

Preparation and Characterization of Poly(organophosphazene) Blends¹

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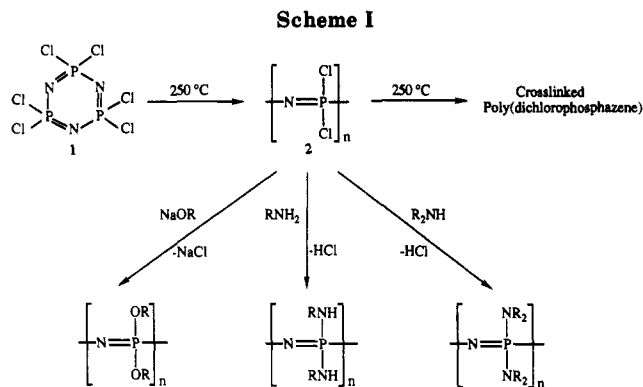
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The synthesis and characterization of polymer blends derived from poly(organophosphazenes) and organic polymers is reported. The miscibility or immiscibility of the materials is influenced by the choice of organic side groups attached to the polyphosphazene backbone and the ratio of the two component polymers. The blends were characterized by DSC analysis and transmission electron microscopy. DSC and TEM characterization data of freshly prepared semimiscible samples are compared to those of samples prepared 5 years previously to determine the permanence of miscibility and estimate the strength of intermolecular interactions between the constituent polymers.

Introduction

An increasing need exists in science and technology for new macromolecular materials with specifically tailored properties. These may be prepared in a number of different ways that include (1) the synthesis of new macromolecules which generate different and unique solid-state properties and (2) the bringing together of existing macromolecular materials in alloys or composites to give materials with properties that are some combination of those of the component macromolecules. Several methods exist to construct multicomponent polymer systems. Graft and block copolymer systems are well-known, as are established multicomponent systems such as filler-reinforced polymers, polymer blends (alloys), polymer laminates, and interpenetrating polymer networks (IPNs). The focus of this paper is the preparation and characterization of a new class of polymer blends composed of poly(organophosphazenes) with organic polymers or with other polyphosphazenes.

Polymer blends or alloys are physical mixtures of two or more polymers. The component macromolecules are held together not by covalent bonds but by intermolecular interactions such as hydrogen bonding, dipole-dipole interactions, or van der Waals forces depending on the functional groups within the polymer system. The role played by different functional groups in these interactions has been reported in detail for organic polymers.^{2,3} However, in some polymer blends, strong intermolecular interactions are not essential because the system may be held together solely by entropic effects. Polymer blends may exist as miscible one-phase systems, as semimiscible systems where miscible domains exist together with phases rich in one of the constituent polymers, or as immiscible multiphase materials systems. In a miscible blend, the interactions between the two different components are presumably stronger than the interactions between the individual molecules of a single species. In an immiscible blend, the reverse is true.³ Many examples exist of both miscible and immiscible systems. A typical example is the one between polycaprolactone and poly(vinyl chloride), where the blend is apparently stabilized by intermolecular hydrogen bonding between of the Cl-C-H unit of the



poly(vinyl chloride) and the proton-accepting character of the carbonyl group of the polycaprolactone.⁴ It has been stated that "hydrogen bonding may be responsible for more miscible systems than any other type of interaction."⁵

It is possible for weakly interacting miscible blends to undergo phase separation over time. Phase separation can be used as a measure of the weakness of intermolecular interactions between the constituent materials. The degree of separation may be determined by comparing characterization data from freshly prepared polymer blends with those prepared in the past. This technique provides tentative clues to the nature and strength of intermolecular interactions within the system.

Poly(organophosphazenes) are a relatively new class of inorganic-organic polymers that contain a flexible backbone of P-N repeating units and with two organic, inorganic, or organometallic groups attached to each phosphorus atom. These polymers are prepared by the thermal ring opening polymerization of hexachlorocyclotriphosphazene (1) at 250 °C to form poly(dichlorophosphazene) (2) which is employed as a reactive macromolecular intermediate.⁶⁻⁸ The chlorine atoms in this polymer are replaced via nucleophilic substitution using, for example, alkoxy, aryloxy or amino reagents to give stable poly(organophosphazene) derivatives.⁶⁻⁸ This process is shown in Scheme I.

Specific polyphosphazenes possess unique differences from most conventional organic polymers, including flame-retardant properties, high resistance to both oil and solvents, high backbone and materials flexibility, and fi-

(1) Parts of this work were reported at the New York ACS Meeting, August 26, 1991. Visscher, K. B.; Manners, I.; Allcock, H. R. *Polym. Prepr. Polym. Mater. Sci. Eng.* 1991, 65, 3-4.

(2) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979, p 207 and references therein.

