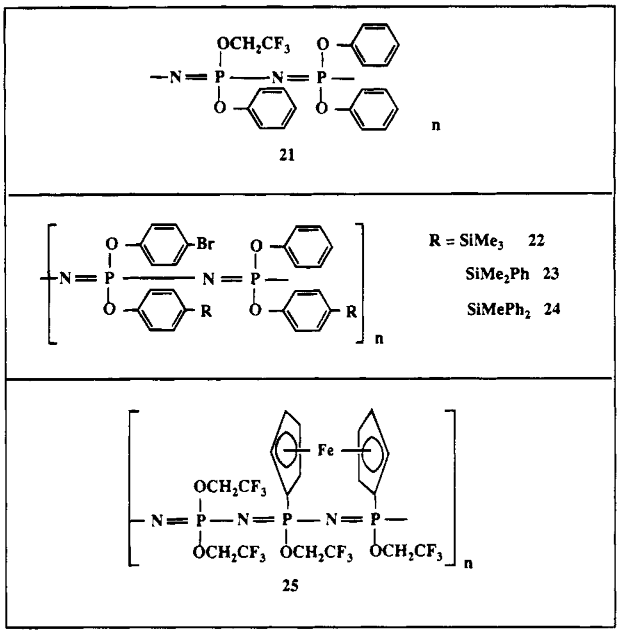


Figure 6. Experiments to monitor the behavior of an amphiphilic polyphosphazene film as a dialysis membrane. (a) Diagram of the apparatus employed for following the diffusion of a solute across the membrane. (b) Structure of the dye Biebrich Scarlet. (c) Concentration versus time profile for the diffusion of Biebrich Scarlet (MW, 556) across a membrane of (open circles) crosslinked $[NP(OCH_2CF_3)_{0.57}(NHCH_3)_{1.43}]_n$ (a variant of structure **17**), and (closed circles) standard cellulose acetate dialysis tubing.

hydrophilic side groups. γ-radiation cross-linking achieves this end. Phenoxy and trifluoroethoxy side groups are less sensitive to γ-rays than methyl or alkyl ether side groups. Hence, some control is possible over the location and maximum density of the cross-link sites. Figure 6 shows a dialysis profile for the diffusion of a small molecule dye through a membrane composed of a cross-linked polymer with 50% trifluoroethoxy and 50% methylamino side groups, compared to the behavior of a standard cellulose acetate membrane. The curve illustrates that the solute diffusion rate can be much faster through the polyphosphazene. Moreover, the selectivity can be altered by changes in the side groups and their ratios.

(b) Membranes for Gas Separations. Gas-transport membranes require a different set of properties from membranes for condensed phase separations. For polyphosphazenes this often means that different types of side groups, or side-group combinations, are required. A series of gas-separation membrane polymers synthesized in our laboratory have been evaluated by W. Koros and co-workers at the University of Texas at Austin.[68] The polymers studied were species **6**, **15**, and those shown in Chart 5. All these polymers showed very high gas diffusion coefficients, with species **6** having a very high transmission coefficient for oxygen.

Chart 5. Polyphosphazenes Studied as Gas-Transport Membranes



The organosilicon derivatives **22**–**24** were designed to be hybrids of organophosphazenes and the high oxygen permeability poly(organosiloxanes) (**2**). However, in the un-cross-linked state, the polymers lacked the strength for testing as membranes. γ-ray cross-linking (3 Mrads) increased their materials' strength without reducing gas permeation. Presumably, the cross-linking process involves C–H bond scission in the CH_3 groups, followed by cross-combination of the resultant carbon radicals. Thus, the polymer chains are probably linked through the organosilicon groups.

6. Interpenetrating Polymer Networks (IPNs). Many polymers can be utilized as useful materials only if combined with other compounds. The practical requirements of strength, impact resistance, and ease of fabrication are often met by the incorporation of polymers into composites. Polymer–polymer composites are of two types—polymer alloys (blends) and interpenetrating polymer networks. The alloying of two different polymers is often complicated by the tendency of the two components to be "incompatible" and to segregate into separate domains. IPNs provide an alternative materials' structure that retards or prevents this phase separation.

An IPN consists of an organogel in which the monomer of one polymer is dissolved in the cross-linked matrix of the other. Polymerization of the monomer (usually a vinyl monomer) then forms an interpenetrating network in which segregation of the two polymers is difficult.[69] If the newly polymerized polymer is also cross-linked, separation of the two is impossible.

The formation of IPNs in which one polymeric component is a polyphosphazene and the other is an organic polymer is a topic of considerable interest. For example, the phosphazene component could confer resistance to burning and impact resistance on a less expensive organic polymer. Amphiphilic materials may be accessible by combining hydrophilic phosphazenes with hydrophobic organic polymers, and vice versa.

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(68) Allcock, H. R.; Nelson, C. J.; Coggio, W. D.; Manners, I.; Koros, W. J.; Walker, D. R. B.; Pessan, L. A. *Macromolecules* **1993**, *26*, 1493.

(69) (a) Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, 1981. (b) Sperling, L. H. *Chemtech* **1988**, *18*, 104.

