

AD-A279 872

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

①

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 17, 1994	3. REPORT TYPE AND DATES COVERED Technical Report No. 17
4. TITLE AND SUBTITLE Synthesis and Characterization of Poly(organophosphazene) Interpenetrating Polymer Networks			5. FUNDING NUMBERS N00014-91-J-1194 Dr. K. J. Wynne R&T Code: 3132007
AUTHOR(S) Karyn B. Visscher, Ian Manners, and Harry R. Allcock*			8. PERFORMING ORGANIZATION REPORT NUMBER
PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry The Pennsylvania State University 152 Davey Laboratory University Park, Pennsylvania 16802			
SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES Prepared for publication in ACS Advances in Chemistry Series			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) Polyphosphazenes are a broad, novel class of inorganic-organic macromolecules. The physical properties of polyphosphazenes can be understood in terms of a highly flexible backbone, with various physical or chemical characteristics tailored by the incorporation of specific side groups. As part of our program to synthesize new materials with hybrid macromolecular properties, the synthesis and characterization of several IPNs containing phosphazene polymers is described.			
14. SUBJECT TERMS phosphazenes, polymers, synthesis, characterization, interpenetrating polymer networks			15. NUMBER OF PAGES 40
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

OFFICE OF NAVAL RESEARCH

Grant: N00014-91-J-1194

R&T Code: 3132007

Dr. Kenneth J. Wynne

Technical Report No. 17

**SYNTHESIS AND CHARACTERIZATION OF POLY(ORGANOPHOSPHAZENE)
INTERPENETRATING POLYMER NETWORKS**

by

Karyn B. Visscher, Ian Manners, and Harry R. Allcock

Prepared for Publication in ACS Advances in Chemistry Series

**Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802**

94-16105



4990

May 17, 1994

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

94 5 27 071

SYNTHESIS AND CHARACTERIZATION OF POLY(ORGANOPHOSPHAZENE) INTERPENETRATING POLYMER NETWORKS

K. B. Visscher, I. Manners, and H. R. Allcock*.

Department of Chemistry

The Pennsylvania State University

University Park, PA 16802

(814) 865-1213 Fax: (814) 865-3314

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/Avail.	
Availability Codes	
Dist	Avail and/or Special
A-1	

Abstract:

Polyphosphazenes are a broad, novel class of inorganic-organic macromolecules with the general formula $[NPR_2]_n$. The physical properties of polyphosphazenes can be understood in terms of a highly flexible backbone, with various physical or chemical characteristics tailored by the incorporation of specific side groups. As part of this program to synthesize new materials with hybrid macromolecular properties, the synthesis and characterization of several IPNs containing the phosphazene polymers poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] and poly[bis(propyl oxybenzoate)phosphazene] with several organic polymers including polystyrene, poly(methyl methacrylate), polyacrylonitrile and poly(acrylic acid) is reported.

Introduction.

Most interpenetrating polymer networks (IPNs) are prepared using organic polymers. With the exception of polysiloxanes (1-8), little work has been published describing the syntheses of IPNs from inorganic-organic polymers. Inorganic-organic polymers generally have a high thermo-oxidative stability coupled with unusual combinations of properties that depend on the side groups attached to the backbone. Some common examples of inorganic-organic polymers include polysilanes, polysiloxanes and polyphosphazenes, depicted in Scheme 1(9). The synthesis and characterization of some of the first interpenetrating polymer networks (IPN) containing poly(organophosphazenes) with organic polymers are described in this paper (10-11).

Scheme 1 near here.

Poly(organophosphazenes) are a unique class of inorganic-organic polymers with alternating phosphorous and nitrogen atoms in the backbone and two organic, inorganic or organometallic side groups attached to each phosphorous (12-16). Their physical properties and applications can be tailored by the choice of the organic side group attached to the backbone. Due to this unique ability to tune their properties and applications by the choice of side groups, polyphosphazenes are an excellent choice for the preparation of IPNs. Table 1 lists some advantages of the polyphosphazene system.

Table 1 near here.

Polyphosphazenes are usually non-burning materials and may be highly flame retardant. This is due to the fact that phosphorous in its highest valency state can interfere with the

combustion pathway. A combination of phosphorous and nitrogen often yields compounds with enhanced flame retardant properties. Secondly, some polyphosphazenes possess a high degree of solvent-and-oil resistance. This makes them valuable materials for many industrial applications such as O-rings, gaskets and fuel lines. Another advantage of the polyphosphazene system is that many of these materials have a high degree of biocompatibility. This property depends on the side group structure, with fluoroalkoxyphosphazenes being of particular interest. Some polyphosphazenes possess high flexibility and low glass transition temperatures (T_g). This characteristic makes many phosphazene polymers useful as low temperature elastomers and flexible thermoplastics. Probably the biggest advantage of the polyphosphazene system is the ease with which the polymeric molecular structure may be tuned to afford different properties and applications. This molecular tuning is accomplished by the linkage of different side groups to the polymer backbone (12-16). IPNs with combinations of poly(organophosphazenes) and other polymers would combine the advantages of polyphosphazenes with those of the other systems.

Poly(organophosphazenes) are prepared by the route summarized in Scheme 2. Commercially available hexachlorocyclotriphosphazene (1) undergoes a thermal ring opening polymerization at 250 °C to form poly(dichlorophosphazene) (2), a long-chain polymer with 15,000 or more repeating units. Poly(dichlorophosphazene) is hydrolytically sensitive, but the system may be stabilized against hydrolysis through halogen replacement reactions using a wide variety of nucleophiles, including sodium alkoxides and aryloxides or primary and secondary amines. These substitution reactions have yielded a large number of stable poly(organophosphazene) derivatives, the properties and applications of which depend on the side group structure (17-19).

Scheme 2 near here

Chart 1 shows examples of phosphazene polymers with different side groups. The first, poly[bis(p-oxybenzoic acid) phosphazene] (3) is water soluble as its sodium salt, and can be ionically cross-linked using calcium or other di or higher valent cation salts (20-22). The second example, poly[bis((3-amino propyl)pentamethyldisiloxane)phosphazene] (4) contains silicon atoms within the side groups and possesses elastomeric properties (23). Poly[bis(2-(2-methoxy ethoxy) ethoxy)phosphazene] (5) is water soluble. It is also an excellent solid solvent for salts such as lithium trifluoromethanesulfonate, and is being developed as a solid electrolyte material (24-28). Finally, when transannular ferrocenyl groups are attached to the polymer backbone, as seen in polymer 6, the system is electroactive and may be used as an electrode mediator material (29).

Chart 1 near here.

Some common applications for poly(organophosphazenes) include O-rings which are flexible at low temperature and have a high solvent-and-oil resistance; oil seal gaskets; fuel lines; shock absorber components with a high level of vibrational energy absorption; and finally carburetor and fuel injector components. As mentioned previously, polyphosphazenes are an excellent choice for these types of applications because of their non-burning characteristics, high flame retardancy, high levels of both solvent-and-oil resistance, and high degree of materials flexibility.

Specific derivatives are also being developed for uses in the field of biomedicine. Figure 1 shows an example of a polyphosphazene/organic polymer IPN which is available commercially as a shock-absorbing denture liner. Poly(organophosphazenes) are employed for dental and oral surgical applications because of their high degree of fungal resistance (30-33).

Figure 1 near here.

Syntheses of Poly(organophosphazenes).

The phosphazene polymers used in this IPN study were synthesized as described in Scheme 3. Polymer 5 was prepared by allowing poly(dichlorophosphazene) (2) to react with the sodium salt of 2-(2-methoxyethoxy)ethanol. The product polymer is poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP) (5). MEEP is an unusual, hydrophilic phosphazene polymer, which is soluble in both water and organic solvents and has a T_g of $-84\text{ }^{\circ}\text{C}$ (24-25). Polymer 7 was prepared by allowing poly(dichlorophosphazene) (2) to react with the sodium salt of propyl p-hydroxybenzoate. This synthesis yields poly[bis(propyl p-oxybenzoate)phosphazene] (POBP) (7) a hydrophobic, elastomeric polymer with a T_g of $-23\text{ }^{\circ}\text{C}$. This polymer is soluble in many organic solvents (21).

Scheme 3 near here.

Both the POBP (7) and MEEP (5) undergo crosslinking when exposed to ^{60}Co γ -radiation (24-25). Scheme 4 shows a mechanism proposed for the cross-linking of MEEP during exposure to ^{60}Co γ -radiation (34). Radiation probably generates radicals on any of the five carbon atoms in the MEEP side chains. Trans-combination of these radicals would form cross-links. Solid, uncross-linked MEEP has little resistance to viscous flow. However, after cross-linking, MEEP has an increased structural integrity and swells, without dissolving, in water or organic solvents. Figure 2 shows a sample of MEEP after cross-linking and after the swelling of a cross-linked portion in water for several hours. Cross-linked MEEP is capable of swelling to over ten times its original volume.

Scheme 4 near here.

Figure 2 near here.

Synthesis of IPNs.

In normal sequential IPN preparation, a monomer is first polymerized and crosslinked using either thermal or radiation techniques, to form a cross-linked polymer matrix (35-36). This cross-linked matrix is then allowed to imbibe a second monomer, a polymerization initiator, and a cross-linker to form a monomer-swollen, cross-linked polymer matrix. The second monomer is then polymerized and cross-linked within the matrix of the first to form the IPN. This general procedure for the preparation of a sequential IPN is shown in Scheme 5.

Scheme 5 near here.

In all the IPN syntheses described here, a preformed phosphazene polymer, either MEEP (5) or POBP (7), was used as the initial cross-linked polymer system. The organic polymers prepared within the polyphosphazene matrix include polystyrene (PS) (8), poly(methyl methacrylate) (PMMA) (9), polyacrylonitrile (PAN) (10), and poly(acrylic acid) (PAA) (11). The structures of the component materials are depicted in Chart 2.

Chart 2 near here.

These organic polymers were chosen because they represent a cross section of common macromolecules. In addition, their ease of polymerization, using thermal methods, for PS and PMMA, and by exposure to ^{60}Co γ -radiation, for PAN and PAA, made them an attractive choice.

Scheme 6 near here.