(3) (a) Coleman, M.; Painter, P. C. *Fourier Transform Infrared Spectroscopy. Appl. Spectrosc. Rev.* 1984, 20, 256-346. (b) Painter, P. C. *Macromolecules* 1988, 21, 666. (c) Painter, P. C. *Macromolecules* 1989, 22, 570. (d) Painter, P. C. *Macromolecules* 1989, 22, 580.

(4) Olabisi, O. *Macromolecules* 1975, 8, 316.

(5) Olabisi, O. In ref 2, p 29.

(6) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* 1965, 87, 4216.

(7) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* 1966, 5, 1709.

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nally the ease by which their properties can be tailored by the choice of organic, inorganic or organometallic side groups.

The objective of this work was the preparation and characterization of polymer blends composed of two different polyphosphazenes or of combinations of polyphosphazenes with organic polymers. It was also a goal of the work to compare the characterization data (DSC and TEM) for samples prepared 5 years ago with those of freshly prepared samples. Characteristics maintained over this period of time would indicate strong intermolecular interactions between the constituent polymers, whereas a change in the material's structure would suggest weak interactions between the parent macromolecules.

Experimental Section

Analytical Equipment and Techniques. Tetrahydrofuran (THF, Aldrich) and dioxane (Aldrich) were distilled from sodium-benzophenone ketyl under a dry nitrogen atmosphere. The organic polymers used were obtained from the following sources: poly(vinyl chloride) (Aldrich), polystyrene (Aldrich), poly(methyl methacrylate) (Cellomer Assoc.), poly(4-vinylpyridine) (Polysciences), poly(vinyl alcohol) (Aldrich), poly(acrylic acid) (Polysciences), and poly(ethylene oxide) (Aldrich). All the organic polymers were used as received.

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 using heating rates of 10, 20, and 40 °C/min, and a helium flow of 10 mL/min was used. Before beginning each run, the samples were annealed for 3 min at 110 °C. The instrument was calibrated with both cyclohexane and indium standards with thermal transitions at -87.06 and 6.54, and at 156 °C, respectively. Transmission electron micrographs (TEMs) were obtained using a JEOL JEM 1200 EXII transmission electron micrograph with a power setting of 80 kV and an exposure time of 1 s. The magnification of all TEM photographs was 14000x. TEM samples were prepared using an LKB Ultratome III microtome.

The synthesis of the phosphazene polymers used in this paper have been reported previously and all possess molecular weights in the range of 1×10^6 .¹³⁻¹⁶

Preparation of Blends. Samples of each component polymer (mol percents from 10% to 90% of each component) were dissolved (with heating) in a common solvent (such as THF or ethanol for hydrophobic polymer blends, or water for aqueous-soluble polymers) or in a cosolvent system (water/THF for blends containing polymer 3 and hydrophobic organic polymers). Because polymer 3 was only slightly soluble in THF, the dissolved polymer solutions were combined and stirred vigorously at room temperature for several hours. The combined mixtures were then cast into films in Teflon-coated dishes. After evaporation of the solvent, the materials were dried in vacuo for 48 h. Following preparation, all samples were stored in air.

Results and Discussion

The structures of the poly(organophosphazenes) and the organic polymers used in this study are depicted in Charts I and II. These materials are representative of several different types of hydrophobic and hydrophilic polymers.

Several ways exist for the characterization of polymer blends, including FT-IR,⁹ differential scanning calorimetry (DSC),¹⁰ and electron microscopy-scanning electron microscopy (SEM), or transmission electron microscopy (TEM).¹¹ The blends discussed here were characterized

