

Formation of Pervaporation Membranes from Polyphosphazenes Having Hydrophilic and Hydrophobic Pendant Groups: Synthesis and Characterization

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ABSTRACT: A series of new polyphosphazene polymers were synthesized using three different pendant groups with the goal of probing structure–function relationships between pendant group substitution and polymer swelling/water flux through thin dense films. Formation of polymers with relative degrees of hydrophilicity was probed by varying the stoichiometry of the pendant groups attached to the phosphazene backbone: *p*-methoxyphenol, 2-(2-methoxyethoxy)ethanol, and *o*-allylphenol. The polymers in this study were characterized using NMR, thermal methods, and dilute solution light-scattering techniques. These techniques revealed that the polymers were amorphous high polymers ($M_w = 10^5$ – 10^7) with varying ratios of pendant groups as determined by integration of the ^1H - and ^{31}P -NMR spectra. Thin dense film membranes were solution-cast with azo-bis(cyclohexane)carbonitrile included in the matrix and crosslinked using thermal initiation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 422–431, 2001

Key words: polyphosphazenes; membranes; NMR analysis; pervaporation; hydrophilic

INTRODUCTION

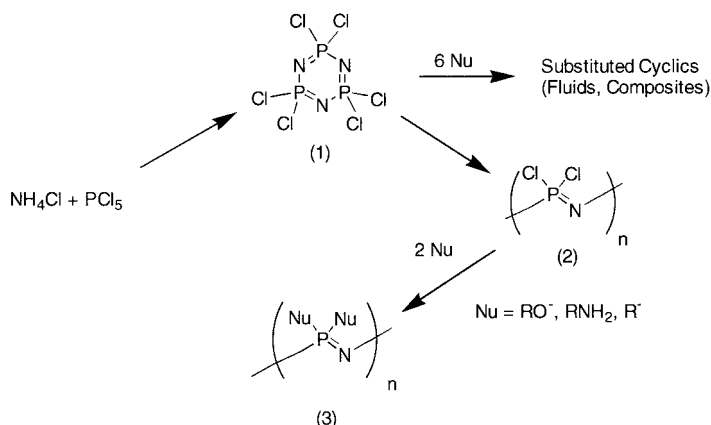
According to a recent report, membranes represent a major growth opportunity for the chemical industry with a projected annual growth of 8.2%, with the largest growth expected in the area of water treatment.¹ In our research effort, we have sought to apply the versatility inherent in polyphosphazene chemistry to membrane separations involving water transport through polymer materials. Polyphosphazenes, hybrid organic–inorganic polymers, have been shown to be effective gas-separation membranes² and liquid pervaporation membranes.³

These characteristics are due to the inorganic nature of the backbone that provides these materials with remarkable chemical and mechanical stability. Additionally, phosphazene materials can be tailored to specific applications through their organic component: the pendant groups attached to the phosphorus atoms of the backbone. Hydrophilic polymers have been synthesized through the attachment of pendant groups such as 2-(2-methoxyethoxy)ethanol (MEE).⁴ Likewise, hydrophobic materials have been synthesized through the attachment of groups such as phenols or aliphatic and aromatic amines. The premise behind our work was to blend these two methodologies to yield membranes with highly controlled solubility characteristics such that chemical selectivity would be enhanced.

Polyphosphazenes are characterized by alternating phosphorus and nitrogen atoms in the

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Scheme 1 Synthetic pathway for the formation of linear polyphosphazene polymers and cyclic trimer-related materials.

backbone with alternating double and single bonds. Numerous syntheses of polyphosphazenes have been reported.^{5–7} These polymers generally are synthesized in a two-step process: First, linear polydichlorophosphazene is formed using either a ring-opening process⁸ from a commercially available phosphonitrilic chloride trimer or via a condensation process.⁹ The second step is nucleophilic substitution of the backbone with the appropriate alkoxide or aryloxide (Scheme 1).^{8,10} This pathway differs from that of typical organic polymers and many inorganic polymers such as siloxanes where the monomer is first given the desired functionality followed by polymerization.

This two-step synthetic approach affords phosphazenes unparalleled versatility with respect to physical and chemical properties. Several polyphosphazene materials exhibit thermal stabilities up to 400°C (ref. 10) and these materials are known to be resistant to degradation by acidic environments. Polyorganophosphazenes are used as flame retardants,¹¹ in medical devices,¹² and as ionic conductors.¹³ The utility of these materials is dictated by choice of the pendant group. The result of this rich chemistry is an opportunity to directly match polymers for specific solubility characteristics.

