

Characterization of 2-(2-Methoxyethoxy)ethanol-Substituted Phosphazene Polymers Using Pervaporation, Solubility Parameters, and Sorption Studies

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ABSTRACT: Two linear phosphazene polymers were synthesized with differing amounts of hydrophilic 2-(2-methoxyethoxy)ethanol (MEE) and hydrophobic 4-methoxyphenol (MEOP) substituted on the backbone. These high polymers were cast into membranes and their permeability to water, methanol, ethanol, and 2-propanol was evaluated as a function of temperature. An additional polymer with a low content of MEE was studied for water permeation and was characterized by trace flux. At higher levels of MEE on the backbone, fluxes of all solvents increased. Solubility also was found to increase with increasing MEE content for all

solvents except water. Unexpectedly, water was found to be less soluble in the higher MEE polymer, although higher membrane fluxes were observed. Diffusion coefficients showed the following trend: methanol \gg 2-propanol $>$ ethanol \gg water. Finally, the affinity of solvents and polymers was discussed in terms of Hansen solubility parameters. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 939–945, 2005

Key words: polyphosphazenes; membranes; hydrophilic polymers; swelling; amorphous

INTRODUCTION

In recent years, the need to purify water and other organic compounds has grown explosively where needs have arisen primarily from the environmental and industrial sectors.¹ Purification of water is required in an environmental setting where pollutants must be separated prior to discharge. Additionally, in an industrial setting, water may be required to be separated from an organic solvent for recycling, thus reducing waste handling and disposal costs. In light of these needs, new materials have been sought for use as water and polar organic passing membranes.

Many polyphosphazene syntheses have been shown to afford facile routes to materials with specific functionality.^{2,3} Unlike conventional organic polymers, polyphosphazenes are most commonly polymerized before addition of chemoselective functionality leading to a two-step process with large variability.⁴ Typical syntheses of polyphosphazenes consist of ring-opening polymerization of commercially available hexachlorocyclotriphosphazene followed by nucleophilic substitution of chlorine with organic pendant groups (Fig. 1). Pendant groups serve

two functions. First, they stabilize the polymer backbone and prevent hydrolytic cleavage. For example, the initial polymerization step yields polydichlorophosphazene, which was shown to be degraded by exposure to water.⁴ Second, pendant groups influence the chemical and physical characteristics of the polymer. Nonpolar groups such as phenols⁵ were shown to form hydrophobic phosphazenes and, conversely, short-chain water-soluble polyethers^{6,7} and amines⁸ were used to form hydrophilic polymers.

Application of polyphosphazenes for membrane separations has been conducted by several groups.⁹ Gas separations using polyphosphazene homopolymers^{10–13} and heteropolymers^{14,15} were studied because of the unique ability to tune the polymer's physical and chemical properties. Specifically, a binary mixture of pendant groups balancing hydrophobic and hydrophilic behavior was investigated; however, these materials lacked sufficient dimensional stability for application as pervaporation membranes.¹⁶ However, the method of synthesizing mixed substituent polymers remained a valid pathway for control of phosphazene structures as shown previously.¹⁷

In a recent contribution, polyphosphazenes containing three pendant groups were synthesized and characterized (see Fig. 1).¹⁸ Polymers were synthesized with a balance between hydrophilic [2-(2-methoxyethoxy)ethanol (MEE)] and hydrophobic [4-methoxyphenol (MEOP)] components. The third pendant group was 2-allylphenol that served as a crosslinking