Chart I. Phosphazene Polymers

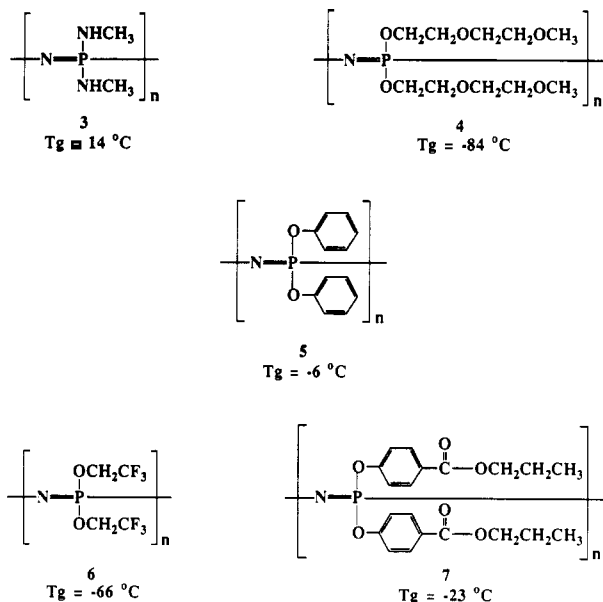
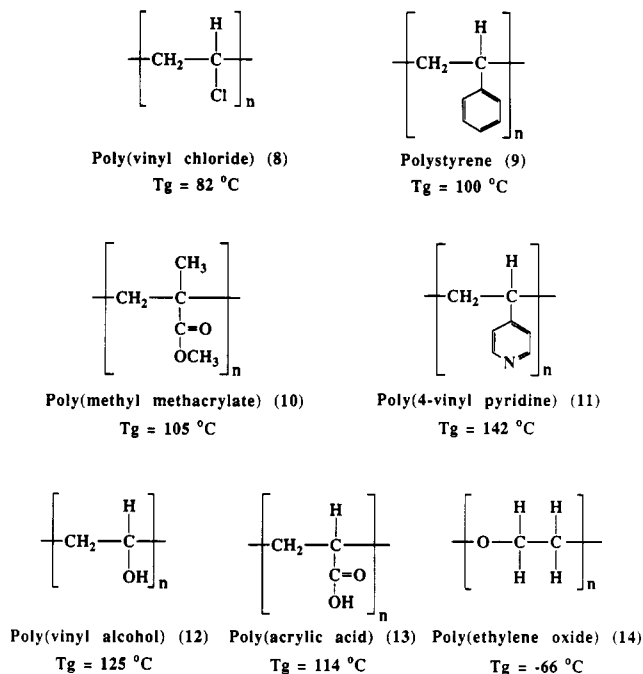


Chart II. Organic Polymers



primarily by DSC and TEM. FT-IR was not used for characterization due to the overlapping peaks of the constituent polymers.

One of the most effective ways to interpret the miscibility of polymers in an alloy is to examine the thermal transitions using DSC. A completely miscible system should have a single glass transition temperature (T_g) located between the values for the component macromolecules. A partially miscible blend will generate either three T_g 's (two for the component materials and a new intermediate T_g) or two T_g 's, displaced from the values of the component polymers. Both the miscibility and strength

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(10) (a) McMaster, L. P. *Macromolecules* 1973, 6, 670. (b) McMaster, L. P. In *Polyblends and Composites*; Platzer, N. A. J., Ed.; American Chemical Society: Washington, DC, 1975. (c) Robard, A.; Patterson, D. *Macromolecules* 1977, 10, 1021. (d) Patterson, D.; Robard, A. *Macromolecules* 1978, 11, 690. (e) Frisch, K. C.; Klempner, D.; Migdal, S.; Frisch, H. L.; Ghirdella, H. *Polym. Sci. Eng.* 1974, 14, 76. (f) Frisch, H. L.; Frisch, K. L.; Klempner, D. *Polym. Sci. Eng.* 1974, 14, 648.

(11) (a) Kato, K. *Jpn Plast.* 1968, 2, 6 (April issue). (b) Matsuo, M. *Jpn Plast.* 1968, 2, 6 (July issue). (c) Thomas, D. A. *J. Polym. Sci.* 1977, 60C, 189.

(12) The first examples of phosphazene/organic polymer blends (poly[bis(trifluoroethoxy)phosphazene]/poly(vinyl alcohol) were investigated by Austin, P. E., Ph.D. Thesis, The Pennsylvania State University, 1984.

of intermolecular interactions within the system may be estimated as a function of time by examining thermal transitions of long-existing and new miscible or semimiscible polymer blends.

Electron microscopy is an excellent method to monitor the topography of the film surface and the phase structure of multicomponent materials. Scanning electron microscopy (SEM) provides information about the film surface, while transmission electron microscopy (TEM) is used to probe the phase structure and domain size of the components within a polymer blend. Electron microscopy is also useful to analyze the potential phase separation of miscible or semimiscible polymer blends after long periods of time. TEM microscopy is especially useful for phosphazene systems due to the fact that the heavier an element, the darker it will appear in the TEM. Therefore, alloys containing phosphazenes do not need to be stained: the phosphazene-containing regions will automatically appear darker than the organic polymer sections.

Phosphazene/Phosphazene Polymer Blends.

Polymer blends containing all pairwise combinations of the polymers poly[bis(methylamino)phosphazene] (3),¹³ poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (4),¹⁴ poly[bis(phenoxy)phosphazene] (5),¹⁵ poly[bis(trifluoroethoxy)phosphazene] (6),¹⁶ and poly[bis(propyloxy benzoate)phosphazene] (7),¹⁷ depicted in Chart I, were prepared using ratios of the starting components that ranged from 10% to 90% of each component. In this way, the miscibility of the systems could be monitored at different concentrations of the constituent polymers.

