Novel Miscible Blends of Etheric Polyphosphazenes with Acidic Polymers

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ABSTRACT: The miscibility of inorganic polyphosphazenes with organic polymers is investigated. The presence of acidic or proton-donating functional groups on the organic polymer is shown to increase the miscibility of the organic polymer with polyphosphazenes containing ethylene oxide side chains. Thus, poly(vinylphenol) (PVPh) is miscible over the entire composition range with poly[bis(methoxyethoxyethoxy)-phosphazene] (MEEP) and with poly[bis(methoxyethoxyethoxyethoxy)phosphazene] (MEEEP) but is not miscible with poly[bis(trifluoroethoxy)phosphazene] or with poly[bis(phenoxy)phosphazene]. Differential scanning calorimetry is used to determine the glass transition temperatures of these blends. The shape of the T_g–composition curves is found to be sigmoidal and is very similar to that reported for blends of polystyrene and poly(vinyl methyl ether). The enthalpy of mixing is determined for low molecular weight model compounds of the polymers. These results show that the interactions between the phenol and the etheric phosphazenes are strong and exothermic, whereas the interactions between the phenol and the trifluoroethoxy and phenoxy phosphazenes are endothermic. Interactions between PVPh and MEEP are also observed via infrared studies. Preliminary studies reveal miscibility of MEEP with a number of styrene or methyl methacrylate copolymers when a small amount of acidic comonomer is introduced.

Introduction

Polyphosphazenes are a class of polymers that show many diverse and interesting properties. Many exhibit liquid-crystalline-like behavior, and most are excellent flame retardants. These polymers are useful in various applications including gasket materials, membranes, biomedical materials, moldings, and coatings.[1a] Etheric polyphosphazenes are defined as containing poly(alkyleneoxy) substituents (such as (methoxyethoxy)ethanol and triethylene glycol monomethyl ether) and have been described by Allcock and Shriver.[1b,2] Etheric polyphosphazenes have the ability to conduct ions when doped with low lattice energy salts and find use as polymeric electrolytes.[1b] There has been little work in the area of polyphosphazene blends, especially of miscible blends. Nonmiscible blends of various polyphosphazenes are known. Blends with siloxanes[3] and other organic polymers[4] have been studied. Aryloxypolyphosphazenes have been blended with organic polymers (polyesters, polyamides, polycarbonates, and polyurethanes) to improve flame retardance.[5] Poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP) has been blended with poly(ethylene oxide) (PEO) to form a polymer electrolyte.[6] The crystallinity of the PEO phase adds dimensional stability to MEEP, which is amorphous and has a glass transition temperature (T_g) of −82 °C. Interpenetrating networks (IPNs) of MEEP with polystyrene or poly(methyl methacrylate) were found to be phase separated.[7] More homogeneous IPNs of polyphosphazenes with polyacrylonitrile (PAN) or poly(acrylic acid) have also been reported.[8] Mixtures of wholly polyphosphazene compositions have been shown to produce miscible blends. These include mixtures of various poly[(fluoroalkoxy)phosphazenes][9] or mixtures of various poly[(aryloxy)phosphazenes].[9,10]

In many cases, the observed miscibility in polymer blends is a direct result of a negative enthalpy of mixing (ΔH_m) contribution to the overall free energy of mixing (ΔG_m),[11,12] the fundamental thermodynamic quantity controlling miscibility.

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

For a blend to be single-phased the requirement that $\Delta G_m < 0$ must be fulfilled. Additionally, the second derivatives of ΔG_m with composition must be zero or positive. For high molecular weight polymers (which have large molar volumes) the combinatorial entropy terms will be small. Therefore, enthalpic contributions usually dominate in polymeric systems. When only dispersive or van der Waals forces are present, the enthalpy of mixing will depend on the square of the difference in the solubility parameters (δ_i) of the two polymers. This difference will always be positive, or zero if δ_i and δ_j are near equal, ultimately leading to contributions to ΔG_m that are unfavorable to mixing. For many systems, however, there exist specific interactions, such as hydrogen bonding or dipolar coupling, which result in negative ΔH_m and contribute favorably to the free energy of mixing. The enthalpy of mixing can then be written in the empirical form

$$\Delta H_m/V = RT(\chi_{ij}/v^0)\phi_i\phi_j \quad (2)$$

where χ_{ij} is the binary interaction parameter, ϕ is the volume fraction, V is the total volume, and v^0 is an arbitrary segment volume, not easily defined for polymers.

Knowledge of the enthalpy of mixing is fundamental to the understanding of polymer–polymer miscibility. Calorimetry is one of the most direct methods of determining this thermodynamic parameter. Unfortunately, the enthalpy of mixing of two high molecular weight polymers cannot be measured directly in the bulk state due to their high viscosities and low diffusion coefficients. An alternative approach (chosen for this work) is to measure the heat of mixing of low molecular weight models of the polymers in question. Low molecular weight polymer analogs have frequently been used in such experiments.[13] The choice of the model structure is important since different models can give somewhat different results. Although this choice remains subjective, valuable insight and quantitative information can be obtained from these measurements. Typically, a model compound is chosen to have a structure that is similar to the monomeric unit

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of the polymer or that is a dimer or cyclic derivative of this unit. Oligomers have also been used elsewhere as models for the corresponding polymers.[14] Mixing can be done readily when the model compounds are in the melt state. Since the enthalpy of mixing results from changes in energy associated with nearest-neighbor contacts, it should be independent of molecular weight, to a first approximation, unless strong steric restrictions associated with the polymer are present. An interaction parameter, χ_{ij} (where $\chi_{ij} = \chi_{ij}/v^0$), between the two compounds can be obtained via these experiments (eq 2).

Free volume, or equation of state, effects are also extremely important in the thermodynamics of polymer mixtures. Although free volume differences are more obvious between a polymer and a solvent (the polymer having a much lower free volume), two polymeric liquids will also have different free volumes because of differing flexibilities of the chain backbones and pendant side groups. These can be reflected by differing values of T_g. The Prigogine–Flory theory predicts that two liquids (or polymers) that have differing free volumes will experience a net contraction upon mixing, leading to a negative contribution to ΔS_m and, thus, a positive contribution to ΔG_m that is unfavorable to mixing.[15] Thus, it is unexpected that two polymers having widely differing T_g's will be miscible. The polymers that are being blended in this study have different free volumes, as evidenced by the large differences in glass transition temperatures (MEEP is a viscous liquid with a T_g of −82 °C and poly(vinylphenol) (PVPh) is a highly self-associated glass with a T_g of 188 °C).

From the above discussion, it is clear that the presence of specific interactions between the polymers is important in promoting their miscibility. In this study the basicity of the etheric side chains of MEEP is shown to increase the miscibility of the polyphosphazene with polymers containing acidic functional groups via hydrogen-bonding interactions. Several miscible pairs of polymers are observed.

Experimental Section

Materials. Reagent grade 2-(2-methoxyethoxy)ethanol (Kodak) and triethylene glycol monomethyl ether (Fluka) were distilled from BaO and stored over molecular sieves. Hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene (>99%, Tracon Industries Corp.) were recrystallized from hexane and sublimed before use. Tetrahydrofuran (THF) was refluxed over sodium benzophenone and distilled. Tetrabutylammonium bromide (Kodak) was dried using an Abderhalden pistol.

