

Metal Ion-Complexing Polyphosphazene-Interpenetrating Polymer Networks

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The synthesis of interpenetrating polymer networks (IPNs) composed of the polyphosphazenes $[\text{NP}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]_n$ (MEEP), or $[\text{NP}(\text{OC}_6\text{H}_4\text{COOPr})_2]_n$ and acidic, ion-complexing organic polymers is reported. These latter polymers included poly(acrylic acid), poly(vinylsulfonic acid sodium salt), poly[bis(undecenyl phosphate)], and poly[(*p*-methylimino-diacetoxy)styrene]. Several of these IPN systems are capable of selective coordination of specific ions and are prototypes for ion-selective membranes. Full, sequential IPNs were prepared, and these materials were characterized by NMR spectroscopy, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). After metal complexation, the conjugate IPNs were analyzed by electron microscopy and X-ray microanalysis. The metal coordination was used to enhance domain contrast in these systems for electron microscopy studies. Because the IPNs based on MEEP are of particular interest for ion-selective membrane applications, the stability of MEEP in acidic, neutral, and basic aqueous media and the response of the polymer to aqueous salt solutions was also examined.

Introduction

The incorporation of metal ions into polymers is of broad interest from both the fundamental and applications points of view. An understanding of the ways in which polymeric ligands can selectively remove metal ions from solution is of widespread interest. So too is the use of metal ion complexation as a means for the identification and visualization of domains in solid polymeric materials systems. From a practical viewpoint, the complexation of ions by porous solids or hydrogels underlies possible solutions to a wide variety of environmental, technological, and biomedical problems. For example, the isolation of precious metals or radioactive isotopes from the environment or the development of medical procedures for the removal of toxic cations from humans can, in principle, be accomplished via the use of ion-selective extraction systems. A general requirement is that the substrate material should have a high contact area and that the polymer and/or its complexes should be insoluble in order to allow a facile separation of the metal-polymer complex from a liquid medium.¹ Many of the systems being studied utilize polymers that bear coordinating units incorporated into the side-group structure.

A number of well-known ion extraction materials are acidic or basic functional forms of common organic polymers such as polystyrene.² The un-cross-linked forms of these polymers often have a high solubility in water, but they can be converted to gels or insoluble matrices in a number of different ways including cross-linking of the polymer, copolymerization of the functionalized monomer with a comonomer that ensures

insolubility or preparation of an interpenetrating polymer network (IPN) with a second polymer. The use of an IPN for ion complexation offers a number of advantages including the prospect that the swellability and permeability of the substrate can be controlled by the choice of the second (noncoordinative) polymer used in the network. In addition, the properties and applications of the final product may be controlled by the choice and concentration of the components in the IPN system.

Interpenetrating polymer networks are multicomponent polymer systems prepared by the polymerization and cross-linking of a monomer within the swollen, cross-linked matrix of a second polymer. The resultant system may form an intimate mixture of the two polymers that are unable to separate from each other even when the system is swollen by a solvent. Thus, once prepared, an IPN is insoluble but is swellable in aqueous or organic media depending on the characteristics of the component polymers.^{3,4} Examples of ion-complexing IPNs that contain polymers with phosphinic acid, phosphonic acid, or phosphate units have been studied by other workers.⁵⁻⁹

The interpenetrating polymer networks described here are comprised of a cross-linked poly(organophosphazene) matrix and a cross-linked organic polymer that bears acidic side groups. Poly(organophosphazenes) are especially useful for multicomponent polymer systems because their properties may be tailored over a broad range by the introduction of different side groups via

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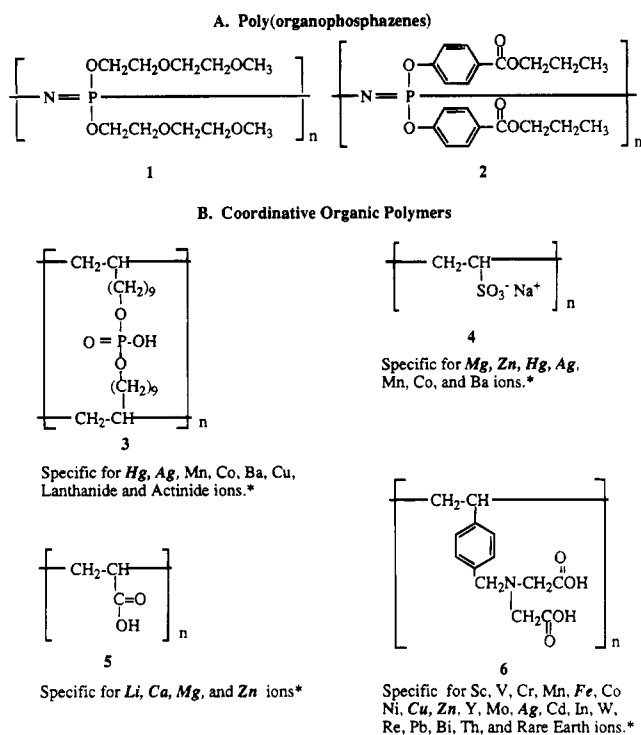
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Chart 1. IPN Component Polymers and Ion Specificities

* Elements in italics used in this investigation.

macromolecular substitution methods.^{10–17} Thus, various side groups can generate water solubility or organic solvent solubility, and other units can be incorporated to facilitate radiation cross-linking, which is the method of choice for the systems to be discussed here. Poly(organophosphazenes) are also a good choice for ion complexing IPNs because they can be designed to be either inert or active as ion-coordination substrates, and this further widens the opportunities for materials optimization.

Two specific polyphosphazenes were chosen for these studies. These are poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (1) and poly[bis(propoxybenzoate)phosphazene] (2) (Chart 1). It has been demonstrated earlier that these two polymers are useful for the formation of IPNs with various organic polymers including polystyrene, poly(methyl methacrylate), poly(acrylonitrile), and poly(acrylic acid).^{18,19} These two polyphosphazenes were chosen in that work and here because they are both appropriate for γ -radiation cross-linking and because polymer 1 is water soluble while polymer 2 is insoluble in water but is soluble in organic solvents such as THF. Thus, these two macromolecules

offer the prospect of forming either hydrogel or organogel cation absorbers. In all cases, the phosphazene polymers served as the initial cross-linked polymer matrix and the polymers shown as 3–6 were formed from their monomers within swollen gels generated from the matrix polymers.

The objectives of this work were to prepare ion-complexing interpenetrating polymer networks containing poly(organophosphazenes) and coordinative organic polymers and to investigate their ion-complexing and ion-exchanging abilities with various metal salts.

Experimental Section

Materials. Vinylsulfonic acid sodium salt (25 wt % solution in water) and acrylic acid (Aldrich) were passed through alumina columns to remove inhibitors and were then stored over 3 Å molecular sieves. ω -Undecylenyl alcohol (Aldrich), phosphorous oxychloride (Aldrich), iminodiacetic acid (Aldrich), and chloromethyl styrene (mixture of meta and para isomers, Polysciences) were used as received. Pyridine (Aldrich) was distilled and stored over 3 Å molecular sieves. Mercury(II) nitrate, magnesium(II) nitrate, calcium chloride, zinc sulfate, silver nitrate, iron(II) chloride, and copper(II) chloride metal salts (Aldrich) were all used as received. The syntheses of polyphosphazene polymers 1 and 2 were described previously.^{20–23} The syntheses of the monomers for polymers 3²⁴ and 6²⁵ have also been reported. Azobisisobutyronitrile (AIBN, Polysciences Inc.) and ethylene glycol dimethacrylate (Aldrich) were used as received. Tetrahydrofuran (THF) was distilled under an atmosphere of dry argon from a sodium benzophenone ketyl drying agent. Hydrochloric acid (12.4 M, VWR), sulfuric acid (18.0 M, VWR), nitric acid (9.0 M, VWR), and phosphoric acid (6.9 M, VWR), Alcon sterile saline solution (pH 7 with a borate buffer), zirconyl chloride (Aldrich), sodium hydroxide (Aldrich), sodium carbonate (Aldrich), sodium bicarbonate (Aldrich), potassium hydroxide (Aldrich), and sodium chloride (Aldrich), were all used as received.