Poly[bis(methylamino)phosphazene] (3) is a colorless, transparent, hydrophilic material which is soluble in water and slightly soluble in organic solvents. This material forms flexible films and has a T_g at +14 °C. It undergoes cross-linking during prolonged exposure to ⁶⁰Co γ -radiation. Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (4) is a transparent, hydrophilic polymer which is soluble in both aqueous and organic solvents. Polyphosphazene 4 has a T_g of -84 °C and can be cross-linked by exposure to ⁶⁰Co γ -radiation to form a material with improved dimensional integrity. In its un-cross-linked form, it has a low resistance to viscous flow. Poly[diphenoxyphosphazene] (5) is an opaque, white hydrophobic material. This polymer, in the solid state, forms microcrystalline films or fibers, is soluble in many organic solvents, and has a T_g at -6 °C. Poly[bis(trifluoroethoxy)phosphazene] (6) is an opalescent, very hydrophobic material which forms flexible microcrystalline films, is soluble in many organic solvents, and has a T_g at -66 °C. Finally, poly[bis(propyloxy benzoate)phosphazene] (7) is a transparent, elastomeric solid which is soluble in many organic solvents. This hydrophobic polymer has a glass transition temperature at -23 °C.

The blending of phosphazenes 3 and 4 created a semimiscible alloy at high loadings of polymer 3 (60% and above). Thermal transitions for both constituent polymers were detected in those samples that contained more than 20% polymer 3. Semimiscibility was indicated by a 20 °C displacement of the T_g of polymer 3 (normally at +14 °C) beginning at 30% of 3 and increasing as the percentage

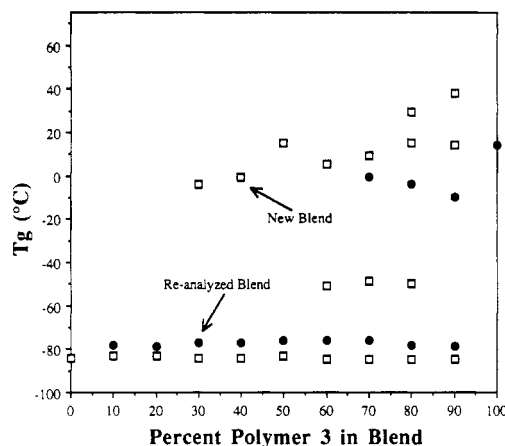


Figure 1. Graphs of T_g (°C) vs percent polymer 3 in old and new poly[bis(methylamino)phosphazene] (3)/poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (4) blends: ●, old blends; □, new blends.

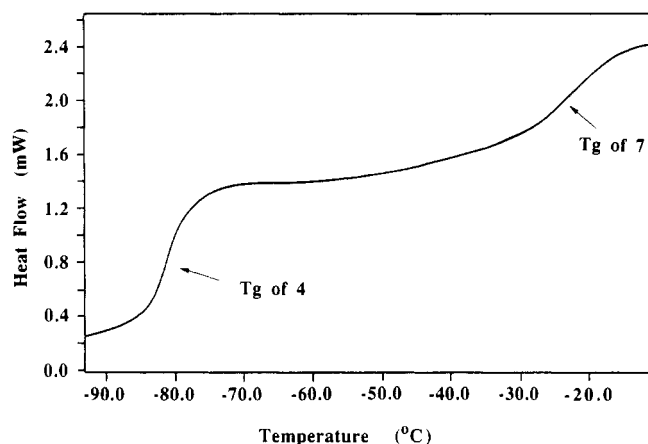


Figure 2. DSC thermogram of a 60%/40% poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (4)/poly[bis(propyloxy benzoate)phosphazene] (7) blend.

of 3 increased in the blend. In addition, new transitions were detected in samples that contained more than 50% polymer 3. These new T_g 's fell between the values of the constituent polymers (+14 °C (3) and -84 °C (4)) and ranged from -52 to -48 °C. This indicated that completely miscible regions existed within the material. This miscibility is probably due to hydrogen bonding, between the two constituent polymers.

Blends of 3 and 4 were reanalyzed by DSC after a period of 5 years. It was found that the transitions from the completely miscible regions no longer existed. This suggests that phase separation occurs slowly in this material. However, some semimiscibility appeared to be retained for samples with high loadings of polymer 3, as seen by a displacement of the T_g values for polymer 3. This suggests that interactions, such as hydrogen bonding or dipole-dipole forces, provide some interactive stability for this material. These results parallel those from related blends of organic polymers containing poly(ethylene imine) and poly(ethylene oxide) which form miscible systems but are not strongly associated with each other.¹⁸ Figure 1 shows T_g 's at various ratios of the starting materials 3 and 4, for both the freshly prepared blends and the 5-year old samples. These hydrophilic blends could be fabricated into flexible films which were rendered insoluble, but swellable, in water when cross-linked by ⁶⁰Co γ -radiation.