Polyphosphazene/organic polymer IPNs were prepared as summarized in Scheme 6. The polymerized polyphosphazene was exposed to ^{60}Co γ -radiation to form a cross-linked polymer matrix (34). The cross-linked matrix was then allowed to swell in a mixture of the organic monomer, azobisisobutyronitrile (AIBN) initiator, and ethylene glycol dimethacrylate cross-linker, until the swollen matrix had increased approximately ten times in volume. The imbibed organic monomer was then polymerized and cross-linked within the polyphosphazene matrix using either thermal techniques (PS and PMMA) or by exposure to additional ^{60}Co γ -radiation (PAN and PAA).

The objective was to incorporate the maximum amount of organic polymer into the cross-linked poly(organophosphazene) matrix. The ratio of components within the IPN system was estimated using ^1H NMR spectroscopy, and the values are depicted in Table 2. The ratios ranged from a 1:1 ratio of polyphosphazene polymer to organic polymer in the MEEP /PS IPN to a 4.5:1 ratio of polyphosphazene to organic polymer in the IPN containing POBP /PAN.

Table 2 near here.

Once prepared, the IPNs were purified and then characterized using conventional methods, including ^1H and ^{31}P NMR spectroscopy, FT-IR spectroscopy, differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) (35-36). ^1H and ^{31}P NMR spectroscopy and FT-IR spectroscopy . FT-IR and NMR analyses are useful mainly to confirm the presence of both macromolecular constituents in the IPN systems, and to monitor the polymerization of the organic monomer by following the loss of vinyl protons.

Characterization.

DSC is an excellent technique for examining the miscibility of the components within an IPN system and for probing the intermolecular interactions that may exist between the component polymers. This may be accomplished by comparing the T_g values of the IPN system with those of its component macromolecules. The displacement of the values of the IPN T_g 's from those of the component materials gives a general indication of both the degree of miscibility within the sample, and of interactions which may take place between the component materials (35-36). The IPN T_g values and those for the component materials are listed in Table 3.

Table 3 near here.

For example, an IPN containing MEEP and polystyrene with glass transition temperatures at -70 and $+57$ °C, can be compared to the T_g 's of the parent component materials which occur at -84 °C (MEEP) and $+100$ °C (PS). This displacement of 15 and 40 °C shows that a good degree of miscibility exists within the system and that strong intermolecular interactions probably exist between the component materials.

In a second example, an IPN containing MEEP and PMMA has T_g 's at -80 and $+112$ °C. These values may be compared to those of the component materials for which transition temperatures are at -84 °C (MEEP) and $+105$ °C (poly(methyl methacrylate)). Because the IPN T_g 's are displaced 5 °C from those of the component materials, it appears that only a low degree of inter-component interactions exist within this system.

Finally, a single glass transition temperature seen in a DSC thermogram indicates a high degree of miscibility within the IPN system and a high degree of intermolecular interactions between the component macromolecules. Two of the polyphosphazene/organic polymer IPNs studied contain a single T_g . MEEP/PAN and POBP/PAA showed single T_g 's at +34 and +54 °C, respectively. These materials apparently enjoy a high degree of miscibility and presumably a high degree of intermolecular interaction.

Scheme 7 near here.

Scheme 7 shows a representation of intermolecular interactions that might exist between a phosphazene polymer and an organic polymer within an IPN system. These interactions include hydrogen bonding, dipole-dipole interactions, and van der Waals forces. The interactions are shown in more detail in Scheme 8.

Scheme 8 near here.

For example, a MEEP side group could undergo hydrogen bonding with the side unit of PAA through the etheric oxygen of the MEEP and the acidic proton of the acrylic acid side group. MEEP could also undergo dipole-dipole interactions with PAN as depicted in Scheme 8. Finally, any poly(organophosphazene) could, in principle, undergo van der Waals interactions with any organic polymer. A good example is POBP and PS .

Each poly(organophosphazene) and organic polymer combination is capable of undergoing one or more type of these different intermolecular interactions, as listed in Table 4. MEEP is a hydrogen bond acceptor and is capable of undergoing dipole-dipole interactions. POBP is also a hydrogen bond acceptor and possesses hydrophobic qualities. Polystyrene is a

hydrophobic material and may undergo van der Waals interactions while PMMA is a hydrogen bond acceptor and undergoes dipole-dipole interactions. PAN undergoes dipole-dipole interactions while PAA is a hydrogen bond donor and also experiences dipole-dipole interactions. It is important to realize that these intermolecular interactions could increase the miscibility of the IPN components by binding the component polymers into a coherent material. However, even when favorable intermolecular interactions are built into the system, it may be impossible to predict the final miscibility of the IPN and whether or not these interactions will influence that miscibility (37-40).

Table 4 near here.

The following are specific descriptions of typical polyphosphazene/organic polymer IPNs. In the first example, an IPN containing MEEP and PAN is an amber, transparent, hard material that swells only slightly in water. This limited swelling behavior could be due to intermolecular interactions such as dipole-dipole interactions between the component materials or to the degree of cross-linking within the system. Its DSC thermogram, shown in Figure 3 contains a single, broad glass transition at +34 °C. This indicates that a high degree of miscibility exists within the system and there are favorable intermolecular interactions between the component polymers. The high degree of miscibility is reflected in the TEM micrograph shown in Figure 4. It shows a widely dispersed, almost web-like structure of the lightly colored organic polymer throughout the darker phosphazene matrix. It is interesting that, due to the relatively high electron density of the polyphosphazene phosphorous-nitrogen backbone, no staining of the sample was required when preparing TEM micrographs of poly(organophosphazenes).

Figure 3 here.

Figure 4 here.

A second example, is an IPN containing POBP and PS. This system forms a tough, opaque, white, elastomeric material which swells in organic solvents. Its DSC thermogram, depicted in Figure 5, shows two T_g 's at +14 and +90 °C. These values are each displaced from those of the component materials by approximately 10 °C. Therefore this system appears to be less miscible than the previous example. The lower degree of miscibility is also reflected in its TEM micrograph shown in Figure 6. Here definite domains of the lightly colored organic polymer are evident dispersed throughout the darker colored polyphosphazene system.

Figure 5 here.

Figure 6 here.

Another example, is an IPN composed of MEEP and PMMA. This IPN is a tough, opaque, white, elastomeric material which swells to a high degree in organic solvents. Its DSC thermogram also shows two T_g 's which occur at -80 and +112 °C. Both values are displaced only 5 °C from the component materials whose T_g values occur at -84 °C (MEEP) and +105 °C (PMMA). This small displacement indicates a very low degree of miscibility within the system and probably reflects the poor intermolecular interactions between the component materials. The low miscibility of the system is also evident from the TEM micrograph shown in Figure 7. Large domains of both the poly(organophosphazene) and the organic polymer throughout the IPN system are clearly evident.

Figure 7 here.

A fourth example, is an IPN composed of POBP and PMMA. This material is opaque with a slight golden hue. It is also elastomeric and swells in organic solvents. Its DSC thermogram shows two T_g 's at +14 and +50 °C. These values are displaced approximately 15 and 50 °C from those of their component polymers which occur at -23 °C (POBP) and +105 °C (PMMA). The larger degree of displacement indicates that this system is more miscible than the previous one. The increased miscibility is also obvious from the TEM micrograph, shown in Figure 8, where a definite domain structure is evident of the lightly colored organic polymer throughout the polyphosphazene matrix.

Figure 8 near here.

The final example is an IPN containing POBP and PAA, a transparent, hard material which swells only slightly in organic solvents. The limited swelling behavior could reflect hydrogen bonding between the POBP and the acrylic acid side groups. This system shows a single T_g at +54 °C in its DSC thermogram which indicates a high degree of miscibility and good intermolecular interactions within the material. This behavior is also reflected in the TEM micrograph (Figure 9) which shows a domain structure of the lightly colored organic polymer bordered by an almost web-like structure of the phosphazene polymer.

Figure 9 near here.

Conclusion.

The synthesis and characterization of novel interpenetrating polymer networks composed of poly(organophosphazenes) and a selected series of organic polymers has been accomplished. Additionally, DSC and TEM methods were used to investigate miscibility and phase structure in the new materials. When the miscibility is low, these IPNs show properties

similar to those of their component polymers but exhibit hybrid properties when the components are highly miscible. Intermolecular interactions such as hydrogen bonding, dipole-dipole interactions or van der Waals forces between the macromolecular components could enhance miscibility within an IPN system. These phosphazene containing IPNs are the first members of new classes of multi-component polymeric materials which may possess unique technological and biomedical properties.

Future work in the area of polyphosphazene/organic or inorganic polymer IPNs includes the preparation of ion specific poly(organophosphazene)/organic polymer IPNs which may be used as ionic filters or ion exchange media. These types of materials could be used for both environmental and biomedical applications. The synthesis and characterization of IPNs composed of poly(organophosphazenes) and polysiloxanes is also being investigated.

Acknowledgement: This work was supported by the Office of Naval Research and the National Institute of Health.

Literature Cited:

1. He, X.W.; Widmaier, J.M.; Herz, J.E.; Meyer, G.C.; *Polymer*, **1992**, *33*(4), 866-871.
2. Frisch, H.L.; Huang, M.W.; *J. Polymer Science, part A* ; **1991**, *29*(1), 131-133.
3. Mukae, K.; Bae, Y.H.; Okano, T.; Kim, S.W.; *Polymer Journal* (Tokyo); **1990**, *22*(3); 206-17.
4. Xiao, H.; Ping, Z.H.; Xie, J.W.; Yu, T.Y.; *J. Polymer Science, part A; Polymer Chem.*; **1990**; *28*(3); 585-594.
5. Mukae, K.; Bae, Y.H.; Okano, T.; Kim, S.W.; *Polymer Journal* (Tokyo); **1990**; *22*(3), 250-265.
6. Arkles, B.; Crosby, J.; in *Advances in Chemistry Series, Volume Date 1987*, vol. no. 224; **1990**; 181-199.