Model Compounds. The molecular structures, melting points, and densities of the model compounds are listed in Table I. Ethylphenol (EPH) was obtained from Eastman Kodak Co. The cyclics $N_3P_3(OCH_2CF_3)_6$, $N_4P_4(OCH_2CF_3)_8$, and $N_4P_4(OC_6H_5)_8$ were prepared following standard literature procedures.[16]

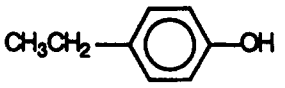
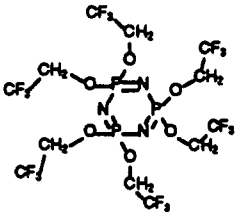
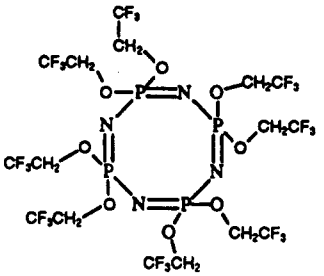
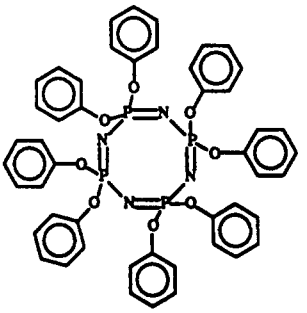
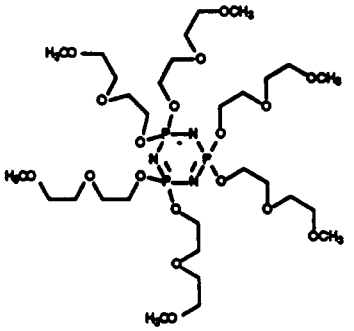
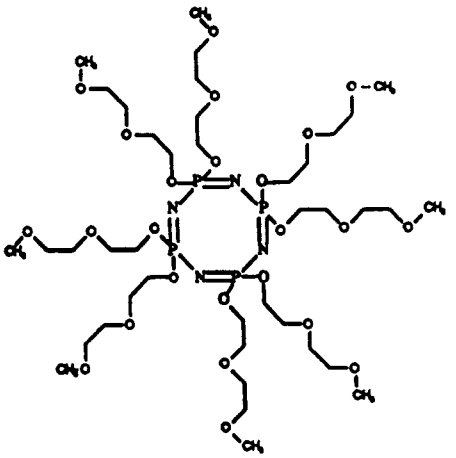
(a) Synthesis of $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_6$. The title compound, $(MEEP)_3$, was prepared by conventional procedures for the synthesis of cyclic phosphazenes,[16,17] combined with procedures used in the MEEP polymer synthesis.[16] Hexachlorocyclotriphosphazene (50 g, 0.14 mol) was dissolved in THF (500 mL), and the mixture was added to a solution of sodium (methoxyethoxy)ethoxide and tetrabutylammonium bromide (0.53 g, 1.6 mmol). The alkoxide was prepared from (methoxyethoxy)ethanol (350 mL, 2.94 mol) and sodium (29.2 g, 1.26 mol) in THF (300 mL). The reaction mixture was refluxed overnight, neutralized with 5% HCl, and poured into a separatory funnel where two layers formed. The top layer was isolated, THF removed with a rotary evaporator, and the excess alcohol removed by vacuum distillation. Final purification was effected by passing 5.0 g of the distillation residue down a short silica column (3 cm × 10 cm) and eluting with dichloromethane, followed by two additional passes through neutral alumina to yield 3.6 g of a clear oil. The ^{31}P NMR spectrum in acetone-d_6 was a singlet at 19 ppm. Gas chromatography showed the product to be greater than 95% pure, but other peaks were present in the chromatogram, all with similar retention times. Attempts to resolve the peaks using GC/MS were unsuccessful. Field desorption mass spectrometry showed two large peaks at m/e 850 and 848, which were assigned to $[M + H]^+$ and $[M - H]^+$ where M^+ is the $(MEEP)_3$ molecular ion. Additionally, several other species were observed. The molecular ions of m/e 864 and 862 were assigned to a cyclic structure, with one of the six side groups terminating in an ethoxy group instead of a methoxy group. The molecular ions of m/e 806 and 804 were assigned to a cyclic with one methoxyethoxy side group. The molecular ion at m/e 894 was assigned to a cyclic with one methoxyethoxyethoxyethoxy group. The molecular ion at m/e 952 was assigned to a cyclic that had a methoxyethoxyethoxyethoxy group and an ethoxyethoxyethoxyethoxy group. The molecular ion at m/e 748 was assigned to a $(MEEP)_3$ molecular ion minus one side group. Further support for these assignments comes from GC/MS analysis of freshly distilled 2-(2-methoxyethoxy)ethanol. Tentative assignments of the molecular ions of methoxyethanol, (ethoxyethoxy)ethanol, (methoxyethoxyethoxy)ethanol, and (ethoxyethoxyethoxy)ethanol were made on the basis of the mass spectral patterns. Assignments were difficult due to the small amount of impurities. Water was also observed in the distilled alcohol.

(b) Synthesis of $N_4P_4(OCH_2CH_2OCH_2CH_2OCH_3)_8$. The synthesis of the title compound, $(MEEP)_4$, was carried out in a manner similar to the $(MEEP)_3$ synthesis described above. Octachlorocyclotetraphosphazene (50 g, 0.14 mol) was dissolved in THF (250 mL), and the mixture was added to a solution of sodium (methoxyethoxy)ethoxide and tetrabutylammonium bromide (0.50 g, 1.6 mmol). The alkoxide was prepared from (methoxyethoxy)ethanol (470 mL, 3.92 mol) and sodium (44.0 g, 1.91 mol) in THF (400 mL). A ^{31}P NMR spectrum of the reaction mixture showed incomplete substitution on the phosphazene ring. The reaction mixture was refluxed for 48 h, neutralized with 5% HCl, and poured into a separatory funnel where two layers formed. The top layer was isolated, THF removed with a rotary evaporator, and the excess alcohol removed by vacuum distillation. Final purification was effected by passing the distillation residue down two short basic alumina columns (3 cm × 10 cm) and eluting with dichloromethane to yield a clear oil. The isolated yield for $(MEEP)_4$ was 19.8 g, which gives an isolated percent yield of 16% based on octachlorocyclotetraphosphazene. The ^{31}P NMR spectrum in acetone-d_6 was a singlet at 1.5 ppm. Field desorption mass spectra showed the major ion at 1133 amu, consistent with $[M + H]^+$ where M^+ is the $(MEEP)_4$ molecular ion. Unlike the trimer, no $[M - H]^+$ ion was observed. Many other peaks were observed between 900 and 1200 amu, but with such low intensities that they could not be identified.

Synthesis of Polymers. The structures and available characterization information of the homopolymers and copolymers used are presented in Table II. Poly(methyl methacrylate) (PMMA) was purchased from Aldrich. Poly(vinyl acetate) (PVAc) was purchased from Polysciences, Inc. Polystyrene (PS) was Styron 666 from Dow Chemical Co. Detailed synthesis and characterization information for poly(vinylphenol) (PVPh), poly(styrene-*co*-vinylphenol) containing 22 mol % VPh (P(S–VPh(22))), poly(styrene-*co*-styrene-4-carboxylic acid) (P(S–CA)), and poly(styrene-*co*-styrene-4-sulfonic acid) (P(S–SA)) is reported elsewhere.[18]

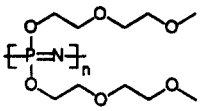
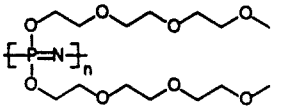
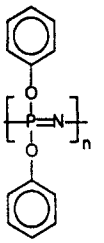
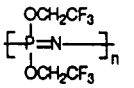
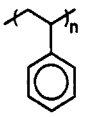
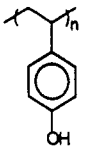
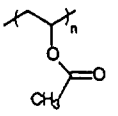
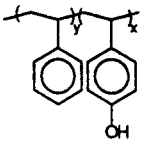
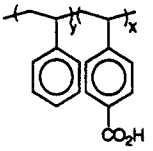
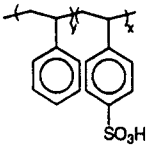
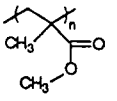
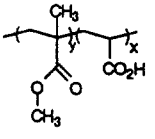
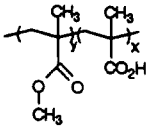
(a) Synthesis of Methacrylate Copolymers. The P(MMA–MAA) and P(MMA–AA) polymers were synthesized using a standard set of reaction conditions. Methyl methacrylate (MMA), acrylic acid (AA), and methacrylic acid (MAA) (Kodak) were purified by elution through a DHR-4 column (Scientific Polymer Products, Inc.) to remove inhibitors. THF (Kodak) was dried over sodium/benzophenone and distilled. Azobis[isobutyronitrile] (AIBN) (Kodak) was recrystallized from methanol. The standard reaction conditions are described below for a polymer prepared from a feed ratio of 80 mol % MMA and 20 mol % AA (P(MMA–AA(20))). All other copolymers were prepared in an analogous manner by varying the feed ratio of AA or MAA. Into a 250-mL round-bottomed flask, equipped with a mechanical stirrer and a reflux condenser, were placed 20 g (0.20 mol) of MMA, 3.60 g (0.05 mol) of AA, 50.15 g (56.6 mL)

