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A study was undertaken to explore the water passing properties of a series of phosphazene polymers versus the attached pendant group structure. Pendant groups containing different numbers of ethyleneoxy groups were synthetically attached to the backbone of phosphazene polymers. Phosphazene polymers facilitate these types of studies because, during their synthesis, the polymer backbone is formed first and then the desired pendant groups are attached through nucleophilic substitution. For these studies, four polymer series were synthesized and tested for their water passing properties. The polymers contained different amounts of ethyleneoxy units. Two different polymer families were synthesized and compared in this work. The critical difference in the two polymer series is that one contained pendant groups with aromatic rings, in addition to the oligioethyleneoxy moieties, while the other has no aromatic rings in its structure. Polymers with phenyl group-containing pendant groups exhibited poor water permeability if they possessed fewer than six ethyleneoxy units. Polymers with more than six ethyleneoxy units inserted between the phenyl ring (tail) and the polymeric backbone exhibited reasonable water permeability. Two additional series of polymers with mixed pendant groups were synthesized and the water passing properties of the phosphazenes varied in proportion to the hydrophilic to hydrophobic balance induced by each individual pendant group. A final study of polymers with shorter pendant groups demonstrated the effect of pendant group on water permeability. These studies suggest that the polyphosphazenes may be tailored for specific water passing applications.

Keywords polyphosphazenes; water transport membranes

INTRODUCTION

Many of the more effective water passing membranes are formed from polymers that contain oxygen atoms. Generally more oxygen atoms in the pendant groups and/or backbone result in higher rates of water transport. However, some polymers that contain oxygen near the backbone and have hydrophobic ends exhibit poor water permeability. A study was undertaken to correlate water permeability with pendant group structure. The pendant groups had varying numbers of oxygen atoms in the form of ethyleneoxy groups attached to the backbone with aryl and alkyl tails. Phosphazene polymers have been studied for years because the two pendant groups attached to the phosphorus atoms can be easily varied enabling structure-property studies while maintaining the same phosphorus-nitrogen backbone.

One of the unique properties of phosphazene polymer synthesis is that the phosphorus-nitrogen (P-N) polymer backbone is first synthesized as the dichlorolinear polymer and then the desired pendant groups are attached through nucleophilic displacement of chlorine. The synthesis and characteristics of many of these materials have been published elsewhere (1–10). The more common traditional organic polymers are synthesized from an initial monomer followed by polymerization. Using this traditional chemistry, it is difficult to obtain a broad spectrum of polymers with consistent backbone structures. The general structure of the phosphazene polymer is shown in Fig. 1 using pendant group A3 (see Table 1) as an example.

EXPERIMENTAL

Synthesis of Polymers

A series of phosphazene polymers were synthesized following the traditional ring opening approach (1–10), and then tested using the FTIR method described in this paper. All of the polymers described here were synthesized in a similar manner. The synthesis for polymer A12 (following) is used below as an example. In a 2-liter round bottom flask a condenser, mechanical stirrer, thermometer, and a nitrogen purge were installed. To this flask was added Igepal CA-210® (82.2 g, 0.28 mol), one l of dry 1,4-dioxane, and freshly cut sodium metal (6.15 g, 0.27 mol). The resulting mixture was stirred at reflux for approximately 48 hours upon which the sodium was consumed. To this solution, poly(bis-chlorophosphazene) (14.0 g, 0.12 mol) was added as a solution in toluene (200 ml). The final mixture was stirred at 75°C for 1.5 hours

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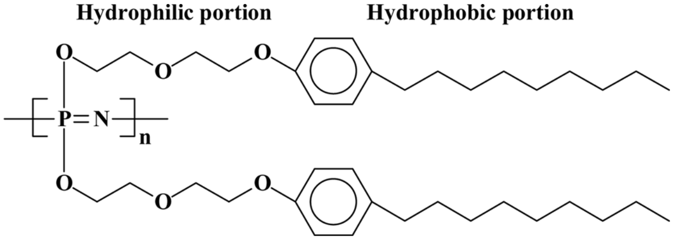