Scheme 10

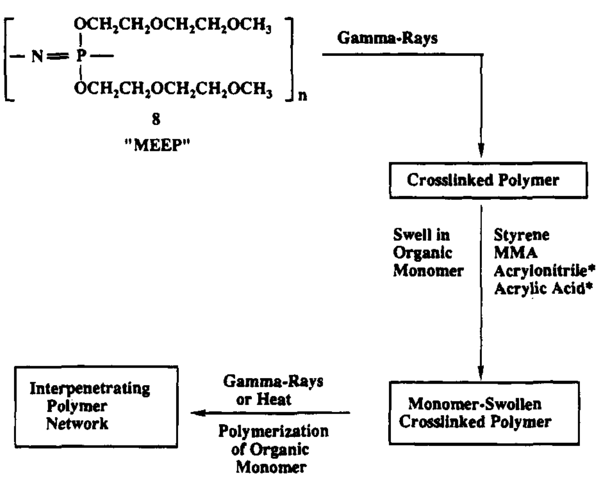
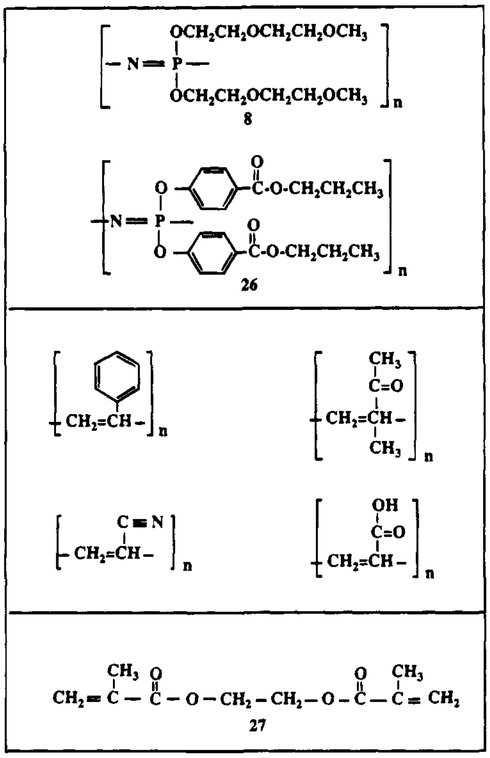


Chart 6. Constituents of Interpenetrating Polymer Networks (IPNs)



One of the key steps in IPN formation is the cross-linking of the first (host) polymer. We have made use of the radiation cross-linking methods described earlier to generate the host polyphosphazene matrix.[70] Imbibition of organic vinyl monomers into this host matrix, followed by thermal- or radiation-induced polymerization and cross-linking of the organic component, then yields an IPN. The process is summarized in Scheme 10 for a case where MEEP is the phosphazene polymer. Chart 6 lists the phosphazene polymers studied most extensively and the organic monomers employed.[70] Ethylene glycol dimethylacrylate (**27**) was the cross-linker for the vinyl polymer. The MEEP/poly(acrylonitrile) system, in particular, yielded a very fine grain composite with a single T_g at a temperature intermediate between those of the two parent polymers. This is an indication of high compatibility and the formation of a new hybrid material.

The potential uses for polyphosphazene IPNs range from nonburning structural composites to biomedical prosthetic materials. Indeed, an IPN of a fluoroalkoxyphosphazene and an organic polymer is currently used in biomedicine.[67]

7. Cross-Linking to Control Surface Reactions. Chemical reactions carried out at the surface regions of polymers provide a means for modification of surface properties without altering the characteristics of the bulk material. Several reactions of this type have been developed for polyphosphazenes.[71-74] However, it is frequently necessary to confine the reaction to the surface layers and to prevent burying of the new surface soon after its formation. Penetration of the surface layers by the reagent and solvent frequently makes this difficult to accomplish. A solution to this problem is to cross-link the surface. In recent work,[74] this has been accomplished by radiation cross-linking the surface of $[NP(OC_6H_4Br)_2]_n$ using γ-rays. The radiation cross section of bromine atoms is sufficiently high that the bulk of the polymer can be unaffected while the surface is cross-linked following C−Br homolytic cleavage and cross combination. This technique allowed a subsequent lithiation and reaction with $CpFe(CO)_2I$ to be restricted to the surface.

8. Coordination Cross-Linking. Coordination cross-linking occurs with polyphosphazenes when a metal-containing reagent reacts with coordination sites on two different polymer chains to link these chains together. The polymer that has been studied in greatest detail for this effect is shown as **29** in Scheme 11.[54,75]

Treatment of polymer **29** in solution with organometallic reagents such as $Fe(CO)_3$ (benzylidineacetone), $[RhCl(CO)_2]_2$, or $Co_2(CO)_8$ resulted in precipitation of the macromolecular complexes. Spectroscopic examination and comparisons with the behavior of small-molecule model compounds, such as **28**, indicated that the cross-links were coordination sites of the types shown in Scheme 11. Other organometallic reagents, such as $H_2Os(CO)_{10}$, first formed soluble complexes with the polymer. However, evaporation of the solvent yielded solids that underwent cross-linking through the organometallic sites, presumably because of the close proximity of the chains in the solid state and the ease of further decarbonylation under these conditions. Complexes of the polymer with $Mn(CO)(-C_5H_5)$ behaved in a similar way. However, treatment of solutions of polymer **29** with solutions of AuCl formed complexes without cross-linking, and this can be attributed to the inability of gold to coordinate to more than one triarylphosphine unit.

Polymers with pendent imidazolyl groups have also been prepared in our program. Although these were synthesized originally as carriers for iron porphyrins (as hemoglobin/myoglobin models),[76,77] they also constitute

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(70) Visscher, K. B.; Manners, I.; Allcock, H. R. *Macromolecules* **1990**, *23*, 4885.

(71) Allcock, H. R.; Rutt, J. S.; Fitzpatrick, R. J. *Chem. Mater.* **1991**, *3*, 442.

(72) Allcock, H. R.; Fitzpatrick, R. J.; Salvati, L. *Chem. Mater.* **1992**, *4*, 769.

(73) Allcock, H. R.; Fitzpatrick, R. J.; Salvati, L. *Chem. Mater.* **1991**, *3*, 1120.