Analytical Equipment and Techniques. ¹H and ³¹P NMR spectra were recorded with the use of a Bruker WM-360 spectrometer operated at 360 and 145.8 MHz, respectively. For ³¹P NMR spectra, positive chemical shifts are downfield from that of external phosphoric acid. For ¹H NMR spectroscopy, chemical shifts were recorded relative to tetramethylsilane at 0 ppm. Solid-state ¹³C NMR spectra were obtained with the use of a CMX solid-state NMR spectrometer operated at 75 and 121 MHz, respectively. ³¹P NMR spectra of some of the MEEP hydrolysis studies were recorded with the use of a JEOL FX-90Q spectrometer operated at 90 MHz. Glass transition temperatures (T_g) were measured with the use of a Perkin-Elmer DSC-7 unit equipped with a PE 7500 computer. The samples (10–30 mg) were analyzed in crimped aluminum pans: heating rates of 10, 20, and 40 °C/min and a helium flow of 10 mL/min were used. The instrument was calibrated with a cyclohexane standard with thermal transitions at –87.06 and +6.54 °C. Infrared spectra were recorded on a Perkin-Elmer 1710 infrared Fourier transform spectrometer. The FT-IR samples were prepared by casting films of the materials on salt plates. GPC data were obtained using a Hewlett-Packard 1090 liquid chromatograph system with a 1037A refractive index detector using THF/(*n*-butyl)₄N⁺Br[–] at a flow rate of 1 mL/min. Transmission electron micrographs (TEMs) were obtained using a JEOL 1200 EXII TEM unit,

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with a power setting of 80 kV and an exposure time of 1 s. The magnification for all TEM photographs was 12076 \times . TEM samples were prepared using an LKB Ultratome III microtome. X-ray microanalyses were obtained using a PGT IMIX Version 6 system attached to either a JEOL JSM 5400 scanning electron micrograph or a JEOL 1200 EXII TEM. SEM X-ray microanalysis samples were prepared by mounting the sample on carbon stubs and sputter coating them with carbon using a Fisons Polaron PS-2 sputter-coater. TEM samples were prepared using a LKB Ultratome III-8800 microtome. Polymers **1** and **2** were cross-linked by exposure to ^{60}Co γ -radiation at the Breazeale Nuclear Reactor at The Pennsylvania State University.

Preparation of Polyphosphazene/Organic Polymer IPNs. All the IPNs in this work were prepared by the method illustrated in the following example. Polymer **1** (0.2 g), which had been cross-linked by exposure to 3 megarad ^{60}Co γ -radiation, was placed in a solution containing 10 mL of vinylsulfonic acid sodium salt (25 wt % in water), 0.05 g of AIBN initiator, and 0.2 mL of ethylene glycol dimethacrylate cross-linker. Polymer **1** was allowed to imbibe the aqueous solution for 48 h or until the volume of the swollen polyphosphazene had increased to 10 times its original value. At this time, the reaction mixture was heated to 80 $^{\circ}\text{C}$ for 12 h. After cooling, the IPN was removed from the reaction mixture and was repeatedly extracted with water (THF for polymer **2**) for 24 h to remove unpolymerized monomer and un-cross-linked organic polymer. Following purification, the IPN was dried rigorously under vacuum and was characterized using ^1H and ^{31}P solution NMR or ^{13}C solid-state NMR spectroscopy, DSC and TEM, and X-ray microanalysis. IPNs prepared from polyphosphazene **2** utilized THF as the solvent.

Preparation of Ion-Coordinated IPNs. IPN bulk samples (0.1 g) were placed in either aqueous or THF solvent solutions of metal salts (approximately 0.1 N) depending on the hydrogel or organogel character of the IPN. The metal salts included mercury(II) nitrate, magnesium(II) nitrate, calcium chloride, zinc sulfate, silver nitrate, iron(II) chloride, and copper(II) chloride. Although it was shown that the fully water- or THF-swollen gels absorbed almost all of their maximum capacity of cations within 1 h of exposure to the metal salt solutions, the IPNs were maintained in contact with the solutions for approximately 340 h to ensure maximum swelling and complete equilibration of each system to the metal salt solutions. The swollen IPNs were then washed and soaked in water or THF for 72 h to remove any metal ions from the surface or uncomplexed ions from the bulk of the material. The samples were then dried in vacuo and were analyzed by TEM and X-ray microanalysis. Control samples that contained only the cross-linked phosphazene polymers were also exposed to the metal salts and then extracted by repeated swelling and washing in water or THF in order to remove loosely adsorbed metal ions. This was done to determine if the phosphazene polymers could complex the metal in the absence of the organic polymers.

Results and Discussion

Ligand Complexation. Several factors influence the ability of a ligand to selectively bind one metal rather than another. These factors include the nature of the ligand, the electronic character of the metal, i.e., its "hardness" or "softness", and the σ - and π -bonding character of the metal.^{26–28} In theory, the basic nitrogen atoms of the phosphazene backbone could be considered weak π -acid ligands and could complex with certain

π -acid metals.^{29,30} The oxygen atoms of the polyphosphazene side groups might also function as ligands.²¹ The ligands deliberately introduced via the organic backbone polymers, $-\text{COO}^-$, $-\text{SO}_3^-$, $-\text{[(CH}_2\text{)}_9\text{O]}_2\text{PO}_2^-$, and $-\text{CH}_2\text{N(CH}_2\text{COO}^-)_2$, generally fall into the category of electron-rich, weak-to-medium strength π -acids which are strong σ donors.

Synthesis of IPNs. As discussed in the Experimental Section, the IPNs were prepared by allowing a radiation cross-linked polyphosphazene matrix to imbibe and swell in a solution mixture of a vinyl monomer, an initiator, and a cross-linking agent. Once the matrix was swollen, the monomer was polymerized within the cross-linked polymer matrix either thermally or by exposure to ^{60}Co γ -radiation.

The phosphazene polymers used in this project, poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP, **1**) and poly[bis(propoxybenzoate)phosphazene] (**2**) were cross-linked by exposure to ^{60}Co γ -radiation to yield materials which swell in but do not dissolve in aqueous or organic media.^{18,19} Radiation cross-linking in these polymers involves homolytic cleavage of aliphatic carbon-hydrogen bonds and cross-combination of the resultant carbon-free radicals. Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP, **1**), with 22 C-H bonds per repeating unit, is particularly sensitive to radiation-induced cross-linking. Poly[bis(propoxybenzoate)phosphazene] (POBP, **2**) has 14 aliphatic C-H groups per repeating unit, which provide the sites for radiation-induced cross-linking.

The four organic polymers used in this study provide a vehicle for the introduction of specific coordination ligands. Poly[bis(undecenyl phosphate)] (**3**) contains a phosphoric acid ester functionality that is specific for complexation to Hg, Ag, Mn, Co, Ba, and Cu ions as well as lanthanide and actinide metal ions. Poly(vinylsulfonic acid sodium salt) (**4**) is similar to the well-known poly[(*p*-sulfoxylato)styrene] which is specific for Mg, Zn, Hg, Ag, Mn, Co, and Ba ions. Poly(acrylic acid) (**5**) bears some resemblance to poly[(*p*-carboxylato)styrene] which is specific for Li and Zn ions. Finally, poly(*N*-(*p*-vinylbenzyliminodiacetic acid)) (**6**) favors the complexation of Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Mo, Ag, Cd, In, W, Re, Pb, Bi, Th, and rare-earth metal ions.

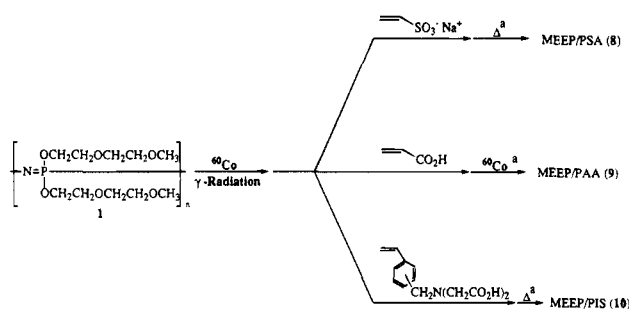
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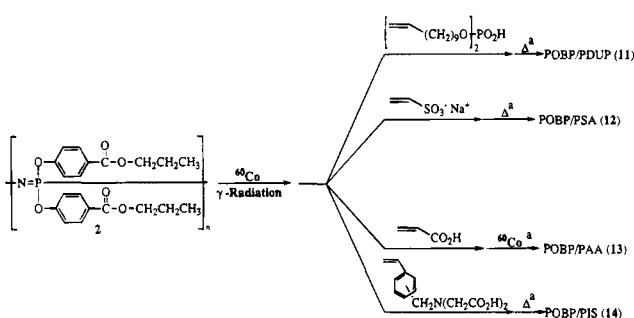
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Scheme 1^a

^a All samples were polymerized using AIBN initiator and ethylene glycol dimethacrylate cross-linker.

Scheme 2^a

^a All samples were polymerized using AIBN initiator and ethylene glycol dimethacrylate cross-linker.