FIG. 1. Example of a typical linear polyphosphazene structure.

at which time the reaction was determined to be at completion using ^{31}P NMR spectroscopy. Purification of the product was accomplished through division of the mother liquor into two portions. Each portion was poured into a mixture of 2-propanol (1875 ml) and water (625 ml) to precipitate the product as a swollen white solid. The product was then collected and dissolved into THF (1l). The THF solution was divided into two portions and each portion was poured into 3l of water. The product was collected and dried, followed by dissolution into THF (1l). A final precipitation was performed into 3l of methanol to obtain an amber colored rubber upon drying under vacuum.

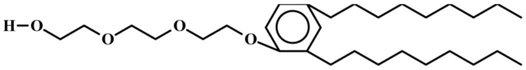
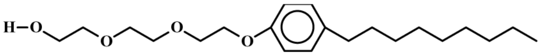
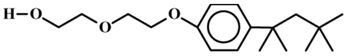
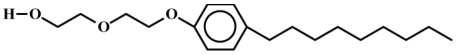
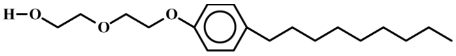
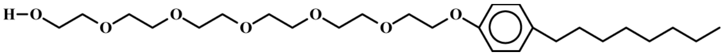
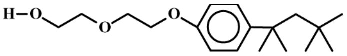
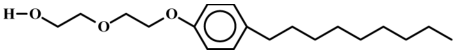
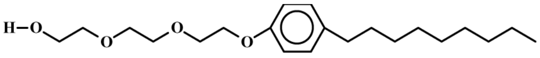
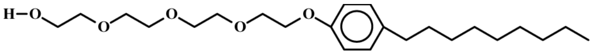
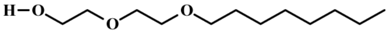
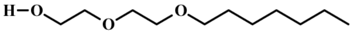
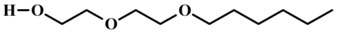
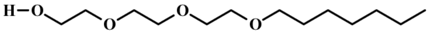
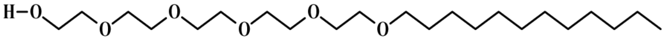
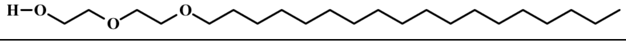
Infrared Spectroscopy

Infrared spectra were acquired on a Bomem MB100 series Fourier Transform Infrared Spectrometer (FTIR) equipped with a gas cell and deuterated triglycine sulphate (DTGS) detector. The gas cell has an optical path length of 20 cm, an internal volume of ~250 mL and 4 mm thick ZnSe windows. The interferometer is operated at $1\,cm^{-1}$ resolution and each spectrum typically consists of 20 coadded scans collected at a rate of ~11 scans/min. The entire optical path of the spectrometer is purged with the same nitrogen used for the permeate purge stream to assure that there is no influence from atmospheric water. The spectrometer is controlled by a data station running Bomem Grams/AI (ABB Bomem and Galactic Industries).

Apparatus

The apparatus and method for water permeation testing is described in reference (11). Briefly, a membrane cell is set up so that dry nitrogen passes through the feed and permeate sides and then into a the FTIR. After it has been established that the cell and membrane are dry, switches are activated sending a recirculating stream of water over the feed side of the membrane. The nitrogen continues to

TABLE 1
Pendant group designations, chemical structures and polymer designations utilized in this study

Material designation	Number of oxygens	Chemical structure
A10	4	
A11	4	
A12	3.3	
A13	3.6	
A14	3	
A16	7	
A2b	3	
A3	2.6	
A8	4	
A9	5	
T19	3	
T21	3	
T21A	3	
T22	4	
T4	5.9	
T7	3.3	

flow over the permeate side and sweeps any permeating water vapor into the FTIR for analysis. A slight pressure of 1 or 2 psi of water is present and the experiments were all run at ambient temperature and pressures.