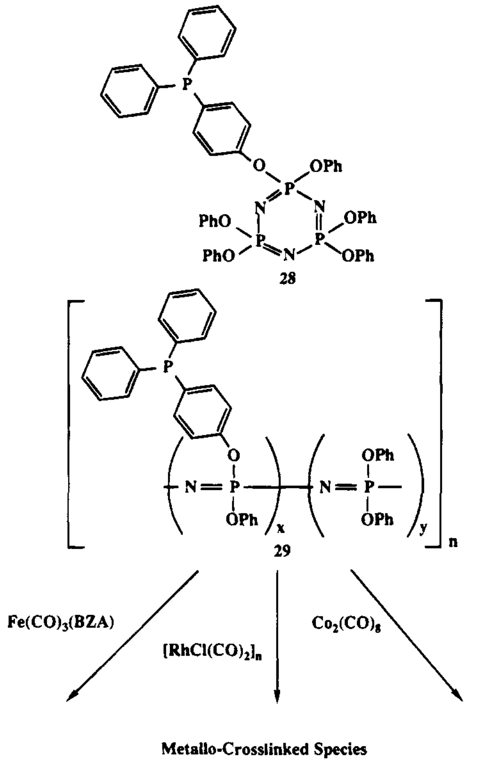
(74) Allcock, H. R.; Silverberg, E. N.; Nelson, C. J.; Coggio, W. D. *Chem. Mater.* **1993**, *5*, 1307.

(75) Dubois, R. A.; Garrou, P. E.; Lavin, K. D.; Allcock, H. R. *Organometallics* **1984**, *3*, 649; **1986**, *5*, 460.

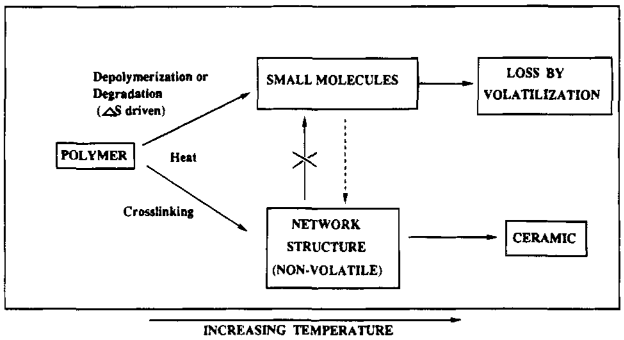
(76) Allcock, H. R.; Greigger, P. P.; Gardner, J. E.; Schmutz, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 606.

(77) Allcock, H. R.; Neenan, T. X.; Boso, B. *Inorg. Chem.* **1985**, *24*, 2656.

Scheme 11



Scheme 12



examples of phosphazene polymers that can be cross-linked by metals.

9. Preceramic Polymers. Un-cross-linked polymers are rarely stable at high temperatures, and polyphosphazenes are no exception. Polymer breakdown can occur via "unzipping" type depolymerization reactions to yield volatile cyclic trimers or tetramers or by random fragmentation.[78-82] However, if reactions can be developed that yield cross-links as a polymer is heated, but before degradation to volatile small molecules occurs, then the thermal stability, rigidity, and strength of the material may be enhanced. Ultimately, continued cross-linking will yield a ceramic. This is illustrated in Scheme 12.

Cross-linking during heating can be accomplished by a number of methods, but the linkage of chains via condensation reactions of side groups is particularly effective, especially if the aim is to reduce the proportion of organic side units in the material en route to a ceramic-type composition.

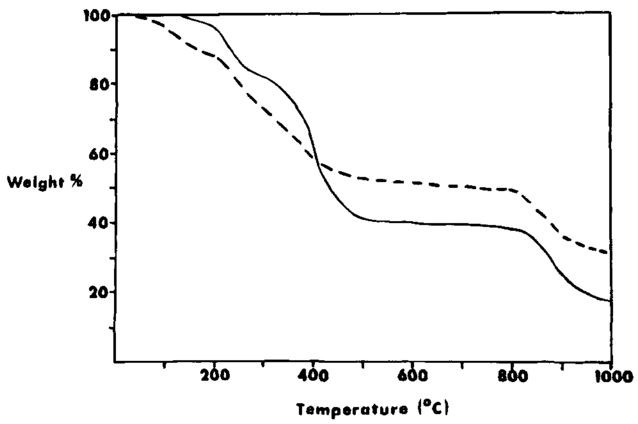
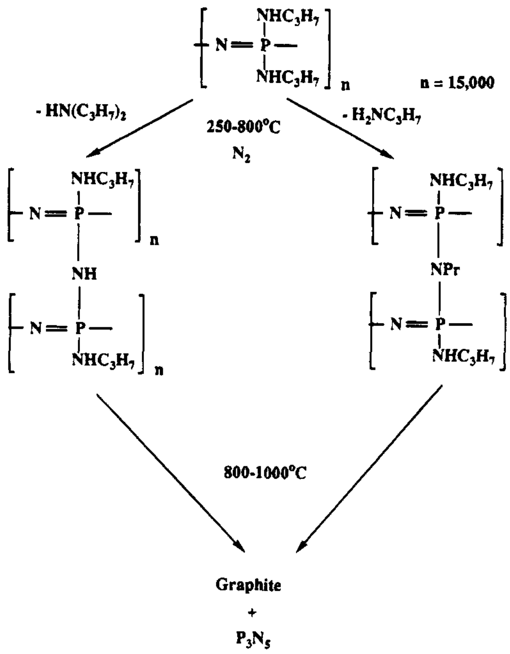


Figure 7. Thermogravimetric analysis weight loss profile for $[NP(NHC_3H_{7-n})_2]_n$ (solid line) and $[NP(NHC_6H_5)_2]_n$ (broken line). Breakdown of the aliphatic amino derivative is accompanied by loss of amines as the condensation cross-linking process proceeds.