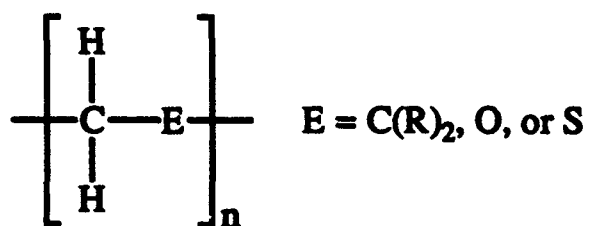
7. Falcetta, J. J.; Friends, G. D.; Niu, G. C. C.; Ger. Off. Patent 2,518,904; 1975.
8. Clark, H. A.; U. S. Patent 3,527,842; 1970.
9. Mark, J. E.; Allcock, H. R.; West, R.; *Inorganic Polymers*; Prentice-Hall Inc.: Englewood Cliffs, N.J., 1992.
10. Allcock, H. R.; Visscher, K. B.; Manners, I., *Macromolecules*, 1990, 23, 4885-4886.
11. Allcock, H. R.; Visscher, K. B.; Manners, I., *Chemistry of Materials* (in press), 1992.
12. Allcock, H. R.; *Phosphorus-Nitrogen Compounds*, Academic Press Inc.: New York, 1972.
13. Penton, H.R. in *Inorganic and Organometallic Polymers*, Zeldin, M.; Wynne, K.J.; and Allcock, H.R. eds.; ACS Symposium Series No. 360; American Chemical Society: Washington D. C., 1988, 272-282.
14. Allcock, H.R., *Chem. Eng. News*, 1985, 63(11), 22.
15. Allcock, H.R., *Angew.Chem.*, 1977, 16, 147.
16. Allcock, H.R. in *Inorganic and Organometallic Polymers*, Zeldin, M.; Wynne, K.J.; and Allcock, H.R. Eds.; ACS Symposium Series No. 360; American Chemical Society: Washington D. C., 1988.
17. Allcock, H. R.; Kugel, R. L., *J. Am. Chem. Soc.*, 1965, 87, 4216.
18. Allcock, H. R.; Kugel, R. L., *Inorg. Chem.*, 1966, 5, 1709.
19. Allcock, H. R.; Kugel, R. L., *Inorg. Chem.*, 1966, 5, 1716.
20. Allcock, H. R.; Kwon, S., *Macromolecules*, 1989, 22, 75-79.
21. Cohen, S.; Bano, M.C.; Visscher, K.B.; Chow, M.; Allcock, H.R. and Langer, R. *J. Am. Chem. Soc.*, 1990, 112, 7832-7833.
22. Bano, M. C.; Cohen, S.; Visscher, K. B.; Allcock, H. R. and Langer, R., *Biotechnology*, 1991, 9, 468-471.

23. Allcock, H. R.; Coggio, W. D., *Macromolecules*, **1990**, *23*, 1626-1635.
24. Blonsky, P.M.; Shriver, D.F.; Austin, P.E.; Allcock, H.R., *J. Am. Chem. Soc.*, **1984**, *106*, 6854.
25. Allcock, H.R.; Kwon, S; Riding, G.H.; Fitzpatrick, R.J.; Bennett, J.L., *Biomaterials*, **1988**, *9* , 509.
26. Allcock, H.R.; Fitzpatrick, R.J.; Gebura, M.; Kwon, S ., *Polym. Prepr.*, **198** 321.
27. Allcock, H. R.; Bennett, J. L.; Dembek, A. A.; Heyen, B. J.; Shriver, D. L., *Chemistry of Materials*, **1989**, *1*, 14-16.
28. Allcock, H. R.; Bennett, J. L.; Dembek, A. A.; Heyen, B. J.; Shriver, D. L., *Polymer Prepr. (ACS Polym. Div.)*, **1989**, *30*, 437-438.
29. Allcock, H. R.; Dodge, J. A.; Manners, I.; Parvez, M.; Visscher, K. B.; *Organometallic Chemistry*, **1991**, *10*, 3098-3104.
30. May, P.; Guerra, L.R.; U.S. Patent 4,251,215; **1981**.
31. Gettleman, L.; Farris, C.L.; Rawls, H.R.; LeBouef, R.J.; U.S. Patent 4,432,730; **1984**.
32. Gettleman, L.; Farris, C.L.; Rawls, H.R.; LeBouef, R.J.; U.S. Patent 4,543,379; **1985**.
33. Gettleman, L.; Gebert, P.H.; U.S. Patent 4,661,065; **1987**.
34. Materials were exposed to ^{60}Co γ -radiation at the Breazeale Nuclear Reactor on the campus of The Pennsylvania State University.
35. Sperling, L.H. , *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, **1981**.
36. Sperling, L.H., *Chemtech.*, **1988**, 104.
37. Coleman, M.; Painter, P. C. *Fourier Transform Infrared Spectroscopy*, in *Applied Spectroscopy Reviews*, **1984**, *20*, no. 3, 256-346.

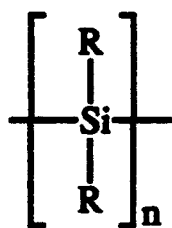
38. Painter, P. C., *Macromolecules*, 1988, 21, 666.
39. Painter, P. C. *Macromolecules*, 1988, 22, 570.
40. Painter, P. C. *Macromolecules*, 1989, 22, 580.

Scheme 1.

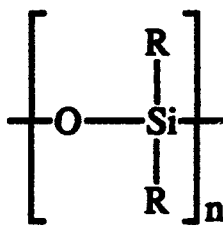
Organic Polymers



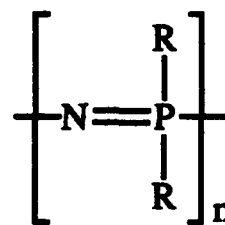
Inorganic Polymers



Polysilane



Polysiloxane



Polyphosphazene

Table 1.

Advantages of Polyphosphazenes as IPN Components
* Non-Burning and Flame Retardant * Solvent and Oil Resistance * Biomedical Compatibility * Materials Flexibility (Low Tg) * Ease of Tuning Molecular Structure

Scheme 2. General Synthesis of Poly(organo)phosphazenes

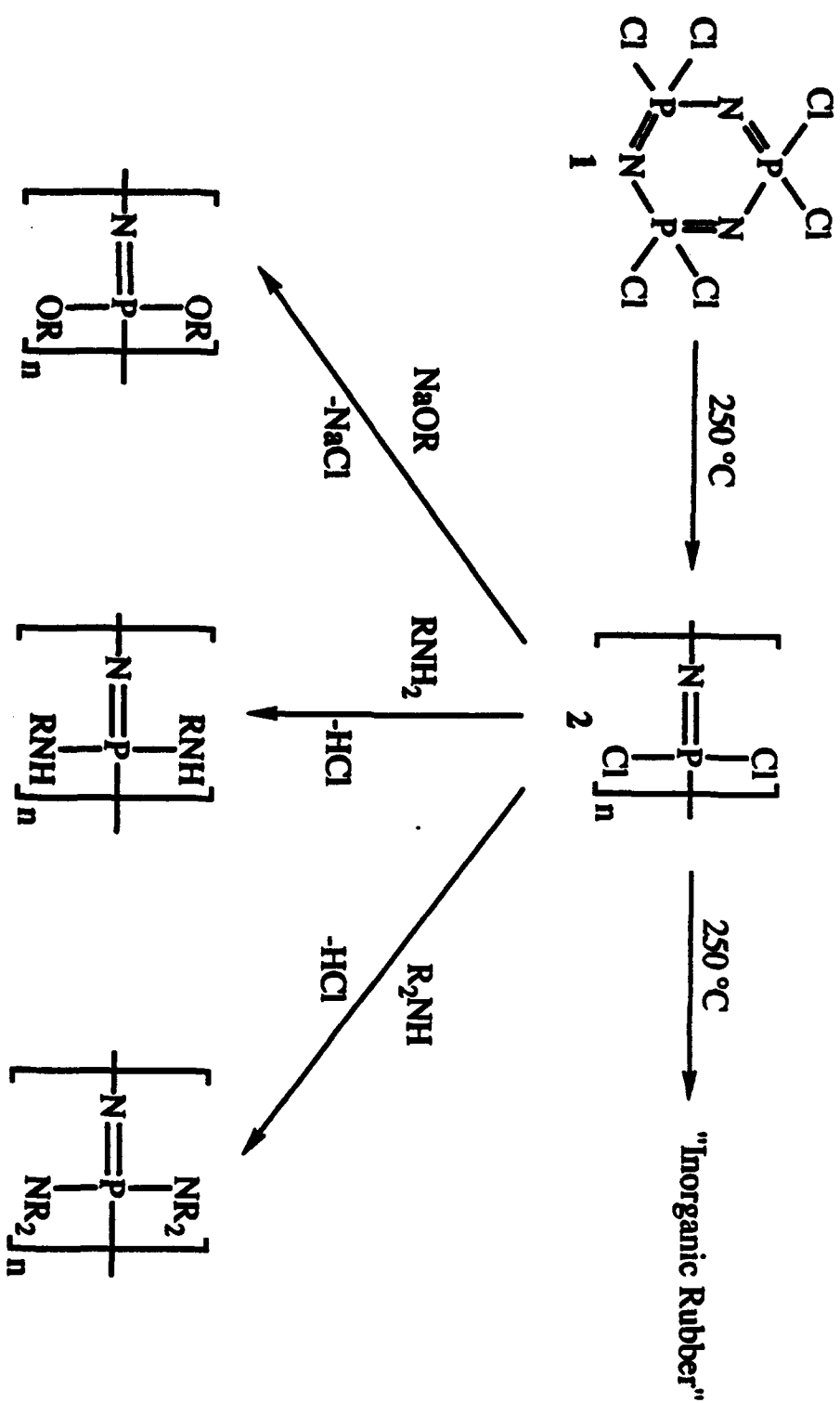
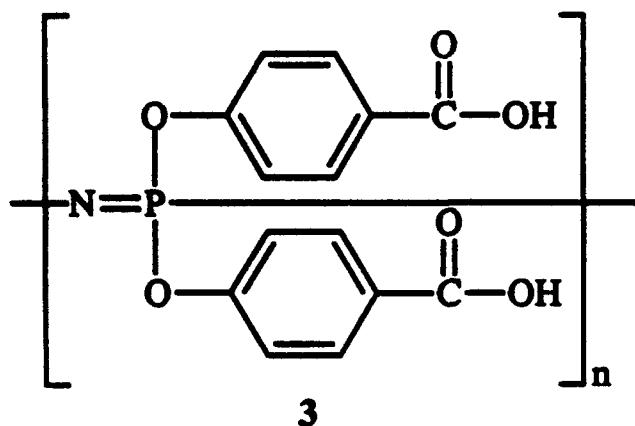