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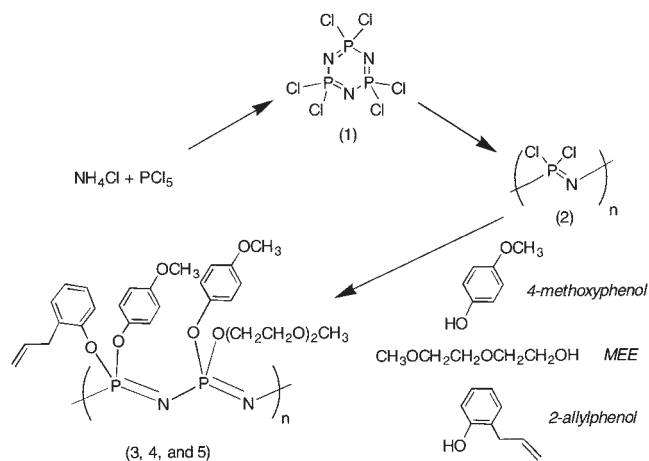


Figure 1 Scheme for the synthesis of polymers 3, 4, and 5.

moiety in small amounts (<15%). It was shown that 2-allylphenol inclusion within the matrix allows for facile polymer crosslinking by using thermal, ultraviolet-free radical initiation, or electron beam irradiation providing increased dimensional stability.¹⁹

Gas permeability studies using these polymers revealed a clear relationship between the amount of MEE substituted onto the polymer and the permeability of CO_2 .²⁰ Further experiments using permanent gases showed no such correlation, suggesting that CO_2 has strong solubility interaction with the MEE pendant groups. Additional correlations were initially sought in liquid permeability experiments; however, no clear relationship was found between MEE content and water flux but there was a positive correlation between polymer swelling and water flux.¹⁸ In a follow-up article, we examined the binary liquid component separation behavior of these polymers.²¹ In this work, the substitution on a family of phosphazene polymers is probed by solvent sorption, pervaporation, and solubility parameters.

EXPERIMENTAL

Methods and materials

Phosphonitrilic chloride trimer was obtained from Esprit Chemicals (Sarasota, FL) and sublimed prior to use. 4-Methoxyphenol, 2-allylphenol, benzoyl peroxide, tetrahydrofuran, diglyme, and sodium hydride (as a 60% dispersion in mineral oil) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Toluene was purchased from Fisher Scientific and was azeotropically distilled prior to use. Methanol, ethanol, and isopropanol were obtained from Fisher Scientific (Pittsburgh, PA) and used as received. NMR analyses were performed on a Bruker (Billerica, MA) DMX300WB operating at a magnetic field strength of 7.04 T. Thermal analyses were ob-

tained by using a TA Instruments (New Castle, DE) model 2910 differential scanning calorimeter (DSC) and a model 2950 thermogravimetric analyzer (TGA). Density measurements were accomplished by using a Micromeritics (Norcross, GA) model Accupyc 1330 pycnometer using nitrogen as the analyte gas. Dilute solution techniques were used to characterize the macromolecular structure of polymer 4.

Tetrahydrofuran (THF) 0.1% tetrabutylammonium bromide (TBABr) filtered through a 0.2- μm filter was used as solvent and all experiments were performed at 23°C. Solution refractive index increment, dn/dc values were obtained by using a Wyatt Technologies (Santa Barbara, CA) OptiLab refractive index detector. High-performance size-exclusion chromatography (HPLC) was performed by using a Waters (Milford, MA) model 2690 solvent/sample delivery system with a column bank of two Styragel HR 5E (4.6 mm id \times 300 mm) solvent efficient columns (Waters, Milford, MA). The columns were kept isothermal at 23°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 by using a Wyatt Technologies DAWN-DSP laser light scattering detector with the F2 flow cell that measures scattered light intensities at angles ranging from 12.3° to 165.1°. The OptiLab refractive index detector was placed in series with the light scattering detector as a concentration detector. Batch mode studies were used for polymer determination of 3 in toluene at 23°C. Toluene was prefiltered through a 0.2- μm filter prior to making dilute solutions in scintillation vials. The average molecular weight and average rms radius for each polymer solution were achieved by using a Wyatt Technologies DAWN-EOS laser light scattering detector utilizing scintillation vials. dn/dc values were obtained with a Wyatt Technologies OptiLab refractive index detector.