DISCUSSION

Thirty-one different polymers were synthesized and characterized for their water permeability. The pendant groups used in this study were either purchased or synthesized using traditional organic coupling reactions from commercially available precursors. Table 1 gives the polymer designations and the corresponding structures. There are four variations in the pendant group substitution pattern:

1. the number of oxygens,
2. with or without a phenyl ring,
3. the number of carbons in the tail end, and
4. with or without an olefinic terminal group.

It should be noted that not all of the oxygen values are integers. This reflects the oliogomeric nature of some of the commercially available materials. For example, A3 has a value of 2.6. This means that most of the pendant groups had three or more oxygens, while there is a significant percentage with has less than three oxygens per pendant group. When the polymers were produced, nuclear magnetic resonance (NMR) was used to determine the relative abundance of each type of pendant group and the average value. Values in the table that are integers indicate that either fine chemicals were used or separations were made to produce pendant groups with only the indicated number of oxygens.

The method described earlier was used to measure the water permeation rates of the polymers (11) and the results are listed in Table 2 with the water permeability data shown in Fig. 2. Two series of mixed pendant group heteropolymers also were synthesized and their water passing properties measured. "Mocon Mylar" was used as the control due to its very well characterized water permeability. The reference value is slightly less than what was measured herein due to the fact that the current film had flowing water on the feed side as opposed to a saturated vapor in the method used to determine the reference values. The poly(dimethyl siloxane) (PDMS) values are similar to those reported in the literature and were used to further validate the system. The averages of three or more runs are reported and the variations are primarily due to the thickness variations among the samples measured.

TABLE 2
Water permeation values for the homo- and hetero-series of polymers

Membrane	$g \cdot \mu m/day/m^2$
Homopolymers	
Mocon Mylar Average	297 ± 24
Mocon Mylar Reference	219
PDMS-b Average	47600 ± 4700
A2b Average	1710 ± 660
A3 Average	1980 ± 560
A8 Average	5400 ± 1500
A9 Average	9600 ± 3000
A10 Average	4900 ± 3600
A11 Average	5360 ± 600
A12 Average	2480 ± 230
A13 Average	5610 ± 300
A14 Average	5200 ± 1100
A16 Average	133000 ± 25000
T4 Average	128000 ± 11000
T7 Average	4390 ± 110
T19 Average	64780 ± 770
T21 Average	126000 ± 14000
T21A Average	125000 ± 11000
T22 Average	127000 ± 12000
Heteropolymers	
HTA1 Average	90000 ± 20000
HTA2 Average	77700 ± 8100
HTA3 Average	47700 ± 2700
HF4 Average	45900 ± 9000
HF5 Average	48600 ± 5000

"A" AND "T" SERIES' HOMOPOLYMER RESULTS

The data in Fig. 2 show a bimodal data distribution. Permeabilities appear to be either high or low with little distribution between these extremes. To adroitly investigate any structure-function relationships in these polymers, the "A" series and the "H" series will be addressed separately. The "A" series are unique in that they all contain aromatic rings in the pendant group structure, although the location of the ring varies with respect to the polymer backbone. For example, polymers A2b, A3, A12, A13, and A14 have the aromatic ring in close proximity to the backbone while A16 is highly removed.

