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Polyphosphazene–Organic Polymer Interpenetrating Polymer Networks

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The synthesis of several new interpenetrating polymer networks composed of polyphosphazenes with organic polymers is reported. Full, sequential IPNs were prepared between poly[bis(methoxyethoxy)ethoxy)phosphazene] or poly[bis(propyloxy benzoate)phosphazene] and several organic polymers including polystyrene, poly(methyl methacrylate), poly(acrylic acid), and polyacrylonitrile. These materials were characterized by NMR and IR spectroscopy, differential scanning calorimetry, and transmission electron microscopy.

Introduction

Multicomponent polymer systems provide a method for the design and assembly of new materials either with hybrid characteristics or with entirely new properties derived from existing polymers.[1] The properties of the multicomponent system may be tailored by variations in the type of starting polymers and by the methods used to prepare the new materials.

Block and graft copolymers,[2] polymer blends,[3] and interpenetrating polymer networks[4] are well-known examples of multicomponent polymer systems. Each system is prepared using a different synthetic route and provides different materials properties. Interpenetrating polymer networks (IPN) are a unique class of multicomponent polymers in which the two component macromolecules are polymerized and cross-linked in close molecular proximity to each other. IPNs possess a cross-linked supramolecular structure, and their properties are often hybrids of those of their component materials. The interpenetrating cross-linked structure restricts molecular migration and eventual phase separation into domains of the separate polymers. In the present work, the synthesis and characterization of interpenetrating polymer networks composed of poly(organophosphazenes) and organic polymers is described. The objective was to combine the characteristics of both the organic and the organic/inorganic polymers into multicomponent polymer systems.

Poly(organophosphazenes) have a number of advantages for use in IPN materials, including the ease with which different types of side groups can be linked to the phosphazene macromolecular chain.[5] Poly(organophosphazenes) have been used for a variety of applications including non-burning, oil-resistant, low-temperature elastomers.[6] Patent reports have appeared of biomedical uses of polyphosphazene IPNs,[7] but to our knowledge, no systematic studies of such materials have been reported in the open literature. Such studies are important because they provide access to a wide range of new materials that combine the advantages of polyphosphazenes (materials flexibility, flame retardance, biomedical compatibility, many accessible molecular structures, coordination to ions, and, in some cases, water solubility) with the attributes of organic polymers (low cost, wide structural variation, and high glass transition temperatures).

In a preliminary communication,[8] the preparation and characterization of IPNs composed of poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP, 1)/polystyrene and MEEP/poly(methyl methacrylate) was reported. In both cases, the MEEP served as the initial cross-linked polymer matrix into which the organic monomer was imbibed prior to its polymerization. In this paper we describe additional IPNs formed between polyphosphazenes and organic polymers and discuss the characterization and properties of the new materials.

Experimental Section

Materials. Styrene (Aldrich), methyl methacrylate (Aldrich), acrylonitrile (Aldrich), and acrylic acid (Aldrich) were passed through alumina columns to remove inhibitors and were then stored over 3-Å molecular sieves. The syntheses of polyphosphazenes 1 and 2 were reported previously.[9] Azobisisobutyronitrile (AIBN, Polysciences Inc.) and ethylene glycol dimethycrylate (Aldrich) were used as received. Tetrahydrofuran (THF) was distilled under an atmosphere of dry argon from a sodium benzophenone ketyl drying agent.

Analytical Equipment and Techniques. ^{1}H and ^{31}P NMR spectra were recorded with the use of a Bruker WM-360 spectrometer operated at 360 and 145.8 MHz, respectively. For ^{31}P NMR spectra, positive chemical shifts are downfield from that of external phosphoric acid. For ^{1}H NMR spectra, chemical shifts were recorded relative to tetramethylsilane at 0 ppm. Solid-state ^{13}C and ^{31}P NMR spectra were obtained with the use of a CMX solid-state NMR spectrometer operated at 75 and 121 MHz, respectively. Infrared spectra were recorded on a Perkin-Elmer 1710 infrared Fourier transform spectrometer. The samples were prepared by pressing swollen IPN gels between salt plates. Glass transition temperatures (T_g) were recorded 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:

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[1] *Multicomponent Polymer Materials*; Paul, D. R., Sperling, L. H., Eds.; Advances in Chemistry Series 211; American Chemical Society: Washington, D.C., 1986.