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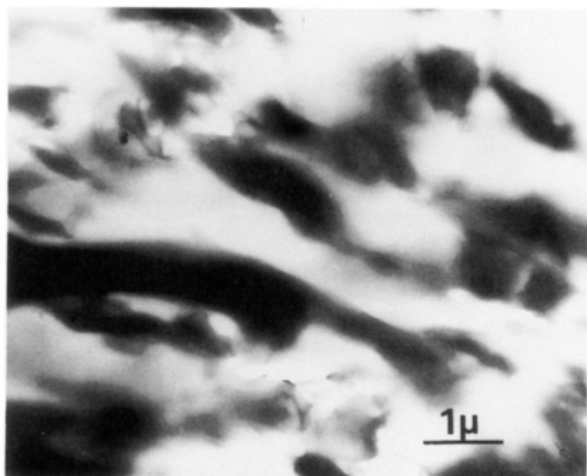


Figure 3. TEM micrograph of a 60%/40% poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (4)/poly[bis(propoxybenzoate)phosphazene] (7) blend.

Other combinations of poly(organophosphazenes) from polymers 3–7 yielded immiscible blends at all concentrations of the starting materials. Figure 2 shows a DSC thermogram for an immiscible system containing poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (4) and poly[di(propoxybenzoate)phosphazene] (7). The material has two T_g 's, close to the values for the component materials. This lack of miscibility is reflected in the TEM micrograph (Figure 3) which shows definite domains of both component materials throughout the solid.

Phosphazene/Organic Polymer Blends. Phosphazene/organic polymer blends were prepared from different ratios of starting materials ranging from 10% to 90% of each component polymer.¹² The organic polymers included poly(vinyl chloride) (8), polystyrene (9), poly(methyl methacrylate) (10), poly(4-vinylpyridine) (11), poly(vinyl alcohol) (12), poly(acrylic acid) (13), and poly(ethylene oxide) (14). The molecular structures and T_g 's of these hydrophobic (8–11) and hydrophilic organic polymers (12–14) are shown in Chart II.

Poly[bis(methylamino)phosphazene] (3) was partially miscible with several of the hydrophobic organic polymers including poly(vinyl chloride) (8), and polystyrene (9). For example, when polymer 3 was combined with poly(vinyl chloride) (8), single T_g 's were detected and were found to decrease in temperature from 10 to 60% loading of polymer 3. These glass transition temperatures were displaced from the T_g 's of the constituent polymers at +14 (3) and +82 °C (8). This semimiscibility could be due, in part, to hydrogen bonding interactions between the proton donor/acceptor properties of the methylamino functionalities of the phosphazene polymer and the proton donor properties of the H–C–Cl units of the organic polymer. Semimiscible blends containing polymers 3 and 8 were reanalyzed by DSC after a period of 5 years. These blends showed a retention of miscibility in the region 10–60% loading of polymer 3. This indicates that the interactions between the components was relatively strong.¹⁹ Figure 4 shows a graph of T_g as a function of the ratio of polymer 3 in the blend for both old and new materials containing polymers 3 and 8.

Blends composed of poly(organophosphazene) 3 and polystyrene (9) were also found to be semimiscible alloys. Single T_g 's were detected in blends with 10–50% loading of polymer 3, and these transitions decreased in temper-

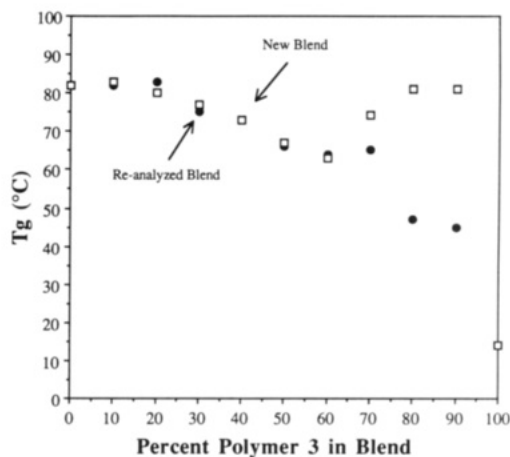


Figure 4. Graphs of T_g (°C) vs percent polymer 3 in old and new poly[bis(methylamino)phosphazene] (3)/poly(vinyl chloride) (8) blends: ●, old blends; □, new blends.