Methods for crosslinking polyphosphazenes can be categorized into two separate areas: radiation-initiated (UV, electron beam, gamma) and chemically initiated (thermal free radical). Use of UV¹⁴ and gamma^{15,16} radiation has been reported for MEE polymers and the use of electron-beam radiation has been recently investigated by this group.¹⁷ Chemical crosslinking is generally performed by the inclusion of a free-radical initiator,

such as benzoyl peroxide, into the polymer matrix during membrane casting. After the solvent has been removed, the membrane is then heated ($\geq 130^\circ\text{C}$) for at least 10 min to effect crosslinking. For this method to be effective, a crosslinking moiety must be incorporated into the structure of the polymer. This moiety must have a sufficiently low carbon–hydrogen-bond activation energy to be easily susceptible to homolytic bond cleavage, such as an allylic group. This article reports our investigations into the simultaneous use of hydrophilic, hydrophobic, and allylic pendant-group attachments to form polymers with the potential to be used for membrane applications.

EXPERIMENTAL

General

All NMR spectra were acquired using a Bruker AC-300P or a Bruker DMX-300WB spectrometer operating at 300.1 MHz (^1H), 75.5 MHz (^{13}C), and 121.5 MHz (^{31}P). Proton NMR spectra were referenced to the residual protons in the deuterated chloroform (7.24 ppm; Cambridge Isotopes). All ^{13}C spectra were referenced to the centerline of the CDCl_3 triplet at 77 ppm. All ^{31}P spectra were referenced to an external H_3PO_4 . Glass transition temperatures were determined using a TA Instruments Model 2910 differential scanning calorimeter and TGA analyses were performed using a TA Instruments Model 2950 thermogravimetric analyzer. Elemental analysis was performed using a Carlo–Erba Instruments EA1108 CHNS-O elemental analyzer.

Dilute solution techniques were used to characterize the macromolecular structures of the polymers. Tetrahydrofuran (Aldrich, Milwaukee, WI), filtered through a 0.02- μm filter, was used as the solvent and all experiments were performed at 22°C. Solution refractive index increment, dn/dc , values were obtained using a Rainin Dynamax RI-1 differential refractive index detector. The instrument constant was determined via calibration using known concentrations of polystyrene standards whose dn/dc values are well known. Laser light-scattering (LLS) measurements were made using a Wyatt Technologies Dawn-DSP system which uses polarized light having a wavelength of 633 nm and measures scattered light intensities at 18 angles ranging from 22.5° to 147°. The instrument was calibrated with toluene that was filtered through a 0.02- μm filter. Dilute solutions in the 10^{-4} to 10^{-5} g/mL range were prepared for scanning on the LLS instrument. Zimm and Debye plots were prepared to obtain weight-average molecular weights M_w , z -average square radii (mean square radii), and second virial coefficients.

High-performance size-exclusion chromatography and detection (HPSEC) was performed using a Waters Model 2690 solvent/sample delivery system with a column bank of two Styragel HR 5E (4.6 mm i.d. \times 300 mm) solvent-efficient columns. The column temperature was maintained at 22°C and operated with a solvent flow rate of 0.3 mL/min. The polymer solutions were filtered through a 0.45- μm filter prior to injection onto the columns. Detection was achieved using the Wyatt Technologies Dawn-DSP laser light-scattering detector with the F2 flow cell that measures scattered light intensities at 16 angles ranging from 12.3° to 165.1°. The refractive index detector described above was placed in series with the light-scattering detector as a total concentration detector.

Synthesis of Polydichlorophosphazene, $(\text{PNC1}_2)_n$ (1)

The dichlorophosphazene polymer was made by ring-opening polymerization¹⁸ of the phosphonitric chloride trimer (Strem, Newburyport, MA), **1**, using a previously described method.¹⁹ An average of 40–45% conversion to the linear polymer, $(\text{PNC1}_2)_n$ was achieved.

Synthesis of Poly{bis[2-(2-(methoxyethoxy)ethoxy]phosphazene} (MEEP) (2)

This polymer was synthesized according to literature procedures²⁰ but was isolated and purified

in 66% yield via a novel route, exploiting the lower critical solubility temperature (LCST) behavior of this material in aqueous solution.

¹H-NMR (D_2O) δ (ppm) 3.3 (3H), 3.5 (2H), 3.7 (4H), 4.1 (2H); ³¹P-NMR δ (ppm) –6.6. ANAL. Calcd: C, 42.4%; H, 7.8%; N, 4.9%. Found: C, 42.5%; H, 7.5%; N, 4.8%. (M_w) = $(2.7 \pm 0.6) \times 10^7$ g/mol, RMS radius = 79.5 ± 0.4 nm; polydispersity (M_w/M_n) = 1.42 ± 0.47 .

All solvents (Aldrich) were anhydrous grade and used as received. The 2-(2-methoxyethoxy)ethanol (Aldrich) was vacuum-distilled prior to use. (bp 62–64°C at 0.7 Torr).

