Correlation of Structure and Function for CO_2 Permeation in Polyphosphazene Membranes

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Abstract

It has been thought that permeation through polyphosphazene membranes of the more condensable gases, such as CO_2 and H_2S, could be enhanced by selection of pendant groups that exhibit higher affinities for these gases. In this paper, over 20 polyphosphazenes with a wide array of pendant groups will be discussed in terms of their CO_2 transport properties. From this work, we have concluded that the pendant group chemical characteristics largely do not play a role in CO_2 transport. More important are the physical characteristics of both the polymer and the gas. For example, permeabilities were found to correlate well to the glass transition temperature of the polymer, regardless of the polarity of the pendant group. Thus, segmental chain motion and physical state of the polymer appear to play a dominant role. This result differs sharply from data taken from liquid transport data that suggests a strong similarity in the solubility properties between the permeant and the polymer is required for higher permeation rates.

Introduction

Polyphosphazenes are an intriguing class of polymers because molecular substitutions can be made onto the phosphorus and nitrogen backbone after polymerization. Chemical functionality is supplied through selection of the pendant group. In general, regardless of pendant group, polyphosphazenes embody a high degree of thermal and chemical stability, although some pendant groups yield more stable polymers as compared to others. For example, many aryloxyphosphazene formulations are stable at temperatures as high as 300 – 400 °C, while many alkoxy-substituted polymers decompose at lower temperatures.[1]

The key advantage of polyphosphazene chemistry for detailed studies of transport mechanisms is that through modification of the pendant groups, polymers with differing chemical and physical characteristics can be formed *without* significantly altering either the polymer backbone structure or the molecular weight. In general, polymer properties are substantially dictated by choice of pendant group. Water soluble polyether pendant groups yield water soluble amorphous, flowing polymers. For instance, poly[bis-2-(2-methoxyethoxy)ethoxyphosphazene] (MEEP) is a flowing elastomer with a glass transition temperature (T_g) of -81°C.[2] Aromatic components, on the other hand, tend to impart hydrophobic character onto the phosphazene backbone. For example, poly[bis-(phenoxy)phosphazene] (PPOP), is a semi-crystalline, hydrophobic, fibrous solid that is only soluble in organic solvents such as toluene, tetrahydrofuran, and chloroform.[3]

Polyphosphazenes containing both hydrophobic and hydrophilic elements have been investigated for gas permeability for the permanent gases (H_2, O_2, N_2, and He) and CO_2.[4] These polymers contained both aromatic components and a polyether component directly attached to the polymer backbone resulting in a terpolymeric structure, Figure 1. In this previous work, a correlation was observed between the content of hydrophilic polyether and the CO_2 permeability where higher polyether containing polymers exhibited higher CO_2 transport. From this work, it was concluded that a chemical interaction between the polyether and CO_2 was responsible for the observed correlation. In this new work, other polymer structures were included in the analysis yielding a more general relationship not between the pendant group and the gas, but between the physical embodiments of the pendant group on the polymer, such as the glass transition temperature, and the gas.

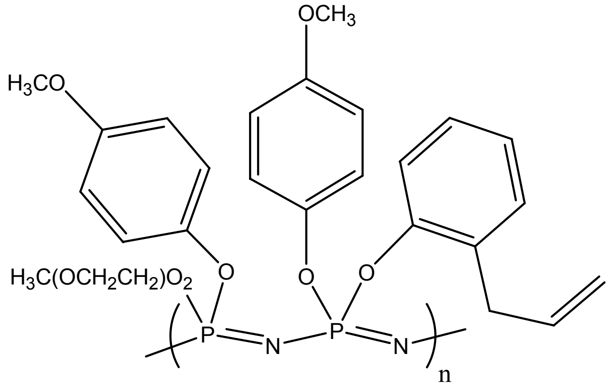


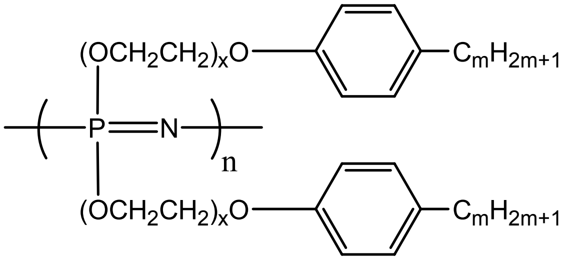
Figure 1. General structure of the phosphazene terpolymers. Pendant groups are randomly substituted resulting in six total possible mers.