Scheme 13



Also vapor deposition phosphorus nitrides

A simple example of this is shown in Scheme 13.[80,81] Here an alkylaminophosphazene polymer is heated. As the temperature is raised through 200 °C, intermolecular side-group condensation reactions occur. These generate cross-links with the concurrent elimination of amines. The loss of side group residues can be followed by thermogravimetric analysis, as shown in Figure 7. Mass spectrometric analysis revealed that the volatile products included n-$C_3H_7NH_2$, $(C_3H_7)_2NH$, and $(CH_3$-$CH{=}CH)(C_3H_7)NH$. Above 800 °C the volatile products included species that deposited from the vapor state to form phosphorus nitride. The remaining nonvolatile residue was a composite of graphite and phosphorus nitride. Arylaminophosphazenes undergo similar condensation cross-linking reactions, as shown for $[NP(NHC_6H_5)_2]_n$ in Figure 7.

An extension of these ideas to boron–nitrogen containing polymers and ceramics has also been made.[82]

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(78) Allcock, H. R.; Cook, W. J. *Macromolecules* **1974**, *7*, 284.

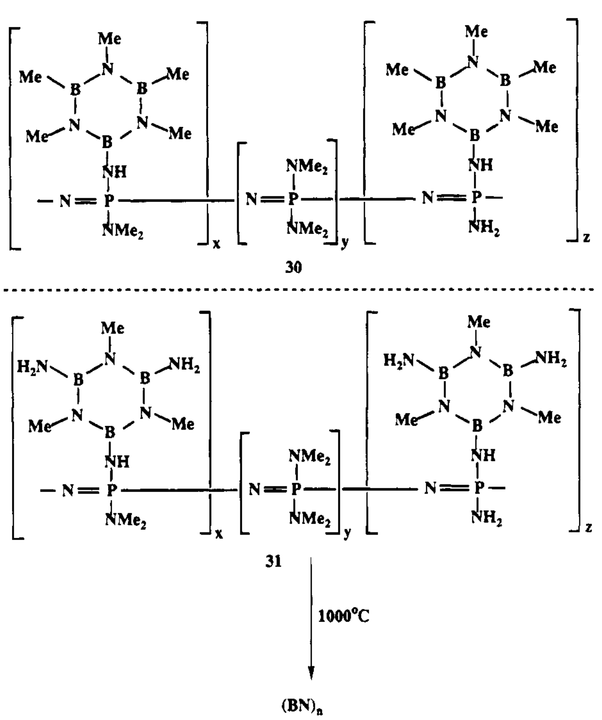
(79) Allcock, H. R.; Moore, G. Y.; Cook, W. J. *Macromolecules* **1974**, *7*, 571.

(80) Allcock, H. R.; McDonnell, G. S.; Riding, G. H.; Manners, I. *Chem. Mater.* **1990**, *2*, 425.

(81) Allcock, H. R.; Kolich, C. H.; Kossa, W. C. *Inorg. Chem.* **1977**, *16*, 3362.

(82) Allcock, H. R.; Welker, M. F.; Parvez, M. *Chem. Mater.* **1992**, *4*, 769.

Scheme 14



The macromolecules shown as **30** and **31** were synthesized to explore the possibility that borazine side groups linked to a polyphosphazene chain might function as a preceramic precursor system to synthesize high temperature materials. The two polymers shown were designed to test the role of $-NH_2$ groups as condensation-cross-link sites—in other words to provide a facile cross-linking mechanism that would prevent random fragmentation or depolymerization before the borazine units could be incorporated into the ceramic matrix (Scheme 14).

In fact, polymer **31** proved to be more resistant to fragmentation at moderate temperatures than did **30**, mainly because the exposed $-NH_2$ groups in **31** underwent facile condensation with their counterparts on neighboring chains, with evolution of ammonia and formation of B−NH−B cross-links. The weight-loss profile at elevated temperatures is shown in Figure 8. Continued pyrolysis at 1300 °C gave crystalline, hexagonal boron nitride.

This provides an example of a preceramic polymer in which the main chain serves mainly as a platform for the elements in the side groups. The polymer backbone facilitates materials' fabrication at moderate temperatures, but heating to higher temperatures leads to loss of the backbone elements as the side units become incorporated into the ceramic. This is perhaps the most unusual of the three routes shown in Figure 9 for the synthesis of ceramics.

10. Hydrogels. *(a) General Observations.* As discussed earlier, hydrogels are formed when cross-linked, hitherto water-soluble polymers, absorb water. A number of polyphosphazenes are soluble in water (Chart 5). This is a useful feature because water-soluble macromolecules are quite rare in synthetic polymer chemistry.

All the polymers in Chart 7 can be cross-linked to form hydrogels, but by far the most attention has been directed toward hydrogels formed from MEEP (**8**) and its close relatives shown in Table 1.

The γ-radiation-induced cross-linking of MEEP was mentioned earlier and follows the mechanism shown in Scheme 15.[61-63] This process allows the average degree of cross-linking per chain to be varied over a wide range according to the radiation dose. Cross-linked MEEP absorbs water to form hydrogels, with the degree of swelling being a measure of the average number of cross-links in the system. A photograph of a MEEP hydrogel is shown in Figure 10.