Table I
Model Compounds

abbrev	T_m (°C)	structure	density (g/mL) [temp (°C)]
EPH	42–45		0.988 [50]
$(TFEP)_3$	49–51		1.518 [120]
$(TFEP)_4$	68–71		1.603 [120]
$(BPP)_4$	85		1.251 [120]
$(MEEP)_3$	liquid		1.175 [50]
$(MEEP)_4$	liquid		1.195 [50]

of THF, and 0.12 g (0.5 wt %) of AIBN. All polymerizations were run at 32 wt % solids and with 0.5 wt % initiator. The reaction mixture was placed under Ar using a Firestone valve, and then transferred to a 60 °C constant-temperature bath. The mixture was polymerized at 60 °C, under Ar, with constant stirring for ~16 h. The resulting solution was allowed to cool to room temperature, and the polymer was isolated by precipitation from ethyl ether and dried in vacuo for 2–4 days. A white polymer was

Table II
Polymers

chem name	abbrev	structure	$\bar{M}_w$[a]	$\bar{M}_w/\bar{M}_n$
poly[bis(methoxyethoxyethoxy)phosphazene]	(MEEP)		3×10^6	
poly[bis(methoxyethoxyethoxyethoxy)phosphazene]	(MEEEP)		$>3 \times 10^6$	
poly[bis(phenoxy)phosphazene]	(PBPP)		$\sim 1 \times 10^6$	
poly[bis(trifluoroethoxy)phosphazene]	(TFEP)		1.5×10^6	
polystyrene (Styron 666)	(PS)		241K	3.0
poly(vinylphenol)	(PVPh)		35.0K[b]	1.7
poly(vinyl acetate)	(PVAc)		218 K[b]	3.5
poly(styrene-*co*-vinylphenol)	P(S–VPh(22))		(x = 22) 95.6 K	2.0
poly(styrene-*co*-styrene-4-carboxylic acid)	P(S–CA(5)) P(S–CA(25))		(x = 5) 318K (x = 25) 58.4K	4.5 2.0
poly(styrene-*co*-styrene-4-sulfonic acid)	P(S–SA(12))		(x = 12) 241K	3.0
poly(methyl methacrylate)	(PMMA)		86.5K[b]	1.8
poly(methyl methacrylate-*co*-acrylic acid)	P(MMA–AA)		(x = 10) 81.5K (x = 20) 77.1K (x = 30) 82.1K	2.0 2.1 2.1
poly(methyl methacrylate-*co*-methacrylic acid)	P(MMA–MAA)		(x = 20) 104K	2.1

[a] Polystyrene equivalent unless noted otherwise. [b] Absolute molecular weight.

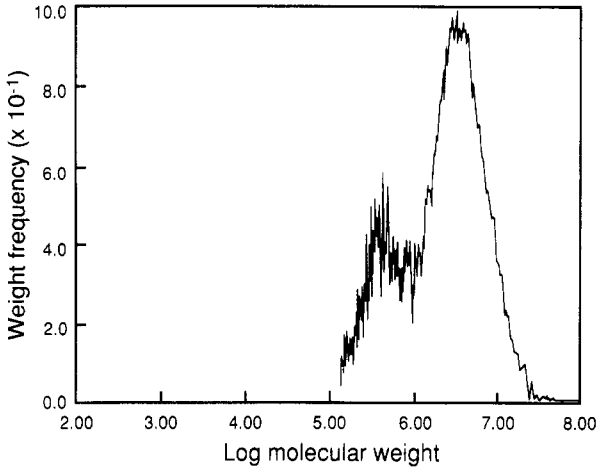


Figure 1. Molecular weight distribution of MEEP as determined by size exclusion chromatography.

obtained in 71.6% yield. Typical yields were 70–85%.

Molecular weight data were obtained by SEC by diazomethylating the acid functionality. The polymers are designated by the mole percentages in the monomer feed. Titrations for carboxylic acids were obtained on selected samples using hexadecyltrimethylammonium hydroxide as titrant in THF/methanol (50/2) as solvent. Typically, MAA was incorporated into the polymer at 90–95% of the feed amount whereas AA was only incorporated at 56–61% of the feed (for example P(MMA–MAA-(20)) was found to contain 18 mol % MAA and P(MMA–AA(20)) was found to contain 11 mol % AA). In all cases the amount of acid incorporated into the polymer was low, and MAA was always incorporated in higher amounts than was AA.

(b) Synthesis of Phosphazene Polymers. The polymers poly[bis(trifluoroethoxy)phosphazene] $[NP(OCH_2CF_3)_2]_n$ (TFEP) and poly[bis(phenoxy)phosphazene] $[NP(OC_6H_5)_2]_n$ (PBPP) were prepared following standard literature procedures.[19] The polymers MEEP and poly[bis(methoxyethoxyethoxyethoxy)-phosphazene] $[NP(OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (MEEEP) were prepared as described previously[2] with additional purification effected by diafiltration in water through an OSMO-52X-20K-(PS)52C column (Osmonics Inc.) and freeze drying (VirTis Freezemobile 25SL). The polymers were isolated as light amber, tacky solids. We state below that the etheric side chains of the MEE–phosphazene seem to be the determining factor governing the miscibility with other polymers. However, structural heterogeneity of the MEE–phosphazene polymer may play some role in determining the properties of the blend. Size exclusion chromatography (Figure 1) on the MEEP polymer indicated that the polymer has a high molecular weight ($\bar{M}_w$ and $\bar{M}_n$ both greater than 10^6) and has a bimodal or multimodal molecular weight distribution.[20] Similar observations have been made by several groups for other phosphazene polymers prepared by the ring-opening method (see ref 21 and references cited therein). As for the (fluoroalkoxy)phosphazene, it was determined that the modes were structurally different. This heterogeneity is caused either by a difference in branching (e.g. the low molecular weight fraction is branched more than the high molecular weight portion) or a chemical difference between the two modes. The same conclusions would be consistent with the chromatograms obtained for MEEP. (Caution should be taken because a Mark–Houwink plot was not obtained during the MEEP molecular weight analysis.) These factors may or may not be important in determining the properties of the MEE–phosphazene polymers in the blend. Work is in progress to test this with MEE–phosphazenes prepared by the condensation method.[22]

Preparation of Blends. The polymer blends were prepared by dissolving each component in a common, good solvent at a level of 5 wt %. The solutions were combined in the appropriate amounts. Most of the solutions were cast into shallow dishes, allowing for slow solvent removal to obtain equilibrium morphology, or knife coated to produce thin films on the order of 24 μm thick, allowing for rapid evaporation of the solvent. Samples for FTIR measurements were spin coated from solution onto KBr disks.

Table III
Blend Results

blend	solvent	film	DSC results[a]
PBPP/PVPh	THF	opaque	2
TFEP/PVPh	THF	opaque	2
MEEP/PVPh	THF	clear	1
MEEEP/PVPh	MEK	clear	1
MEEP/PS	THF, MEK	opaque	2
/P(S–VPh(22))	THF	clear	3
/P(S–VPh(22))	MEK	clear	1
/P(S–CA(5))	THF, MEK	opaque	3
/P(S–CA(25))	MEK	opaque	1
/P(S–CA)	THF	clear	4
/P(S–SA(2))	THF	~clear	2
/P(S–SA(12))	THF	clear gel	3
/P(S–SA(12))	MEK	clear gel	3
/P(S–SA(12))	pyr	clear	4
/PMMA	THF, MEK	opaque	2
/PVAc	THF	opaque	2
/P(MMA–AA(10))	MEK	clear	1 or 4
/P(MMA–AA(20))	MEK	clear	1 or 4
/P(MMA–AA(30))	MEK	clear	1
/P(MMA–MAA(20))	MEK	clear	1

[a] DSC results: 1, a single T_g at each composition; 2, two T_g values at each composition unshifted from the values of the individual polymers; 3, two T_g values, but shifted from those of the individual polymers; 4, undetermined.