[2] *Contemporary Polymer Chemistry*, 2nd ed.; Allcock, H. R., Lampe, F. W., Eds.; Prentice-Hall: Englewood Cliffs, NJ, 1990, and references therein.

[3] Manson, J. A.; Sperling, L. H. *Polymer Blends and Composites*; Plenum Press: New York, 1976.

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

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[6] Penton, H. R. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; *ACS Symp. Ser.* **1988**, *360*, 272–282.

[7] See, for example, U.S. Patent 4,543,379, U.S. Patent 4,661,065, and U.S. Patent 4,432,730.

[8] Visscher, K. B.; Manners, I.; Allcock, H. R. *Macromolecules* **1990**, *22*, 4885–4886.

[9] (a) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1972**, *5*, 231–232. (b) Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854. (c) Cohen, S.; Bano, M. C.; Visscher, K. B.; Chow, M.; Allcock, H. R.; Langer, R. *J. Am. Chem. Soc.* **1990**, *112*, 7832–7833.

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Scheme I

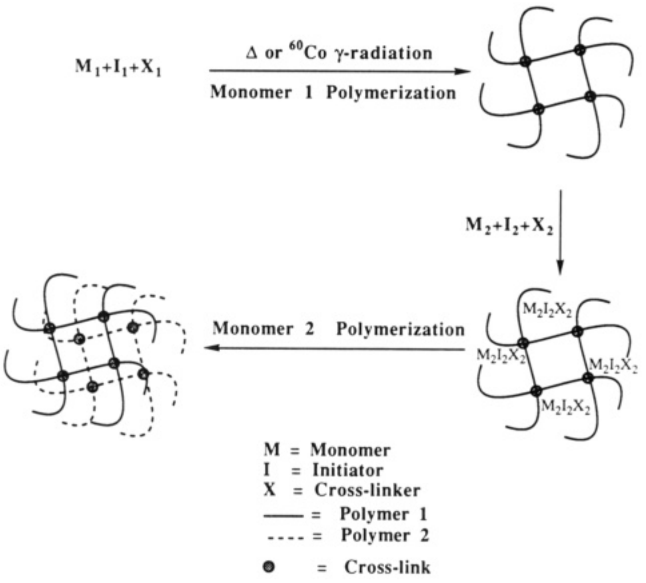
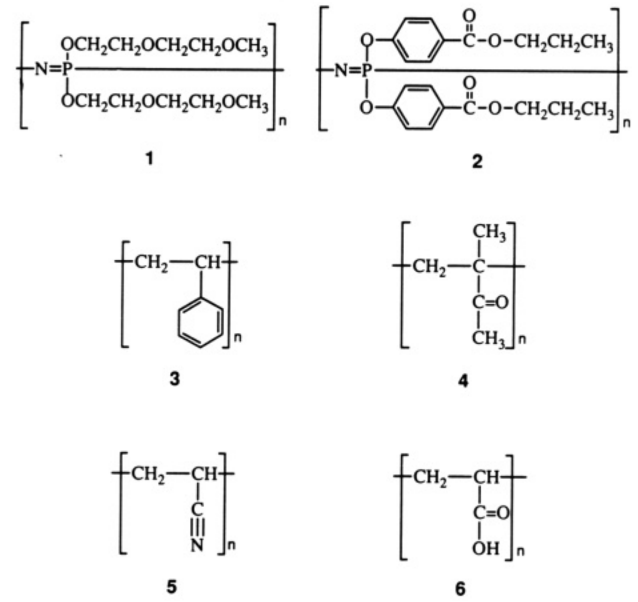
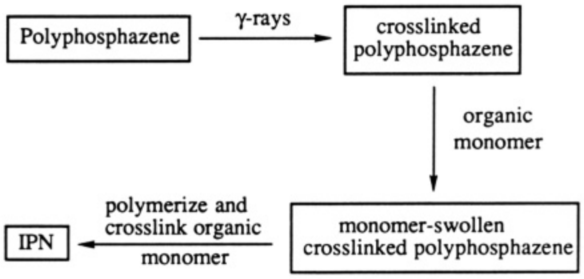