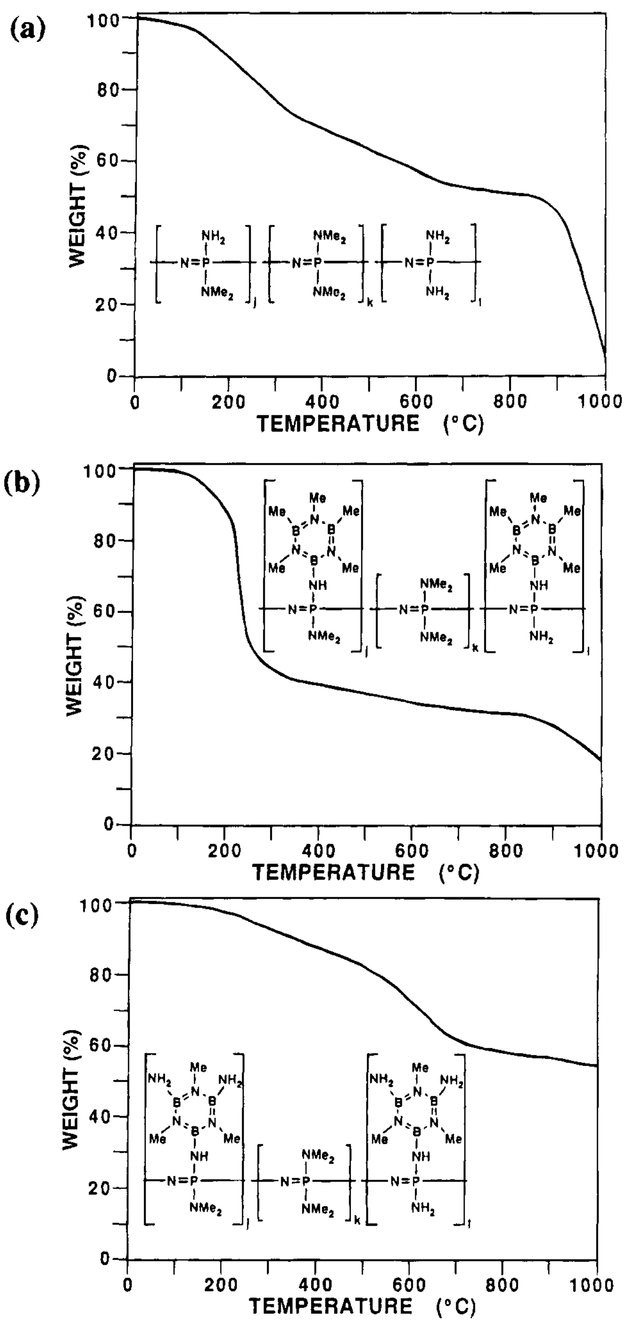


Figure 8. Thermogravimetric analysis weight loss profiles for the pyrolysis of (a) an aminophosphazene polymer with amino side groups but no borazine units, (b) a polymer with amino side groups and borazine units that lack amino substituents, and (c) a polymer similar to the one shown in (b) but with amino condensation groups linked to the borazine units. The curves illustrate the principle that amino condensation groups favor crosslinking at 150−200 °C, retard depolymerization and fragmentation, and increase the yield of ceramic.

(b) Lower Critical Solution Temperatures. MEEP and its closely related polymers, shown in Table 1, are unusual in the sense that they show a lower critical solution temperature (LCST) in water.[83] This means that the polymers, although soluble in water at room

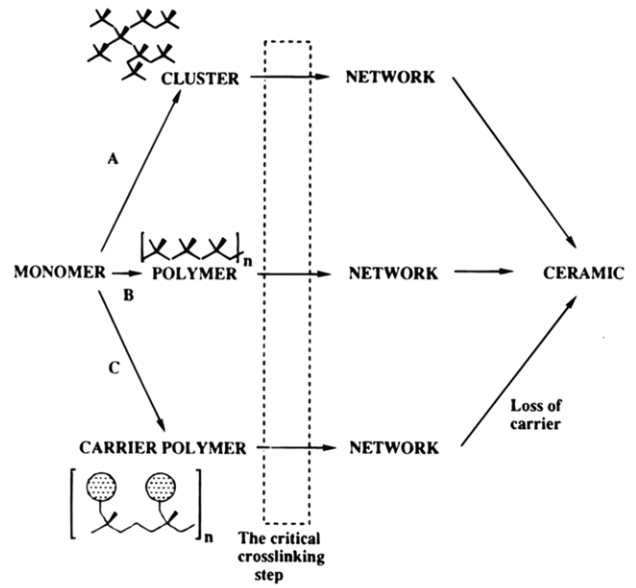
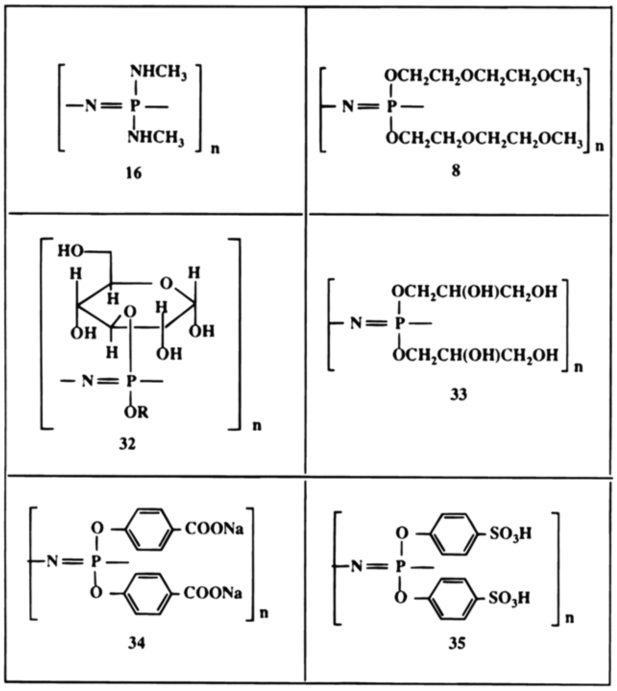


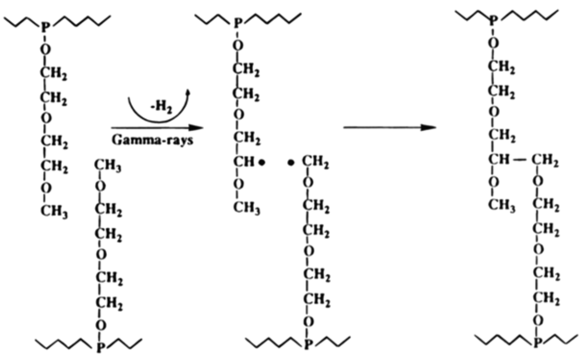
Figure 9. Three routes for the conversion of small-molecules to ceramics. The cross-linking step is critical for lowering the volatility of the system and reducing depolymerization or random chain fragmentation within the intermediate temperatrure range.