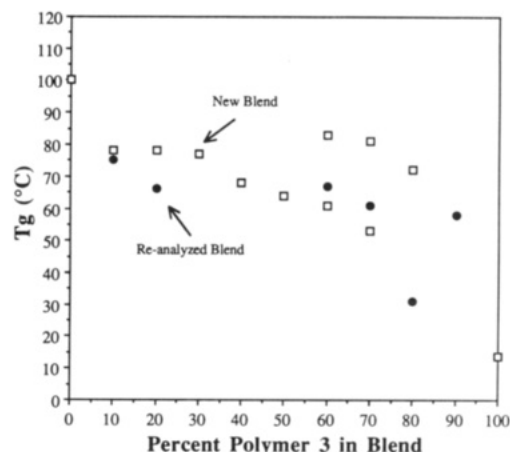


Figure 5. Graphs of T_g (°C) vs percent polymer 3 in old and new poly[bis(methylamino)phosphazene]/polystyrene (9) blends: ●, old blends; □, new blends.

ature (from 80 to 60 °C) as the loading of phosphazene polymer increased. Above 50% 3, two T_g 's were found in the DSC thermogram. This suggests that both miscible sections and phases rich in polystyrene exist within the material. In the poly[bis(methylamino)phosphazene]/polystyrene blends, miscibility is probably encouraged through the weak proton accepting/electron donating nature of the aromatic groups of 9 and the proton donating/accepting character of the primary amino groups of polymer 3. The thermal transitions of blends containing polymers 3 and 8 were reanalyzed after a period of 5 years. Slight deviations were found between the two sets of DSC data, which may indicate a small amount of phase separation over time. These data are not surprising in view of the fact that aromatic hydrocarbons possess only weak donating/proton accepting capabilities. A graph that illustrates T_g as a function of the percentage of polymer 3 in the blends for both old and new blends is shown in Figure 5.

Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (4) was allowed to interact with poly(vinyl alcohol) (12) and was found to be semimiscible at all concentrations of the constituent polymers. In all the 4/12 samples, T_g 's from 4 were present at approximately –84 °C (which is the normal T_g of 4) and in some cases, T_g 's close to the value of polymer 12 were detected, although these were displaced slightly from their normal value of +125 °C. However, T_g 's were also detected in each sample at temperatures between those of the constituent polymers. These intermediate

(19) Olabisi, O. In ref 2, p 210.

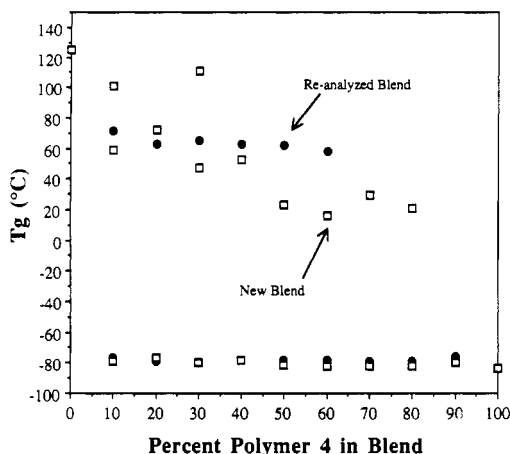


Figure 6. Graphs of T_g ($^{\circ}\text{C}$) vs percent polymer 4 in old and new poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (4)/poly(vinyl alcohol) (12) blends: ●, old blends; □, new blends.

transitions were found in the range of +75 to +30: they moved to lower temperatures as the loading of polymer 4 increased. This semimiscibility can be attributed to strong hydrogen bonding resulting from the proton-accepting capabilities of the etheric side groups of 4 and the strong proton donor/acceptor properties of the alcohol groups of the organic polymer. The miscibility in this system parallels that of an analogous organic polymer blend containing poly(ethylene oxide) and poly(vinyl alcohol), which is a highly interactive combination.²⁰ Blends containing polymers 4 and 12 were reanalyzed by DSC after 5 years and, although slight deviations occurred from the recent data, the materials were still semimiscible. Thus, the intermolecular interactions between the constituent polymers are quite strong. Figure 6 shows the thermal transitions plotted as a function of the percent of polymer 4 in the blend for both the old and new data.

Blends containing polymer 4 and poly(acrylic acid) (13) were prepared and were also found to be semimiscible. Most samples had T_g 's at -84°C corresponding to polymer 4, and some showed transitions displaced slightly from $+125^{\circ}\text{C}$ which corresponds to the T_g of polymer 13. As in the previous systems, the new T_g 's were found in an intermediate temperature range compared to the pure materials. These intermediate T_g 's, in the range of $+100$ to -60°C , were found for blends containing between 10 and 60% polymer 4. The values moved to lower temperatures as the loading of polymer 4 increased. Miscibility in this set of blends may also be influenced by hydrogen bonding between the moderate proton accepting etheric side groups on the phosphazene and the strong proton donating/accepting carboxylic acid side groups pendant to the organic polymer. This miscibility is also seen in the analogous organic polymer blends between poly(ethylene oxide) and poly(acrylic acid).²¹ As in the other systems, the thermal transitions of the polymer 4/13 blends were reexamined by DSC after 5 years, and although a slight deviation exists between the corresponding values, the blends retained their miscibility over time. This persistent miscibility is due to the strong hydrogen bonding within the system. Figure 7 shows the T_g 's of the system in relation to the percent incorporation of polymer 4 for both the old and new polymer blends.