Synthesis and characterization of poly[(4-methoxyphenoxy)_{0.98}(2-(2-methoxyethoxy)ethoxy)_{0.76}(2-allylphenoxy)_{0.26}phosphazene](3)

Poly[bis(chloro)phosphazene], 2, was prepared from phosphonitrilic chloride trimer, 1, by using the method of Allcock.^{22–25} Polymer 3 was synthesized from 2 by using the following method. A reactor was assembled by using a dry 2-L three-neck flask equipped with a condenser, mechanical stirrer, and a nitrogen purge. To a solution of poly[bis(chloro)phosphazene] (32.9 g, 284 mmol) in 400 mL of THF was added a previously prepared solution of sodium 2-allylphenoxide. This phenoxide solution was prepared by reacting 2-allylphenol (11.4 g, 84.9 mmol) with sodium hydride (in mineral oil) (3.4 g, 85 mmol) in 300 mL of dry THF. The phenoxide-polymer solution was

mechanically stirred for 2 h with mild heating ($\sim 60^\circ\text{C}$). A solution of sodium 4-methoxyphenoxide and sodium 2-(2-methoxyethoxy)ethoxide was prepared from the room temperature reaction of 4-methoxyphenol (52.8 g, 426 mmol) and 2-(2-methoxyethoxy)ethanol (21.3 g, 178 mmol) with sodium hydride (27.3 g, 683 mmol) in 400 mL of dry THF. This solution was introduced into the polymer solution and the resulting mixture was heated to 110°C for 15 h upon which it was judged to be complete by ^{31}P -NMR spectroscopy. The reaction was subsequently cooled to $\sim 50^\circ\text{C}$ where it was precipitated into 3 L of deionized water. Crude polymer was observed to float to the surface. This material was then collected, dried, and dissolved into THF, followed by precipitation into water. Collected polymer was then precipitated twice from THF into hexanes yielding, once dry, 42.2 g of a brown elastomer in 51% yield.

Polymer 3 characterization data: ^1H -NMR (CDCl_3) δ (ppm): 7.3 (brs), 7.0 (brs), 6.9 (brs), 6.5 (brs), 6.1 (brs), 4.9 (brs), 3.9 (brs), 3.5 (brs), 3.3 (brs). Integrated ^1H -NMR: methoxyethoxyethanol (MEE) 38%, 4-methoxyphenol 49%, and 2-allylphenol 13%. ^{31}P -NMR (CDCl_3) δ (ppm): -8, -12, -18. DSC $T_{g'}$ -18°C . TGA T_d 313°C . (M_w) = $(1.4 \pm 0.2) \times 10^7$, rms radius = 354.9 ± 26.4 nm, 2nd virial coefficient = $(-1.75 \pm 0.9) \times 10^{-4}$. Density, 1.2547 g/cm 3 .

Synthesis and characterization of poly[(4-methoxyphenoxy) $_{0.96}$ (2-(2-methoxyethoxy)ethoxy) $_{0.96}$ (2-allylphenoxy) $_{0.08}$ phosphazene] (4)

Polymer 4 was synthesized by using a literature method. 21

Polymer 4 characterization data: ^1H -NMR (CDCl_3) δ (ppm): 7.3 (brs), 7.0 (brs), 6.9 (brs), 6.5 (brs), 6.1 (brs), 4.9 (brs), 3.9 (brs), 3.5 (brs), 3.3 (brs). Integrated ^1H -NMR: methoxyethoxyethanol (MEE) 48%, 4-methoxyphenol 48%, and 2-allylphenol 4%. ^{31}P -NMR (CDCl_3) δ (ppm): -8, -12, -13, -18. DSC $T_{g'}$ -43°C . TGA T_d 288°C . M_w = $(3.1 \pm 0.2) \times 10^6$. Polydispersity index (M_w/M_n), 3.09 ± 0.49 . Density, 1.2495 g/cm 3 .