Synthesis of {PN[2-(2-methoxyethoxy)ethoxy] (*p*-methoxyphenoxy)}_n (3)

A solution of $(\text{PNC1}_2)_n$ (**1**) (12.2 g, 0.11 mol) was made with toluene (200 mL; Fisher, Pittsburgh, PA) and 5.6 g of tetra-*n*-butylammonium bromide (Aldrich). To this was added to a solution of *p*-methoxyphenoxy formed from 5.7 g (0.046 mol) of *p*-methoxyphenol (Aldrich), 1.8 g (0.047 mol) of sodium hydride (Aldrich, as a 60% suspension in mineral oil), and 150 mL of THF. Once added, a degree of gelation occurred and stirring was performed through use of a mechanical stirrer. The mixture was stirred for 3 h. A solution of sodium 2-(2-methoxyethoxy)ethoxide was prepared by reacting 22.2 g (0.185 mol) of 2-(2-methoxyethoxy)ethanol (Aldrich) with 7.1 g (0.185 mol) of sodium hydride (as a 60% suspension in mineral oil) in 200 mL of dry THF. This solution was then added to the polymer solution using a pressure-equalizing addition funnel followed by heating at 108°C for 18 h. Reaction progress was monitored by ³¹P-NMR spectroscopy. Once substitution was complete, the polymer was precipitated into water twice and hexane twice sequentially from THF to obtain a tan-colored gum in 26% yield.

¹H-NMR (CDCl_3) δ (ppm) 7.1 (brs), 6.7 (brs), 3.9 (brs), 3.5 (brs), 3.3 (brs), integration: MEE 77%, MEOAr 23%. ¹³C-NMR (CDCl_3) δ (ppm) 155.7, 146.0, 122.1, 113.9, 71.9, 70.2, 65.0, 58.8, 55.4. ³¹P-NMR (CDCl_3) δ (ppm) –8.3, –12.8, –16.9. (M_w) = $(1.46 \pm 0.2) \times 10^8$, RMS radius = 222.9 ± 34.9 nm, 2nd virial coefficient = $(5.22 \pm 4.0) \times 10^{-6}$. DSC T_g –60°C.

Preparation of Poly{bis[4,2(2-methoxyethoxyethyl)carboxylatophenoxy]phosphazene} (4)

Polymer **4** was prepared according to literature procedures.²¹

Synthesis of a Representative {PN[2-(2-methoxyethoxy)ethoxy](*p*-methoxyphenoxy)*o*-allylphenoxy]}_{*n*}(5)

(Polymers 5–9 were prepared using similar methods; the exact method for the preparation of 5 is shown here.) A solution of (PNCl₂)_{*n*} (1) (16.8 g, 0.14 mol) was made with toluene (200 mL) in a 2-L three-neck flask equipped with a mechanical stirrer. To this was added a solution of alkoxides/aryloxides formed from 21.8 g (0.18 mol) of *p*-methoxyphenol, 11.4 g (0.10 mol) of 2-(2-methoxyethoxy)ethanol (MEE), 6.4 g (0.05 mol) of *o*-allylphenol (Aldrich), 12.2 g (0.30 mol) of sodium hydride (as a 60% suspension in mineral oil), and 300 mL of THF. To this mixture was added 400 mL of diglyme (Aldrich) and then it was heated. THF and toluene were removed by a Dean–Stark trap until the reaction reached a stable reflux temperature of 115°C. Reaction progress was monitored by ³¹P-NMR spectroscopy. After 15 h, the completed polymer reaction was precipitated into water twice followed by hexane twice sequentially from THF to obtain a tan-colored gum in 48% yield. The product was characterized for molecular weight, NMR spectra, and thermal transitions.

Polymer 5: ¹H-NMR (CDCl₃) δ (ppm) 7.1 (brs), 6.7 (brs), 3.9 (brs), 3.5 (brs), 3.3 (brs). ¹³C-NMR (CDCl₃) δ (ppm) 155.7, 146.0, 122.1, 113.9, 71.9, 70.2, 65.0, 58.8, 55.4. ³¹P-NMR (CDCl₃) δ (ppm) –8.3, –12.8, –16.9. (*M*_w) = (1.2 ± 0.1) × 10⁷, RMS radius = 179.5 ± 11.8 nm, 2nd virial coefficient = (–1.33 ± 1.0) × 10^{–5}. DSC *T*_g –25°C. Polymer 6: (*M*_w) = (1.9 ± 0.3) × 10⁶, RMS radius = 47.6 ± 7.6 nm, *M*_w/*M*_n = 1.13, DSC *T*_g 3°C, 25% yield. Polymer 7: (*M*_w) = (3.2 ± 0.1) × 10⁶, RMS radius = 61.3 ± 2.0 nm, 2nd virial coefficient = (2.9 ± 2.0) × 10^{–4}, DSC *T*_g –19°C, 83% yield. Polymer 8: (*M*_w) = (4.0 ± 0.6) × 10⁶, RMS radius = 141.1 ± 11.5 nm, 2nd virial coefficient = (1.48 ± 2.0) × 10^{–4}, DSC *T*_g –36°C, 28% yield. Polymer 9: (*M*_w) = (6.7 ± 0.6) × 10⁵, RMS radius = 74.1 ± 9.1 nm, 2nd virial coefficient = (–4.54 ± 2.0) × 10^{–4}, DSC *T*_g –10°C, 37% yield. Chemical shifts for the ³¹P-, ¹H-, and ¹³C-NMR data for all of these polymers were similar to those for polymer 5.