Thus, the organic backbone polymers chosen provide a range of selectivities for different metal ions that forms a starting point for the development of this system. The structures of the component polymers and their ionic specificities are summarized in Chart 1.

Schemes 1 and 2 illustrate the synthetic routes used to prepare the IPNs. Poly(organophosphazene) polymers 1 and 2 were each exposed to 3 Mrad of ⁶⁰Co γ -radiation to cross-link the polymers before IPN preparation. In all examples, AIBN was used as the polymerization initiator for the coordinative monomer, and ethylene glycol dimethacrylate was employed as the cross-linking agent. The presence of two vinyl groups in bis(undecenyl phosphate) provided a second intrinsic route for cross-linking. Bis(undecenyl phosphate), vinylsulfonic acid sodium salt, and *N*-(*p*-vinylbenzyliminodiacetic acid) were polymerized thermally while acrylic acid was polymerized by exposure to additional ⁶⁰Co γ -radiation. Bis(undecenyl phosphate) and *N*-(*p*-vinylbenzyliminodiacetic acid) were polymerized in a toluene medium. Control studies were performed to determine the overall effect and contribution of the initiator and/or cross-linking agent to the overall IPN synthesis.

Of the eight IPN permutations, the only system that proved to be unsuitable for coordination studies was that prepared from MEEP (1) and poly[bis(undecenyl phosphate)] (3), because the phosphoric acid monomer reacted with the cross-linked MEEP. The phosphazene hydrogel de-cross-linked and/or degraded when the monomer-swollen, cross-linked matrix was heated, irradiated with ⁶⁰Co γ -radiation, or simply exposed to the monomer for more than 48 h. As will be discussed, MEEP is sensitive to strong mineral acids, and it is assumed that phosphorus-oxygen bond cleavage occurs in this system.

Table 1. ¹H and ¹³C NMR Data^a

IPN	δ ppm
1/4	3.4, 3.5, 3.6, 4.0 (OCH ₂ of 1)
	1.9 (CH ₂ of 4), 3.2 (CH of 4)
1/5 ^b	66.0, 68.5, 71.2 (OCH ₂ of 1)
	26.2 (CH of 5), 179.0 (CO ₂ of 5)
1/6	3.4, 3.5, 3.6, 4.0 (OCH ₂ of 1)
	1.2 (CH ₂ CH of 6), 2.8 (CH ₂ CH of 6)
	7.2 (Ph of 6), 3.0 (PhCH ₂ N of 6)
	3.2 (NCH ₂ CO ₂ of 6)
2/3	0.9 (CH ₃ of 2), 1.3 (CH ₂ of 2)
	4.1 (CO ₂ CH ₂ of 2), 6.6, 7.4 (Ph of 2)
	1.2 (CH ₂ -CH of 3 (polymerized branch))
	5.0 (CH ₂ =CH of 3 (unpolymerized branch))
	1.5 (CH ₂ -CH of 3 (polymerized branch))
	5.8 (CH ₂ =CH of 3 (unpolymerized branch))
2/4	1.7, 2.0 (CH ₂ 's of 3), 4.1 (CH ₂ O of 3)
	0.9 (CH ₃ of 2), 1.7 (CH ₂ of 2)
	4.1 (CH ₂ of 2), 6.6, 7.4 (Ph of 2)
	1.9 (CH ₂ of 4), 3.4 (CH of 4)
	115.3, 122.5, 129.4, 159 (Ph of 2)
	170.0 (CO ₂ of 2), 67.0 CO ₂ CH ₂ of 2
2/5 ^b	22.3 (CH ₂ of 2), 21.0 (CH ₃ of 2)
	10.0 (CH ₂ of 5), 40.0 (CH of 5)
	181.0 (CO ₂ of 5)
	0.9 (CH ₃ of 2), 1.7 (CH ₂ of 2)
	4.1 (CO ₂ CH ₂ of 2), 6.6, 7.4 (Ph of 2)
	1.2 (CH ₂ CH of 6), 2.6 (CH ₂ CH of 6)
2/6	7.2 (Ph of 6), 3.3 (PhCH ₂ N of 6)
	3.6 (NCH ₂ CO ₂ of 6)

^a All ¹H NMR samples were studied as swollen gels in CDCl₃.
^b Samples containing polymer 5 were more easily characterized by solid-state ¹³C NMR due to difficulties in swelling the samples in CDCl₃.

Table 2. IPN Component Ratios^a

MEEP/PSA (1/4)	14:1	POBP/PSA (2/4)	3.6:1
MEEP/PAA (1/5)	1:1	POBP/PAA (2/5)	2:1
MEEP/PIS (1/6)	7.6:1	POBP/PIS (2/6)	7:1
POBP/DUP (2/3)	2.5:1		

^a Based on ¹H NMR integration.

Characterization. The IPNs were characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM).

NMR characterization data for the IPNs are shown in Table 1. These data confirmed the presence of both polymeric components and provided a means for estimating the polymer component ratios. ¹H NMR characterization was accomplished by examination of the spectra of IPN gels swollen by CDCl₃. IPNs that contained polymer 5 did not swell appreciably in CDCl₃; therefore NMR characterization was accomplished using ¹H analysis for a sample that was lightly swollen by CDCl₃ or by solid-state ¹³C NMR spectroscopy. Table 2 summarizes the ratios of the components in each of the IPN systems, as determined by ¹H NMR spectroscopy.

DSC analysis was used as an initial probe of the compatibility between the two polymers in each IPN and, by inference, the degree to which the component polymers formed an evenly dispersed network in the hydro- or organogels. A miscible IPN generates only one glass transition (*T_g*) detectable in the DSC spectrum, located between the values of the component polymer *T_g*'s. In a semi-miscible IPN, either two *T_g*'s are detected, displaced toward the center of the spectrum from the values of the parent polymers, or three transitions are found, with two displaced toward the center of the spectrum and one *T_g* lying between the

Table 3. Glass Transition Temperature (DSC) Data

IPN	T_g (°C)	IPN	T_g (°C)
1/4	-79/-1/+32/+58	2/4	-12/+1/+31/+76
1/5	-41/+3.5	2/5	-15/+54
1/6	-75	2/6	+11
2/3	-15/+15/45		

^a "Parent polymer" T_g 's: **1** = -84 °C; **2** = -23 °C; **3** = +5.3 °C; peak at +33 °C; **4** = -1, +32, 58 °C; **5** = 106 °C; **6** = +112 °C.

values of the component polymers. This third transition indicates the existence of regions of significant compatibility between the two component materials. In a totally immiscible material, two T_g 's may be found at the T_g values of the component polymers. None of these IPNs were completely miscible. The DSC analyses indicated that IPNs composed of **1/5**, **2/5**, and **2/6** were semimiscible mixtures (with T_g displacements of 40/100, 10/50, and 35 °C for component **2** in **2/6**, respectively). IPNs composed of **1/4** and **2/4** were found to be immiscible by DSC. IPNs **2/3** and **1/6** were on the verge of being immiscible, with T_g displacements of only 10/10 °C for polymers **2** and **3** and 9 °C or less for polymer **1**. The DSC characterization data are shown in Table 3.

Electron microscopy is probably the most effective way to identify domain structures in an IPN system. IPNs that appear to be miscible by DSC analysis may possess a definite domain structure that can be detected by TEM analysis. Several of the uncomplexed IPNs (**1/6**, **2/6**, **1/5**, **2/5**, and **2/3**) were studied by TEM in order to provide data for comparison with the complexed analogs. Species **1/4** and **2/4** could not be studied by TEM in the uncomplexed state because of experimental difficulties with sample preparation due to the softness of the materials. An example TEM photograph of **2/3** is shown in Figure 1a, which illustrates the rather featureless domain structure before complexation. A comparison of this photograph with those obtained after metal complexation (Figure 1b) illustrates the enhanced contrast and visualization of domain structure that can be obtained by metal coordination.

Metal Ion Absorption Experiments. (a) *IPNs Based on MEEP (1).* MEEP was used as the comacromolecule in specific IPNs to ensure that these systems would function as extensively swollen hydrogels which would expose the incoming metal ions to the maximum number of coordination sites. Control experiments were performed initially in which samples of cross-linked **1** (with no comacromolecule in the network) were exposed to aqueous solutions of mercury(II) nitrate, magnesium(II) nitrate, calcium chloride, zinc sulfate, silver nitrate, iron(II) chloride, and copper(II) chloride for 340 h to ensure complete swelling of the network and maximum exposure to the salts. The complexes were then extracted by repeated washings, soaking, and swelling with water over 72 h. These studies were carried out to determine if the MEEP component of the IPNs complexed metal ions independently. These materials were analyzed by X-ray microanalysis. Polymer **1** complexed traces of iron but did not retain Hg^{2+} , Mg^{2+} , Ca^{2+} , Zn^{2+} , Ag^+ , or Cu^{2+} . This result was taken as tentative evidence that the MEEP matrix would not interfere with cation coordination at the organic polymer active sites.