Synthesis and characterization of poly[(4-methoxyphenoxy) $_{1.44}$ (2-(2-methoxyethoxy)ethoxy) $_{0.46}$ (2-allylphenoxy) $_{0.10}$] (5)

The synthesis of Polymer 5 was discussed in a previous work. 18

Polymer 5 characterization data: ^1H -NMR (CDCl_3) δ (ppm): 7.3 (brs), 7.0 (brs), 6.9 (brs), 6.5 (brs), 6.1 (brs), 4.9 (brs), 3.9 (brs), 3.5 (brs), 3.3 (brs). Integrated ^1H -NMR: methoxyethoxyethanol (MEE) 23%, 4-methoxyphenol 72%, and 2-allylphenol 5%. ^{31}P -NMR (CDCl_3) δ (ppm): -8, -12, -18. (M_w) = $(6.7 \pm 0.6) \times 10^5$, rms

radius = 74.1 ± 9.1 nm, 2nd virial coefficient = $(-4.54 \pm 2.0) \times 10^{-4}$. DSC $T_{g'}$ -10°C . TGA T_d 300°C .

Membrane formation

Membranes were prepared by using a solution casting method. Casting solutions were made from THF with 2% (wt %) polymer and benzoyl peroxide (2% with respect to polymer mass). These solutions were stirred at room temperature for 12–24 hs. The solutions were then centrifuged to remove any suspended particulate matter before use. Membranes were formed by directly applying freshly prepared casting solutions to Whatman Anopore $^{\text{®}}$ (Maidstone, UK) ceramic membranes (47-mm-diameter with $0.2\text{-}\mu\text{m}$ pore size). The THF solvent was allowed to evaporate, leaving transparent and defect-free thin dense films as a discrete layer on the ceramic membrane. Defect-free films ($5\text{--}20$ μm thick) were most easily obtained by slowing the evaporation rate of the THF solvent such that bubbles did not appear. Crosslinking was accomplished by heating at 130°C for a minimum of 10 min. The crosslinking process did not result in any physically observable changes to either the polymer film or the ceramic support.

Pervaporation

Membranes were loaded into filtration membrane cells obtained from Millipore, Inc. (Bedford, MA) that were modified for pervaporation experiments by introducing a second port on the feed side to allow for continuous flow. Feed solution flow rate over the membrane was ~ 50 mL/min. A diaphragm vacuum pump provided a permeate side pressure of 56 mmHg. Temperature control was provided by using a constant temperature water bath to heat the feed solution. Temperature of the membrane was monitored by using a calibrated thermocouple attached to the membrane cell. Permeates were collected cryogenically and quantified gravimetrically over 6–9 h per experiment. Each flux measurement represents four to seven replications. All feed solutions were doped with green food coloring dye [a mixture of FD&C Blue 1 (Brilliant Blue FCF) and FD&C Yellow 5 (Tartrazine) in a water/propylene glycol base (McCormick, Hunt Valley, MD)]. All membranes were leak-checked by using compressed nitrogen to probe for defects. Membranes that allowed a steady stream of gas were rejected.

Solubility, diffusivity, and permeability coefficients

Solubility coefficients were determined through immersion of crosslinked polymer samples in solvent for at least 7 days or until no mass gain was observed. Coefficients were determined by using a literature method. 26

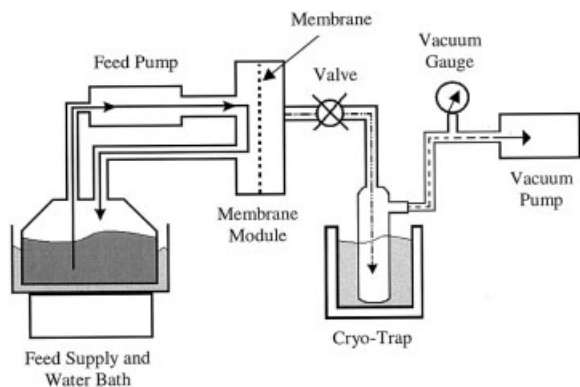


Figure 2 Pervaporation apparatus.