Chart I



Scheme II



heating rates of 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. Polymers **1** and **2** were cross-linked by exposure to ^{60}Co γ-radiation at the Breazeale Nuclear Reactor at the Pennsylvania State University. Transmission electron micrographs (TEMs) were obtained using a Philips 300 transmission electron micrograph with a power setting of 80 kV and an exposure time of 1 s. The magnification of both TEM photographs was 15000×. TEM samples were prepared using a LKB Ultratome III microtome.

Preparation of Polyphosphazene/Organic Polymer IPNs. All the IPNs studied in this paper were prepared by the method described in the following example. Polymer **2** (0.2 g), which had been cross-linked by exposure to 3 Mr ^{60}Co γ-radiation, was immersed in a solution of 10 mL of styrene, 0.05 g of AIBN initiator, and 0.2 mL of ethylene glycol dimethacrylate cross-linker. No solvent was used during the IPN preparation. The suspension was stirred at room temperature in the absence of light for 48 h or until the volume of the swollen polyphosphazene had increased 10 times. At this point, the reaction mixture was heated to 80 °C and was stirred for 12 h. After cooling, the IPN was removed from the reaction mixture and was repeatedly extracted with THF to remove unpolymerized monomer and uncross-linked organic polymer. Following purification, the IPN was dried rigorously under vacuum and was characterized using ^{1}H and ^{31}P NMR, ^{13}C and ^{31}P solid-state NMR, and IR spectroscopies and DSC and TEM techniques.

Results and Discussion

In general terms, IPNs are prepared by the polymerization of a monomer within the cross-linked matrix of another polymer.[4] A general outline of the preparation of interpenetrating polymer networks is shown in Scheme I. This procedure results in an intimate mixing of the macromolecular components and provides greater opportunities for intermolecular interactions between the two polymers than may be found in conventional polymer blends (alloys) or in graft or block copolymer systems. The intimate mixing of the components in IPNs also generates a much finer and more integrated domain structure than would be possible in most other multicomponent polymer systems.

Synthesis of IPNs. Two phosphazene polymers served as the initial cross-linked polymer matrices for this work, poly[bis(2–(2–methoxyethoxy)ethoxy)phosphazene], (MEEP, **1**) and poly[bis(propyloxy benzoate)phosphazene] (POBP, **2**, Chart I). Poly[bis(2–(2–methoxyethoxy)ethoxy)phosphazene] (MEEP) is a hydrophilic, water-soluble material that is being studied as a solid ionic conduction matrix for energy storage applications.[9,10] Poly[bis(propyloxy benzoate)phosphazene] (POBP, **2**) is a hydrophobic, elastomeric material which is soluble in many organic solvents. Exposure of both polymers to ^{60}Co γ-radiation induces cross-linking to yield materials that absorb organic monomers to form organogels. The degree of swelling is controlled by the γ-radiation dose and the resultant cross-link density.

Four organic monomers were polymerized within the cross-linked phosphazene matrices of **1** and **2**. The organic polymers derived from these monomers are depicted in Chart I. Polystyrene, poly(methyl methacrylate), polyacrylonitrile, and poly(acrylic acid) were chosen for their ease of synthesis from the monomer, their range of functional groups, and their hydrophobic or hydrophilic materials character. For example, polystyrene and poly(methyl methacrylate) are hydrophobic polymers, while polyacrylonitrile and poly(acrylic acid) are hydrophilic in nature. IPNs that contain phosphazene and organic polymers with varying hydrophobicities could lead to materials with interesting surface or bulk properties.