The MEEP-containing IPNs were then immersed in solutions of the same metal ions to determine their

coordination properties. During this time, the migration of colored cations into the hydrogel could be followed visually (green for Fe^{2+} , blue-green for Cu^{2+} , and red for Ag^+). The IPN adducts were then washed and soaked in water for 72 h to remove uncoordinated metal ions. The materials were dried in vacuo, and the samples were sectioned to determine if the color was concentrated only at the surface or was uniform throughout the material. In all cases, the color changes were uniform throughout the solid. In some cases, changes also occurred in the physical properties of the material. For example, IPN **1/4** became markedly less flexible after complexation.

Exposure of the IPN adducts to solutions of aqueous sodium chloride or sodium hydroxide for 340 h provided an evaluation of the ease of replacement of the metal ions by sodium ions.³¹ The metallosulfonic acid IPNs were treated with 2 M NaCl, the carboxylic acid IPNs with 1 M NaCl, the methylimidodiacetic acid IPNs with 1 M NaOH, and the phosphoric acid IPNs with 2 M NaCl. The metal ion complexed IPNs were also exposed to pure water for 340 h to determine if the complexed ions could be removed by prolonged extraction.

(b) *IPNs Based on Polymer 2.* The use of polymer **2** as a component of the IPNs was based on the idea that a hydrophobic or amphiphilic comacromolecule would allow metal ion complexing from organic media. For example, the presence of **2** in an IPN would convert an essentially water-soluble or hydrophilic polyelectrolyte system into one that would swell in organic solvents and function as an organogel. The complexation experiments were carried out with the same salts as used in the MEEP systems but with THF employed as the solvent for ingress of the ions and washing of the complexes and as the ion extraction medium. All the conditions and concentrations were the same as for the MEEP-based systems.

First, it was found that cross-linked **2**, in the absence of another polymer, bound silver ions very strongly, and that the silver ions could not be extracted after repeated washings with THF. Second, complexation took place between the IPNs based on **2** and cations specific to the organic polymer component. As in the case of the MEEP-based IPNs, metal coordination resulted in a marked decrease in the flexibility of the materials. For example, IPNs **2/4**, **1/5**, and **2/5** were flexible or elastomeric before exposure to the metal ion solutions but were less flexible after complexation and solvent removal.

Characterization of the Metal-Complexed IPNs. The solvent-free, metal-complexed IPNs and the non-complexed control samples were examined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with the details of the TEM and SEM micrographs being probed by X-ray microanalysis. A phosphazene polymer, with its P=N backbone, appears darker in TEM micrographs than a totally organic polymer (this can sometimes eliminate the need to stain

(31) Sodium salts, normally sodium chloride or sodium hydroxide of varying strengths, are used to regenerate commercially available ion exchange media that possess different acidic functionalities by replacing the complexed metal ions with sodium ions.

(32) Allcock, H. R.; Pucher, S. R. *Macromolecules* **1992**, *25*, 5573.

(33) (a) Bailey, F. E.; Callard, R. W. *J. Appl. Polym. Sci.* **1959**, *1*, 56. (b) Saito, S. *J. Polym. Sci. A* **1969**, *7*, 1789. (c) Schick, M. J.; Atlas, S. M.; Eirich, F. R. *J. Phys. Chem.* **1962**, *66*, 1326.

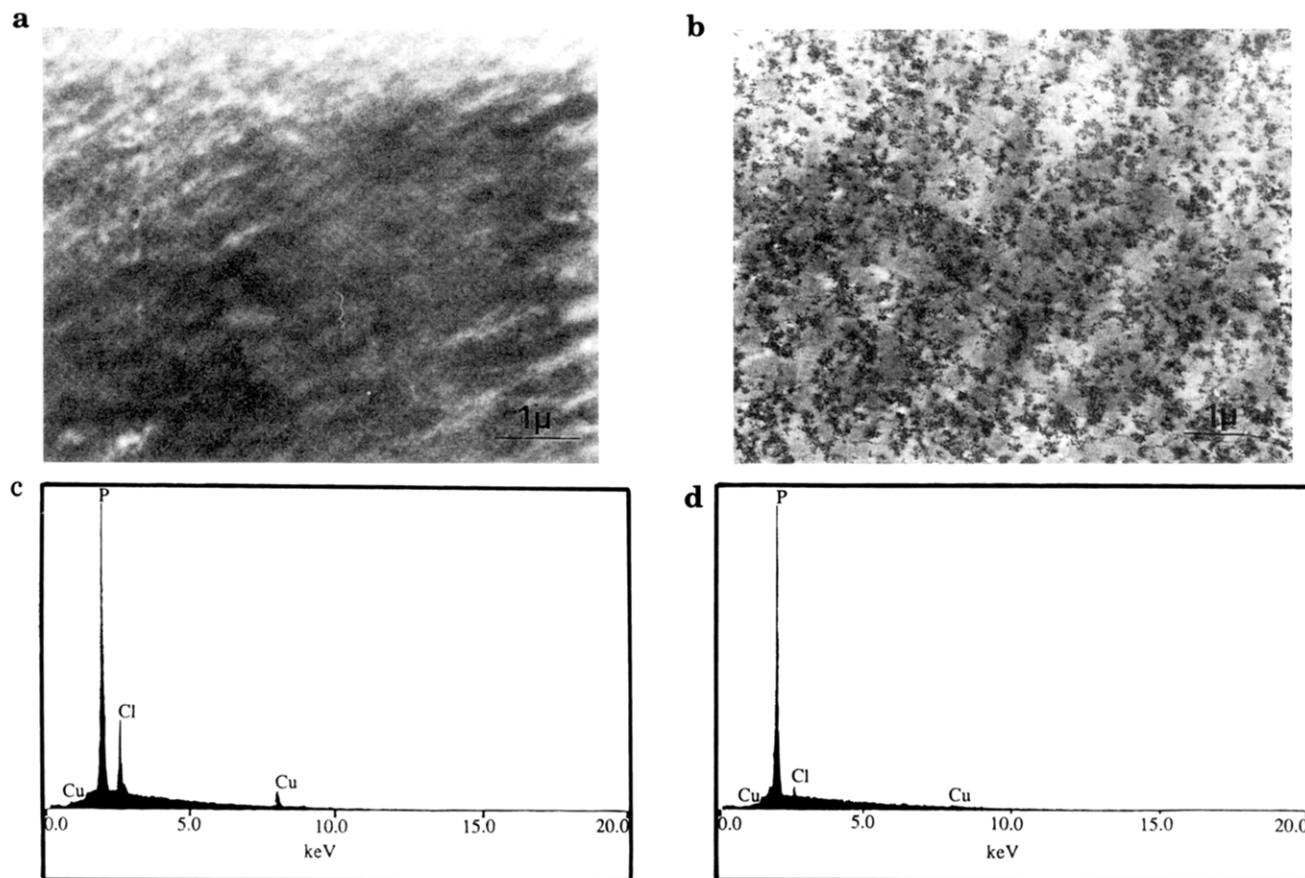


Figure 1. (a) Transmission electron micrograph of IPN **2/3** before metal complexation. (b) Transmission electron micrograph of **2/3** after complexation with copper. (c) X-ray microanalysis of **2/3**/Cu complexed IPN. (d) X-ray microanalysis of **2/3**/Cu complexed IPN after extended exposure to aqueous NaCl.

the samples to determine the domain structure). However, domains with complexed metal ions should appear even darker than the phosphazene polymer, and it was of interest to explore the effect of complexation on the visualization of the domain structure. The identification of the different regions was accomplished by TEM X-ray microanalysis of the domains in each metal-complexed IPN and by comparison with the corresponding uncomplexed IPNs and the species formed by displacement of the metal ions by treatment with aqueous sodium ion. The level of complexation of metals was estimated qualitatively by SEM X-ray microanalysis of the metal ion peaks in the bulk materials. This method did not provide a reproducible quantitative analysis, but it did give a clear indication of relative levels of metal ions in the different domains, including the presence of sodium ions following treatment with NaCl or NaOH.