Membrane-casting Method

The thin dense film membranes used in this study were formed by solution-casting. Casting solutions were made through dissolution of the polymer (2%) in THF followed by addition of 2% (poly-

mer weight percent) azo-bis(cyclohexane)carbonitrile, a free-radical initiator. The solutions were cast onto a solid substrate. For the TGA measurements, the substrate was a piece of smooth tempered glass. For the pervaporation experiments, porous ceramic disks were employed (AnodiscTM, 0.2 μm pore size). The solvent was allowed to slowly escape after solution casting, forming a film on the support. The membranes were thermally crosslinked in an oven at 130°C for at least 10 min prior to use. The materials on glass support were removed through immersion in water to aid the separation of the film from the substrate. The membranes used in this study were on the order of 50 μm in thickness.

Pervaporation Experiments

The membranes on porous supports were loaded into cells obtained from the Millipore (Bedford, MA) and modified for pervaporation experiments. Modification of the Millipore cells was accomplished to allow a pumping system to flow the feed solution over the membrane at approximately 50 mL/min. A diaphragm vacuum pump capable of providing a transmembrane pressure differential of 550 mmHg was installed on the system with a cryo-trap between the pump and the cell. Temperature control was provided by using a constant temperature water bath to heat the feed solution. Temperature was measured at the cell using a thermocouple. Permeates were collected for 6–8 h and quantified gravimetrically. Transmembrane fluxes are reported in terms of L m^{–2} h^{–1}, where L is the volume of the permeate; m², the membrane area (0.0017 m²); and h, the experimental time.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymer 3

In an earlier article,²² we reported the synthesis of linear phosphazene high terpolymers containing *p*-methoxyphenol (MEOAr) and 2-(2-methoxyethoxy)ethanol (MEE) pendant groups. That particular study indicated that synthetic progress can be monitored by ³¹P-NMR spectroscopy, where three distinct mers were observed corresponding to phosphorus atoms substituted in the following manner: PN(MEE)₂ (–8 ppm), PN(MEE)(MEOAr) (–12 ppm), and PN(MEOAr)₂ (–18 ppm). During the course of the reaction, a

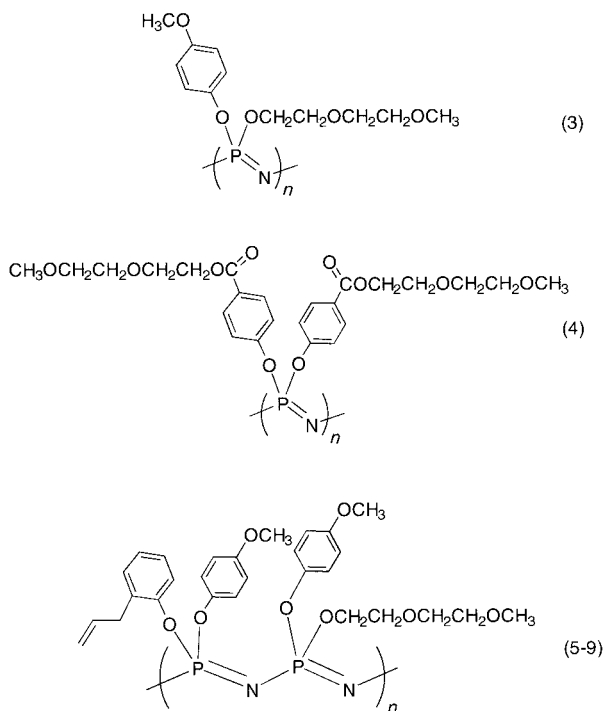


Figure 1 Representative structures of polymer **3**, polymer **4**, and polymers **5-9**.

monochlorinated intermediate was noted at -15 ppm. Syntheses are considered complete upon the disappearance of this resonance. Polymer **3** (Fig. 1) is an example of an MEE–MEOAr terpolymer. ^{31}P -NMR characterization of polymer **3** (Fig. 2) gave the expected three resonances that were integrated to give the following percentages of mers: $\text{PN}(\text{MEE})_2$ 56%, $\text{PN}(\text{MEE})(\text{MEOAr})$ 42%, and $\text{PN}(\text{MEOAr})_2$ 2%. DSC analysis of this polymer reveals only one feature: the T_g measured at -60°C . With no other significant features, it was expected that this polymer would require mechanical stabilization to function as an effective pervaporation membrane. Therefore, the inclusion of an additional moiety was required to provide a venue for facile crosslinking.