The details concerning the preparation of the individual blends are reported in Table III. The blend samples were dried under vacuum from ambient temperature to a temperature that is close to or above the glass transition temperature (T_g) of the blend. The maximum drying temperature was, however, kept below 170 °C to prevent degradation.

Experimental Techniques. The enthalpies of mixing were obtained using a Setaram C-80 temperature-controlled calorimeter. A reversing mechanism ensures proper mixing of the two compounds. These are placed in separate chambers arranged as concentric cylinders with the top of each cell open to a small common vapor space. Typically, the total sample volume used was 2 mL. All of the measurements were performed at a common temperature (50.0 or 90.0 ± 0.1 °C), chosen such that all components are in the melt state and have a low viscosity.

When literature values were not available, the densities of the components were measured in the melt state using calibrated pycnometers.

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 or a Du Pont 990 thermal analyzer equipped with a data-analysis program by Laboratory Micro Systems, Inc. The heating rate used was 20 °C/min and the glass transition temperature is taken as the midpoint in the change in heat capacity with temperature.

FTIR spectra were obtained using either a Bio-Rad (Digilab Division) FTS-7 spectrometer (3240-SPC) or a Nicolet 60SX FTIR spectrometer at a resolution of 4 cm^{-1}.

Gas chromatography (GC) was carried out on a Hewlett-Packard 5890A capillary gas chromatograph using a J. & W. Scientific Co., 15-m, DB-5 narrow-bore, 0.25-μm film thickness capillary column. Gas chromatography/mass spectrometry (GC/MS) was performed using a Hewlett-Packard GC/MS 5987A System. Field desorption mass spectrometry (FDMS) was carried out using a Varian/Finnigan MAT-731 spectrometer.

Results and Discussion

Model Studies for Blends of PVPh with Polyphosphazenes. The heats of mixing of ethylphenol (EPH) (a model for poly(vinylphenol)) with several model compounds for polyphosphazenes containing different side groups were measured, and the results are shown in Figure 2. EPH was chosen to represent the potential hydrogen bond donor capable of interacting with the phosphazenes. Since the various model phosphazenes have different

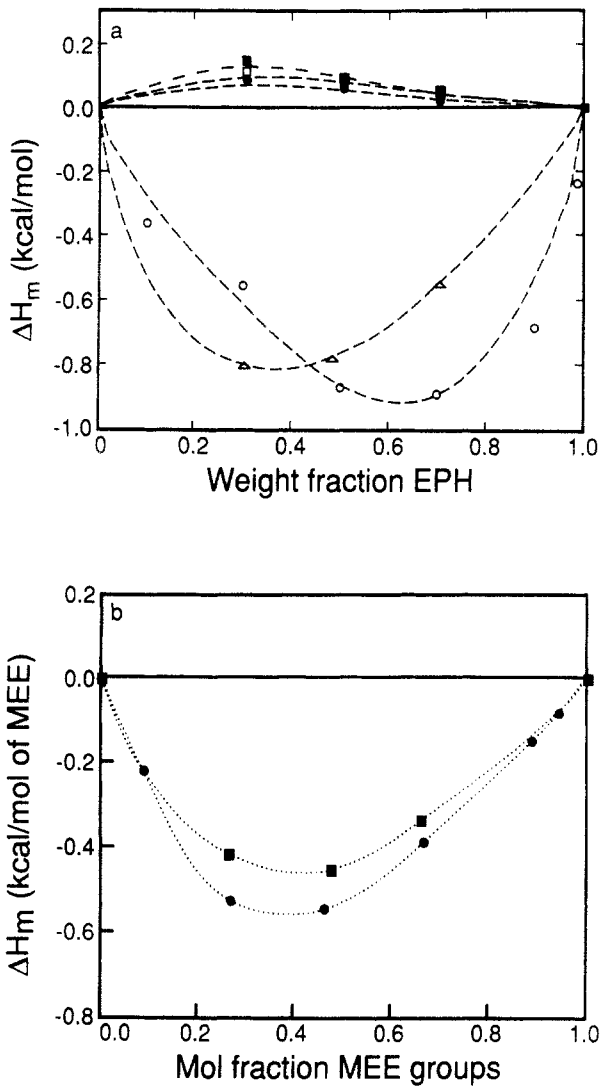


Figure 2. (a) Composition dependence of the heats of mixing for mixtures of EPH with (●) $(TFEP)_4$, (■) $(TFEP)_3$, and (□) $(BPP)_4$ at 90 °C, and (○) $(MEEP)_3$ and (△) $(MEEP)_4$ at 50 °C. (b) Composition dependence of the heats of mixing for mixtures of EPH with (●) $(MEEP)_3$ and (■) $(MEEP)_4$, normalized by the number of MEE side groups per molecule.

melting points, some of the measurements were carried out at slightly different temperatures to ensure that all components would be in the melt state. Typically, the measured value of ΔH_m will decrease slightly as the temperature is increased. However, these slight variations in temperature are not thought to greatly influence the conclusions drawn from this study. In Figure 2a the results are plotted in kilocalories per mole as a function of the weight fraction of EPH. As a result of the mismatch in the molecular weights of the phosphazene compounds relative to that of EPH, the curves for the analog models do not have similar symmetry with respect to composition. An alternate way of comparing the heats of mixing of EPH with each of the two MEEP models is illustrated in Figure 2b. The number of moles of the MEEP model compound has now been normalized by the number of methoxyethoxyethoxy (MEE) side groups present in each. For example, the MEEP trimer has six MEE groups and the tetramer has eight.

Two conclusions can be drawn from these results. The first is that different models for the same polymer, that is, a trimer or tetramer, give very similar values for the enthalpy of mixing with EPH. The second is that the side groups on the phosphazene are the most important factor in determining the interactions with the phenol. EPH is a hydrogen bond (or proton) donor and will exhibit an exothermic interaction with a basic compound. Certain classes of organophosphazenes display properties of Lewis bases. In particular, the amino- and alkyl-substituted phosphazenes are readily alkylated on the backbone nitrogen atom.[23] Additionally, low oxidation state transition metals have been shown to form stable complexes or salts with these phosphazenes.[24] Other classes of phosphazenes are less basic, with the (fluoroalkoxy)-phosphazene representing an extreme. These trends are also observable from the basicity measurements of many cyclic phosphazenes, although the etheric phosphazenes have not been studied. The alkoxyphosphazenes are the closest analogs to the etheric phosphazenes, with pK_a' values (determined in nitrobenzene) ranging from −1.9 to +2.1.[25] Thus, the ring nitrogens in the ethyleneoxy-substituted phosphazenes are not expected to be readily protonated or to be hydrogen bond acceptors.[26] For these reasons, it is not surprising that coordination of cations from low lattice energy salts in MEEP is thought to take place at the etheric oxygens, without the participation of the skeletal nitrogen atoms.[1b] It is then reasonable that the phosphazene compounds containing the phenoxy $(BPP)_4$ or the trifluoroethoxy $(TFEP)_x$ side groups exhibit no favorable interactions with EPH. Only the MEEP models, which have long ethoxy-containing side groups that can in themselves act as hydrogen bond acceptors, show favorable (exothermic) interactions with EPH. This would suggest that the miscibility of these polyphosphazenes with other polymers will be governed primarily by the nature of the side groups.

The physical property variations of poly(organophosphazenes) are often dictated by the side groups on the polymer.[27] MEE- and MEEE-phosphazene polymers are high molecular weight, amorphous polymers with T_g values (midpoint of DCS endotherm) of −82 and −78 °C, respectively. The low T_g suggests a considerable amount of free volume associated with the etheric side groups and an inherent flexibility of the phosphorus–nitrogen backbone. Long alkylene oxide side groups result in crystallization of the side group.[2] However no evidence of crystallinity has been reported in the MEE- or MEEE-phosphazene polymers.[1b] A partial explanation why the MEE-phosphazenes are amorphous[28] may be that the etheric side groups consist of several different types of ethers. The mass spectrum of the "pure" $(MEEP)_3$ cyclic showed many different molecular ions, consistent with a variety of side groups on the ring (see Experimental Section). The presence of the various alkylene oxides on each of the cyclics may hinder crystallization of the model compounds. The extent of this effect on polymer and blend properties is unclear. However, it is reasonable to assume that the MEE and MEEE polymers are not truly homopolymers consisting of a single side group moiety.