The results are shown in Table 4. On the basis of the dimensions of the SEM X-ray microanalysis peaks, the strongest metal complexation was detected for the systems **1/4** with Hg and Ag; for **1/5** with Mg, Zn, and Ca; and for **1/6** with Zn, Ag, Fe, and Cu. Weaker complexation was seen for the systems **1/4** with Mg and Zn. Within the series based on polymer **2**, strong complexation was detected only for the **2/3**/Ag and **2/4**/Mg systems and for **2/6** with the Fe system. Weaker complexation was detected for systems composed of **2/3**/Hg and Cu, **2/4** with Zn, **2/5**/Mg and Zn, and **2/6** with Zn, Ag, and Cu. Release of the complexed ions was achieved by treatment of most of the IPN metal complexes with sodium ions, but specific examples were found where the complexation of the transition metal

ions could not be reversed by exchange with sodium ions under mild conditions (**1/6**/Ag, Fe, Cu; **2/3**/Cu; **2/4**/Ag; **2/5**/Mg; **2/6**/Ag, Fe, Cu). Solvent extraction of the complexed metals by treatment of the IPNs with water or THF occurred in a few cases (see Table 4). It should be noted that removal of the metal ions by treatment with acids was precluded for the IPNs that contained MEEP since, as will be discussed, that polymer undergoes degradation under strongly acidic conditions.

Complexation as a Means for Domain Visualization. The following description provides specific information about the way the materials structure of the metal-IPNs was established. Several uncomplexed IPNs, including **1/6**, **2/6**, and **2/3**, were characterized by TEM as controls. It should be noted that species **2/3** contains phosphorus atoms in both component polymers. Hence, the domain contrast in this system was insufficient to allow a visualization of the internal phase structure. The IPNs containing **1/4**/Ag, **1/6**/Cu, **1/6**/Ag, **1/6**/Zn, **2/3**/Cu, and **2/4**/Hg were also analyzed by TEM. All the TEM micrographs of the metal derivatives showed regions of complexation of the metal ions within the IPN. Figure **1a** shows a TEM representation of IPN **2/3** before reaction with a metal salt. In comparison (Figure **1b**) the bright green system formed between IPN **2/3** and copper ion clearly revealed granules or clusters attributed to copper ions dispersed throughout the material. This copper complexation was confirmed by X-ray microanalysis. Figure **1c** summarizes the SEM X-ray microanalysis of the bulk **2/3**/Cu sample, and the presence of copper was clearly detected. Further X-ray microanalysis studies were undertaken using the TEM

Table 4. Metal Ion Complexation Data from X-ray Microanalysis Data

IPN	metal ion complexation	sodium ion replacement	solvent-induced replacement
1/4-			
Mg	<i>b</i>	<i>c</i>	<i>f</i>
Zn	<i>b</i>	<i>c</i>	<i>g</i>
Hg	<i>a</i>	<i>c</i>	<i>f</i>
Ag	<i>a</i>	<i>c</i>	<i>g</i>
1/5-			
Mg	<i>a</i>	<i>c</i>	<i>g</i>
Zn	<i>a</i>	<i>c</i>	<i>g</i>
Ca	<i>a</i>	<i>c</i>	<i>g</i>
1/6-			
Zn	<i>a</i>	<i>c</i>	<i>f</i>
Ag	<i>a</i>	<i>d</i>	<i>g</i>
Fe	<i>a</i>	<i>d, h</i>	<i>g</i>
Cu	<i>a</i>	<i>d</i>	<i>g</i>
2/3-			
Hg	<i>b</i>	<i>c</i>	<i>f</i>
Ag	<i>a</i>	<i>c</i>	<i>g</i>
Cu	<i>b</i>	<i>d</i>	<i>f</i>
2/4-			
Mg	<i>a</i>	<i>c</i>	<i>f</i>
Zn	<i>b</i>	<i>c</i>	<i>g</i>
Hg	<i>a</i>	<i>c</i>	<i>f</i>
Ag	<i>a</i>	<i>d</i>	<i>g</i>
2/5-			
Mg	<i>b</i>	<i>d</i>	<i>g</i>
Zn	<i>b</i>	<i>c</i>	<i>g</i>
2/6-			
Zn	<i>b</i>	<i>c</i>	<i>f</i>
Ag	<i>b</i>	<i>d</i>	<i>g</i>
Fe	<i>a</i>	<i>d</i>	<i>g</i>
Cu	<i>b</i>	<i>d</i>	<i>g</i>

^a Strongest complexation. ^b Weak complexation. ^c Complete replacement by sodium ion. ^d Partial sodium ion replacement. ^e Complete loss of metals after exposure to solvent. ^f Partial loss of metal ions after exposure to solvent. ^g No loss of metal ions after solvent exposure. ^h Decomposition of polyphosphazene.

in which the metal-rich domains were compared to the metal-poor regions. TEM X-ray microanalysis showed a definite lack of copper in the "lighter" areas. Figure 1d shows the X-ray microanalysis of the material after exposure to NaCl. It is evident that most of the copper had been displaced by the sodium ions.

Figure 2a shows a TEM micrograph for 2/4 after complexation with mercury. The mercury-rich regions appear as dark spots evenly dispersed throughout the material. The presence of the mercury was confirmed by the data in Figure 2b which shows the results of an SEM X-ray microanalysis of the 2/4/Hg bulk material after metal complexation. The dark spots in the TEM micrograph were further probed by TEM X-ray microanalysis and compared to lighter areas in the micrograph. This confirmed the presence of mercury in the dark regions and a lack of mercury in the light areas of the TEM micrograph. The displacement of mercury ions is evident in Figure 2c, which illustrates the X-ray microanalysis of the same system after extended exposure to aqueous NaCl. The data indicated a lack of mercury and the presence of sodium. Thus, the coordination of mercury to this IPN is reversible.

The extensive complexation of silver ions in the 1/4 IPN is clearly visible in Figure 3a. The regions rich in silver ions are evident from the dark patches throughout the material. We are currently exploring the nature of this metal clustering. This material has a deep rust red color which extends through the entire sample. Figure 3b is an SEM X-ray microanalysis of the bulk 1/4/Ag system which demonstrates the presence of silver ions

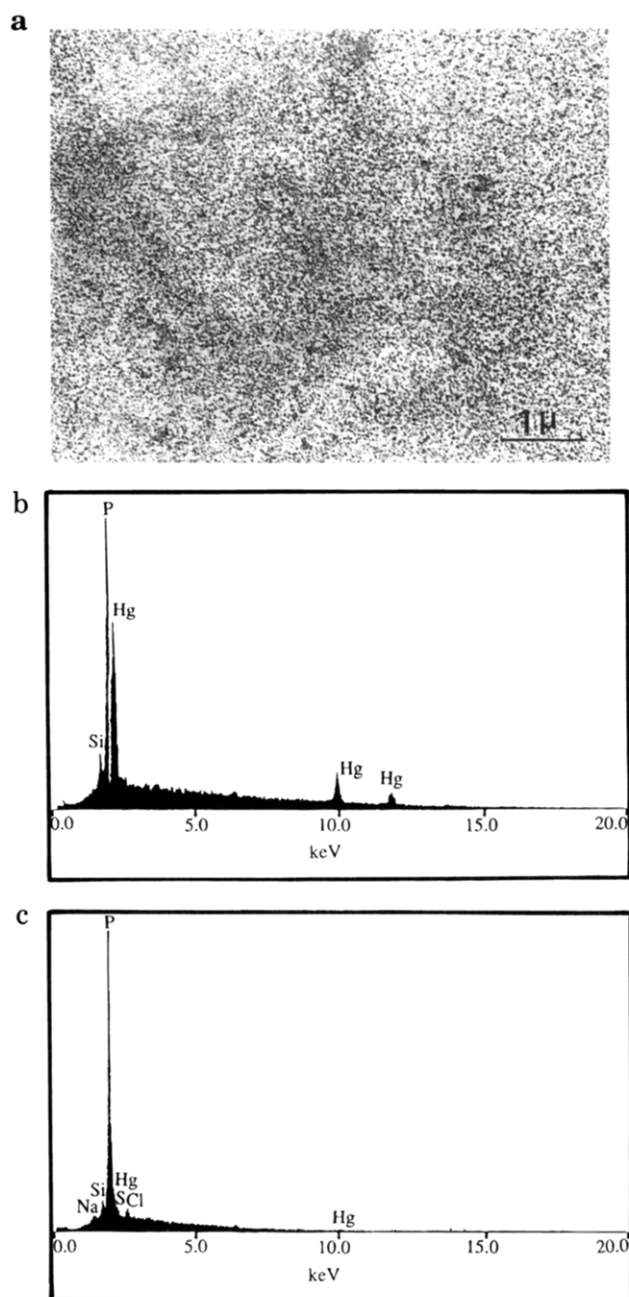


Figure 2. (a) Transmission electron micrograph of IPN 2/4 after complexation with mercury. (b) X-ray microanalysis of 2/4/Hg complexed IPN. (c) X-ray microanalysis of 2/4/Hg complexed IPN after extended exposure to aqueous NaCl.

in the material. The dark patches evident throughout the TEM micrograph were further characterized by TEM X-ray microanalysis which indicated the presence of silver in the dark regions and the absence of silver in the light areas of the micrograph. Figure 3c shows the disappearance of these silver ions when the IPN was treated with aqueous NaCl. Thus, this material can reversibly exchange silver ions.