Synthesis and Characterization of Polymers 5–9

To facilitate crosslinking, allylic sites were added into the pendant group mix through the addition of a third pendant group generating polymers **5-9** and were initially reported.²³ *o*-Allylphenol was added to the mixture of MEE and *p*-methoxyphenol in amounts ranging from 5 to 16% of the available phosphorus sites to yield elastomeric phosphazene polymers (Fig. 1). The synthetic

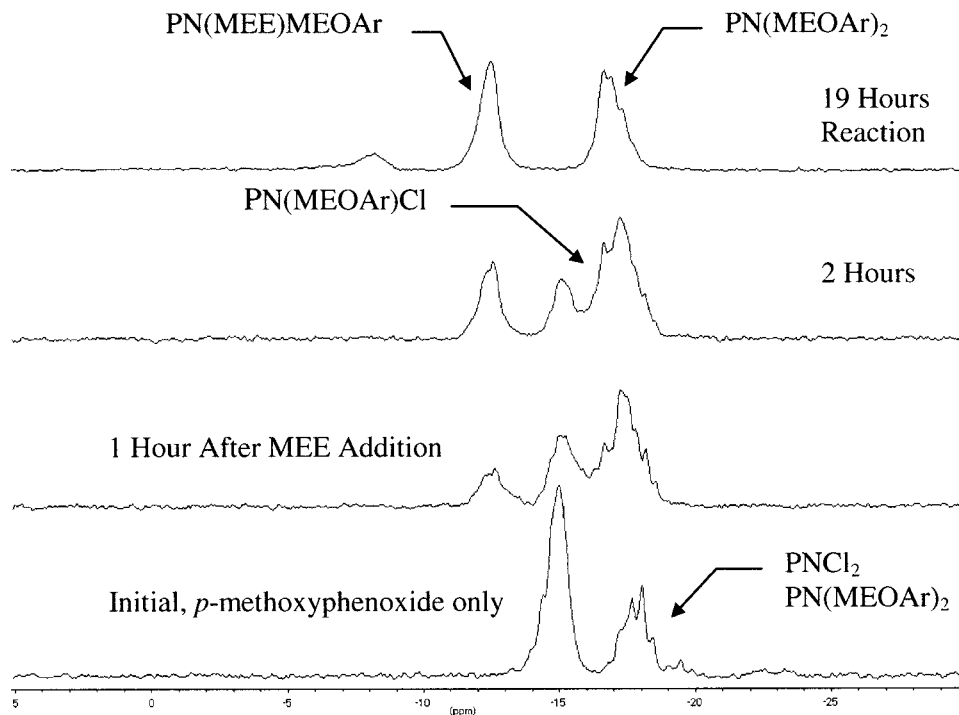


Figure 2 Reaction progress of linear PNCl_2 substitution by MEE and *p*-methoxyphenol. Reaction progress is presented from bottom with completion shown in the top spectrum.

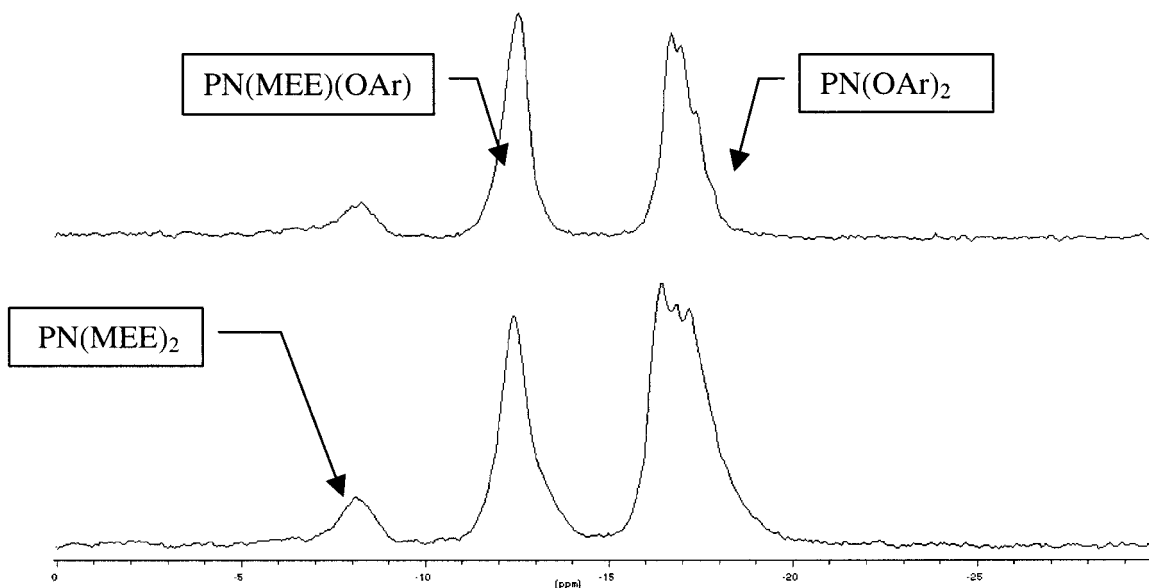


Figure 3 ^{31}P -NMR spectra of phosphazene polymers substituted with (lower, polymer **5**) MEE/*p*-methoxyphenol/*o*-allylphenol and (upper, polymer **3**) MEE/*p*-methoxyphenol.

methods employed were similar to that employed for terpolymer **3**, where all three nucleophiles were prepared in one reaction vessel, with each in approximately 10% excess as compared to phosphorus substitution sites. This method was compared to sequential nucleophile addition methods and it was observed that the one reaction vessel method gave the highest lot-to-lot reproducibility.