In a further attempt to characterize the interactions between EPH and $(MEEP)_4$, FTIR was performed on this mixture at 50 °C. The results are shown in Figure 3, which shows the hydroxyl region of the absorbance spectrum. Both a 5/5 and a 3/7 mixture by weight of EPH and $(MEEP)_4$ were examined since these were the compositions for which the stronger enthalpy of mixing values were observed (see Figure 2a). The OH band of EPH is quite broad and may be deconvoluted into several overlapping bands. The band that occurs at higher wavenumbers (ca. 3525–3540 cm^{-1}) is due to free or unassociated hydroxyls. The lower frequency bands are due to hydrogen-bound hydroxyls. $(MEEP)_4$ has no contribution to the infrared spectrum in the region above 3000 cm^{-1}. The intensity of

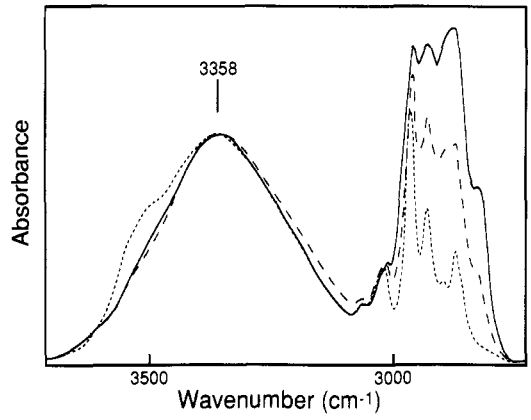


Figure 3. Hydroxyl stretching region of the infrared spectra for pure melts of (- - -) EPH and (– – –) a 50/50 wt % mixture and (—) a 30/70 wt % mixture of EPH and $(MEEP)_4$ at 50 °C.

the peak at ca. 3520 cm^{-1} decreases substantially upon the addition of $(MEEP)_4$ to EPH. This suggests that heterointeractions are occurring between the two components. The position of the peak maximum for the associated hydroxyls (3358 cm^{-1}) remains unshifted for the blends relative to pure EPH. The reason for this absence of a shift in peak maximum is not fully understood since one is observed when the polymers are blended (as will be dicussed below). The difference between the models and polymers may be due to the cyclic nature of the phosphazene models.

Miscibility of Polyphosphazenes. The miscibility of PVPh with the three classes of polyphosphazenes discussed in the heats of mixing section was determined, and the results are presented in Table III.

Both the PBPP and TFEP polymers exhibit no miscibility with PVPh, as seen from the DSC results shown in Figure 4. In each case the blend exhibits T_g values and melting endotherms characteristic of the pure components. (Note that the location of the melting transition in the TFEP polymer depends on thermal history[29] that may be different in the blend.)

On the other hand, polyphosphazenes containing etheric side groups (MEEP and MEEEP) show complete miscibility with PVPh throughout the composition range. All of the miscible blends were optically transparent. The composition dependence of T_g for these miscible blends is shown in Figure 5. The shape of the T_g–composition curve is unusual and is identical for both series of blends. It is reminiscent of that seen for blends of polystyrene (PS) with poly(vinyl methyl ether) (PVME), another blend with a very large spread between the T_g values of the pure components.[30] Blends of polymers that strongly interact often show positive deviations of T_g from the weight-average values. Although the present polymers show strong heteroassociations, as seen from the heats of mixing studies and FTIR, the composition dependence of the T_g shows a strong negative deviation from additivity at low PVPh compositions. The shape of the T_g–composition curve suggests a destabilizing effect on the PVPh chains at high polyphosphazene compositions. Since the high T_g of PVPh is largely a result of strong self-associations, when a small amount of PVPh is present in an excess of MEEP (or MEEEP), most of the self-associations of the PVPh chains will be disrupted. This leads to an increase in mobility of the PVPh chains relative to their original state and a decrease in the blend T_g below additivity. Many equations based on free volume theory and thermodynamic mixing relations have been proposed to explain the composition dependence of T_g in miscible binary blends,

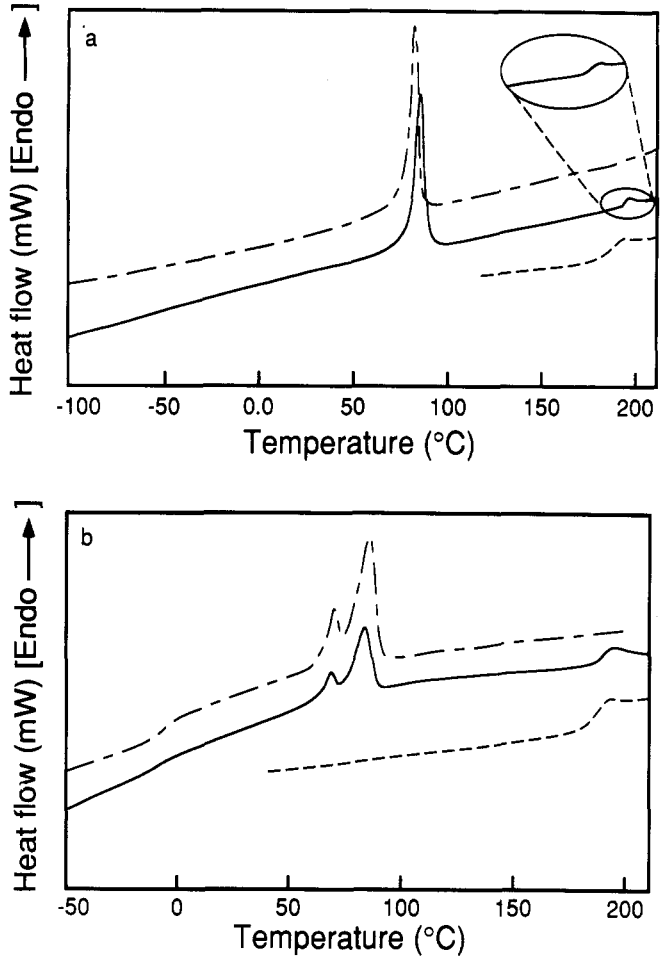


Figure 4. DSC traces for (a) (- - -) PVPh, (– – –) TFEP polymer, and (—) a 50/50 blend of PVPh and TFEP polymer and (b) (- - -) PVPh, (– – –) PBPP polymer, and (—) a 50/50 blend of PVPh and PBPP polymer.

and several reviews have been published on this subject.[31-34] Most of these equations predict a monotonic variation of T_g with composition. These simple linear equations, as well as the quadratic equation by Kwei[31] (which has been successful in fitting the composition dependence of T_g for miscible blends of strongly interacting polymers), fail to reproduce the shape of the data of this study; a higher order virial equation is required. This third-power equation (eq 3) (with respect to the concentration of the more rigid polymer) for the composition dependence of T_g was proposed by Brekner, Schneider, and Cantow.[35] It is based on the Flory–Huggins lattice theory and assumes that binary contact interactions influence both the conformational redistributions in the neighborhood of the heterocontacts and the free volume distribution in the blend. This equation has been shown to successfully fit data on PS/PVME blends. The equation is given by

$$(T_g - T_{g1})/(T_{g2} - T_{g1}) = (1 + K_1)w_{2c} - (K_1 + K_2)w_{2c}^2 + K_2 w_{2c}^3 \quad (3)$$

where w_{2c} is given by $[Kw_2/(w_1 + Kw_2)]$ and represents the corrected weight fraction of the component with the higher T_g and accounts for the changes of the volume fractions in the glass transition range of the blend due to the different expansion coefficients. K is (as in the Gordon–Taylor (G–T) equation) given by $K = K'(T_{g1}/T_{g2})$, where K' accounts for the ratio of the densities of the polymers at T_g (ρ_1/ρ_2) and for possible deviations from the universal value of the Simha–Boyer[36] constant relating $\Delta\alpha$ (the difference in the expansion coefficient in the glass