Figure 4a shows a TEM micrograph for 1/6 after complexation with copper. This material has a brilliant blue color. The copper ions were detected as the dark spots throughout the TEM micrograph, and the presence of copper was confirmed in the bulk sample by SEM X-ray microanalysis shown in Figure 4b. The dark spots in the TEM micrograph were investigated using TEM X-ray microanalysis and compared to regions of the micrograph without dark spots. The dark areas

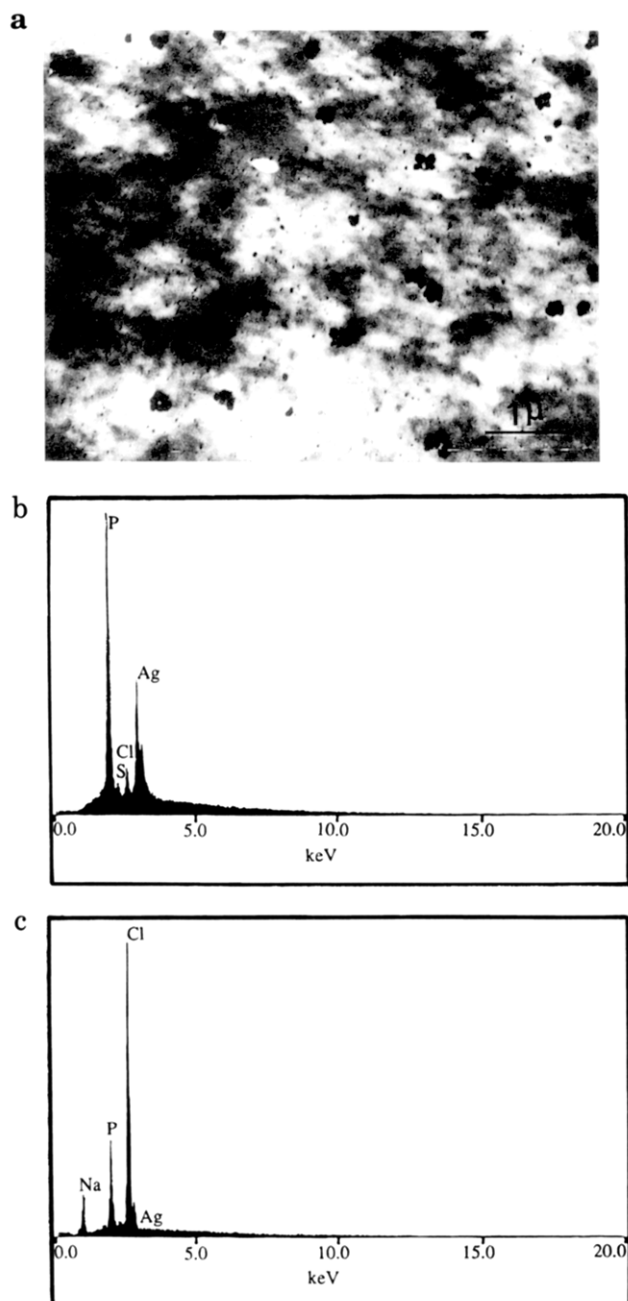


Figure 3. (a) Transmission electron micrograph of 1/4 IPN after complexation with silver. (b) X-ray microanalysis of 1/4/Ag complexed IPN. (c) X-ray microanalysis of 1/4/Ag complexed IPN after extended exposure to aqueous NaCl.

contained copper and the other regions contained no copper. This IPN is different from those described previously because it tends to retain the complexed copper ions even after extended exposure to NaOH solutions. This behavior is attributed to the presence of polymer **6**, which is a strong chelating material. Figure 4c shows an X-ray microanalysis of 1/6/Cu after extended exposure to NaOH solution. Peaks for both copper and sodium are evident, and little difference exists in the intensity of the copper peaks in Figure 4b, and c. In principle, strong acids might be used to remove the copper ions but, as stated previously, this could decompose the phosphazene polymer.

Figure 5a shows a TEM micrograph of the same 1/6 IPN after complexation with zinc ions. Again, the zinc-rich regions appear as extensive dark areas throughout the material. The presence of zinc was confirmed in the

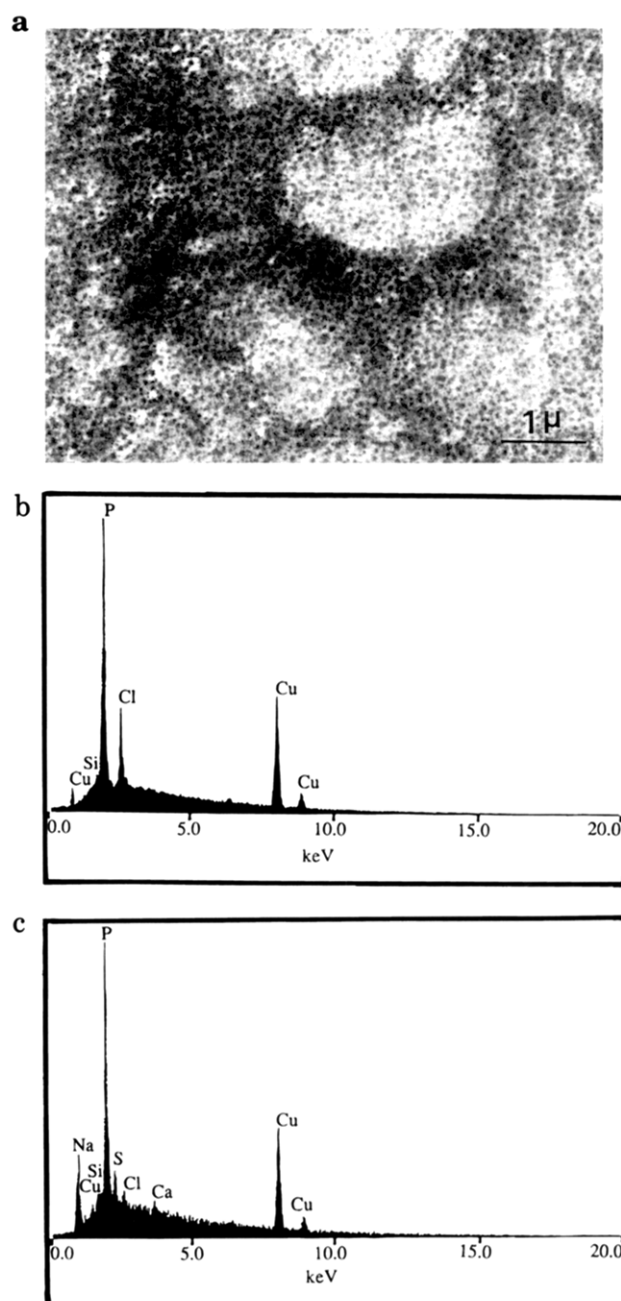


Figure 4. (a) Transmission electron micrograph of IPN 1/6 after complexation with copper. (b) X-ray microanalysis of 1/6/Cu complexed IPN. (c) X-ray microanalysis of 1/6/Cu complexed IPN after extended exposure to aqueous NaOH.

bulk material by the SEM X-ray microanalysis data shown in Figure 5b. The dark patches in the TEM micrograph were examined by TEM X-ray microanalysis and were compared to the light regions. The dark areas were found to contain zinc, whereas the light regions contained no zinc ions. Figure 5c shows the SEM X-ray microanalysis of the bulk 1/6/Zn sample after extended exposure to NaOH. The disappearance of the peaks corresponding to zinc suggests that the zinc ions are not bound as tightly as were the copper ions in the previous example and may be removed by exposure to Na ions. This difference in complexation could be due to the fact that copper is more electron deficient than zinc and better able to complex to this particular ligand.