In our previous work, we have observed a strong correlation between the permeability of gases and the glass transition temperature (T_g) of the polymer. Specifically, the permeability of gases increases as the polymer T_g decreases for a self consistent polymer series. This has been explained as being a result of increased polymer fluxional motion, since T_g can be thought of as a relative measure of polymer motion. Applying this relationship to water transport, as shown in Fig. 3, can reveal similar relationships. For example, the "A" series data show a general trend of increasing water permeability with decreased T_g. As indicated in the plot, the water permeability for A16 is significantly higher than the other polymers, which may be a result of the placement of the aromatic ring far from the

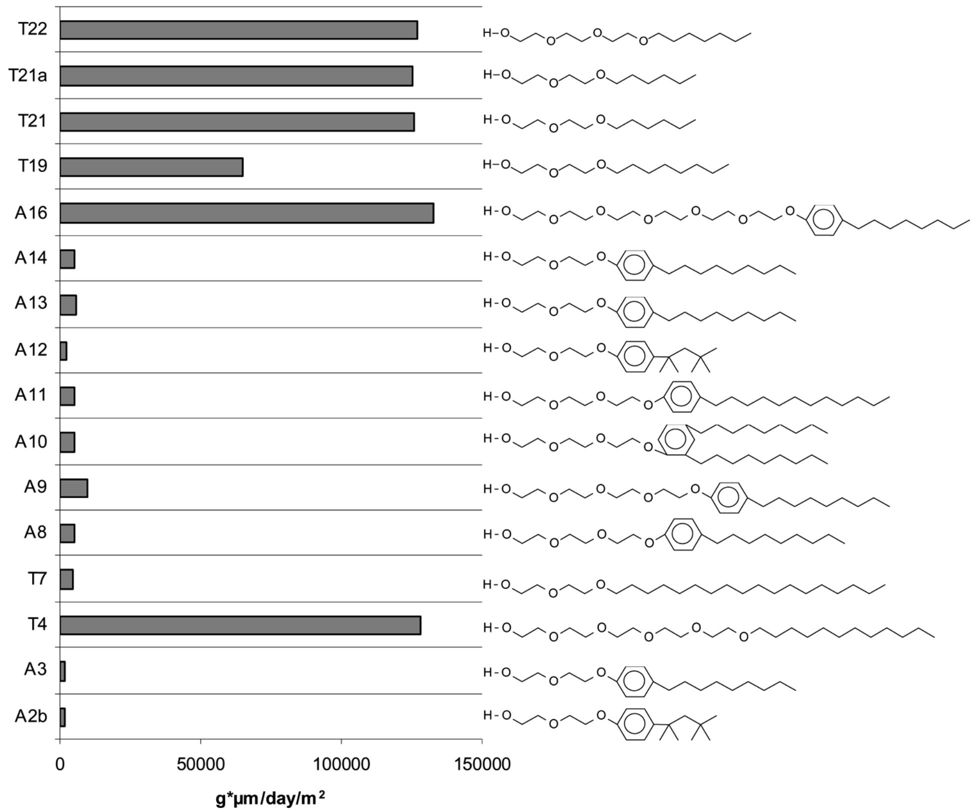


FIG. 2. Water permeation rates for both the "A" and "T" polymers with their pendant group structures.

polymer backbone. Even considering only the lower permeability polymers, it can be observed that the placement of the aromatic ring closer into the polymer backbone results in higher T_g values and lower permeability.

To further investigate the role of the aromatic ring, the "T" series of polymer was synthesized that contained no aromatic functionality. As shown in Fig. 3, the T_g values for this series appears to be lower overall than what was observed for the corresponding "A" series, which is a direct reflection of the role of the aromatic ring in the polymer structure. Most interestingly, the water permeability data show no trend of increasing permeability with decreasing T_g, suggesting that perhaps a theoretical maximum in water permeability has been reached. Furthermore, the "T" polymer series data are consistent with those measured for A16, which supports a theoretical maximum and also suggests that the displacement of the aromatic ring far from the backbone negates its influence on water permeability, although some effect is still observed on T_g. It also should be noted that the "T" series and A16 form swollen gel-like materials in water at equilibrium. These gel-like materials probably represent a maximum in water solubility without polymer dissolution. Thus rates of water transport can be directly correlated to the solubility of water within the polymeric membrane.

