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POLYPHOSPHAZENE MEMBRANES: PART 1. ISOPROPANOL/DYE SEPARATIONS

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ABSTRACT

Research has been conducted at the Idaho National Engineering and Environmental Laboratory to determine the characteristics of phosphazene polymers when used as membranes for chemical separations. Phosphazene chemistry allows tailoring of the polymers' mechanical and chemical properties to suit particular applications. Separations discussed in this paper are models for several applications needed in the chemical industry. Ligands on the polymers tested have included modified sugars, various glycols, and substituted phenols. In some cases all of the substituents on the polymer were the same entity. In other cases, up to three different ligands were attached in attempt to develop polymers with all of the needed properties. Physical properties of the different materials varied from film forming rubbers to sticky materials. Some of the polymers gave good fluxes, excellent separations, and lasted for weeks, while others started out with good properties but failed rapidly. A description of the separation performance relative to the separation of isopropanol from dye is given in this paper.

INTRODUCTION

Polymeric thin films (polyphosphazenes and others) have been utilized as semipermeable membranes that can perform chemical separations.[1-10] In some cases, the films are deliberately produced with holes or pores that can perform separations on the basis of size differences of the components in the feed (filtration, ultrafiltration, microfiltration). In other cases, thin, dense pinhole-free films are used as membranes and separate on the basis of solubility differences.[11]

Thus, it is advantageous to be able to easily modify the chemical structure of a polymer in order to tailor separation performance as well as its chemical, thermal, and mechanical properties to a specific application.

Phosphazene polymers consist of a backbone having alternating phosphorus and nitrogen atoms. There are also alternating single and double bonds on the polymer backbone. In addition, each phosphorus is bound to two other substituents; it is these substituents or ligands that are easily substituted.[12] Adjustments to the polymers' properties can also be made by forming polymers with different backbone structures, as shown in Fig. 1.

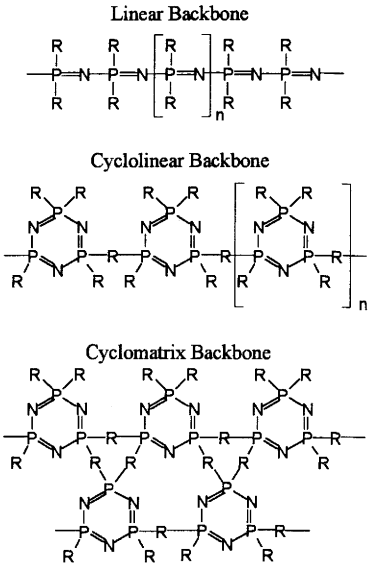


FIGURE 1. Polyphosphazene backbone structures

All of the 'R' groups in the Fig. 1 represent possible substitution sites. Even though the Rs represents all substituents, it is important to realize that mixtures of differing groups may be employed. Thus, it is possible to independently vary both the side groups and the backbones to produce materials with specific properties. "A huge variety of substituents can be linked to P atoms; no other polymeric system exists with the same versatility . . . It is therefore possible to taylor the properties of polyphosphazenes (hydrophilicity/hydrophobicity, solubility, chemical affinity, etc.) for most specific separation needs in different membrane operations."[13]

In order to develop a database on the relationship between the structure and the performance of phosphazene polymers, a series of phosphazene polymers was tested against a feed consisting of isopropanol and a dye. This separation is a model for several applications needed in the chemical industry. Ligands on the polymers tested have included modified sugars, various glycols, and substituted phenols. In some cases, up to three different ligands were attached in an attempt to develop a polymer with all of the needed properties. This paper gives the experimental results.

Of the several membrane separation techniques available, pervaporation is the method employed in this work.[14, 15] Pervaporation is a membrane process that has been characterized as "selective

evaporation." It is a very useful process for the separation of liquid mixtures, especially if one is more volatile than the other. In this process, the feed liquid is passed along one side of the membrane. The more soluble component permeates through the membrane, at which point it encounters a reduced pressure on the backside and vaporizes. Thus there is a phase change from a liquid to a vapor. Described in terms of the solution-diffusion model, the process is comprised of the following three steps:

1. sorption of the components from a liquid phase at the membrane surface;
2. diffusion of the sorbed components through the polymer matrix; and
3. evaporation from the polymer into the vapor phase on the permeate side of the membrane.