A TEM micrograph of 1/6 after complexation with silver ions is shown in Figure 6a. This micrograph is

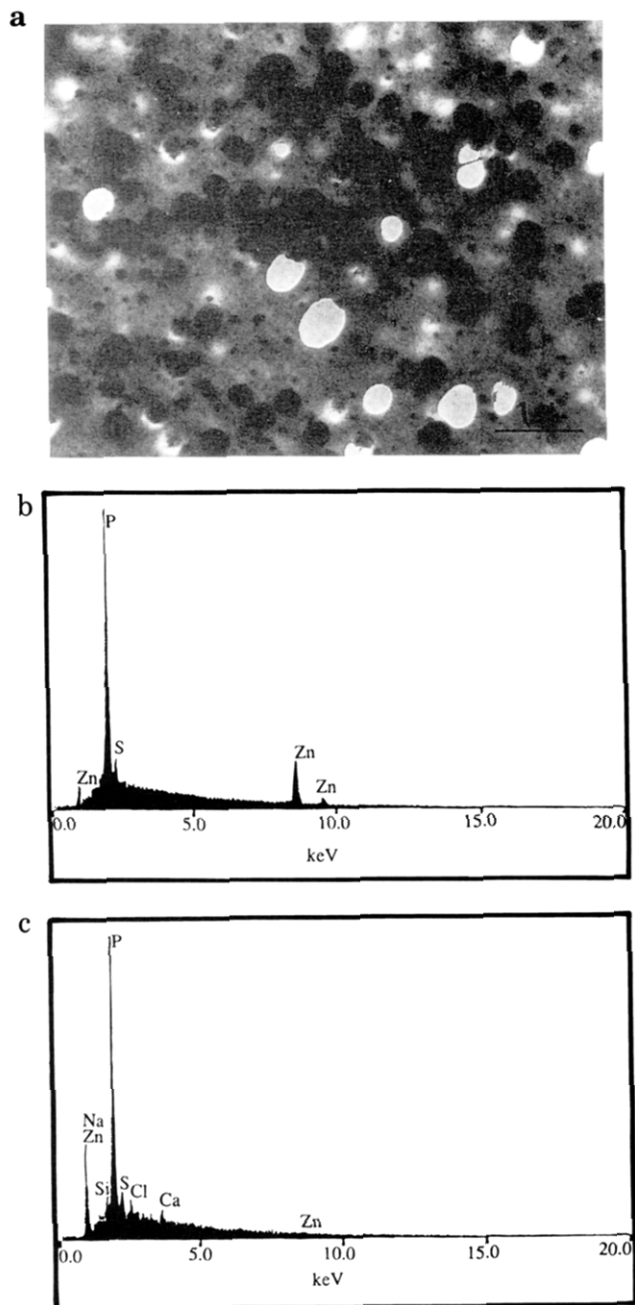


Figure 5. (a) Transmission electron micrograph of 1/6 IPN after complexation with zinc. The distinctive light-toned circular regions are from voids in the material. (b) X-ray microanalysis of 1/6/Zn complexed IPN. (c) X-ray microanalysis of 1/6/Zn complexed IPN after extended exposure to aqueous NaOH.

very similar to that in Figure 5a where both samples show the metal ions as dark spots throughout the IPN. The 1/6/Ag has a dark red/rust color. The presence of silver in the bulk material was confirmed by the SEM X-ray microanalysis data in Figure 6b, and the dark spots were shown by TEM X-ray microanalysis to contain silver ions, but no silver was detected in the light regions of the IPN. This IPN behaves similarly to the 1/6/Cu system in that the silver ions, like copper, are complexed very strongly to the organic polymer. The X-ray microanalysis data for 1/6/Ag after extended exposure to NaOH solution is shown in Figure 6c. The concentration of silver ions is similar in both Figures 6b and 6c, but the clustering of silver ions is more noticeable in Figure 6c.

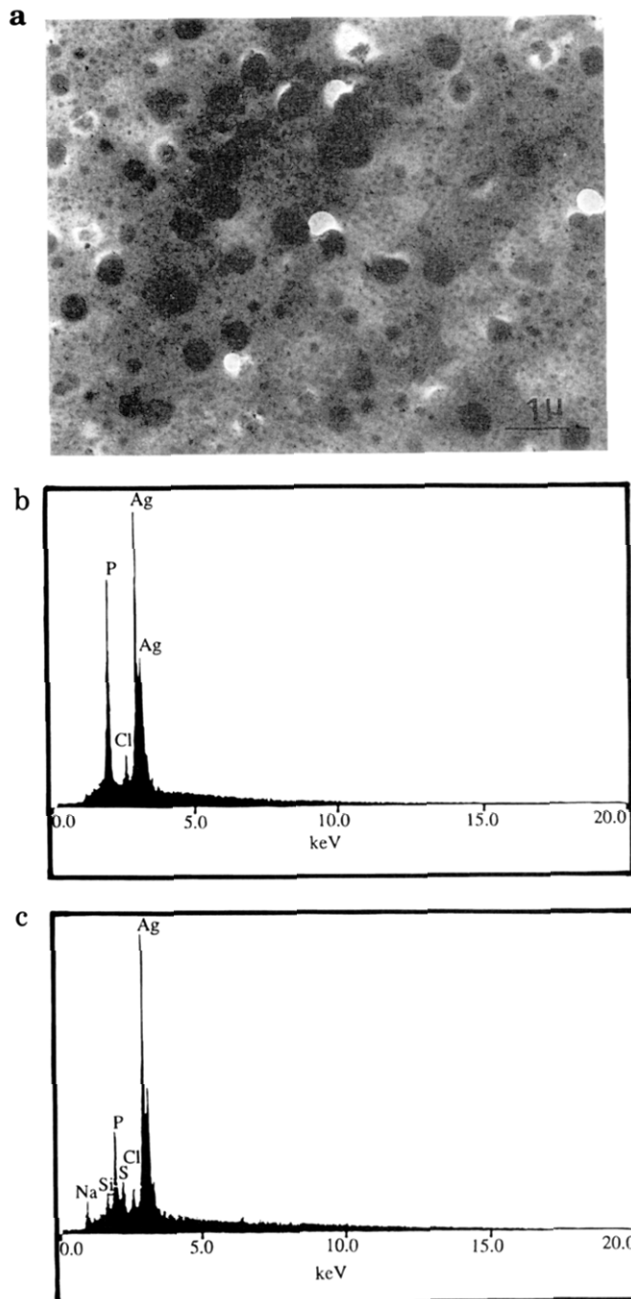


Figure 6. (a) Transmission electron micrograph of IPN 1/6 after complexation with silver. (b) X-ray microanalysis of 1/6/Ag complexed IPN. (c) X-ray microanalysis of 1/6/Ag complexed IPN after extended exposure to aqueous NaOH.

Stability of MEEP in Aqueous Media at Different pH Conditions. The instability of MEEP in the presence of monomer 3 raised questions about the behavior of this polymer in acidic media in general. For this reason, a series of experiments was undertaken to assess the long-term stability of this polymer in aqueous media over a broad pH range. It was found that MEEP is stable for long periods of time in contact with neutral or basic aqueous media, but undergoes slow hydrolysis under acidic conditions.

Stability of MEEP in near-neutral or basic aqueous media: First, it was found that MEEP is stable in borate buffered saline solution at pH 7.0 at room temperature and at 37 °C for long periods of time. No changes were detected by ^{31}P NMR spectroscopy over 8 weeks at either temperature. Second, the polymer is stable for years

in slightly acidic media at room temperature. For example, a sample of MEEP, which had been cross-linked by 7 Mrad of ^{60}Co γ -radiation (roughly 45 cross-links/15 000 repeat unit chain) and had been swollen to a hydrogel and stored in pH 6.5 water, retained its hydrogel properties without decomposition for 5 years. Only after this time did the material eventually dissolve in the aqueous medium, a process that appeared to be the consequence of hydrolysis. ^{31}P NMR spectra of the hydrolyzate contained a major peak at -7 ppm from the MEEP structure and a small peak at -3 ppm, which was attributed to phosphates generated by hydrolysis. FT-IR spectra contained the characteristic phosphazene stretching peaks as well as peaks attributed to amine functionalities (3500 and 1650 cm^{-1}) and ammonium ions (1950 cm^{-1}). The molecular weight of the starting material (before cross-linking) was estimated to be in the region of 1×10^6 , but GPC analysis showed that the hydrolyzed sample now had a molecular weight of approximately 4×10^4 . Increases in temperature from 37 to 90°C induced detectable hydrolysis within 10 days at pH 6.5 to give phosphates, that were identified by ^{31}P NMR spectroscopy and by the zirconyl chloride test.