RESULTS AND DISCUSSION

Pervaporation of water

Pure water, spiked with dye, was used as the feed in pervaporation experiments employing polymers 3, 4,

and 5 by using a standard apparatus (Fig. 2). Experiments were carried out at different temperatures to allow for a comparison of relative performances and a determination of activation parameters. The general trend noted for polymers 4 and 5 was increased flux with increased temperature (Fig. 3). Additionally, polymer 4 exhibited more flux as a function of temperature than did polymer 3. All fluxes for both polymer membranes were obtained with 100% rejection of the dye, indicating that the membranes were defect-free.

Magnitudes of flux for these two polymers were found to correspond well to an Arrhenius analysis of the data (Fig. 3). Activation energies of permeation (E_p) were calculated to be 84.0 and 80.1 KJ/mol for polymers 3 and 4, respectively. From these results, there appears to be slight lowering of E_p because of increased MEE content corresponding to increased fluxes. Also suggested is an interaction between the MEE pendant group and water that enhances permeability of the membranes.

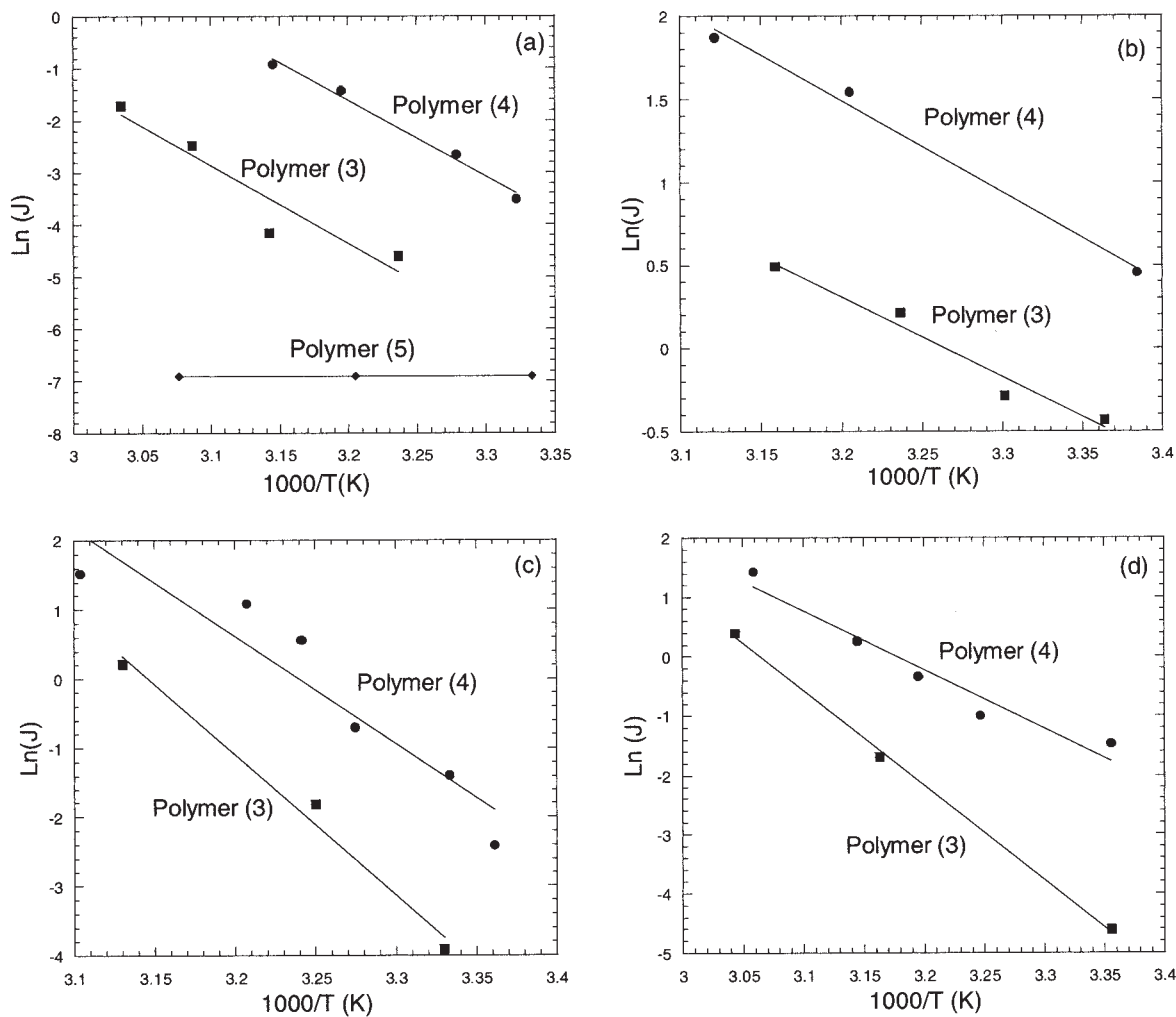


Figure 3 Arrhenius plots for showing pervaporation results for (a) water, (b) methanol, (c) ethanol, and (d) 2-propanol.

TABLE I
Activation Energy of Permeation (E_p) Values for
Polymers 3 and 4

Polymer	Water (KJ/mol)	Methanol (KJ/mol)	Ethanol (KJ/mol)	2-Propanol (KJ/mol)
3	84.0	1.3	128.3	80.3
4	80.1	6.5	88.7	40.1

Trace fluxes were observed from membranes cast from polymer 5, substituted with 23% MEE, regardless of temperature. MEOP, as a pendant group, is nonpolar and was shown to give very specific solubility behaviors where water was found to be a nonsolvent.²¹ Substitution of 23% of the backbone phosphorus atoms with MEE appears to be insufficient in providing significant affinity for water; thus, the membrane was hydrophobic and an ineffective medium for water transport.

Pervaporation of methanol, ethanol, and 2-propanol