Usually, the permeate is collected by cryogenic trapping. The separation is governed by the chemical nature of the permeating species and the membrane material, the morphology of the membrane, and the process operating conditions. Since the dye has no appreciable vapor pressure, these experiments are basically pure component separation tests to compare the permeabilities of the different polymers with isopropanol (IPA). The inclusion of the dye functions mainly for the detection of leaks or pinholes in the membranes.

EXPERIMENTAL

The linear polymers used in this study were produced using a two-step process.[16] First the linear dichloro-substituted polyphosphazene, was produced, and then a nucleophilic substitution process was used to attach specific side groups.

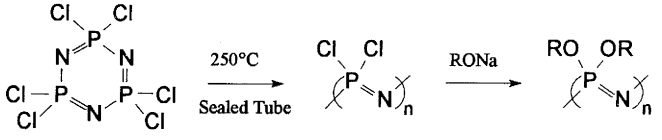


FIGURE 2. Synthetic Pathway for linear Polyphosphazenes.

The linear polymers were produced by the following procedure.

1. Hexachlorocyclotriphosphazene was polymerized under vacuum at 250°C for 48 h.
2. The polymerized material was dissolved in toluene and purified by precipitation into heptane.
3. The pure poly(dichlorophosphazene) was dissolved in dry toluene and added to

tetrahydrofuran (THF) + diglyme solution containing 20 mole percent excess sodium phenoxide. (Mole percentages are based on the number of moles of chlorine in poly(dichlorophosphazene.)

4. This solution was refluxed at approximately 115°C for 42 h. THF was removed using a Dean-Stark trap until a constant reflux temperature of 115°C was achieved.
5. After cooling, the reaction mixture was precipitated into a large excess of methanol.
6. The solids were separated by filtration and were washed with water and methanol to remove occluded sodium chloride.
7. The polymer was purified by dissolving in tetrahydrofuran and precipitated into a large excess of water.
8. Air-drying was done for 12 h, followed by vacuum drying for 2 days.

The molecular weights of the polymers tested ranged from 6 million to 60 million. They all have low glass transition temperatures (T_g) in the range of -30 to -60°C, indicating that they are rubbery polymers in the temperature range tested.

The separation configuration was a simple pervaporation system. The feed mixtures were circulated continuously. Most runs continued for several hours and then stopped, and the permeate volumes were measured and analyzed. A schematic picture of the setup is seen in Fig. 3. Although the cell in the figure appears to be a flat sheet type, in most cases porous ceramic tubes were coated on the inside with the polymer and housed in specially designed cells. Reagent- grade isopropanol was used without further purification. Rose Bengal dye was used as received.

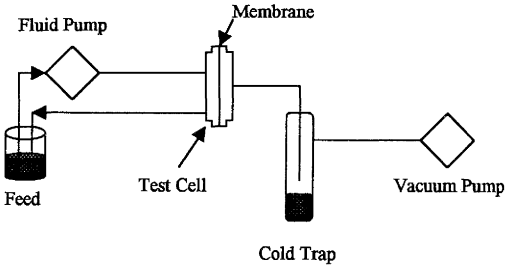


FIGURE 3: Pervaporation Schematic.

Membranes were cast using from 3 to 7% polymer solutions in THF. For flat sheet membranes, the films were either cast on glass plates, lifted off, and transferred to the cell, or they were cast directly onto the support. Whenever a ceramic tube was used, the membrane was cast directly onto the inside surface of the tube, air dried, and in some cases heated. Feed flow rates and permeate vacuum pressures are given in Table 1. The temperature was 22°C in all the runs.