Chart 7. Water-Soluble Polyphosphazenes



temperature, nevertheless precipitate from solution as the temperature is *raised* above the LCST (Figure 11). The phenomenon is a consequence of the amphiphilic nature of polymers in which the backbone nitrogen atoms and the side-group oxygens are hydrophilic, but the CH_2 groups and terminal CH_3 units are hydrophobic. At room temperature, hydrogen bonding between water molecules and the hydrophilic sites predominates over hydrophobic interactions. However, at higher temperatures, as the hydrogen-bonding forces become weaker, the hydrophobic interactions determine the behavior, and the polymer molecules precipitate. The exact temperature of the LCST depends on the length of the side chains and the hydrophobiciy of the terminal unit (Table 1). Note that a hydrophilic terminal group eliminates the LCST behavior.

Scheme 15



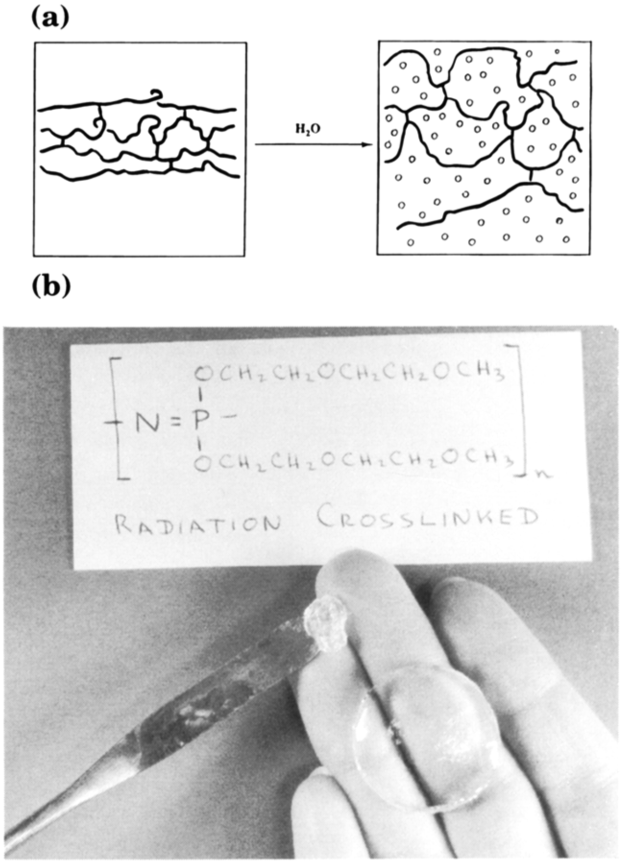


Figure 10. (a) Radiation-cross-linked MEEP absorbs water to the limit defined by the average number of cross-links per chain. (b) Photograph showing a hydrogel formed from cross-linked MEEP following absorption of water by the polymer network.

When these same polymers are cross-linked, the LCST phenomenon becomes translated into an unusual characteristic of the hydrogels. At room temperature, the systems absorb water to form hydrogels. However, if the hydrogels are heated through the LCST, they extrude water at this temperature and collapse to a tight, "insoluble" network (Figure 11). Lowering of the temperature reverses the process, and the cycle can be repeated indefinitely.

Uses for this phenomenon can be foreseen in medicine for the release of imbibed drugs at the LCST or for use in devices that open or close valves in the circulatory, renal, or drug release devices.

(c) Enzyme Entrapment. The process of cross-linking polymers such as MEEP to hydrogel networks has also

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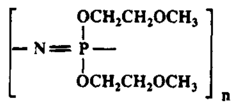
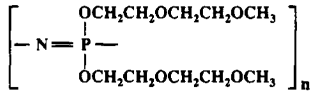
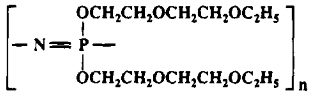
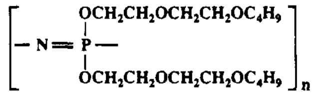
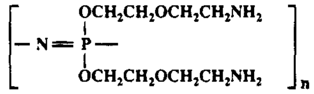
(83) Allcock, H. R.; Pucher, S. R.; Turner, M. L.; Fitzpatrick, R. J. *Macromolecules* **1992**, *25*, 5573.

Table 1. Lower Critical Solution Temperatures (LCST) for MEEP and Related Polymers[a]

	water solubility at 25 °C	LCST (°C)
 $[-N{=}P(OCH_2CH_2OCH_3)_2-]_n$	sol	30
 $[-N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2-]_n$	sol	80
 $[-N{=}P(OCH_2CH_2OCH_2CH_2OC_2H_5)_2-]_n$	sol	38
 $[-N{=}P(OCH_2CH_2OCH_2CH_2OC_4H_9)_2-]_n$	sol	51
 $[-N{=}P(OCH_2CH_2OCH_2CH_2NH_2)_2-]_n$	sol	none

[a] Hydrogels extrude water at the same temperatures as the LCCTs.