In a typical example of an IPN synthesis, as depicted in Scheme II, a sample of MEEP cross-linked with 3 Mrad of ^{60}Co γ-radiation was allowed to swell in a mixture of methyl methacrylate monomer, azobisisobutyronitrile (AIBN) initiator, and ethylene glycol dimethacrylate, which was used as a cross-linking agent. The absorption of these small molecules took place in the absence of light

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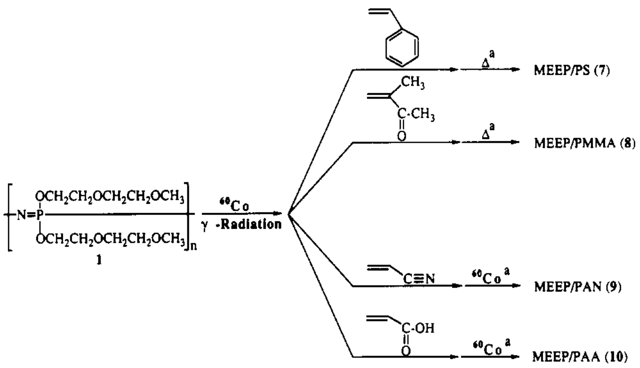
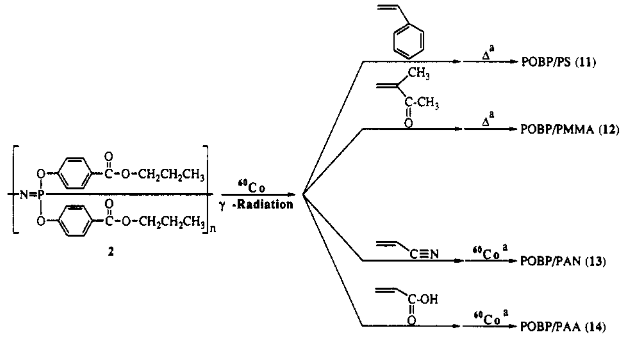
(10) (a) Allcock, H. R.; Kwon, S.; Riding, G. H.; Fitzpatrick, R. J.; Bennett, J. L. *Biomaterials* **1988**, *9*, 509. (b) Allcock, H. R.; Fitzpatrick, R. J.; Gebura, M.; Kwon, S. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1987**, *28*, 321.

Scheme III



[a] All samples were polymerized with AIBN initiator and ethylene glycol dimethacrylate cross-linker.

Scheme IV



[a] All samples were polymerized with AIBN initiator and ethylene glycol dimethacrylate cross-linker.

during 48 h. The cross-linked phosphazene expanded to more than 10 times its original volume and weight. Following this step, the imbibed monomer was polymerized and cross-linked within the cross-linked MEEP matrix either thermally or, in some cases, by exposure to additional ^{60}Co γ-radiation. After polymerization, the IPN was purified by multiple extractions with water and tetrahydrofuran (THF) to remove both unpolymerized monomer and free (un-cross-linked) polymer not incorporated into the IPN. Following purification, the IPNs were dried rigorously in vacuo and were characterized fully by IR, ^{1}H and ^{31}P NMR spectroscopy, ^{13}C and ^{31}P solid-state NMR spectroscopy, differential scanning calorimetry, and transmission electron microscopy.

The synthetic pathways used to prepare IPNs 7–14 are illustrated in Schemes III and IV. Phosphazene polymers 1 and 2 were each exposed to 3 MRad of ^{60}Co γ-radiation to induce cross-linking. For the organic components, AIBN was used as the polymeric initiator, and ethylene glycol dimethacrylate was employed as the cross-linker. Equivalent amounts of initiator and cross-linker were used for each sample. Polystyrene and poly(methyl methacrylate) were polymerized thermally while both polyacrylonitrile and poly(acrylic acid) were polymerized by additional exposure to ^{60}Co γ-radiation.