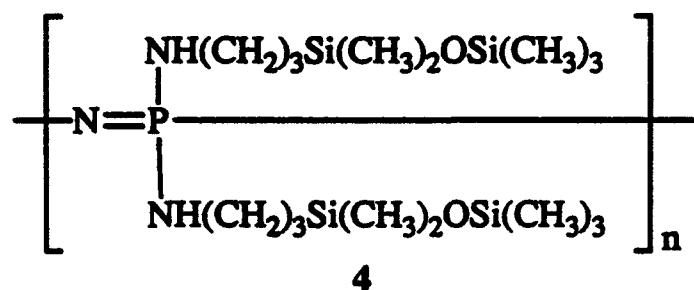


Figure 1. Poly(organophosphazene) shock absorbing denture liner. (Reprinted courtesy of Dr. L. Gettleman)(24)

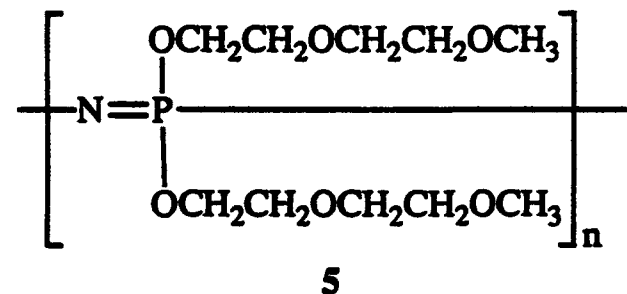
Chart 1. Examples of Poly(organophosphazenes)



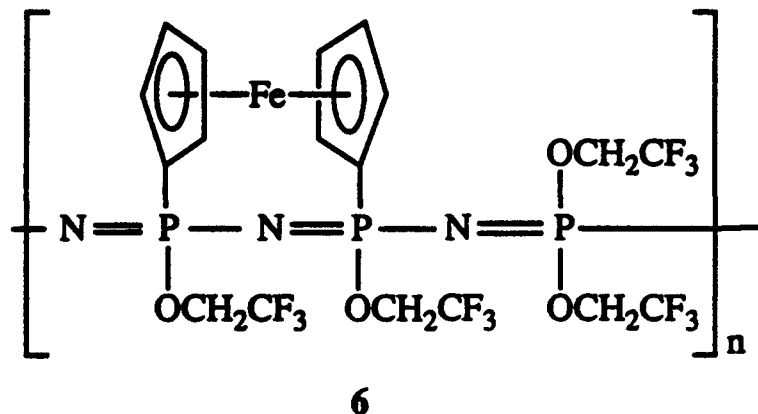
**Water Soluble as Sodium Salt,
Cross-linkable by Ca^{2+} Ions**