Poly[bis(phenoxy)phosphazene] (5) was allowed to form an alloy with polystyrene (9) and was found to be semimiscible in concentrations between 10 and 70% loading of

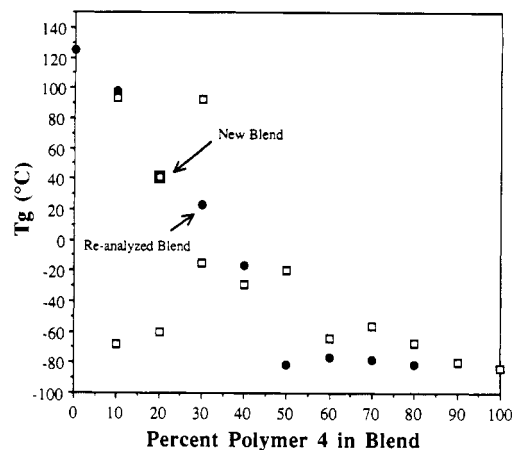


Figure 7. Graphs of T_g ($^{\circ}\text{C}$) vs percent polymer 4 in old and new poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (4)/poly(acrylic acid) (13) blends: ●, old blends; □, new blends.

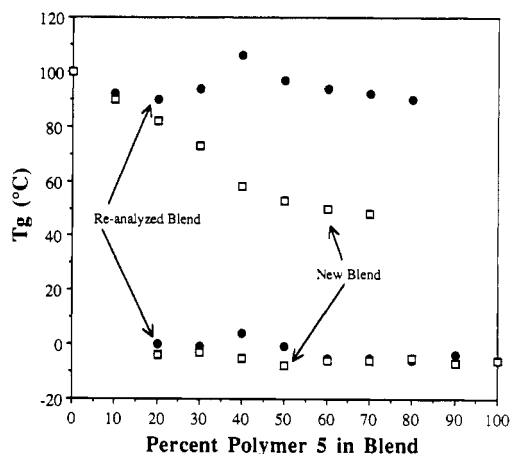


Figure 8. Graphs of T_g ($^{\circ}\text{C}$) vs percent polymer 5 in old and new poly[bis(phenoxy)phosphazene] (5)/polystyrene (9) blends: ●, old blends; □, new blends.

polymer 5. In every sample, a T_g was detected at -6°C , which is the T_g for polymer 5. Thus, domains exist in the blend which are composed solely of polymer 5. Additional transitions existed in an intermediate range ($+90$ to $+50^{\circ}\text{C}$) distinct from the constituent polymer T_g 's (-6 (5) and $+100$ (9)). These intermediate transitions fall at lower temperatures as the loading of polymer 5 increases in the system. This semimiscibility could be due, in part, to the similarity of the aromatic, hydrophobic side groups. Many examples exist of miscible systems containing polystyrene together with either a polystyrene of different tacticity, or a polystyrene derivative.²² However, after 5 years, these polymer blends became totally phase separated. DSC thermograms show transition for the constituent polymers, but no intermediate peaks were present. This illustrates the relative weakness of the interactions. The DSC data comparing T_g 's for different percentages of polymer 5, for both old and new blends, are shown in Figure 8.

TEM micrographs were obtained for samples of both old and new blends containing polymers 5 and 9 in ratios of 50%/50% of each polymer and are shown in Figures 9 and 10. The TEM for the recently prepared alloy, shown in Figure 9, shows a phase-separated material presumably containing regions composed solely of polymer 5 and regions containing the miscible portions of the blend. The

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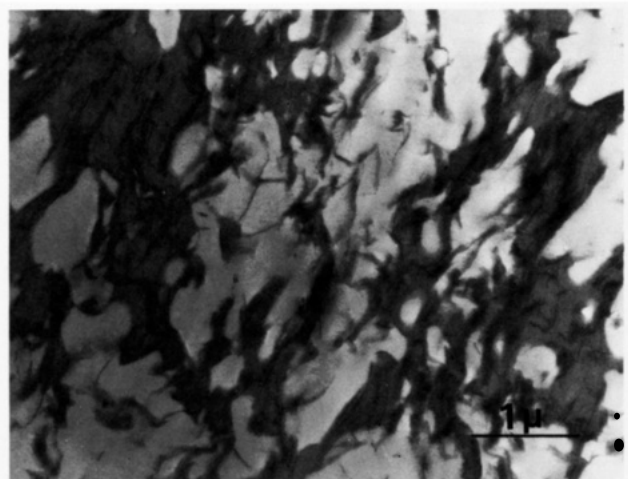


Figure 9. TEM micrograph of 50%/50% newly prepared poly[bis(phenoxy)phosphazene] (5)/polystyrene (9) blend.