Methanol, ethanol, and 2-propanol were found to readily permeate through membranes cast from both polymers 3 and 4. Measured fluxes were significantly higher for all alcohols tested when compared to water with 100% rejection of the dye. Fluxes as high as 4–6 Kg/M² h were measured by using membranes cast from polymer 4. Similar to the water experiments, pervaporation of the three alcohols revealed increased fluxes with increased temperature. Additionally, fluxes for polymer 4 were larger than for 3 at similar temperatures. Methanol was observed to have higher permeability than either ethanol or 2-propanol between 25 and 30°C. Methanol also exhibited the least degree of temperature susceptibility. Fluxes of ethanol were far more susceptible to temperature changes. 2-Propanol exhibited the lowest temperature susceptibility likely due to its larger molecular size as compared to the two other alcohols.

Temperature susceptibility may be probed by using an Arrhenius analysis that quantifies this behavior in terms of activation energy. Arrhenius plots (Fig. 2) and E_p values (Table I) for the alcohols show that methanol has by far the lowest E_p for both polymers. E_p for polymer 4 was somewhat higher than the corresponding value for 3. The significance of this difference is not clear; however, the magnitude of both values suggests that methanol is highly permeable through both polymers. Ethanol and 2-propanol exhibited significant differences in E_p between the two polymers, ~ 40 KJ/mol, where polymer 4 was less than polymer 3. A curious behavior observed was the larger E_p values for ethanol as compared to 2-propanol. One would have predicted based on molecular

size that the barrier to permeation would have been higher for 2-propanol. A possible explanation for this behavior could be an increased plasticization of the polymer induced by 2-propanol that serves to lower the barrier for transport. Nevertheless, these data suggest that the increased amount of MEE on polymer 4 facilitates the transport of both ethanol and 2-propanol, although 2-propanol is less permeable, especially at higher temperatures.