Elastomer

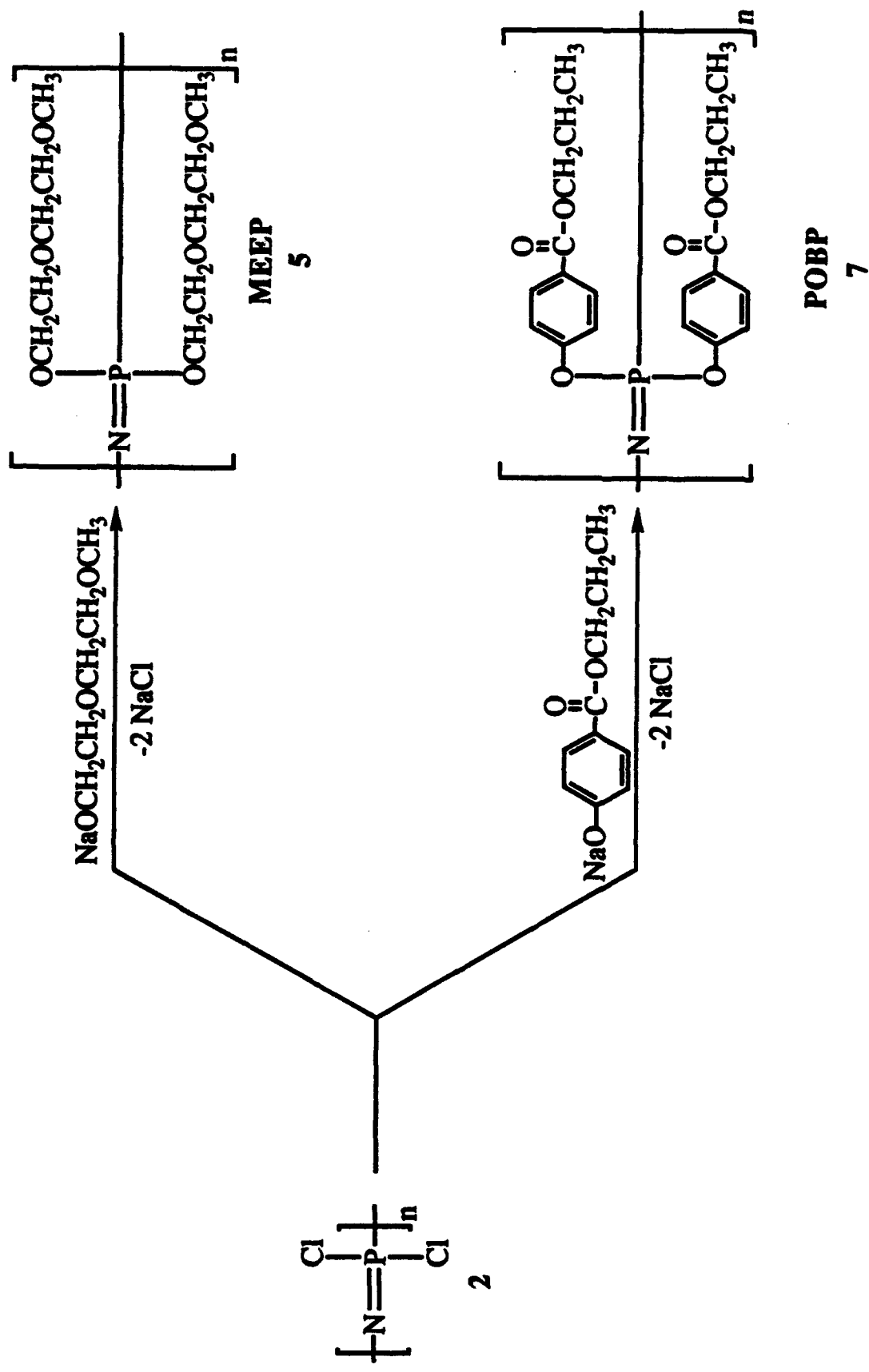


**Water-Soluble,
Solid Electrolyte**

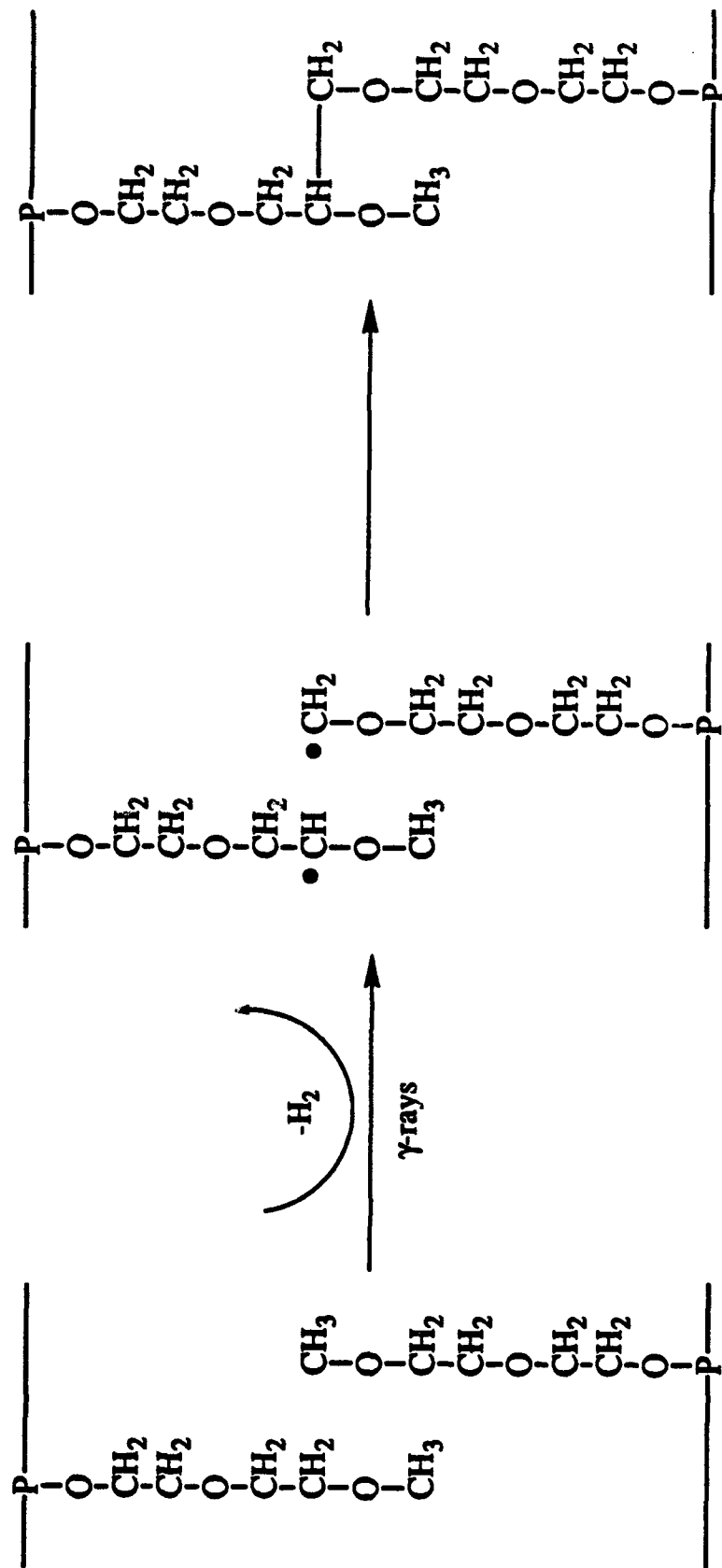


Electroactive Material

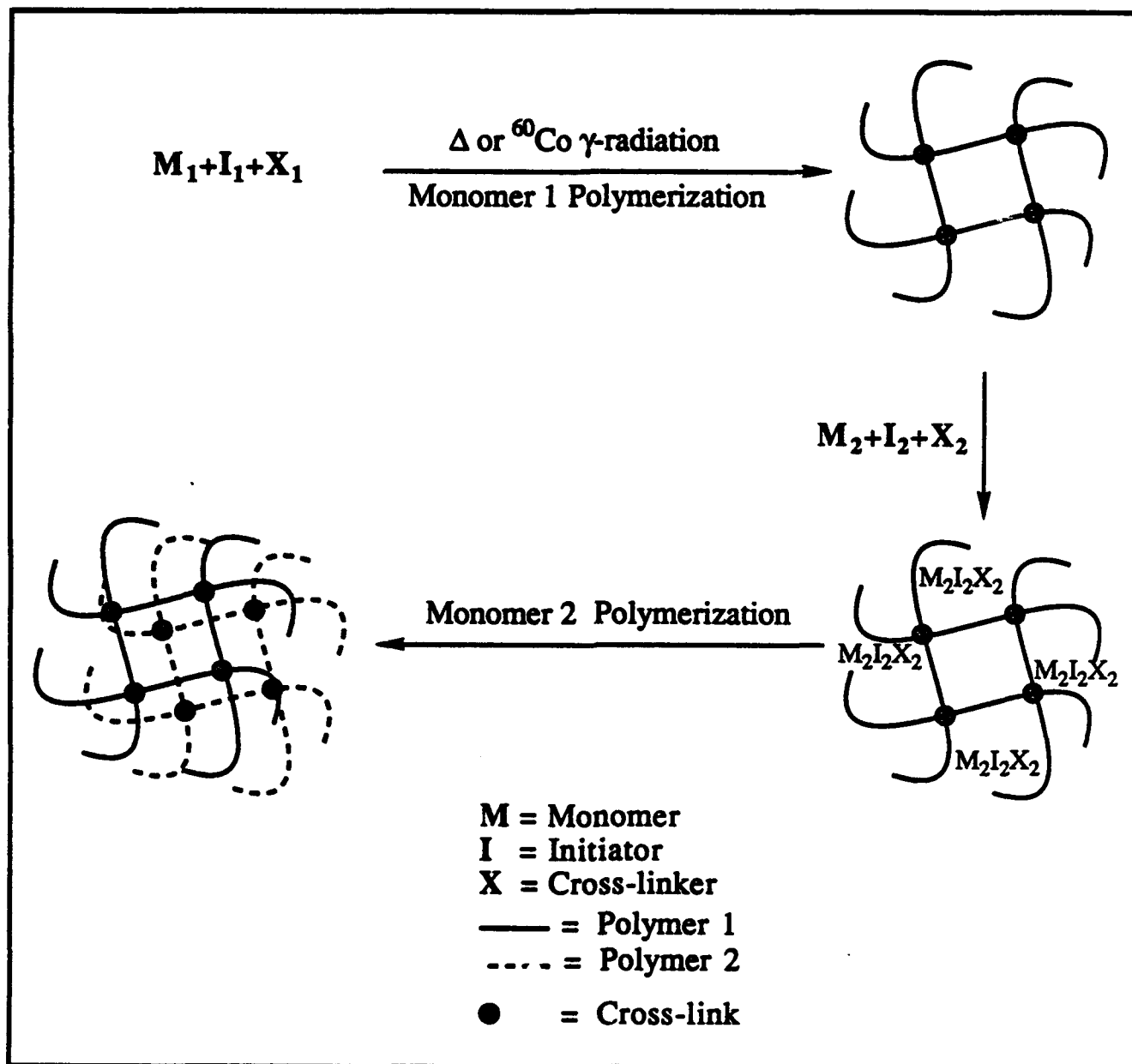
**Scheme 3. Synthesis of Poly(organophosphazenes)
Used in This Work**



Scheme 4. Crosslinking of Poly(organophosphazenes) by ^{60}Co γ -Radiation (12)



Scheme 5. Schematic Representation of IPN Preparation



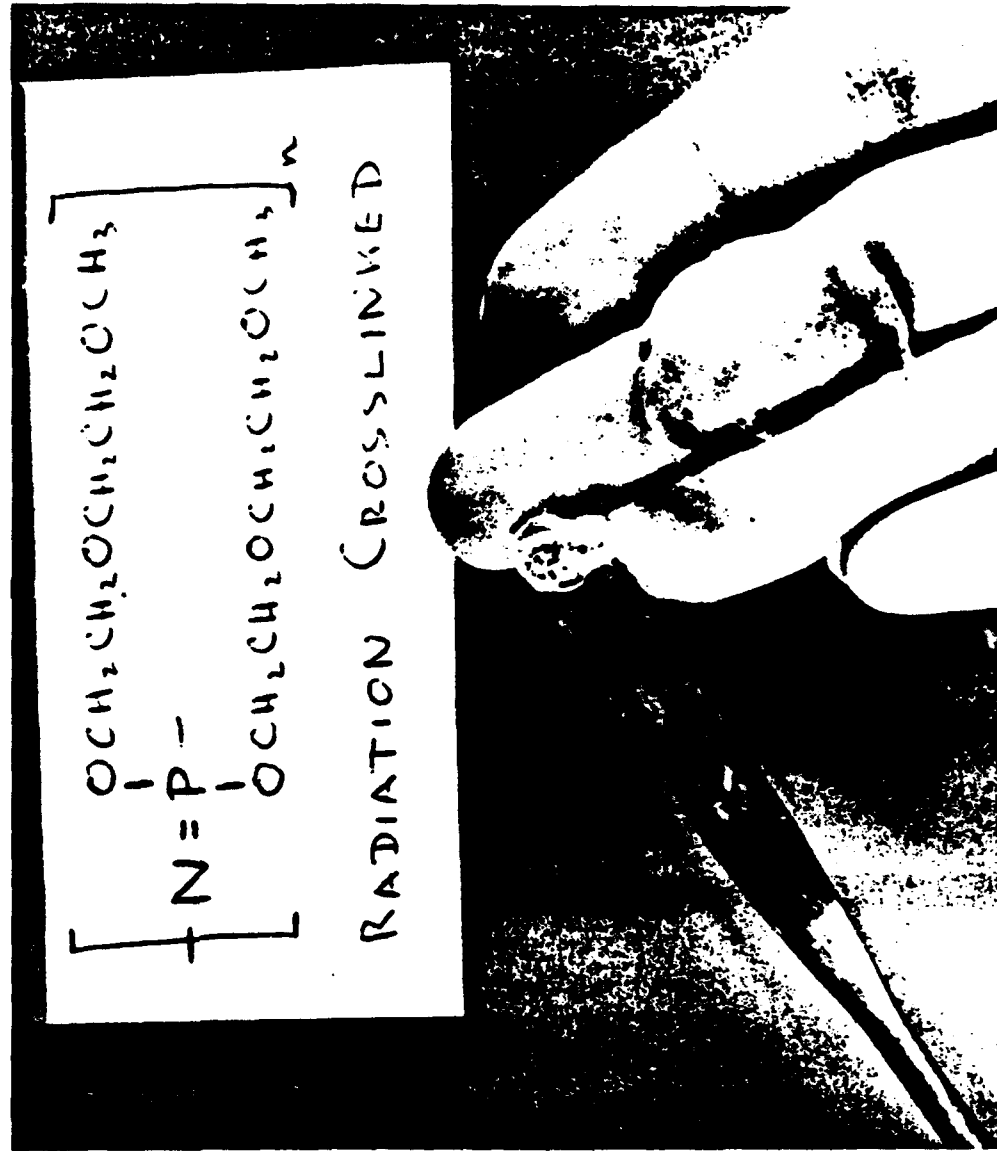
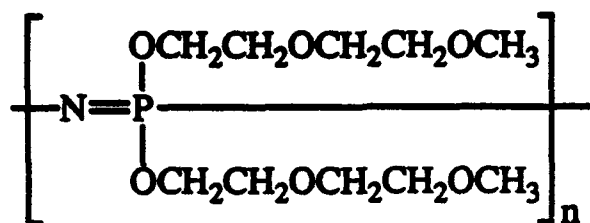


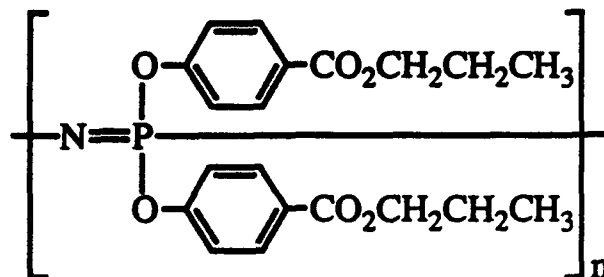
Figure 2. MEEP after cross-linking and after swelling in water for several hours. (Reprinted courtesy of Dr. H. R. Allcock)(12)

Chart 2. IPN Component Polymers

Poly(organophosphazenes)

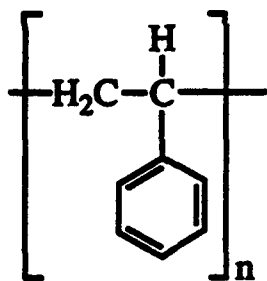


MEEP (5)

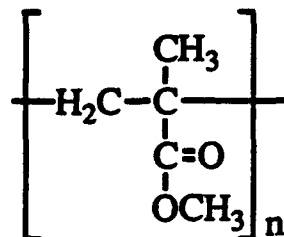


POBP (7)

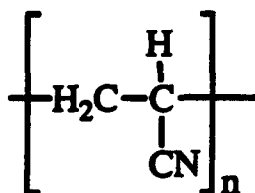
Organic Polymers



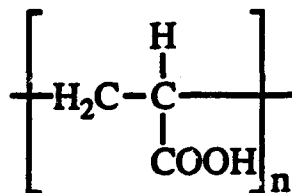
Polystyrene (PS) (8)



Poly(methyl methacrylate) (PMMA) (9)



Polyacrylonitrile (PAN) (10)



Poly(acrylic acid) (PAA) (11)