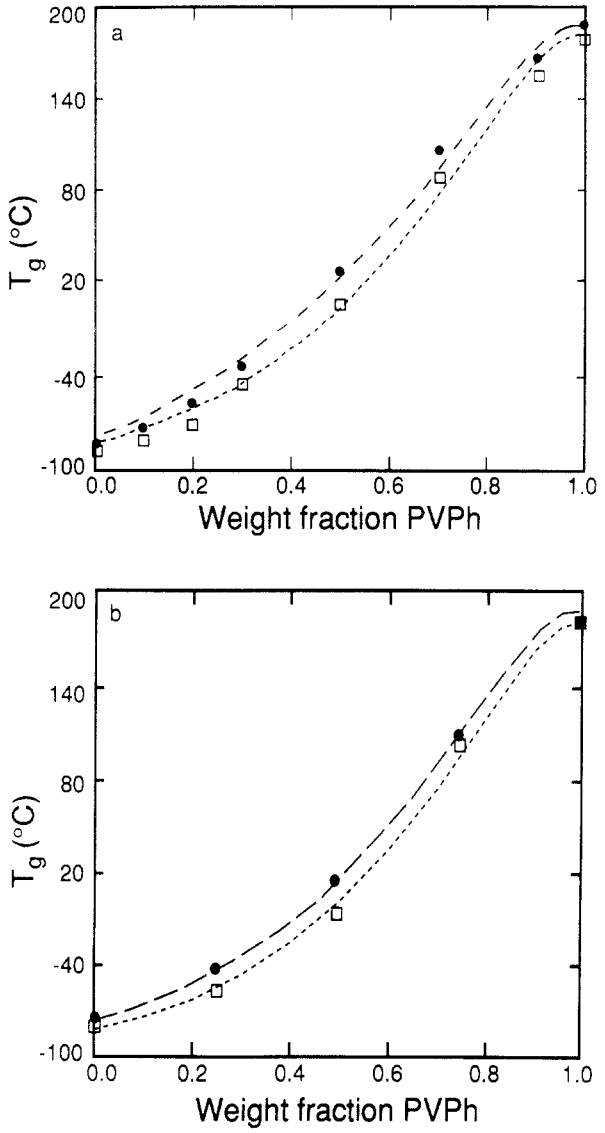


Figure 5. Composition dependence of the glass transition temperature for blends of (a) PVPh with MEEP [(□) onset and (●) midpoint] [the curves are fits to eq 3 fixing $K' = 1.00$. (- - -) represents the onset data with $K_1 = -1.15$ and $K_2 = -1.30$, and (– – –) represents the midpoint data with $K_1 = -1.20$ and $K_2 = -1.00$] and (b) PVPh with MEEEP [(□) onset and (●) midpoint] [the curves are fits to eq 3 fixing $K' = 1.00$. (- - -) represents the onset data with $K_1 = -1.15$ and $K_2 = -1.50$ and (– – –) represents the midpoint data with $K_1 = -1.20$ and $K_2 = -1.40$].

and liquid states) and T_g. In cases where the polymers have similar densities, the value for K' generally falls within the 0.8–1.2 range.[35] It has been suggested that[34,35] K_1 is associated with the interaction energy differences between hetero- and homomolecular contacts. It also includes energetic perturbations in the local environments of the contacts. K_2 considers the differences only between the energetic perturbations in the molecular surroundings of the binary contacts. Both can be related to orientation effects of the heterointeractions in the blend and are affected by molecular weight. If one assumes identical effects of the neighborhood perturbations ($K_2 = 0$ and K_1 finite), then eq 3 is equivalent to the Kwei equation. For conditions of volume additivity (K_1 and $K_2 = 0$), G–T equation is obtained.

The data for the two MEE–polyphosphazene/PVPh blends were fit to eq 3. Figure 5a shows the DSC values for the T_g of the MEEP/PVPh blends. Assuming similar densities at T_g, the value for K' was fixed at 1.0 and K_1 and K_2 were varied. These results are illustrated by the

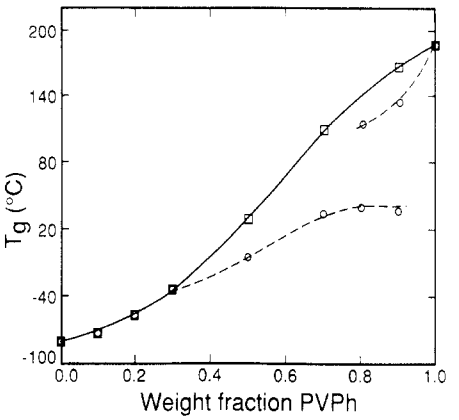


Figure 6. Composition dependence of the glass transition temperature (midpoint) for blends of PVPh with MEEP which were (□) knife coated from THF and (○) cast slowly from THF.

dashed curves in Figure 5. The best values obtained for K_1 fall between −1.0 and −1.2, and those for K_2 fall between −1.0 and −1.5, depending on whether the onset or midpoint data were used. These values are consistent with those determined for high molecular weight PS/PVME blends.[34] Figure 5b shows the data for the MEEEP/PVPh blend. The best values for K_1 and K_2 were similar to those determined for the MEEP/PVPh blends, although K_2 was consistently somewhat less negative.

Solvent Effects. Often, the equilibrium miscibility of a polymer pair is difficult to determine experimentally. This is particularly true in systems having strong interactions between components when the blends are prepared via solvent techniques. This is a result of solvent-induced phase separation since the solvent will interact more strongly with one component of the blend than with the other.[37] These effects confound the miscibility issue in several systems involving hydrogen bonding.[18,38] However, due to limited quantities of the polymers used in this study, it was necessary to prepare most of the blends via solvent casting techniques. Initially, the blends of MEEP and PVPh prepared by solution casting thick films from THF showed some tendencies to phase separate (producing opaque films) at higher PVPh compositions (higher T_g range). The DSC results for a series of blends prepared this way are shown in Figure 6 and are compared to those discussed above prepared by knife coating, in which the solvent is removed more rapidly. One may argue that by rapid removal of the solvent a nonequilibrium homogeneous morphology may be trapped in the blend. However, subsequent annealing above the T_g of the blend should result in phase separation of the two components. This did not occur in these systems.

The difficulty remains in finding a solvent system in which solvent-induced phase separation effects are less likely to occur. MEK (2-butanone) is a good candidate since it dissolves both the MEE–polyphosphazenes and PVPh. Also it has been reported that blends of PMMA and PVPh, which were found to phase separate when cast from THF, were single-phase when cast from MEK.[18] The miscibility of the latter system was confirmed by melt blending and precipitation experiments. Blends of MEEEP and PVPh were prepared from MEK and showed no tendency to phase separate. Extreme care was taken to ensure complete removal of solvent prior to the determination of T_g, since solvents to which PVPh can hydrogen bond are strongly retained in these blends. Therefore, the sigmoidal nature of the T_g–composition curves is believed to be real and not due to residual solvent. Furthermore, the blend compositions for which the T_g

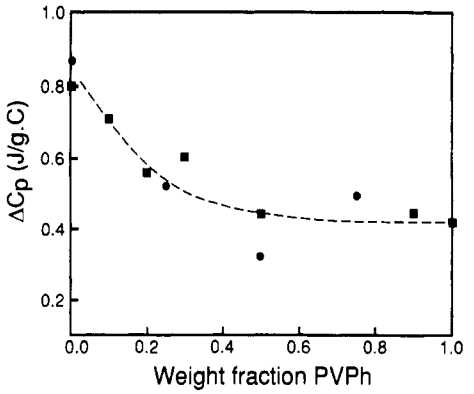


Figure 7. Composition dependence of ΔC_p for blends of PVPh with (■) MEEP and (●) MEEEP.

falls below additivity are those of low PVPh content and of lowest T_g. Both conditions would facilitate removal of solvent relative to the higher PVPh composition, higher T_g blends.