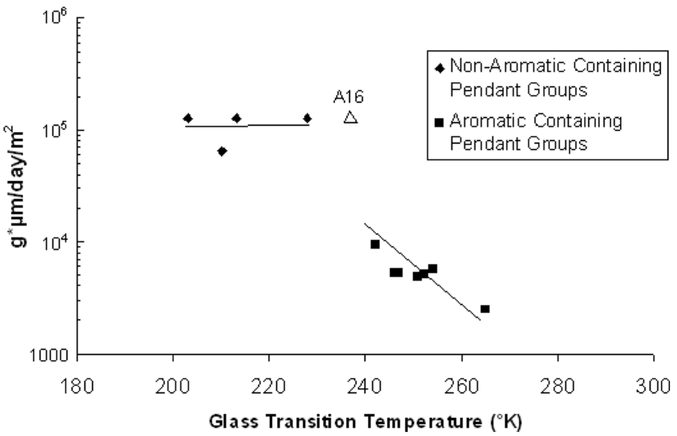


FIG. 3. Plot of water permeability vs. T_g for selected polymers at various temperatures.

"HTA" AND "HF" SERIES' HETEROPOLYMER RESULTS

Two heteropolymer series ("HTA" and "HF" Series) were synthesized. The "HTA" is a combination of A9 and T4 pendant groups. The "HF" series of heteropolymers consists of mixtures of fluorinated pendant group materials mixed with "T" series groups.

"HTA" Hetero Polymers

The "HTA" heteropolymer series consists of a systematic pendant group variation of two homopolymers ranging from: 100% A9 to 100% T4. A9 is a low water passing, phenyl ring containing polymer, while T4 is a high water passing material with no phenyl rings, Fig. 4. In addition to the two homopolymers, A9 and T4, three mixtures of pendant groups with compositions shown in Fig. 4 were tested for their water permeation properties. The polymers containing the higher percentage of the better water passing pendant group T4 produced materials with higher water passing properties. T4 and its relatives are somewhat sticky and not very rigid making it difficult to obtain accurate thickness measurements, which could explain the variability in our data. These results show that the polymers' properties can be modified not only by changing the structure of the pendant groups, but also by making heteropolymers that consist of blends of different pendant groups on the same polymer backbone. To achieve the same types of results the polymers' performance can be predicted assuming that performance of the homopolymers is known.

"HF" Heteropolymers

In an attempt to further modulate the performance of these polymers, hydrophobic fluorine containing pendant groups were placed on the polymeric backbone. Specifically, two polymers were synthesized using fluorinated alcohol, F2, and "T" alcohols T22 and T21A, to form polymers designated HF4, and HF5, respectively. The structure of each pendant group is shown in Fig. 5. Performance of each polymer also is shown in Fig. 5 with the performance of its corresponding "T" series homopolymer. For HF4 and HF5, an expected drop in performance was observed with the addition of the hydrophobic F2 alcohol onto the polymer backbone. HF4 is roughly 50% of each pendant group; however, it has a permeability of only 36% of the T22 homopolymer analogue.

HF5 utilizes pendant group T21A that has similar water permeability as the T22 polymer. But in this case, only 27% of the attached pendant groups are the T21A with the balance consisting of F2 pendant group. Despite this imbalance in favor of the more hydrophobic material, the overall water permeation rates are nearly identical to those of HF4. These results suggest that the structure-function relationships in these materials are probably more complex than a simple linear application would suggest.

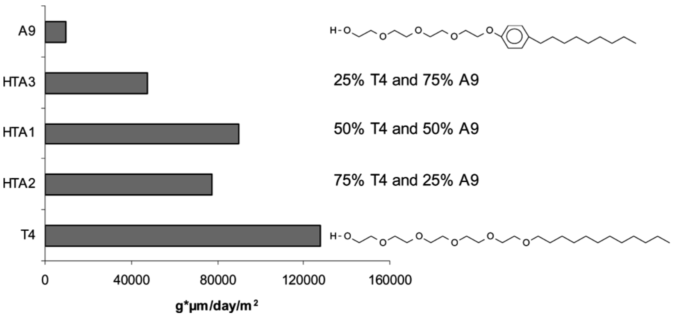


FIG. 4. Water permeation rates and compositions of a series of "HTA" heteropolymers.