For each IPN system investigated, two control experiments were performed. The controls helped to determine the importance of both the initiator and cross-linker in the IPN synthesis. In the first control, a sample of cross-linked polyphosphazene was swelled with organic monomer and initiator with no cross-linking agent present. In the second, a sample of cross-linked polyphosphazene was swollen only with monomer. In all cases, the control prepared with monomer and initiator yielded semi-IPNs, in which only the polyphosphazene was cross-linked. The presence of the un-cross-linked organic polymer was detected by ^{1}H NMR and infrared spectroscopy. The un-cross-linked polymer could, theoretically, be removed by extraction with solvent. In the second control set, where neither initiator nor cross-linker was present, little or no organic polymer could be detected by ^{1}H NMR or infrared spectroscopy following heating. However, polymerization did occur in all the systems irradiated with ^{60}Co γ-radiation, since radicals produced by γ-radiation initiate the organic monomer polymerization process.

Table I. IPN Component Ratios[a]

MEEP/PS (7)	1:1	POBP/PS (11)	2.5:1
MEEP/PMMA (8)	3:1	POBP/PMMA (12)	1.5:1
MEEP/PAN (9)	1:1	POBP/PAN (13)	4.5:1
MEEP/PAA (10)	1:1	POBP/PAA (14)	2:1

[a] Based on NMR integration.

Table II. ^{1}H NMR Data[a]

IPN	δ, ppm
7	3.38, 3.53, 3.65, 4.05 (OCH_2 of 1) 1.25, 1.65 (CH of 3), 7.2 (Ph of 3)
8	3.65 (br) (OCH_2 of 1) 0.85, 0.98 (CH_2 of 4), 1.85 (CH_3 of 4) 3.65 (CO_2CH_3 of 4)
9	3.38, 3.52, 3.65, 4.05 (OCH_2 of 1) 1.60 (CH_2 of 5), 2.45 (CH of 5)
11	0.93 (CH_3 of 2), 1.68 (CH_2 of 2) 4.11 (CO_2CH_2 of 2), 6.63, 7.46 (Ph of 2) 1.45 (CH_2 of 3), 1.69 (CH of 3) 7.10 (Ph of 3)
12	0.94 (CH_3 of 2), 1.68 (CH_2 of 2) 4.13 (CH_2 of 2), 6.63, 7.46 (Ph of 2) 0.94 (CH_3 of 4), 1.86 (CH_2 of 4) 3.76 (CO_2CH_2 of 4)

[a] All samples were studied as swollen gels in $CDCl_3$.

Table III. Infrared[a] **Data**

IPN	ν, cm^{-1}
7	3000 (C–H of 1 and 3), 1670, 1590 (aromatic C=C of 3), 1200 (P=N stretch of 1)
8	2900 (C–H of 1 and 4), 1720 (C=O stretch of 4), 1200 (P=N stretch of 1)
9	2981 (C–H stretch of 1 and 5), 2238 (C≡N of 5), 1457 (CH_2 stretch of 3) 1200 (P=N stretch of 1)
11	2961 (C–H of 2 and 3), 1723 (C=O stretch of 2), 1603 (aromatic C=C of 2 and 3) 1200 (P=N stretch of 2)
12	2977 (C–H of 2 and 4), 1723 (C=O stretch of 2), 1603 (C=C aromatic stretch of 2), 1460, 1365 (CH_3 stretch of 2 and 4), 1200 (P=N stretch of 2)

[a] All samples were studied as thin films between salt plates.

The polyphosphazene/organic polymer IPN systems were prepared with the maximum amount of organic polymer allowed by the monomer imbibition process. The volume of the cross-linked phosphazene polymers increased up to 10 times during exposure to the organic monomers. The ratios of the component materials were determined roughly by integration of the NMR spectra and are depicted in Table I. These ratios ranged from a 1:1 mixture in many of the MEEP IPNs to 3:1 and 5:1 ratios in some of the IPNs-derived POBP (2). MEEP (1) tended to imbibe more of the organic monomers than did POBP (2).