**Scheme 6. Experimental Procedure for Preparation
of Poly(organophosphazene) IPNs**

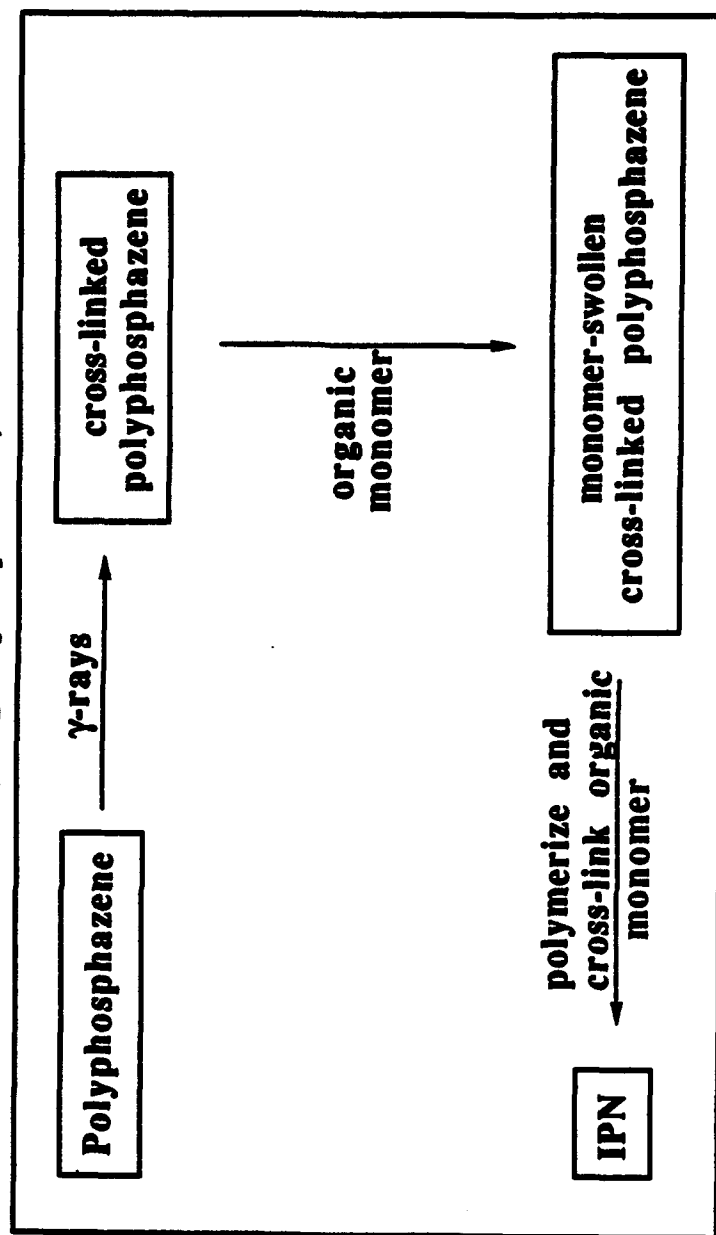


Table 2. IPN Component Ratios^a

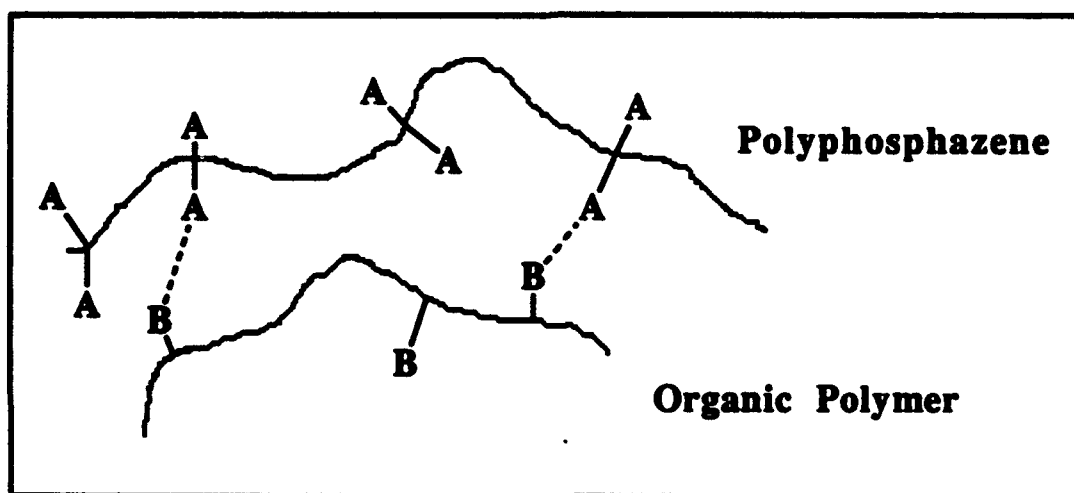
MEEP/PS (5/8)	1 : 1
MEEP/PMMA (5/9)	3 : 1
MEEP/PAN (5/10)	1 : 1
MEEP/PAA (5/11)	1 : 1
POBP/PS (7/8)	2.5 : 1
POBP/PMMA (7/9)	1.5 : 1
POBP/PAN (7/10)	4.5 : 1
POBP/PAA (7/11)	2 : 1
a: Based on NMR integration	

Table 3. DSC Data and Tg's of Individual Component Polymers

<u>IPN</u>	<u>T_g (°C)^a</u>
MEEP/PS (5/8)	-70/+57
MEEP/PMMA (5/9)	-80/+112
MEEP/PAN (5/10)	+34
MEEP/PAA (5/11)	-41/+3.5
POBP/PS (7/8)	-14/+92
POBP/PMMA (7/9)	-14/+50
POBP/PAN (7/10)	-9/+51
POBP/PAA (7/11)	+54

**a: Component Polymer Tg's: MEEP(5)= -84 °C; POBP(7)= -23 °C;
PS(8) = 100 °C; PMMA(9) = 105 °C;
PAN(10) = 106 °C; PAA(11) = 85 °C**

Scheme 7. Schematic Illustration of Intermolecular Interaction



Scheme 8. Possible Molecular Level Interactions

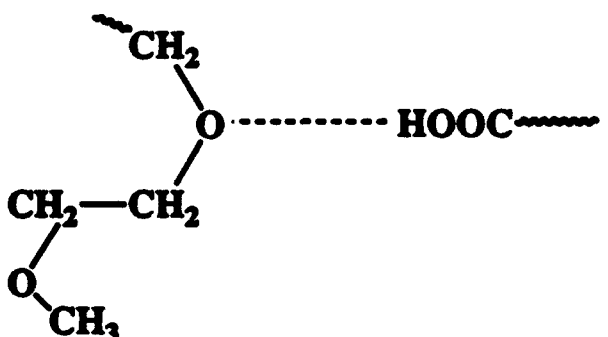
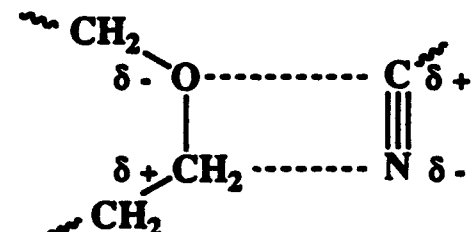
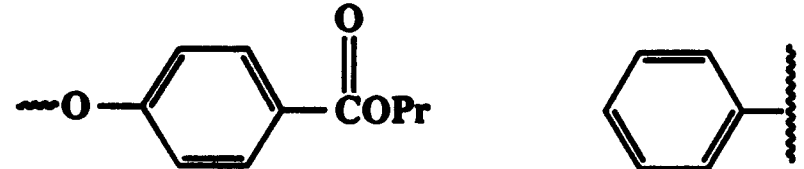
Polyphosphazene	Organic Polymer
Hydrogen Bonding 	
Dipole-Dipole 	
van der Waals Interaction 	

Figure 3. DSC Thermogram of MEEP(5)/PAN(10) IPN.

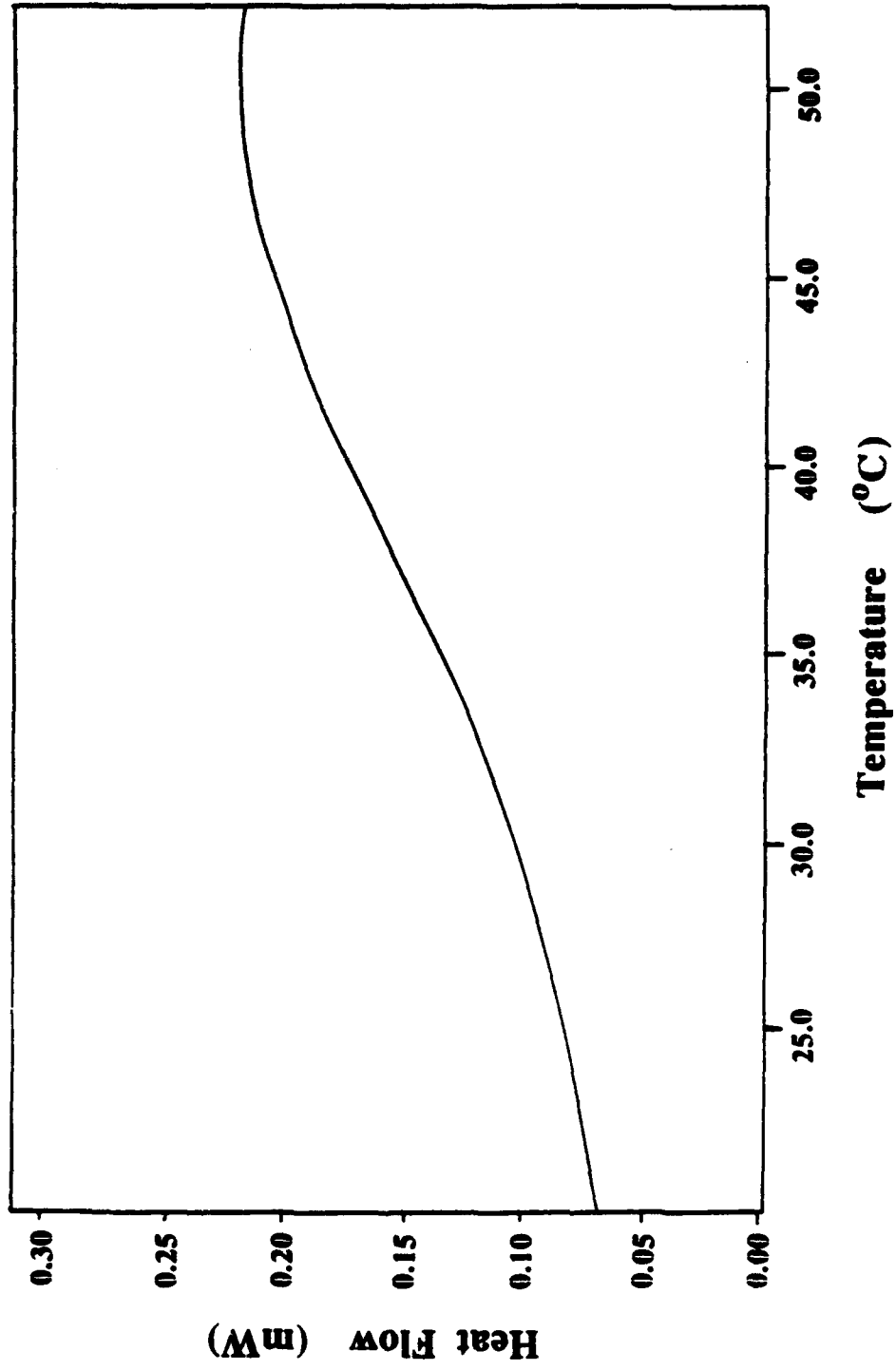
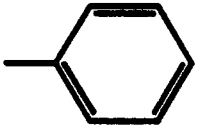