The progress of the synthesis of polymers **5–9** was followed by ^{31}P -NMR spectroscopy. A spectrum (Fig. 3) of purified polymer **5** was similar to that observed for terpolymer **3**. However, one significant difference was the peak assigned to the bis-aryloxy-substituted phosphorus (-17 ppm). With the inclusion of *o*-allylphenol, an envelope of three possible phosphorous species was observed. A further clarification of these assignments was provided by polymer **6**, which possessed a relatively low content of MEE: 8% of the total. The aryloxy-bound phosphorous envelope in the ^{31}P spectrum (Fig. 4), approximately -17 ppm, shows three distinct peaks with a sharp resonance at -16.8 ppm corresponding to $\text{PN}(\text{MEOAr})_2$; thus, the other two peaks at -17.7 and -17.3 ppm are assigned to homogeneously substituted bis(*o*-allylphenol)-substituted phosphorus and the expected heterogeneously aryloxy-substituted phosphorus, respectively.

The ^{31}P -NMR data was integrated to determine relative percentages of each phosphorus

species. These include $\text{PN}(\text{MEE})_2$, $\text{PN}(\text{MEE})\text{OAr}$, and $\text{PN}(\text{OAr})_2$; however, it should be noted that OAr signifies both the *o*-allylphenol and the MEOAr pendant groups, due to the lack of significant resolution for reliable integration of the envelope at -17 ppm. From these data, it is observed that the majority of the hydrophilic moiety, MEE, is attached to phosphorus in a heterogeneous manner. The clear exception to this observation is polymer **8**, where approximately half of the MEE is attached in the form of $\text{PN}(\text{MEE})_2$, in contrast to polymers **5**, **7**, and **9**, where this percentage does not exceed 38%.

The relative ratios of pendant groups (Table I) on the polymers were determined by curve-fitting deconvolution of ^1H -NMR spectra collected with a 60-s delay between scans to ensure complete relaxation. The amount of *o*-allylphenol varied between 11 and 16% with the exception of polymer **9**, which was measured at 5%. Polymers **5**, **7**, **8**, and **9** all contain amounts of MEE between 23% and 38%, which gives them a degree of hydrophilicity as bulk polymers. Polymer **6** shows no macroscopic hydrophilic behavior such as surface wetting due to an extremely low hydrophilic pendant group content.

Thermal analyses of polymers **5–9** reveal that the glass transition temperature, T_g , for each as the only significant feature, suggesting that the materials are amorphous. The Fox equation²⁴ de-