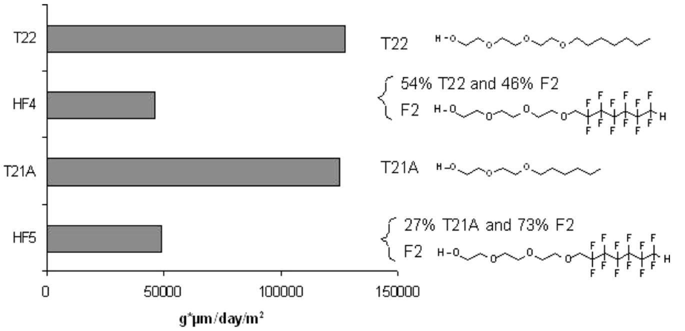


FIG. 5. Water permeation rates and compositions for the "HFA" series of heteropolymers.

SINGLE OXYGEN PENDANT GROUP SERIES

The final set of polymers to be discussed is comprised of a series of phenolic pendant groups without oligioethyleneoxy units. This series also explores the effects of various substitutions on the phenyl rings as well as alkyl chain length spacing between the phosphorus bound oxygen and the phenyl ring.

Poly(bisphenoxy) phosphazene (PPOP) is hydrophobic and is an excellent film forming polymer. PPOP hydrophobicity is seen in Fig. 6 where the water permeability is

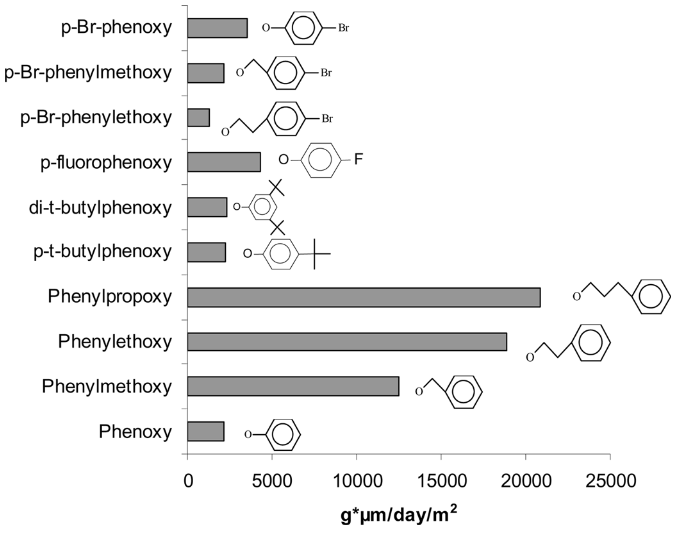


FIG. 6. Water permeation values of polymers synthesized from pendant groups containing one oxygen and one phenoxy group, the "single oxygen pendant group series."

relatively low. Use of phenylmethanol, 2-phenylethanol, and 3-phenylpropanol as pendant groups represents spacers between the phosphorus bound oxygen of one, two, and three methylene units, respectively. Increasing the number of methylene spacer units increases the water permeability, (See Fig. 6).

Addition of bulky side substituents onto PPOP results in polymers that are equally as hydrophobic but are less dense, suggesting a higher fractional free volume, as has been demonstrated through gas permeation measurements (10). Mono-t-butyl substituted and di-t-butyl PPOP polymers showed nearly identical water passing performance with each other and with the parent PPOP material suggesting that increases in free volume do not add to water permeability and that permeation is dictated more by solubility than diffusion.