TABLE 1. PERMEATE FLUXES AND OPERATING CONDITIONS FOR PERVAPORATION TESTS.[a]

Table Entry No.	Polymer Type	Flux (L/m^2-h) High	Low	Ave	Permeate Color	Vac (in-Hg)	Feed Flow Rate (mL/min)
1	First di-substituted phosphazene	4.91	3.23	4.02	clear	-22	1000
2	First di-substituted phosphazene	4.46	3.15	3.90	clear	-22	1000
3	First di-substituted phosphazene	4.35	3.30	3.68	clear	-22	1000
4	First di-substituted phosphazene	4.20	2.20	3.36	clear	-22	1000
5	First di-substituted phosphazene	3.20	2.40	2.81	clear	-22	1000
6	First di-substituted phosphazene	1.10	0.09	0.77	clear	-26	30
7	First di-substituted phosphazene	1.57	0.58	0.85	clear	-26	30
8	Second di-substituted phosphazene	0.38	0.12	0.20	clear	-26	30
9	Second di-substituted phosphazene	0.34	0.17	0.22	clear	-18	10
10	Second di-substituted phosphazene	0.26	0.13	0.17	clear	-26	30
11	Second di-substituted phosphazene	0.19	0.08	0.13	clear	-26	30
12	Second di-substituted phosphazene	0.15	One pt.	-	clear	-26	30
13	Second di-substituted phosphazene	0.08	0.05	0.07	clear	-26	30
14	First tri-substituted phosphazene	0.15	0.09	0.11	clear	-26	30
15	First tri-substituted phosphazene	0.14	0.05	0.07	clear-pink	-24	30
16	First tri-substituted phosphazene	0.11	0.05	0.78	clear	-23	1000
17	First tri-substituted phosphazene	0.00	0.00	0.00	-	-23	1000
18	Second tri-substituted phosphazene[b]	0.21	0.09	0.13	clear	-26	30
19	Second tri-substituted phosphazene[c]	0.16	0.03	0.08	clear	-20	50
20	Two component IPN[c]	0.06	0.03	0.05	clear	-22	50
21	Three component IPN	0.00	0.00	0.00	-	-26	30

[a]The polymers used in this study are listed in descending values of the highest flux rates observed. In all cases, the feed solution contained 0.25 ppm Rose Bengal dye and the polymers were coated on the inside of 0.2 μm pore size alumina porous ceramic tubes. The separations were run in the pervaporation mode at 22°C.
[b]These polymers were tested using a 3 PPM Rose Bengal Dye.
[c]These polymers were tested using a 1 PPM Rose Bengal Dye

RESULTS AND DISCUSSION

Two strategies for developing polymers with good fluxes, separations, and physical properties were employed. One strategy was to synthesize linear polyphosphazenes with multiple ligands attached to the same backbone (*i.e.*, di- and tri-substituted) to give the polymer suitable performance. The other approach was to form interpenetrating polymer networks (IPN) by mixing at least two mono-substituted phosphazene polymers. Both techniques were used; however, only two IPN's were included herein for comparison.

More than twenty runs were made in which di- and tri-substituted phosphazenes were utilized. The side groups were combinations of hydrophilic, hydrophobic, ionic, and/or other modifier

groups. Examples of a few of the kinds of ligands possible are given in Fig. 4. Table 1 gives the experimental conditions, fluxes, and separation performance of these materials. The first thirteen entries are derived from membranes cast from two different di-substituted polymers. Polymers 14 through 19 are two tri-substituted combinations. The last two formulations in the table are IPN's of 100%-substituted polymers. They were mixed in ratios similar to the ratios of the ligands on the di- and tri-substituted materials so that the two approaches could be compared.

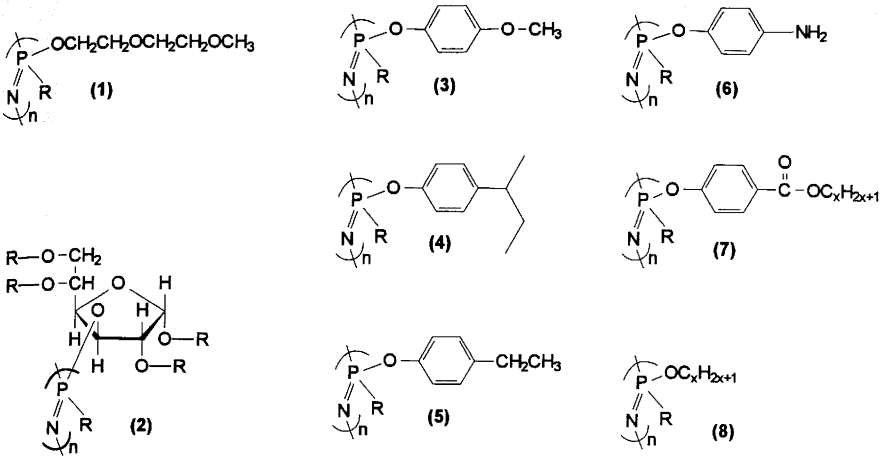
First Di-substituted Phosphazene Polymer.