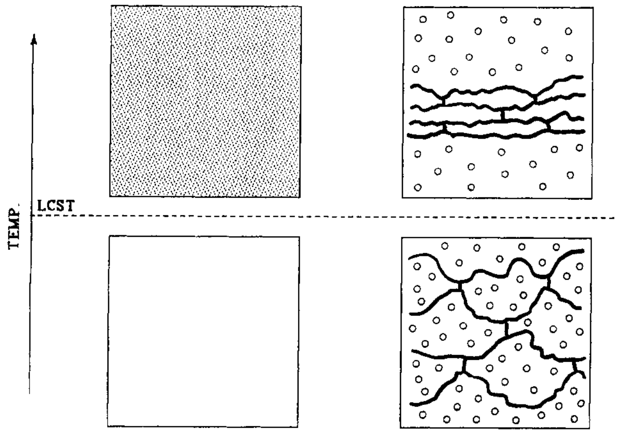


Figure 11. Un-cross-linked, water-soluble polyphosphazenes with etheric side groups become insoluble in water as the temperature is raised above the lower critical solution temperature (LCST, left). Hydrogels formed from the same polymers after cross-linking extrude water when heated above the same temperature (right).

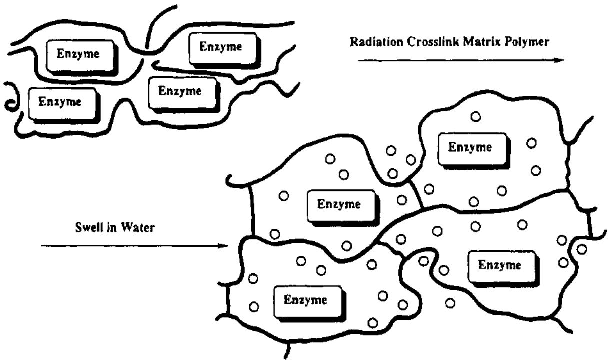


Figure 12. Enzyme molecules, such as urease, can be trapped within the polymer MEEP by γ-irradiation of the polymer enzyme congugate. Subsequent swelling of the system by absorption of water yields a hydrogel that contains immobilized urease which converts urea to ammonia at a rate that is more than 80% of that of the free enzyme in solution.

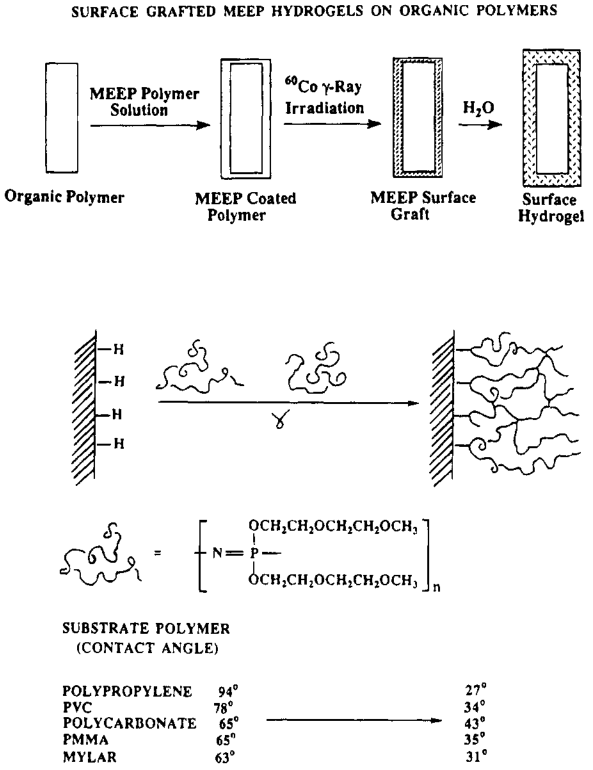


Figure 13. Radiation cross-linking of MEEP can also be accomplished in tandem with the grafting of this polymer to the surfaces of other polymers. The grafting process results in a marked decrease in the contact angle to water, an indication of the increased hydrophilicity of the surface. The MEEP surface-grafted systems can be used to form surface hydrogels following absorption of water, and these are of biomedical interest both from the viewpoint of blood and endothelial cell compatibility and because they display an antimicrobial character.

been used for the immobilization of enzymes.[84] In a typical procedure, an aqueous solution of MEEP and the enzyme urease was cast into a film by water evaporation, and the solid was cross-linked by γ-irradiation (Figure 12). The resultant material was then swelled in water to form a hydrogel. The hydrogel retained the enzyme molecules during prolonged extraction cycles with water, which indicated that the enzyme was physically trapped within the cross-linked matrix and perhaps also covalently linked to the MEEP. The conjugate hydrogels retained the enzymic activity of the urease as defined by its ability to convert urea to ammonia. This illustrates many possible uses for these hydrogels in biochemistry and medicine.

(d) Hydrogel Grafting onto Polymer Surfaces. Finally, the γ-radiation cross-linking of MEEP has been used to graft hydrogels to the surfaces of other polymers—both other polyphosphazenes and conventional organic polymers.[85] This process is shown in Figure 13. Grafting to the surface occurs by the same chemistry as that used for the MEEP cross-linking. Carbon radicals formed from the MEEP combine with carbon radicals generated from the C−H or C−Cl sites at the surface of the substrate polymer.

The importance of this process in technology and medicine is that it provides a method for covalently binding a hydrogel to an otherwise hydrophobic surface.

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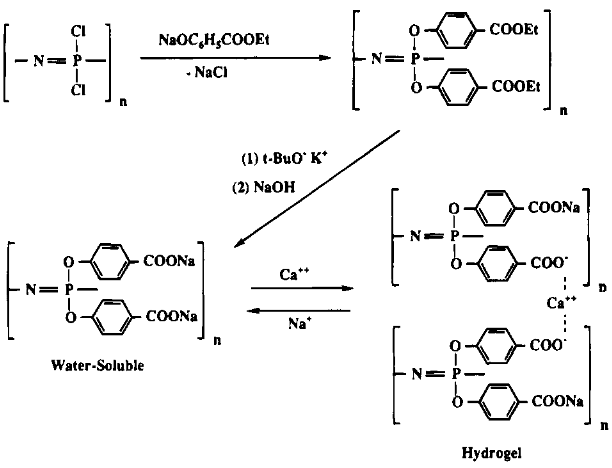
(84) Allcock, H. R.; Pucher, S. R.; Visscher, K. B. *Biomaterials* **1994**, *15*, 502.