Four halogenated polymers are shown in Fig. 6. Two are PPOP substituted with either bromine or fluorine at the para position, while the other two are polymers substituted with 4-bromophenylethanol and 4-bromophenylmethanol. The p-fluorophenoxyphosphazene showed a slightly higher water flux than PPOP or the other bromine substituted polymers. Adding one or two carbon atom spacers between the oxygen and the phenyl group on the bromo-containing phosphazenes did not have the same impact as it did on phenylethoxyphosphazene. A general observation is that none of the halogen substitutions on the phenyl ring made a significant difference on water passing performance.

CONCLUSIONS

Over twenty different phosphazene polymers were made and tested for their water transport values. From this work, it can be concluded that higher water permeability can be obtained from membranes formed from lower T_g polymers. Inclusion of aromatic functionalities close to the polymer backbone serves to create membranes with lower water permeability. This is a conclusion that has also been observed in previous gas transport research. Omission of aromatic functionalities from pendant groups generally results in lower T_g polymers with significantly higher water permeability. However, there appears to be a limit to the water transport rate with decreasing T_g because no further increase in water permeability was observed with increasing spacer groups attached to the polymer pendant groups. Modulation of the water permeability can be accomplished through adroit selection of pendant groups to give specific performance or can be controlled through formation of polymers using pendant group mixtures. By balancing the relative speciation of hydrophobic and hydrophilic pendant groups, polymer membranes with specific water passing characteristics can be formed and characterized.

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REFERENCES

1. Peterson, E.S.; Stone, M.L.; McCaffrey, R.R.; Cummings, D.G. (1993) *Separation Science and Technology*, 28 (1–3): 423–449.
2. Peterson, E.S.; Stone, M.L.; McCaffrey, R.R.; Cummings, D.G. (1993) *Separation Science and Technology*, 28 (1–3): 271–281.
3. Peterson, E.S.; Stone, M.L.; Bauer, W.F.; Gianotto, A.K. (1992) *Proceedings of the International Conference on Effective Industrial Membrane processes, Benefits and Opportunities*, 6 (21), Euromembrane 92-Paris, Paris, France, pp. 381–387.
4. Peterson, E.S.; Stone, M.L.; Cowan, R.L.; Stewart, F.F.; Orme, C.J. (1995) *Proceedings of Euromembrane '95 Conference*, Bath, England, 1995, Paper CP14, pp. I377–I381.
5. Stewart, F.F.; Peterson, E.S.; Stone, M.L.; Singler, R.L. (1997) *Polymer Preprints*, 38 (1): 836.
6. Stewart, F.F.; Peterson, E.S.; Busse, S.C.; Orme, C.J. (1997) *Chemistry of Materials*, 9 (1): 155–163.
7. Stewart, F.F.; Lash, R.P.; Singler, R.E. (1997) *Macromolecules*, 30 (11): 3229–3233.
8. Luther, T.A.; Stewart, F.F.; Budzien, J.L.; LaViolette, R.A.; Bauer, W.F.; Harrup, M.K.; Allen, C.W.; Elayan, A. (2003) *J. Phys. Chem. B*, 107: 3168–3176.
9. Stewart, F.F.; Luther, T.A.; Harrup, M.K.; Orme, C.J. (2004) In: *Phosphazenes: A Worldwide Insight*, Gleria, M.; De Jaeger, R., eds.; Nova Science Publishers, Inc., New York: Chapter 24, 573–590.
10. (a) Orme, C.J.; Klaehn, J.; Stewart, F.F. (2004) *Journal of Membrane Science*, 238: 47–55. (b) Bauer, W.F.; Stone, M.L.; Orme, C.J.; Harrup, M.K.; Luther, T.A. (2006) *Polymer Testing*, 25 (5): 642–649.
11. Bauer, W.F.; Stone, M.L.; Orme, C.J.; Harrup, M.K.; Luther, T.A. (2006) *Polymer Testing*, 25 (5): 642–649.