Hansen parameter analysis

Hansen solubility parameters were determined for polymers 3 and 4 by using a literature method (Table II).²¹ To these were added the parameters for methanol, ethanol, isopropanol, and water. The data include parameters^{27,28} describing the dispersive interactions, δ_d , the polar interactions, δ_p , and the hydrogen bonding interactions, δ_h , in addition to δ_t and δ_v derived from the previous values and described in eqs. (1) and (2). It should be noted that δ_t corresponds with the single-value Hildebrand parameter. Additionally, δ_v is presented because this parameter represents both the dispersion and the polar influences while negating the hydrogen bonding contribution,²⁹

$$\delta_v = (\delta_d^2 + \delta_p^2)^{1/2} \quad (1)$$

$$\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \quad (2)$$

Hansen parameters were derived as an improvement on the single-parameter Hildebrand values, which were shown to describe well interactions between nonpolar systems, however, were inadequate to describe interactions in polar systems. In general, the application of Hansen parameters to solubility is to look for similarity, where it is expected that a polymer and a permeate with similar parameters are mutually miscible. Polymers 3 and 4 have closely corresponding Hansen parameters allowing a reflection of the ramifications of the increased MEE content. Polymer 4 is somewhat more polar than polymer 3, attributable to

TABLE II
Hansen Solubility Parameters for Solvents
and Polymers 3, 4, and 5

Material	δ_d	δ_p	δ_h	δ_v	δ_t
3	19.9	7.7	6.2	21.3	22.2
4	20.0	8.3	6.6	21.7	22.6
5	19.8	7.0	5.7	21.0	21.8
Methanol*	15.4	12.3	22.3	19.7	29.8
Ethanol*	15.8	8.8	19.4	18.1	26.5
2-Propanol*	15.8	7.2	16.0	17.4	23.6
Water*	12.3	31.3	34.2	33.6	48.0

* Ref. 28.

the MEE content as shown by a larger δ_t . In this instance, the larger δ_t is due to all three primary Hansen parameters being larger.

Clearly, the data show that the polymers and each solvent have appreciable degrees of polarity such that δ_t corresponds well between the polymers and the longer chain alcohols that are, in general, less polar. Thus, 2-propanol is less polar than methanol and this is reflected by a lower δ_t . Relative contributions to δ_t can be examined by using δ_v , which negates δ_h from the δ_t calculation. Trending of δ_v with respect to the alcohols shows that the shorter chain alcohols give δ_v values closer to that of the polymers. Thus, polarity of the solvents as compared to the polymers is fundamentally different. Magnitudes of the δ_h values show that although the polymers may participate in hydrogen bonding as an electron donor, there are no acceptor sites on any of the pendant groups including the MEE chains. Additionally, the data show that MEE contributes to the δ_d parameter that represents attractive forces that do not involve dipole-dipole or hydrogen bond attraction. Increased intermolecular attractions described by δ_d potentially could be due to the sp^3 hybridized oxygen and carbon chain of the MEE pendant group that measures nine atoms in length giving 22 degrees of motional freedom in the MEE chain alone. With little significant steric hindrance in the MEE chain, a significant amount of fluxionality is present. Evidence for this fluxionality can be observed macroscopically in the low glass transition temperature (T_g) measured for poly[bis-(2-(2-methoxyethoxy)ethoxy)phosphazene] (-82°C) as opposed to phosphazenes with other pendant groups such as amines or phenols.⁴