Characterization. The IPNs 7–14 were characterized by ^{1}H and ^{31}P NMR and in selected cases by solid-state ^{13}C and ^{31}P NMR spectroscopy, infrared spectroscopy, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). The characterization data are shown in Tables II–IV.

The NMR spectra of IPNs 7–14 were studied together with the NMR spectra of the IPN control samples and the

Table IV. DSC Data

IPN	T_g, °C	parent polymers[a]
7	−70/+57	1/3
8	−80/+112	1/4
9	+34	1/5
10	−41/+3.5	1/6
11	−14/+92	2/3
12	−14/+50	2/4
13	−9/+51	2/5
14	+54	2/6

[a] "Parent polymer" T_g's: 1 = −84 °C; 2 = −23 °C; 3 = 100 °C; 4 = 105 °C; 5 = 106 °C; 6 = 85 °C.

individual component polymers **1**–**6**. NMR analysis is useful mainly to confirm the presence of both macromolecular constituents and to monitor the polymerization of the organic monomer by following the loss of vinyl protons. Because the IPNs were insoluble, but swelled in many solvents, samples were studied as swollen gels in $CDCl_3$ (the materials increased up to 10 times in volume when swollen in $CDCl_3$). The NMR peaks were broad due to the polymeric nature of the components and the method of sample preparation. This is a common problem for many polymer systems. For example, IPN **9** showed broad ^1H NMR peaks at 3.38, 3.52, 3.65, and 4.05 ppm for the OCH_2 and OCH_3 protons of **1**, 1.60 ppm for the CH_2 protons of **5**, and 2.45 for the CH proton of **5**. In the case of IPNs **10** and **13**, solid-state ^{13}C and ^{31}P NMR spectra were obtained because the material did not swell appreciably in $CDCl_3$. Solid-state ^{13}C NMR confirmed both the presence of both polymeric constituents and the absence of residual organic monomer.

Infrared spectroscopy was also used to confirm the presence of both parent polymers in the IPN. The IR spectra of IPNs **7**–**14**, the component polymers **1**–**6**, and the control samples were studied as thin films prepared by pressing the swollen gels between salt plates. In a typical example, the infrared spectra recorded for IPN **9** showed a C–H stretch at 2981 cm^{-1} for both constituents, a nitrile band at 2238 cm^{-1} for **5**, a CH_2 stretch at 1457 cm^{-1} for **5**, and the very characteristic P=N skeletal vibrations for **1** at 1200 cm^{-1}.

Differential scanning calorimetry (DSC) is one of the most important techniques for the characterization of IPNs. DSC provides an estimate of the composition and the homogeneity of an IPN as well as the degree of intermolecular interaction between the component macromolecules. For IPNs with minimal intermolecular interactions, two thermal transitions (T_g) may be detected, displaced from the values of the component polymer transitions. The stronger the interaction between the polymers and more homogeneous the system, the more obvious is the displacement of the T_g's from their original values. In a completely homogeneous system, only one transition will be detected in a temperature region between those of the component T_g's. Every poly(organophosphazene)/organic polymer IPN prepared in this work showed evidence of some interaction of the component macromolecules based on the location of T_g's in the DSC thermograms and their displacement from the T_g's of the component materials.

Figure 1 shows the DSC spectra for IPN **9**. This material is a clear, amber colored glassy material which yields a single, broad DSC transition at 34 °C. This indicates a high degree of homogeneity in the system and a significant amount of intermolecular interaction between MEEP (**1**) and polyacrylonitrile (**5**), the T_g's of which occur at −84 and 85 °C (**5**), respectively. This high degree of miscibility could be due to strong van der Waals and polar interactions between the MEEP (**1**) and acrylonitrile (**5**) side groups. A single transition was also found for IPN **13**. This hard, transparent, light yellow material composed of poly[bis(propyloxybenzoate)phosphazene] (**2**) and poly(acrylic acid) (**6**) had a T_g at 54 °C which is intermediate between those of the parent polymer at −23 °C (**2**) and 85 °C (**6**). The ester (**2**) and acrylic acid (**6**) side groups are capable of hydrogen bonding interactions as well as dipolar attractions.