(85) Allcock, H. R.; Fitzpatrick, R. J.; Visscher, K.; Salvati, L. *Chem. Mater.* **1992**, *4*, 775.

Scheme 16



The changes in contact angles shown in Figure 13 illustrate this point. Moreover, it is a process that converts ordinary polymer surfaces to blood- or tissue-compatible interfaces that may also discourage colonization by microorganisms.[86]

11. Microencapsulation of Bioactive Species. The final example involves the ionic cross-linking of a water-soluble phosphazene polyelectrolyte, and the use of this principle for the formation of hydrogel microcapsules. The process is being used for the microencapsulation of mammalian cells, proteins, antigens, and a range of other biologically active species. The chemistry is based on the reactions of poly[bis(carboxylatophenoxy)phosphazene] and its sodium salt (**34**), synthesized by the route shown in Scheme 16 and Figure 14.[87,88]

This polymer is insoluble in neutral or acidic aqueous media but is soluble as its sodium or potassium salt to form a polyelectrolyte solution. Addition of this to an aqueous solution of a divalent or trivalent cation (Ca^{2+} or Al^{3+}) results in an exchange of cations and a coupling of polymer chains through salt formation with the multivalent ions. This is illustrated in Scheme 16.

Through a collaboration with the group of R. S. Langer at MIT,[88-92] this process has been utilized as a microencapsulation system in the following way. A solution or suspension of hybridoma mammalian cells, proteins, or other bioactive species in an aqueous solution of polymer **34** is sprayed as fine droplets into a solution of calcium chloride in water. Each droplet consists of a bioactive unit surrounded by a coating of the polymer solution which coagulates to a hydrogel on contact with the Ca^{2+} solution. The microspheres formed in this way are then separated and incorporated into biochemical and biomedical reactor devices. The hydrogel coating allows nutrients and small-molecule metabolic products to diffuse in or out of the capsule but protects the encapsulated species from, for example, antibodies or protein hydrolysis enzymes. Hybridoma liver cells have been microencapsulated in this way.[88]

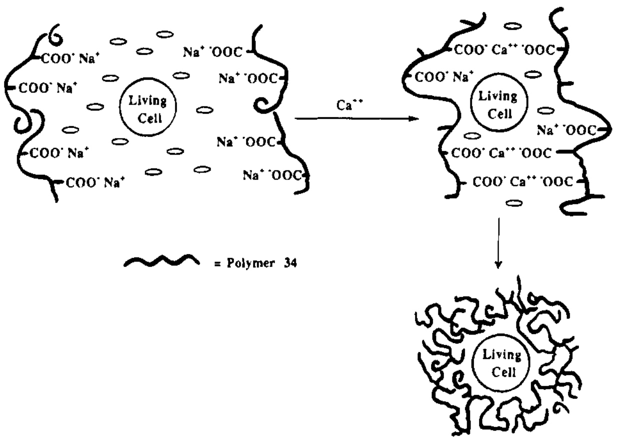


Figure 14. Ionic cross-linking of the water-soluble polymer, $[NP(OC_6H_4COONa)_2]_n$, occurs when solutions of this polymer are brought into contact with divalent or trivalent cations. In the presence of biologically active units, such as living mammalian cells or proteins, the cross-linking process results in the formation of a microcapsule around each active species. (Cohen, S.; Bano, M. C.; Visscher, K. R.; Chow, N.; Allcock, H. R.; Langer, R., in refs 88–90). The resultant microspheres are proving to be of considerable interest in the fields of artificial organ research, biotechnology, and the delivery of biologically active agents to the body.

E. Conclusions

Cross-linking reactions are often a neglected aspect of polymer materials science. Yet they provide a critical means for the conversion of polymers that are mainly of academic interest into materials that have important uses. Polyphosphazene research has reached a stage where hundreds of different side groups and side group combinations can be incorporated into these polymers. However, it is the development of cross-linking methods, such as those described here, that provides the key to the technological and medical developments of the future.

Acknowledgment. Aspects of this work were funded by the U.S. Army Research Office, the Office of Naval Research, the National Institutes of Health, and Virus Research Institute, and this support is very much appreciated. Many co-workers at The Pennsylvania State University contributed to the development of cross-linking methods, especially C. Kolich, G. Moore, T. X. Neenan, M. Gebura, S. Kwon, G. H. Riding, J. Bennett, K. Lavin-Riding, T. L. Evans, N. Tollefson, T. Fuller, K. B. Visscher, S. R. Pucher, R. J. Fitzpatrick, M. F. Welker, I. Manners, G. A. Schrubbe-McDonnell, A. A. Dembek, and C. Cameron.

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(86) Allcock, H. R.; Pucher, S. R.; Fitzpatrick, R. J.; Rashid, K. *Biomaterials* **1992**, *13*, 857.

(87) Allcock, H. R.; Kwon, S. *Macromolecules* **1989**, *22*, 75.

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

(89) Bano, M. C.; Cohen, S.; Visscher, K. B.; Allcock, H. R.; Langer, R. *Bio/Technology* **1991**, *9*, 468.

(90) Cohen, S.; Bano, C.; Visscher, K. B.; Chow, M. B.; Allcock, H. R.; Langer, R. S. *Pct Int. Appl.* **1992**, *45*.

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

(92) Andrianov, A. K.; Payne, L. G.; Visscher, K. B.; Allcock, H. R.; Langer, R. *Polym. Prepr. (ACS Div. Polym. Chem.)* **1993**, *34*, 233.