Table 4. Participating Side Groups and Possible Interactions

Polyphosphazene	
$\text{—OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ (5)	H-Bond Acceptor Dipole-Dipole
—O—  —COOPr (7)	H-Bond Acceptor Hydrophobic
Organic Polymer	
 (8)	Hydrophobic
—COOMe (9)	H-Bond Acceptor Dipole-Dipole
$\text{—C}\equiv\text{N}$ (10)	Dipole-Dipole
—COOH (11)	H-Bond Donor Dipole-Dipole

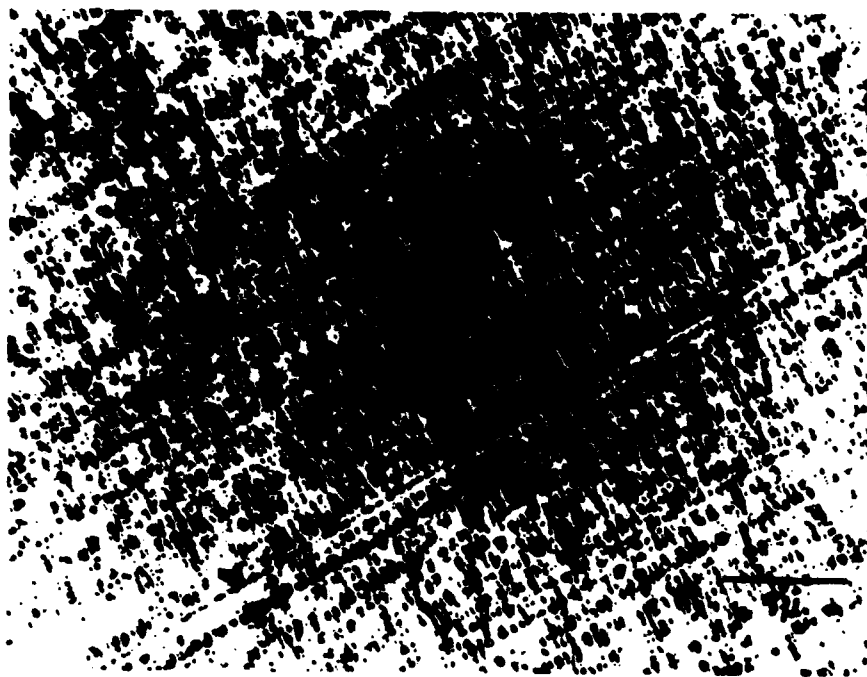


Figure 4. TEM Micrograph of MEEP(5)/PAN(10) IPN.

Figure 5. DSC Thermogram of POBP(7)/PS(8) IPN.

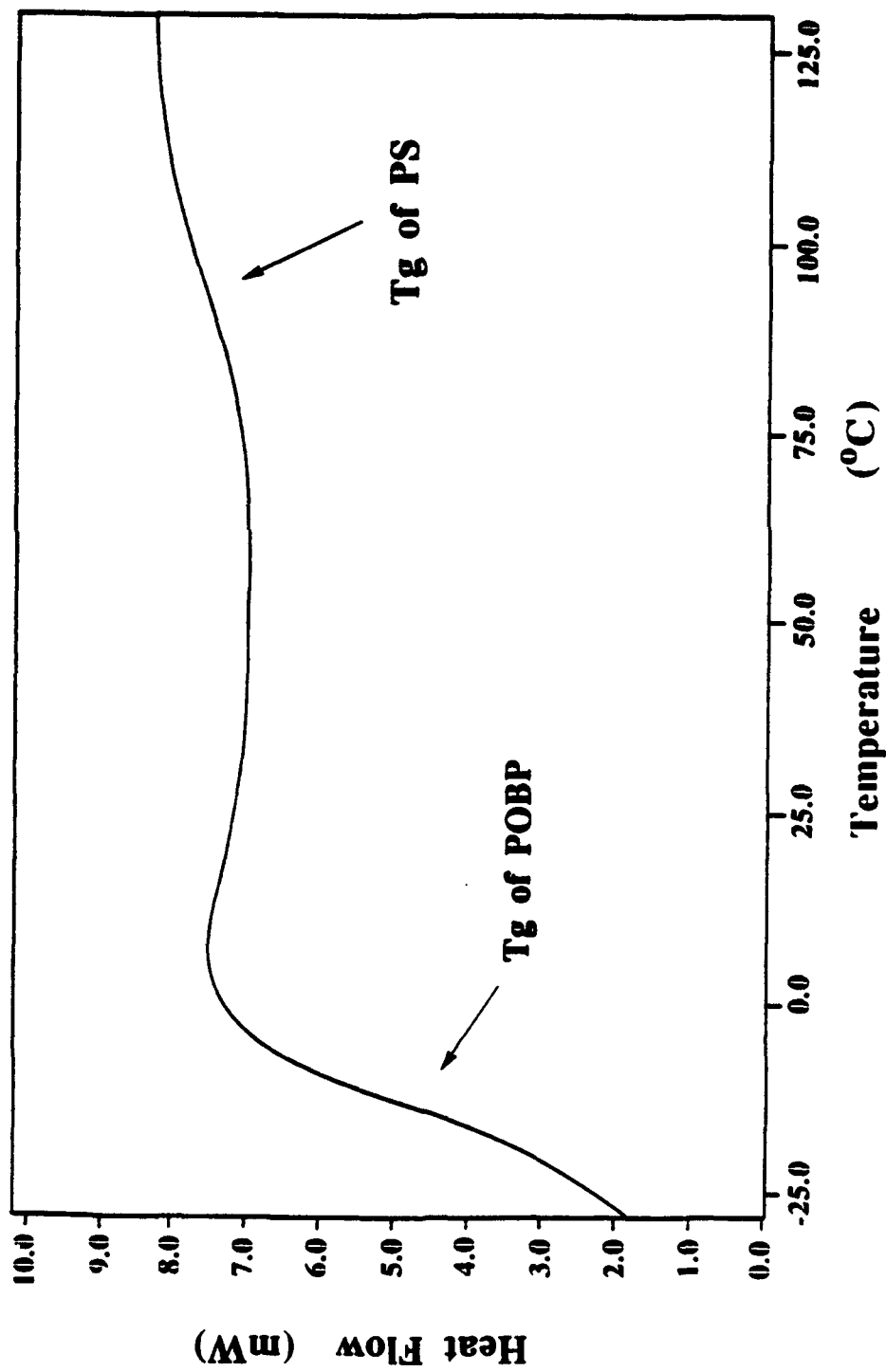




Figure 6. TEM Micrograph of POBP(7)/PS(8) IPN.

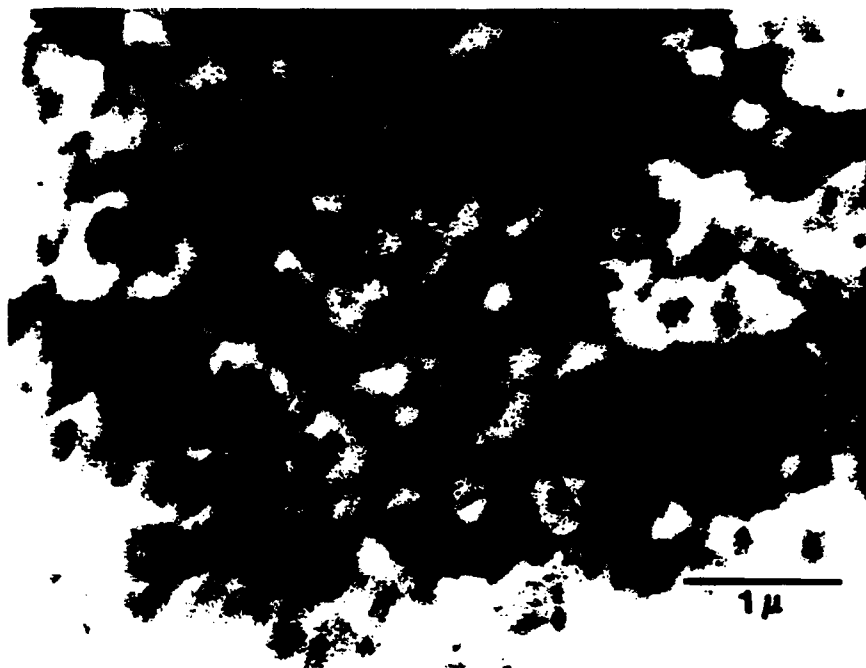


Figure 7. TEM Micrograph of MEEP(5)/PMMA(9) IPN.



Figure 8. TEM Micrograph of POBP(7)/PMMA(9) IPN.