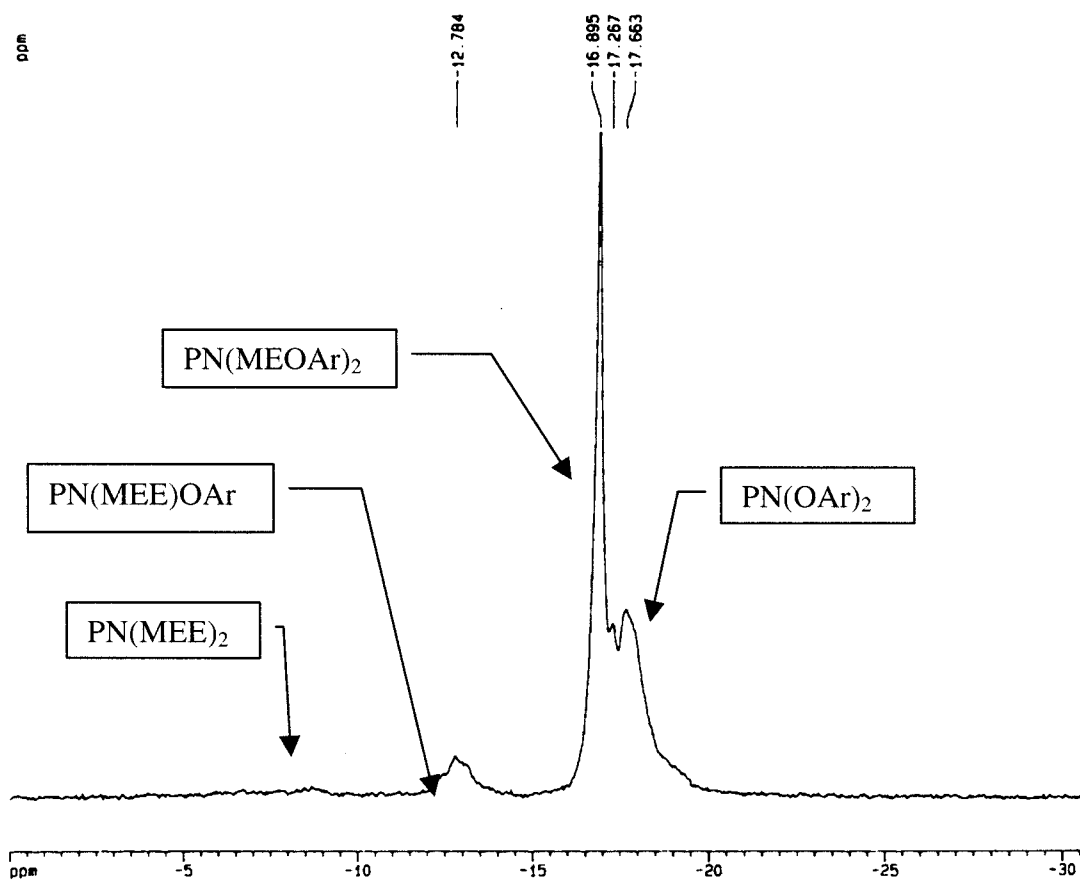


Figure 4 ^{31}P -NMR spectrum of polymer 7. OAr represents both aromatic pendant groups. The two smaller peaks in the aromatic-bound phosphorus envelope (-16 to -18 ppm) are assigned to the two other possible distributions: bis(*o*-allylphenol) and the mixed pendant group PN(MEOAr)(*o*-allylphenol).

describes the relationship between the T_g of an organic copolymer and the T_g values of each homopolymer. We recently described a phosphazene terpolymer where the T_g could be predicted with a high level of accuracy from the relative amounts

of each pendant group and the T_g values from each of the phosphazene homopolymers.²⁵ Application of this relationship to the new polymers is problematic due to the need to know the T_g values of each homopolymer, which are known for MEE-

Table I Speciation of Phosphorus Substitution and Pendant-group Composition Taken From Integration of NMR Spectra

Polymer	^{31}P -NMR Data			^1H -NMR Data		
	PN(MEE) ₂ (%)	PN(MEE)OAr (%)	PN(OAr) ₂ (%)	MEE (%)	MEOAr (%)	<i>o</i> -Allyl Phenol (%)
5	6	32	62	31	58	11
6	3	8	89	8	79	13
7	5	30	65	25	59	16
8	20	45	35	38	46	16
9	8	26	66	23	72	5

Experimental error = $\pm 2\%$.

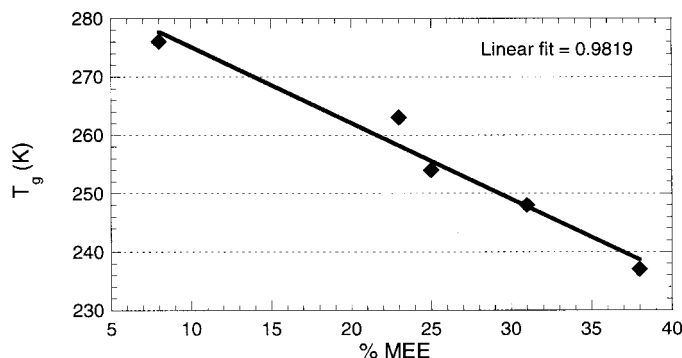


Figure 5 Plot of T_g versus percent of MEE on polymers 5–9 as measured by integration of $^1\text{H-NMR}$ spectra.

and *p*-methoxyphenol-substituted polymers, -79 and 7°C , respectively. However, the 100% *o*-allylphenol-substituted phosphazene cannot be synthesized due to *in situ* crosslinking during synthesis that yields an intractable solid; thus, an accurate application of the Fox equation is not possible. A less rigorous analysis of the data can be made that suggests that the T_g values measured for polymers 5–9 correspond to the level of MEE: the more of the polyether pendant group, the lower the T_g (Fig. 5). A trendline gives an R value of 0.98, suggesting a high degree of linearity, providing validation for this analysis.

Thermally crosslinked membranes using polymers 5–9 were formed and their ability to swell in water was measured (Table II). Portions of these thin films were immersed in water for at least 3 weeks to ensure equilibrium swelling. The content of water absorbed by each membrane was quantified by TGA. Water uptake into the polymer (percent swelling) of each polymer was calculated from at least five duplicate experiments by measuring mass loss from ambient temperature to 110°C . Dry sample analyses of each polymer were also performed to verify that mass losses in this region were only attributable to the loss of water. Contrary to expectations, no clear correlation between the content of the hydrophilic MEE on the polymer and the water-swelling amount was observed.