Heat Capacity. The composition dependence of the measured changes in heat capacity at T_g (ΔC_p) of the blends of MEE–polyphosphazenes with PVPh is plotted in Figure 7. Both MEE–polyphosphazenes exhibit very large ΔC_p values. A major contribution to the heat capacity of a polymer melt comes from the creation of free volume or holes[39] and from changes in the conformational degrees of freedom.[40] In the context of Wunderlich's[39] approach, the change in specific heat at T_g will be proportional to the number of beads in a polymer unit. A bead is defined as the smallest molecular unit whose movement can change the hole equilibrium. Both MEEP and MEEEP, which have several ethylene oxide (EO) units in each side group, would be divided into a large number of beads, each contributing to ΔC_p. MEEEP has two additional EO groups per polymer unit and exhibited a larger value for ΔC_p than observed for MEEP. In addition to the side group contributions, the polymer backbone of the phosphazene is inherently flexible and would increase both the free volume and the conformational degrees of freedom of the chains in the melt. Therefore, these polymers would be expected to show large values of ΔC_p. In fact, these values are somewhat larger than corresponding poly(itaconate esters) containing ethylene oxide units in the side chains on a stiffer carbon backbone. The reported ΔC_p values for the latter polymers with two and three EO units per side chain are 0.56 and 0.68 J g^{-1} K^{-1}, respectively,[40] slightly lower than those observed for the corresponding MEEP (0.8 J g^{-1} K^{-1}) and MEEEP (0.87 J g^{-1} K^{-1}). A more in-depth study of the heat capacity of these polyphosphazenes is currently in progress. PVPh also exhibits a larger ΔC_p than would be expected for a high-T_g polymer. This is probably a result of strong internal secondary forces that increase the internal energetics of the chain. High values for ΔC_p have been observed for many alcohols.[39] The composition dependence of ΔC_p for both blends is similar. An initial large decrease in ΔC_p is observed upon the addition of PVPh to the polyphosphazene, suggesting a loss in the free volume associated with the MEEP chains. ΔC_p seems to remain somewhat constant as more PVPh is added. In the figure, the dashed line is only drawn as a visual guide.

Infrared Studies. FTIR spectra on the PVPh/MEEP blend were obtained to determine the specific nature of the interactions. Shown in Figure 8a is the hydroxyl stretching region of the absorbance spectra of PVPh and a 1/1 blend of MEEP/PVPh. The maximum in the OH peak for PVPh is shifted significantly to lower wavenumbers upon addition of MEEP, indicating a strong interaction of the hydroxyl groups with MEEP. (The model compounds did not show as much shift, however.) The magnitude of this shift is consistent with that observed in blends of PVPh with ether-containing polymers such as poly(ethylene oxide) and poly(vinyl methyl ether).[41] The amount of unassociated OH groups in PVPh (represented by the peak at 3520 cm^{-1}) is also observed to decrease significantly upon addition of MEEP, similar to the results observed for the model compounds, shown in Figure 3.

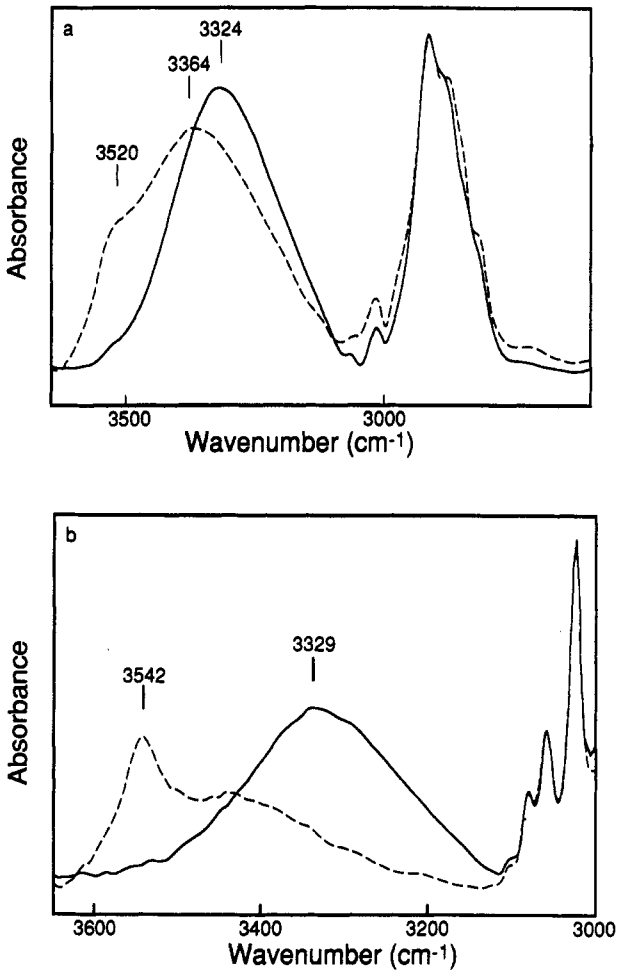


Figure 8. Hydroxyl stretching region of the infrared spectra for 50/50 wt % mixtures of (a) PVPh and MEEP cast from MEK and (b) P(S–VPh(22)) and MEEP cast from MEK. The dashed curves are the spectra for a digital addition of the spectra of the pure components.

Blends of MEEP with copolymers of styrene and vinylphenol were also studied. The hydroxyl stretching region of the infrared spectrum for P(S–VPh(22)), and a 1/1 blend with MEEP is shown in Figure 8b. The relative intensities of the free to the hydrogen-bound OH peaks for P(S–VPh(22)), which are larger than for the homopolymer, are reduced significantly upon addition of MEEP. In addition, the maximum for the hydrogen-bound peak in the copolymer blend is shifted to lower wavenumbers. In fact, the shape and peak position of the OH band for this blend is almost identical to that observed for the MEEP/PVPh 1/1 blend. The miscibility of these two polymers was difficult to determine unambiguously by DSC. The blends were prepared from both MEK and THF. All were optically transparent. Two very broad transitions, shifted from the T_g values of the pure components, were observed by DSC for the blends cast from THF, indicating a certain degree of inhomogeneity. On the other hand, a single T_g is observed at each

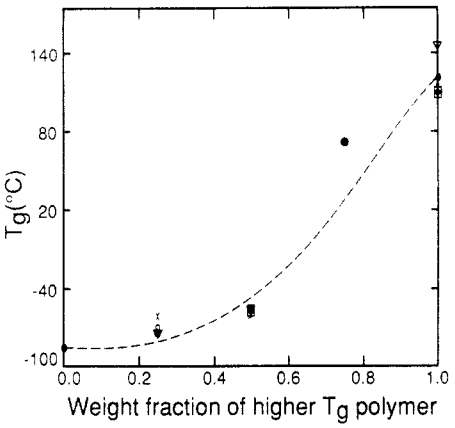


Figure 9. Composition dependence of the glass transition temperatures (onset) for blends of MEEP with (●) P(S–VPh-(22)), (○) P(MMA–AA(10)), (×) P(MMA–AA(20)), (□) P(MMA–AA(30)), and (▽) P(MMA–MA(20)). The dashed curve is given by eq 3 with $K' = 1.0$, $K_1 = -0.5$, and $K_2 = -1.7$.

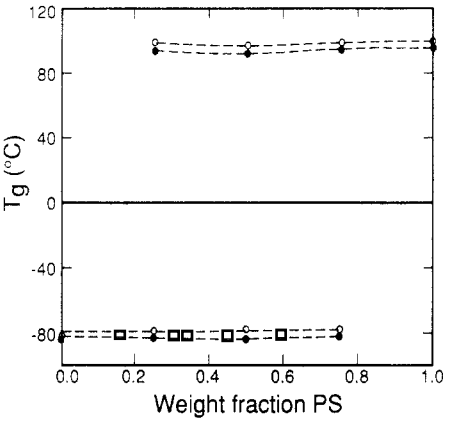


Figure 10. Composition dependence of the glass transition temperature for blends of MEEP and PS [(●) onset and (○) midpoint].

composition for the blends prepared from MEK. The DSC results for these blends, shown in Figure 9, reveal that, up to 50 wt % P(S–VPh(22)), the temperature of the glass transition does not increase significantly. Using a value of $K' = 1.0$, eq 3 (shown by the dashed curve in Figure 9) did not effectively fit the data. The observed behavior could also be described by the theory presented by Kovacs and Braun[33] where the lower T_g polyphosphazene is considered to act like a polymeric plasticizer and has a dominant role in determining the shape of the T_g–composition curve up to relatively high concentrations of the more rigid polymer. However, more work is required before an in-depth analysis can be made. The FTIR data for this blend are taken as evidence that strong interactions between these polymers are occurring. In addition, when solutions of this blend (1/1 by weight) were cast onto a microscope slide, they were clear and did not undergo phase separation (the presence of a cloud point) until heated to ca. 220 °C.