The possibility was considered that the hydrolytic sensitivity of MEEP at pH 6.5 and 90°C was due to the presence of phosphorus-chlorine bonds that had not been replaced during the original polymer synthesis reaction. This is an exceedingly difficult explanation to disprove since there are an average of 30 000 side groups per macromolecule, and only a few unreacted chlorine atoms could in principle sensitize the system to reaction with water, replacement of chlorine by hydroxyl, and initiation of a hydrolytic breakdown of the macromolecule. These chlorine atoms might be detectable by elemental analysis of the polymer, but elemental analyses of the MEEP before hydrolysis showed only 0.046% chlorine in the material. It is unclear whether these chlorine atoms were due to unsubstituted sites on the polymer, salts trapped within the polymer, or merely the result of the error inherent in the analysis itself. Moreover, it is difficult to exclude the possibility that the room-temperature aqueous dialysis procedure used for purification of the MEEP before the hydrolysis experiments brought about hydrolysis of residual P-Cl bonds and thereby introduced hydroxyl side units that remained quiescent until the temperature was raised for the 90°C experiments.

The hydrolytic behavior of MEEP in bases was also studied. Samples of cross-linked and un-cross-linked MEEP were exposed to solutions of NaOH (up to 10 M), Na_2CO_3 (up to 3.5 M), and NaHCO_3 (up to 1.5 M). Un-cross-linked samples of MEEP dissolved in all concentrations of NaOH lower than 1.25 M (the MEEP was only partially soluble in 1.25 M NaOH). ^{31}P NMR spectroscopy indicated no decomposition of the polymer after a period of one month at 25°C . Similarly, no polymer decomposition was detected in solutions of the other two bases.

It should also be noted that un-cross-linked MEEP precipitates from solution in the presence of high concentrations of NaOH, KOH, NaCl, and CaCl_2 . Hydrogels derived from MEEP also shrink and extrude water under these circumstances. For example, aqueous solutions of MEEP, when titrated with aqueous solutions of these salts or bases, underwent polymer

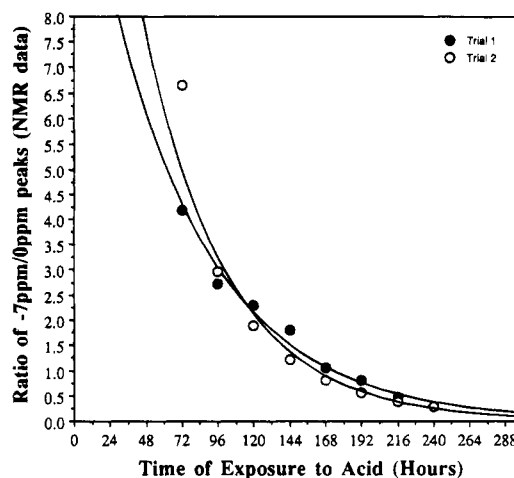


Figure 7. Hydrolysis of MEEP in 12.4 M aqueous hydrochloric acid as detected by the ratios of the ^{31}P NMR peaks for $\text{NP}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ units at -7 ppm to those for phosphate at 0 ppm. Each initial bulk sample of MEEP weighed approximately 0.1 g.

Table 5. Molecular Weights of MEEP after Exposure to Concentrated Acid

complex	un-cross-linked, 24 h	cross-linked, 72 h	cross-linked, 2 weeks
MEEP/HCl (12.0 M)	7.5×10^3	3.3×10^3	3.4×10^3
MEEP/ H_2SO_4 (18.0 M)	2.7×10^4	1.3×10^4	5.4×10^3
MEEP/ HNO_3 (9.0 M)	6.4×10^4	1.9×10^4	3.0×10^3
MEEP/ H_3PO_4 (6.9 M)	1.3×10^5	3.8×10^4	2.7×10^4

precipitation at concentrations of 1.0 M NaOH, 1.0 M KOH, 3 M NaCl, or 5 M CaCl_2 . This precipitation may reflect a competition by the ions for the water molecules in the polymer hydration sheath, in the same way as has been proposed for poly(ethylene oxide).³³ Whatever the explanation, it indicates that the degree of swelling of MEEP hydrogels and the IPN hydrogels can be controlled by the concentration of salts and bases in solution, and this clearly has implications for the use of these materials as ion-exchange species.

MEEP hydrolysis by exposure to strong acids: Cross-linked MEEP hydrogels dissolved in strong acids such as HCl ($\text{p}K_a = -7.7$), H_2SO_4 ($\text{p}K_a = -5.2$), HNO_3 ($\text{p}K_a = -1.4$), and H_3PO_4 ($\text{p}K_a = +2.2$) after 72 h. The solutions were brought to neutral pH and the products were analyzed by ^{31}P NMR, FT-IR, and GPC methods. ^{31}P NMR analysis showed new peaks at -3 and 0 ppm (phosphates) in addition to the MEEP peak at -7 ppm. Infrared spectroscopy showed peaks at 3500 and 1640 cm^{-1} and a characteristic ammonium ion peak at 1950 cm^{-1} . GPC analysis indicated a significant decrease in molecular weight, from 1×10^6 for the starting material, to approximately 1×10^4 for the hydrolyzed species. After 2 weeks of exposure to the strong acids at room temperature the un-cross-linked polymer molecular weight had decreased to approximately 5×10^3 . The relationship between ^{31}P NMR hydrolysis peaks for cross-linked MEEP and exposure time to 12.4 M HCl is shown in Figure 7. Samples of un-cross-linked MEEP were also exposed to strong acids for 24 h. GPC molecular weight data for both the cross-linked and un-cross-linked MEEP experiments are shown in Table 5.

The effect of different acid strengths on the hydrolysis was also investigated by exposure of MEEP to different concentrations of HCl ranging from 12.4 to 0.024 M for 24 and 48 h time periods. In all cases, the ^{31}P NMR

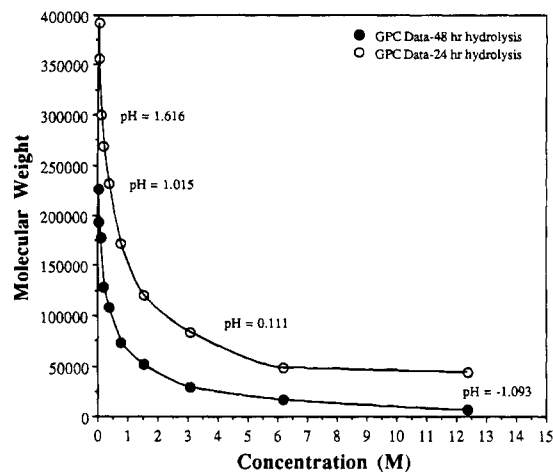


Figure 8. Molecular weight decline of MEEP after exposure to different concentrations of hydrochloric acid during 24 and 48 h at room temperature. The molecular weights were estimated by gel permeation chromatography.

spectra revealed the presence of hydrolysis product peaks at -3 and 0 ppm at high concentrations of acid, with the peaks increasing in height with increased reaction time. FT-IR analysis showed the normal phosphazene stretching bands as well as a possible NH stretch at 3500 cm^{-1} , an NH_2 stretch at 1640 cm^{-1} and the characteristic NH_4^+ stretch at 1950 cm^{-1} —all of which had been observed in the other hydrolysis experiments. GPC analysis showed an almost logarithmic molecular weight loss for the samples exposed to acid for both 24 and 48 h. These molecular weight data are depicted in Figure 8.

We speculate that the hydrolysis of MEEP under acidic conditions follows a pathway in which protonation of the backbone nitrogen atoms or cleavage of a P–O side group linkage generates a phosphazane structure (P(O)–NH–) which would be sensitive to hydrolytic cleavage.

Conclusions

Ion-complexing IPNs composed of poly(organophosphazenes) and organic polymers can function as ion-exchange materials and may be useful as cation removal matrices. The MEEP systems are probably more appropriate for use in aqueous ion-exchange devices because of the hydrophilic nature of the IPNs. The poly-[bis(propoxy benzoate–phosphazene)] systems worked well for cation removal from organic media.

The use of IPNs for metal complexation (rather than, for example, copolymers) has the advantage that the ratios of the component side groups can be varied easily by changes in the ratios of the two polymers without the introduction of block copolymer components and without regard to the reactivity ratios of two different monomers. The “contact volume” available for complexation within an IPN may also be modified by controlling the degree of cross-linking of the IPN component polymers. The advantage in the use of the polyphosphazenes in these systems is the way in which the hydrophilicity, hydrophobicity, and coordination properties of the matrix can be controlled by the choice of the appropriate side groups and their ratios. The radiation stability of the phosphazene backbone is an added advantage when radiation-induced cross-linking via organic side groups is employed.

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