Dry polymer samples were analyzed by TGA to determine decomposition temperatures for polymers 5–9. Thermograms for these polymers were generally characterized by minor mass loss up to 200°C , where a sharp mass loss was noted. Decomposition points for these polymers were calculated as the onset points for the observed sharp mass losses. A somewhat linear trend was noted

except for data recorded for polymer 8, where the decomposition point was higher than would be expected from the data obtained for the other four polymers (Fig. 6). Of the series presented in this work, polymer 8 stood out as somewhat different from the others because, although soluble in common membrane-casting solvents such as THF, turbidity was evident. A similar TGA experiment was conducted on poly bis[2-(2-methoxyethoxy)ethoxy]phosphazene (MEEP) (2), representing an endpoint where there is no aromatic content (Fig. 6). With the addition of this data point, nonlinear behavior clearly is observed for the entire data set. In the absence of the MEEP data point, a trend exists that suggests that the polyether pendant group (MEE) is responsible for the observed lower-temperature decomposition: the greater the percentage of MEE on the backbone, the lower the temperature at which decomposition begins. With the addition of the MEEP T_d point, these data suggest that MEE/aromatic blends experience greater thermal destabilization relative to what

Table II Maximum Polymer Swelling in Water Solvent (Ambient Temperature) and Transmembrane Fluxes of Water from a Water-dye Feed Using Polymers 5–9 at 50°C

Polymer	Swelling (%)	Flux ($\text{L m}^{-2}\text{h}^{-1}$)	Separation Factor (% Rejection)
5	150	0.15	99+
6	17	0.02	99+
7	400	0.27	99+
8	25	0.06	99+
9	146	0.16	99+

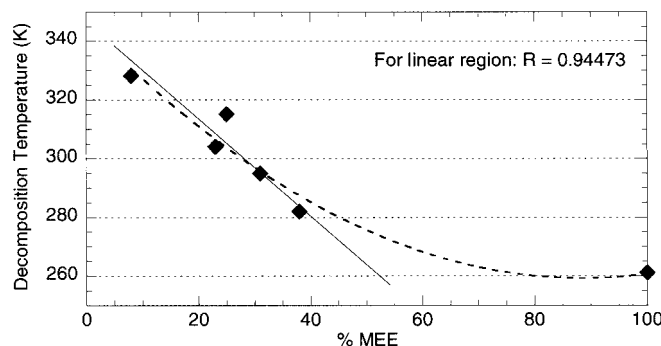


Figure 6 Plot of decomposition temperature as measured by TGA versus percent of MEE. Data point at 100% MEE substitution is poly{bis[2-(2-methoxyethoxy)ethoxy]-phosphazene}.

would predicted from the data obtained for polymers **5–9**.

Pervaporation Experiments

Pervaporation experiments were performed with membranes formed from polymer **3** using an ethylene glycol–water feed stream. The flux of water through the membrane declined steadily over a period of days, suggesting mechanical instability of the polymer. Presumably, the polymer was mechanically destabilized through polymer creep and drawn into the pores of the ceramic support, thus substantially inhibiting water transport. Another polymer, poly{bis[4,2(2-methoxyethoxyethyl)carboxylatophenoxy]phosphazene}, **4**, incorporating an amphiphilic pendant group (Fig. 1), also rapidly failed in the pervaporation experiments. Failures of membranes formed from polymer **4** were characterized by dye passage into the permeate trap. Crosslinked membranes synthesized from polymers **5–9** all formed stable films and were studied using pervaporation. Measured membrane fluxes are shown in Table II and were mechanically stable for the lifetime of the experiment, approximately 10 days. Additionally, no dye transport across the membrane was observed.

As a further test of membrane durability, a separation at high pH was performed. Phosphazenes are generally regarded as stable in highly acidic media; however, they are known to decompose in basic environments. A membrane formed from polymer **5** without crosslinking was exposed to a feed stream of 20% aqueous ethylenediamine, where it was observed to rapidly decompose. A second membrane was formed from polymer **5** and crosslinked. The crosslinked material was exposed to the feedstream and found not to de-

compose. This membrane formulation was used in a pervaporation experiment where the water fluxes observed were comparable to the neutral pH water–dye separations (Table III).

CONCLUSIONS

This article described a method for forming tailored phosphazene polymers for use as membranes in pervaporation separation processes. Of the factors that appear to be critical, selection of the appropriate pendant group for attachment onto the phosphazene backbone must be done to match the solubility characteristics of the selected permeate. However, this type of polymer modification alone does not provide for the ability to “fine tune” the performance characteristics of the membrane, suggesting that other factors such as morphology and crosslink density also play a role in polymer membrane transport. This observation is supported by the fact that transmembrane water flux and polymer water swelling, while correlating well to each other, do not correlate in a linear fashion with the amount of MEE

Table III Pervaporation Testing of a Crosslinked Polyphosphazene in 20% Aqueous Ethylenediamine Performed on Duplicate Membranes

Polymer	Flux (L m ⁻² h ⁻¹)	Temperature (°C)	Separation Factor (% Rejection)
6	0.11	35	92
6	0.14	38	84

on the polymer backbone. Additionally, swelling and transmembrane flux do not enjoy a proportional correlation. Polymer swelling varied by over a factor of 10 while the magnitudes of transmembrane flux varied by a factor of 5.

The mechanical stability of membranes formed from polymers outlined here was enhanced through the synthetic addition of *o*-allylphenol to the pendant group mix. This pendant group provided the labile carbon–hydrogen bonds that formed crosslinks within the phosphazene membrane matrix. Due to the amorphous nature of these phosphazenes, crosslinking is necessitated for long-term membrane durability and this was demonstrated.

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