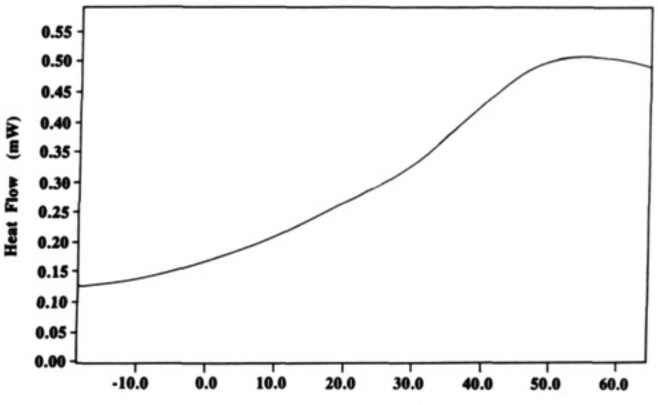


Figure 1. DSC thermogram of a MEEP/polyacrylonitrile IPN.

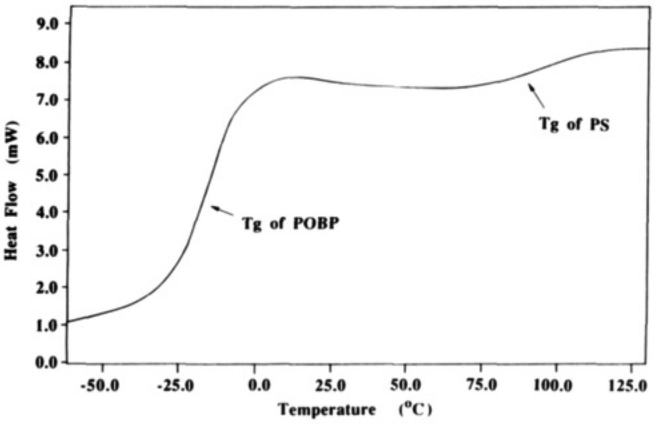


Figure 2. DSC thermogram of a poly[bis(propyl oxybenzoate)phosphazene]/polystyrene IPN.

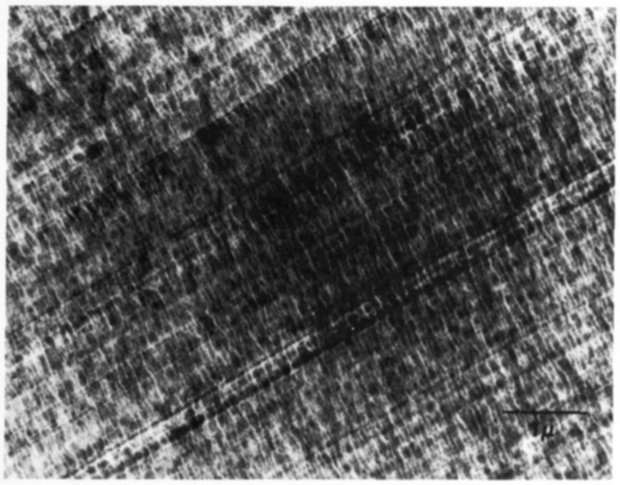


Figure 3. TEM micrograph of a MEEP/polyacrylonitrile IPN.

Another example is shown in Figure 2 in which the DSC plot for IPN **11** is shown. This system contains POBP (**2**) and polystyrene (**3**). The IPN is an opaque, white, slightly elastomeric solid with two glass transitions occurring at −14 and 92 °C. Its composition (2.5:1) was determined