Other Miscible Blends. For comparison purposes, the miscibility of MEEP with PS, cast from both THF and MEK, was determined. All samples prepared were opaque and showed two distinct glass transitions at each composition, as plotted in Figure 10. This strengthens the idea that the miscibility of the MEE–polyphosphazenes with PVPh is due to specific interactions between the hydroxyl group of PVPh and the etheric side chains of the polyphosphazene. These ideas were extended to find other, new miscible blends. Several acidic-type polymers, their structures shown in Table II, were evaluated as potential candidates. In many instances, however, the results were somewhat ambiguous, most probably as a result of the solvent preparation techniques used. Nonetheless, strong interactions were observed between MEEP and several of these polymers and are discussed below.

Blends of MEEP with random copolymers of styrene and styrene-4-carboxylic acid (P(S–CA)), where the CA content was 5 and 25 mol %, resulted in opaque films. All the blends with P(S–CA(5)), prepared from THF or MEK, showed two distinct glass transitions, although the T_g curve for the low-T_g component of a 50/50 blend prepared from MEK was broadened substantially. A blend (50/50) of MEEP and P(S–CA(25)) showed a single, narrow T_g at a temperature that is substantially lower than additivity. Perhaps a second phase is actually present (opaque sample), for which the ΔC_p was too small to detect. Nonetheless, both results show that there is some intermixing of the P(S–CA) with the MEEP phase. Blends of MEEP with a random copolymer of styrene and styrene-4-sulfonic acid (containing 12 mol % SA) (P(S–SA(12))) were more promising. When the blends were prepared from THF or MEK, the polymers immediately formed a gel that dried to a clear film. Two T_g values were detected for these samples, although the values were substantially shifted from those of the individual components. When pyridine was used as the common solvent, a clear, stable solution was obtained from which a clear film could be cast. Unfortunately, no T_g was detected by DSC.

Since the etheric side chains of the MEE–polyphosphazenes seem to be the determining factor governing its miscibility with other polymers, another approach to finding miscible systems is to compare MEE(E)P miscibility with the miscibility of an organic polymer that it resembles, e.g., poly(ethylene oxide) (PEO). PEO is known to be miscible with PMMA[42] and PVAc.[43] Therefore, blends of MEEP with both of these polymers were prepared. Neither polymer showed miscibility with the MEE–polyphosphazene. This is not terribly surprising since one is comparing, on the one hand, a polymer containing short ethylene oxide side chains on an inorganic backbone with a linear homopolymer essentially consisting of one extremely long ethylene oxide side chain. The miscibility between PEO and PMMA (or PVAc) is not driven by strong interactions but is the result of a balance between dispersive and interactive forces. Even slight changes in the makeup of one of the polymers (going from a C—C to a P=N backbone) could disrupt this balance, resulting in immiscibility.

Introducing a small amount of acidic functionality to the acrylate polymer, however, is enough to induce miscibility. Blends of several copolymers of methyl methacrylate (MMA) and either acrylic acid (AA) or methacrylic acid (MAA) with MEEP were prepared. These blends were shown to be miscible by their optical transparency and the absence of phase separation indicated by a cloud point below ca. 200 °C. An attempt was also made to characterize them via their glass transition temperatures using DSC. The data for several blend pairs are shown in Figure 9. Only a few compositions were examined for each polymer pair. For the blends of MEEP with the acid-containing methacrylate copolymers, no T_g was discernible by DSC at the lower MEEP compositions. The similarity in the behavior at high MEEP compositions for the different blends is interesting. A single T_g is observed at each composition, which shifts only slightly to higher temperature as the more rigid polymer is added, up to about 50 wt % of the latter. These results are similar to those observed for the P(S–VPh(22)) blend. The work

presented in this section is only intended to be cursory. Further work is currently in progress using dynamic mechanical spectroscopy and dielectric relaxation to better define the T_g–composition curves of these MEEP blends.

Conclusions

Blends of several classes of polyphosphazenes with acidic organic polymers were investigated. The miscibility of the polyphosphazenes was controlled by the nature of the substituents along the phosphazene backbone. Hence, etheric polyphosphazenes such as MEEP and MEEEP are found to be miscible with poly(vinylphenol) (PVPh) over the entire composition range, whereas phenoxy (PBPP) and trifluoroethoxy (TFEP) polyphosphazenes are shown to be immiscible with PVPh. The enthalpy of mixing was determined by solution calorimetry for low molecular weight models of these polymers. The results indicate that strong interactions occur between the phenol and the MEEP models but not between the phenol and the other phosphazenes. FTIR analysis of the PVPh/MEEP blend also supports hydrogen bonding between the ethoxy side chains and the hydroxyl group of PVPh.

The observed shape of the T_g–composition curve, as well as the values for the fitting parameters K_1 and K_2, for the PVPh/MEE(E)P blends are similar to those reported for PS/PVME blends. Limited miscibility has been suggested to explain the compositional dependence of the T_g curve for the PS/PVME blend, which is believed to be microheterogeneous and undergoes phase separation at fairly low temperatures.[44] Stronger, hydrogen-bonding-type interactions have been shown to occur in the PVPh/MEEP blends (the absence of a detectable cloud point below 200 °C (where chemical reactions or decomposition is probable) supports this hypothesis). Thus, although the T_g–composition curves have similar characters (for PS/PVME and PVPh/MEEP), the interactions are different. This is consistent with the ideas that the miscibility (and the T_g) is influenced both by the energetic interactions between the polymers and by the associated free volume distribution due to conformational rearrangements of the chains in the neighborhood of the interacting contact points. Although the strong decrease in ΔC_p in the PVPh/MEE(E)P blends upon the addition of small amounts of PVPh suggests a loss in the free volume associated with the MEE(E)P chains, a corresponding and proportional increase in the T_g is not observed. In fact, T_g remains significantly below additivity, probably a result of a loss of stiffness of the more rigid PVPh chains. Further investigations of this anomaly are currently underway.

Preliminary evidence suggests that whereas MEEP is not miscible with PS or with PMMA, the addition of minor amounts of proton-donating monomers via copolymerization with styrene or methyl methacrylate enhances the miscibility of these polymers with the etheric polyphosphazenes. The glass transition temperatures of these blends remain far below what would be predicted from additivity of T_g's up to about 50 wt % of the more rigid polymer. These blends are currently being investigated by dynamic mechanical spectroscopy and dielectric relaxation so as to better define the molecular dynamics at the glass transition.

The dimensional stability of MEEP is improved by the incorporation of the higher T_g acidic polymer (50/50 mixtures by weight are not tacky and form free-standing self-supporting films). The fact that the T_g of the blend remains unusually low indicates that good ionic conductivity would be retained.

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References and Notes

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Registry No. PVPh, 59269-51-1; PVAc, 9003-20-7; (PS)(PVPh) (copolymer), 72317-19-2; (PS)(PCA) (copolymer), 28854-56-0; (PS)(PSA) (copolymer), 68491-85-0; PMMA, 9011-14-7; (PAA)(PMMA) (copolymer), 25322-25-2; (PMA)(PMMA) (copolymer), 25086-15-1; EPH, 123-07-9; $(TFEP)_3$, 1065-05-0; $(TFEP)_4$, 562-88-9; $(BPP)_4$, 992-79-0; $(MEEP)_3$, 131841-09-3; $(MEEP)_4$, 119256-93-8; $Cl_6N_3P_3$, 940-71-6; $MeO(CH_2)_2O(CH_2)_2ONa$, 19278-10-5; $Cl_8N_4P_4$, 2950-45-0.