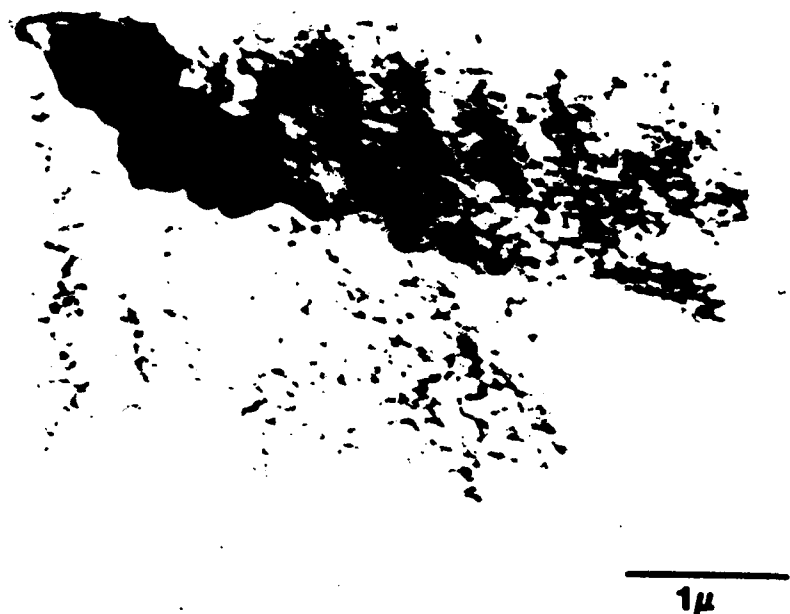


Figure 9. TEM Micrograph of POBP(7)/PAA(11) IPN.

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research Chemistry Division, Code 313 800 North Quincy Street Arlington, Virginia 22217-5000	(1)*	Dr. Richard W. Drisko (1) Naval Civil Engineering Laboratory Code L52 Port Hueneme, CA 93043
Defense Technical Information Center Building 5, Cameron Station Alexandria, VA 22314	(2)	Dr. Harold H. Singerman (1) Naval Surface Warfare Center Carderock Division Detachment Annapolis, MD 21402-1198
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	(1)	Dr. Eugene C. Fischer (1) Code 2840 Naval Surface Warfare Center Carderock Division Detachment Annapolis, MD 21402-1198
Dr. Robert Green, Director Chemistry Division, Code 385 Naval Air Weapons Center Weapons Division China Lake, CA 93555-6001	(1)	Dr. Bernard E. Douda (1) Crane Division Naval Surface Warfare Center Crane, Indiana 47522-5000
Dr. Elek Lindner Naval Command, Control and Ocean Surveillance Center RDT&E Division San Diego, CA 92152-5000	(1)	

* Number of copies to forward

DR. HARRY R. ALLCOCK
DEPARTMENT OF CHEMISTRY
PENNSYLVANIA STATE UNIV.
UNIVERSITY PARK, PA 16802

DR. ANDREW R. BARRON
DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MA 02138

DR. KURT BAUM
FLUOROCHEM, INC.
680 SOUTH AYON AVENUE
AZUSA, CA 91702

DR. FRANK D. BLUM
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MISSOURI - ROLLA
ROLLA, MO 65401

DR. ALEXANDER S. BLUMSTEIN
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MASSACHUSETTS
LOWELL, MA 01854

DR. LEONARD J. BUCKLEY
AIRCRAFT DIVISION, CODE 6064
NAVAL AIR WARFARE CENTER
P.O. BOX 5152
WARMINSTER PA 18974-0591

PROF. TOBY M. CHAPMAN
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH PA 15261

DR. ROBERT E. COHEN
DEPARTMENT OF CHEMICAL ENGINEERING
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MA 02139

PROF. JOSEPH M. DESIMONE
DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF NORTH
CAROLINA AT CHAPEL HILL
CHAPEL HILL, NC 27599-3290

DR. RANDOLPH S. DURAN
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF FLORIDA
GAINESVILLE, FL 32611

DR. CURTIS W. FRANK
DEPARTMENT OF CHEMICAL ENGINEERING
STANFORD UNIVERSITY
STANFORD, CA 94305

DR. JEAN M. FRECHET
DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NY 14853

DR. JOSEPH A. GARDELLA
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BUFFALO
BUFFALO, NY 14214

DR. JAMES R. GRIFFITH
CODE 6120
DEPARTMENT OF THE NAVY
NAVAL RESEARCH LABORATORY
4555 OVERLOOK AVENUE, SW
WASHINGTON, DC 20375-5000

DR. ROBERT H. GRUBBS
DEPARTMENT OF CHEMISTRY
CALIFORNIA INST. OF TECHNOL.
PASADENA, CA 91124

DR. I. I. HARRUNA
DEPARTMENT OF CHEMISTRY
MORRIS BROWN COLLEGE
ATLANTA, GA 30314

DR. JAMES F. HAW
DEPARTMENT OF CHEMISTRY
TEXAS A&M UNIVERSITY
COLLEGE STATION, TX 77843

DR. ALAN J. HEEGER
DEPARTMENT OF PHYSICS
UNIV. OF CALIFORNIA
SANTA BARBARA, CA 93106

DR. HATSUO ISHIDA
DEPARTMENT OF MACROMOLECULAR SCIENCES
CASE WESTERN RESERVE UNIV.
CLEVELAND, OH 44106

DR. RICHARD B. KANER
DEPARTMENT OF CHEMISTRY & BIOCHEMISTRY
UNIVERSITY OF CALIFORNIA, LA
LOS ANGELES CA

DR. JOHN F. KEANA
UNIVERSITY OF OREGON
EUGENE, OR 97403

DR. JEFFREY T. KOBERSTEIN
INSTITUTE OF MATERIALS SCIENCE
UNIVERSITY OF CONNECTICUT
STORRS, CT 06268

PROF. HILARY S. LACKRITZ
DEPARTMENT OF CHEMICAL ENGINEERING
PURDUE UNIVERSITY
WEST LAFAYETTE IN 49707

PROF. RICHARD M. LAINE
DEPT. OF MATERIALS SCIENCE
AND ENGINEERING
THE UNIVERSITY OF MICHIGAN
H.H. DOW BUILDING
ANN ARBOR MI 48105-2137

DR. GEOFFREY LINDSAY
CHEMISTRY DIVISION - CODE 3858
NAVAL WEAPONS CENTER
CHINA LAKE, CA 93555

PROF. ALAN G. MACDIARMID
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA
CHEMISTRY BUILDING
PHILADELPHIA PA 19104-6323

DR. ASLAM MALIK
AEROJET PROPULSION DIVISION
P.O. BOX 13222
SACRAMENTO CA 95813-6000

DR. LON J. MATHIAS
DEPARTMENT OF POLYMER SCIENCE
UNIVERSITY OF SOUTHERN MISSISSIPPI
HATTIESBURG MS 39406-0076

DR. KRZYSZTOF MATYJASZEWSKI
DEPARTMENT OF CHEMISTRY
CARNEGIE-MELLON UNIVERSITY
PITTSBURGH, PA 15213

DR. ALON MCCORMICK
CHEMICAL ENGINEERING & MATERIALS
SCIENCES DEPARTMENT
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MN 55455

DR. JAMES E. MCGRATH
DEPARTMENT OF CHEMISTRY
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VA 24061

DR. JAMES A. MOORE
DEPARTMENT OF CHEMISTRY
RENSSELAER POLYTECHNIC INSTITUTE
TROY, NY 12180-3590

DR. GEORGE MUSHRUSH
DEPARTMENT OF CHEMISTRY
GEORGE MASON UNIVERSITY
FAIRFAX, VA 22030

DR. MICHAEL L. MYRICK
DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA SC 29208

PROF. A. NATANSON
QUEENS UNIVERSITY
KINGSTON ONTARIO
CANADA K7L 3N6

DR. DOUGLAS C. NECKERS
DEPARTMENT OF CHEMISTRY
BOWLING GREEN UNIVERSITY
BOWLING GREEN, OH 43403

DR. BRUCE M. NOVAK
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CA 94720

DR. CHRISTOPHER K. OBER
MATERIALS SCIENCE & ENGINEERING
BARD HALL, CORNELL UNIVERSITY
ITHACA NY 14853-1501

DR. PETER N. PENTAURO
DEPARTMENT OF ELECTRICAL ENGINEERING
TULANE UNIVERSITY
314 GIBSON HALL
NEW ORLEANS LA 70118-5698

DR. VIRGIL PERCEC
DEPARTMENT OF MACROMOLECULAR SCIENCES
CASE WESTERN RESERVE UNIV.
CLEVELAND, OH 44106-2699

DR. MICHAEL F. RUBNER
MATERIALS SCIENCE & ENGINEERING
DEPARTMENT
MASSACHUSETTS INST. OF TECH.
CAMBRIDGE, MA 02139

DR. JACOB SCHAEFER
DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY
ST. LOUIS, MO 63130

DR. JERRY I. SCHEINBEIM
DEPARTMENT OF MECHANICAL
& MATERIALS SCIENCES
RUTGERS UNIVERSITY
PISCATAWAY, NJ 08854

DR. RICHARD R. SCHROCK
DEPARTMENT OF CHEMISTRY, 8-331
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
77 MASSACHUSETTS AVENUE
CAMBRIDGE, MA 02139

DR. R. SHASHIDHAR
CENTER FOR BIO/MOLECULAR SCIENCE & ENG.
NAVAL RESEARCH LABORATORY
CODE 60909
WASHINGTON DC 20375-5320

DR. ARTHUR W. SNOW
CHEMISTRY DIVISION
NAVAL RESEARCH LABORATORY
MATERIALS CHEMISTRY BRANCH
CODE 6120
WASHINGTON DC 20375

PROF. SAMUEL I. STUPP
DEPT OF MATERIALS SCIENCE & ENGINEERING
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN
1304 WEST GREEN STREET
URBANA, IL 61801

DR. C. S. SUNG
INSTITUTE OF MATERIALS SCIENCE
UNIVERSITY OF CONNECTICUT
STORRS, CT 06268

DR. JAMES M. TOUR
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, SC 29208

PROF. S. K. TRIPATHY
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF LOWELL
LOWELL, MA 01854

DR. DAVID M. WALBA
DEPARTMENT OF CHEMISTRY & BIOCHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, CO 80309

DR. C. H. WANG
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEBRASKA
LINCOLN, NE 68588-0304

DR. ROBERT WEST
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN-MADISON
MADISON WI 53706

DR. MICHAEL E. WRIGHT
DEPARTMENT OF CHEMISTRY
UTAH STATE UNIVERSITY
LOGAN, UT 84322

DR. LUPING YU
DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF CHICAGO
970 E. 58TH STREET
CHICAGO IL 60637