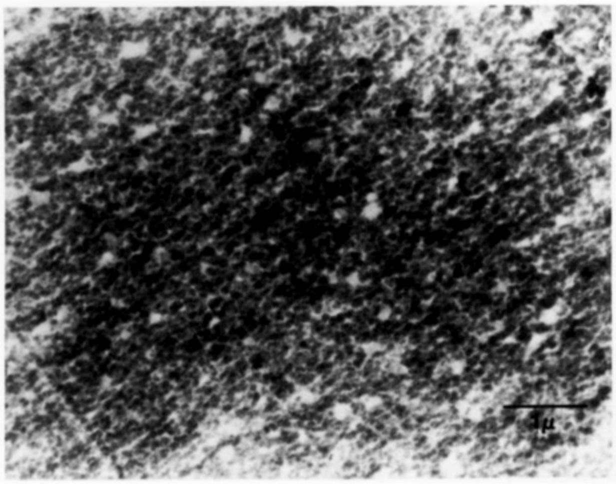


Figure 4. TEM micrograph of a poly[bis(propyl oxybenzoate)phosphazene]/polystyrene IPN.

roughly by NMR integration and also by comparing the heights of the two T_g endotherms. An indication of the significant intermolecular interaction between the constituents is indicated by the (~10 °C) displacement of the T_g's from their original values of −23 (**2**) and 100 °C (**3**).

The homogeneity of the samples was also measured using transmission electron microscopy (TEM). Here, the phase separation of the constituents into individual domains can be seen clearly. The smaller the domain size, the more homogeneous is the sample and the greater the degree of mixing within the sample. Figures 3 and 4 show transmission electron micrographs for IPNs **9** and **11**.

Figure 3 shows a transmission electron micrograph of IPN **9** (MEEP (**1**)/polyacrylonitrile (**5**)). Note the regularity of the small, evenly spaced, almost weblike domain structure. These small domains, along with the single T_g endotherm found in the DSC spectra discussed earlier, show that this is a microheterogeneous, semimiscible system, which could display very different properties from either of its component polymers—MEEP and polyacrylonitrile.

The TEM micrograph of IPN **11** POBP (**2**)/polystyrene (**3**) is shown in Figure 4. This material also possesses a definite domain structure, but the domains are much larger and are well separated, which indicates a less homogeneous structure. This low degree of homogeneity is reflected by the DSC spectra from IPN **11**, which showed two distinct T_g endotherms close to the values for the component polymers. This material should possess properties that are hybrids of the component polymers.

Conclusions. IPNs **7**–**14** represent the first well-characterized interpenetrating polymer networks based on a phosphazene polymer system. The physical properties of these IPNs range from soft and pliable materials to hard and brittle substances, depending on the nature of the component macromolecules. Possible uses for these materials are being studied, especially in biomedical technology.

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Pulsed Laser-Assisted Chemical Vapor Deposition of W, Mo, and V Thin Films

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A pulsed laser is used to deposit W, Mo, and V films on SiO_2/Si(100) surfaces, from the corresponding metal hexacarbonyl precursor, at two wavelengths, 562 and 281 nm. Film compositions and sputter depth profiles are analyzed with a scanning Auger microprobe. In general, films are contaminated with carbon and oxygen impurities. Film surfaces contain a greater amount of impurities than the bulk of the films. This is most likely due to surface reactions with unreacted hexacarbonyl, following irradiation, and atmospheric gases, during transfer to the analysis chamber. The bulk compositions of W and Mo films are, on average, 65–81% metal, 8–13% carbon, and 10–22% oxygen. An even greater amount of carbon and oxygen is incorporated in the V films at both wavelengths. The results presented here for pulsed laser deposition are compared to previous continuous laser deposition studies.

Introduction

There has been much interest in recent years in the deposition of thin metallic films by laser-assisted chemical vapor deposition (LCVD) because of its important applications in microelectronics device fabrication.[1] In LCVD, a substrate held in a chamber with the vapor of the organometallic precursor is laser irradiated. The organometallic decomposes, and a metal film is deposited on the substrate. One group of precursors that has received a great deal of attention is the metal carbonyls.

Cr, Mo, W, Fe, and Ni films have been produced from the corresponding carbonyl with both continuous-wave (CW)[2-8] and pulsed[2,9-17] laser sources. Carbonyl precursors

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