Diffusion and solubility coefficients

An examination of solubility in both polymers was made through swelling experiments where cross-linked polymer samples were immersed in solvent until equilibrium was observed. Percent swelling and density information were used to calculate solubility in grams of solvent per cm^3 of polymer (Table III) at 22°C . For polymer 4, the trend for increasing solubility was methanol \gg ethanol $>$ 2-propanol $>$ water. By using the exponential regressions from the Arrhenius plots, permeability coefficients at 22°C for all four solvents were calculated with the following trend: methanol \gg 2-propanol $>$ ethanol \gg water. Methanol was an order of magnitude larger than the other alcohols, which in turn were an order of magnitude larger than water. From the permeability and solubility coefficients, diffusion coefficients were calculated that mirrored the permeability coefficients, suggesting that diffusion is a dominant influence in permeation through polymer 4.

TABLE III
Permeability, Diffusion, and Solubility Coefficients for Polymers 3 and 4 at 22°C

	$P (\times 10^{-9})$ (g/cm \times s)	$D (\times 10^{-9})$ (cm^2/s)	S (g/ cm^3)
<i>Polymer 3</i>			
Water	0.3	0.1	2.2
Methanol	230	290	0.79
Ethanol	3.0	4.9	0.6
2-Propanol	2.3	7.2	0.3
<i>Polymer 4</i>			
Water	5.2	9.9	0.5
Methanol	650	420	1.6
Ethanol	40	27	1.5
2-Propanol	51	50	1.0

By using the same method, polymer 3 was evaluated in terms of permeability, solubility, and diffusion coefficients (Table III). Permeability coefficients for this polymer were found to have the following order: methanol \gg ethanol $>$ 2-propanol \gg water. This differs from the above result where 2-propanol $>$ ethanol. However, it should be noted that there was a relatively small difference between these two solvents. Solubility coefficients for the solvents corresponded well to polymer 4, except the value for water was far higher than expected. By using these values, diffusion coefficients were calculated that gave the same trend as polymer 4: methanol \gg 2-propanol $>$ ethanol \gg water.

A comparison of the data from the two polymers yielded the trend where lower diffusion coefficients were observed for the less polar polymer 3. It can also be said that the greater percentage of hydrophobic MEOP groups on polymer 3 provides resistance to diffusion. Thus, phosphazene heteropolymers can be thought of as random copolymers (treating both the MEOP and the 2-allylphenol pendant groups as hydrophobic) where the physical and chemical characteristics are a blend of the characteristics of the homopolymers. Phosphazenes with higher levels of MEE substitution would then be envisioned to have more MEE-like characteristics and potentially act as membranes capable of higher fluxes of solvents with affinity for the MEE. Likewise, polymer membranes with less MEE and more MEOP would be expected to have lower polar organic and water permeabilities.

CONCLUSION

Described in this article is a method for the increasing affinity of water and short-chained alcohols for polyphosphazenes by synthetic tailoring of the polymer. Increased MEE content on the polymer backbone has been found to give increased permeabilities to water, methanol, ethanol, and 2-propanol as mixtures

with dyes. However, enhancement in bulk flux of the three alcohols was achieved to a much greater degree than for water. Solubility and diffusion coefficients reveal a stronger affinity for the alcohols with MEE than for water. Hansen solubility parameters predicted for the polymers were also found to correspond more closely with values for the alcohols than for water. These data taken together address the chemical affinity of the phosphazene in terms of the individual components that form the polymer. Attachment of the MEE pendant group to the phosphazene yields a phosphorus-carbon ether terminus to an organic polyether, which is polar and has an affinity for water and alcohols, however, has no hydrogen bonding capability. As a homopolymer, MEE induces a wide range of solubilities in which the polymer is completely soluble in the four test solvents. As a hydrophobic component (MEOP) is added into the polymer, relative differences in affinity become observable. A lower affinity for water than the alcohols is attributable to the lack of hydrogen bonding capability of the MEE pendant group. To improve water permeation, these data suggest that other pendant groups should be attached to the phosphazene polymer that more closely interact with water through both the polar and the hydrogen-bonding mechanisms.

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