Table entry numbers 1through 5 were all performed on the same membrane. Table entry number 6 was a separate batch of polymer. In addition, table entry number 7 consisted of a different ratio of the same two ligands. These polymers were devised to contain groups that would have an affinity to the alcohol and have an open structure by the addition of a bulky group. These polymers formed nice films; however, they swelled in isopropyl alcohol (isopropanol, IPA) to the point of dissolution. The large flux values shown in Table 1 are somewhat suspect because most of the polymer cast on the surface of the tubes was probably swollen and sloughed off into the feed solution. The fact that there were high fluxes and clear permeates could have resulted from a very thin layer of the polymer either adhering to the surface or being trapped in the pores of the support. If this is the case, then the polymer was actually performing the desired separation. However, the dissolved polymer in the feed may have had an affinity to the dye, tying it up and preventing it from going through the pores in the tube.

The fact that the polymers swelled greatly (dissolved in some cases) is very encouraging. It means that if there is a way to modify the structure to limit the swelling, while at the same time maintaining the alcohol affinity, a very useful membrane would result. Several methods are presently being investigated.

Second Di-substituted Phosphazene Polymer.

This series of polymers was designed to have high affinity for the alcohol through the use of the same side group used in the first polymer but to have less "swellability" (solubility) by the inclusion of a different second group. This scheme worked quite well. The polymers were much less swollen and had very good mechanical properties when exposed to the IPA. The difference in the performance observed was small even though the substituent ratios were varied by as much as 30%. This may be due to variations in the thickness of the membranes cast inside the tubes, making quantitative permeability comparisons difficult. The fluxes were quite good,[17] and in all cases the membranes remained intact and showed no dye penetration.



(1) Glycols
(2) Sugars (protected and unprotected)
(3) *p*-Methoxyphenoxy-
(4) *p*-Isobutylphenoxy-
(5) *p*-Ethylphenoxy-
(6) Amino- containing
(7) Phenoxy esters
(8) Longer chain alcohols

FIGURE 4. Examples of types and families of potential ligands.

First Tri-substituted Phosphazene Polymer.

In an effort to try to improve the mechanical and thermal stabilities of a series of polymers, attempts were made to add a third group to the backbone that is known to have good thermal and chemical properties. These materials showed much better physical properties and also maintained good separation performances.

Second Tri-substituted Phosphazene Polymers.

The different set of ligands used for these two polymers worked quite well. The flux rate was good, and it is felt that this family of polymers has excellent potential and should be further investigated.

IPN's (Nos. 20 and 21 in Table 1).

The first IPN tested was a mixture of a very hydrophilic material and a very hydrophobic material. Even though the membrane formed a good film, its performance as a membrane was not good. The second IPN gave unexpected results. It is a mixture of the 100% substituted polymers of one

of the tri-substituted polymers reported on earlier. However, this mixture gave no flux. The reasons for this are not clear at this time and are being investigated.

SUMMARY AND CONCLUSIONS

This was a straightforward attempt to show two things. First, that phosphazene polymers are easily modified to produce materials with a wide variety of properties. Second that these changes in structure affect the materials' abilities to perform as membranes. The purpose of this study was to start to develop a database of polyphosphazene membrane properties and performance relative to isopropanol permeabilities. Eight side groups were selected, and polymers were both synthesized and mixed in a series of twenty-three different tests, as discussed previously.

One di-substitued series of polymers was highly soluble in IPA. It was easy to coat tubes and make films. High fluxes and clear permeates were observed, but the integrity of the polymer films needs to be further investigated and improved.

Another di-substituted series swelled some but did not dissolve. This illustrates one of the main features of the phosphazenes. They can be easily modified to change their properties. These polymers showed good fluxes and complete dye retention. Adding a third type of property-modifying group can further improve the chemical, mechanical, and separation characteristics of these polymers.

Another strategy for tailoring the properties is to blend or mix polymers to give IPNs. A limited number of blends were reported herein. Some provided stable films, but with reduced fluxes. This is an area of opportunity that will be further investigated in the future.

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