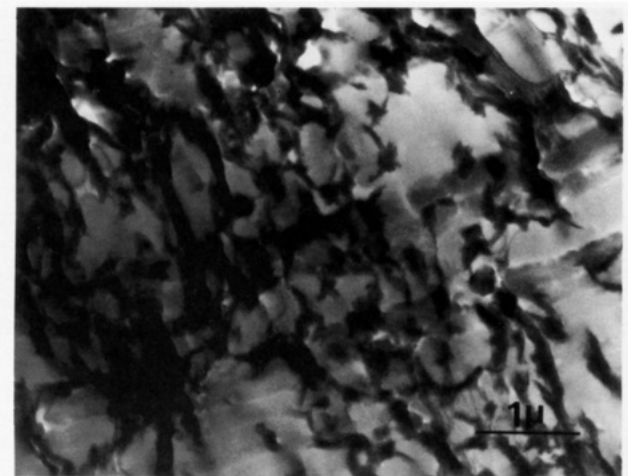


Figure 10. TEM micrograph of a 50%/50% old poly[bis(phenoxy)phosphazene] (5)/polystyrene (9) blend.

phases that contain polymer 5 only are darker than the regions containing the miscible combinations. The phases in Figure 9 are almost in a "free-flowing" arrangement whereas the phases in Figure 10 seem more regimented, and the separation between the domains seems to be more rigid and distinct.

Polymer blends containing 5 were also semimiscible with poly(methyl methacrylate) (10). Glass transition temperatures for the constituent polymers were -6 (5) and $+105$ °C (10) and transitions were found in each sample at -6 °C and also displaced from 105 °C. This suggests a low degree of miscibility within the system. Blends containing polymers 5 and 10 were reanalyzed by DSC after 5 years and, although some differences exist between the old and new materials, some miscibility remained in the system. Figure 11 illustrates the T_g of the polymer blends at various concentrations of polymer 5 for both the old and new blends.

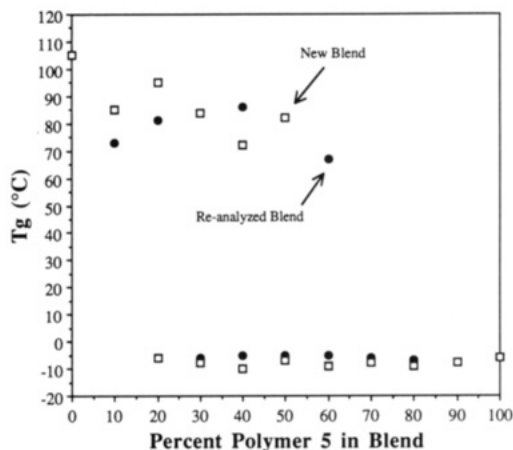


Figure 11. Graphs of T_g (°C) vs percent polymer 5 in old and new poly[bis(phenoxy)phosphazene] (5)/poly(methyl methacrylate) (10) blends: ●, old blends; □, new blends.

Conclusions. The preparation and characterization of polymer blends containing poly(organophosphazenes) and organic polymers has been accomplished. These blends contain a variety of functional groups which allow for intermolecular interactions such as hydrogen bonding, dipole-dipole interactions, or van der Waals forces within the alloy. A similarity of functional groups in two constituent polymers might also contribute to the miscibility of a polymer blend. The strength of these interactions and the tendency for miscibility were determined by comparing DSC and TEM data of freshly made samples of semimiscible polymer blends with those prepared 5 years ago. Those materials with strong interactions between the constituent polymers retained their miscibility while the weakly interacting samples underwent phase separation over time. These results can be seen clearly when comparing the blends composed of poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (4) and either poly(vinyl alcohol) (12) or poly(acrylic acid) (13) and those containing poly[bis(phenoxy)phosphazene] (5) and polystyrene (9). The blends containing polymer 4 are capable of strong hydrogen-bonding interactions between the components, and these materials retained their semimiscibility over a long period of time. However, polymers 5 and 9 interact mainly via weaker van der Waals forces and totally phase separated after 5 years.

Both miscible and immiscible phosphazene alloys are of considerable interest as membranes, biomaterials, or flame retardant materials due to the ease of tailoring of their properties and the broad opportunities that exist for combining a wide range of polyphosphazenes with many different organic polymers.

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