Experimental Methods

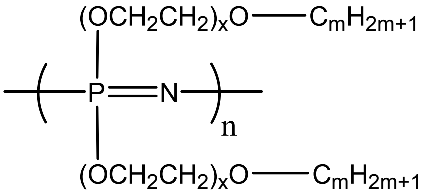
Organophosphazenes were synthesized from poly[bis-(chloro)phosphazene] (PNCl2) and purified using previously published methods.[5, 6] Membranes were formed using the solution casting method. Casting solutions, generally 5-10% (w/w) polymer, were stirred until complete polymer dissolution was observed. The solutions were centrifuged to assure that no suspended particulate matter was present, which could cause defects in the membrane films. Casting was conducted directly onto a ceramic support (Whatman Anodisk®, 0.2 µm pore size).[7] The membrane formed as the solvent evaporated from the film. Covering the drying membranes with a glass vessel (beaker, crystallizing dish, etc.) controlled evaporation rates such that defect free films were formed. Film thicknesses were approximately 150 µm as measured using a Mitutoyo caliper. PNCl2 also was formed into a membrane using the solution casting method. To prevent reaction of the polymer with atmospheric moisture, the polymer was dissolved in dry toluene and stored in solution under dry nitrogen for periods up to one week. Membrane casting was performed in a glove bag with a dry nitrogen purge. Upon complete removal of solvent, the membrane was rapidly mounted into a cell housing and connected to the gas permeation instrument for analysis. Permeabilities were determined using literature methods where the permeate volume was 1021.5 ml, the membrane area was 3.2 cm^2, and the initial feed gas pressure was 30 psi.[8, 9]

Results and Discussion

Seven new phosphazene polymers were synthesized employing commercially available surfactants as the pendant groups. Generalized structures for these pendant groups and the resulting polymers are located in Table 1. Two distinct types of surfactants were employed that have one key difference. Both types contained hydrophilic polyethers, terminated in a hydroxyl group for attachment to the polymer backbone phosphorus, and hydrophobic aliphatic groups. For five of the pendant groups, an aromatic ring separated the hydrophilic and hydrophobic moieties, see Structure (A). The other two had these groups joined directly to each other without the aromatic spacer, see Structure (B).



(A)



(B)

Table 1. Polymer Characterization Data.

Polymer # Pendant Group (Structure)	Polyether chain length (x)	Aliphatic Chain (C_mH_{m+1}) (m)	^{31}P NMR (σ, ppm)	T_g (° C)	M_w (g/mol)	Density (g/ml)
1 Igepal CA-210 (A)	1.52	8.31[1]	-6.3	11.0	1.4×10^6	1.07
2 Igepal CO-210 (A)	1.63	9.19	-6.7	-11.0	2.2×10^6	1.04
3 Igepal CO-430 (A)	4.75	9.20	-7.3	-33.0	4.5×10^6	1.09
4 Triton X-114 (A)	8.25	8.07[1]	-7.3	-39.0	6.5×10^5	1.11
5 Igepal DM-530 (A)	8.57	2×9.11[2]	-7.1	-41.0	3.7×10^6	1.06
6 Brij-72 (B)	2.36	18.21	-7.2	-39.0 (T_m 22.0)	3.7×10^5	0.99
7 Brij-30 (B)	4.89	12.19	-7.3	-45.0 (T_m –5.0)	2.5×10^6	1.02

[1] Branched tert-octyl groups.

[2] Two aliphatic chains with m = 9.11 are substituted on the aromatic ring at the ortho and para positions.

Characterization data for the resulting polymers is shown in Table 1. P-31 NMR was used to directly observe the polymer backbone where the homopolymers were observed as singlets. Little significant difference in the data suggests that electronic effects from immediately neighboring groups of the observed nucleus are responsible for the chemical shift, while more remote groups, such as the aromatic rings or the alkyl chains play no significant role. H-1 NMR spectroscopy was used to determine the structure of each pendant group, which was required because they are obtained as technical grade mixtures of closely related compounds. Integration of the NMR data provided average structures for each group, as shown in Table 1.

Unlike the NMR data, the more remote moieties do appear to have an effect on the thermal analytical data obtained for these polymers. A broad range of T_g data was obtained for these materials, from +11 °C to –45 °C, Table 1. Additionally, polymers **6** and **7** showed melt transitions (T_m) at 22 °C and -5 °C, respectively. In general, more flexible polyphosphazenes have lower T_g values, while more sterically encumbered polymers have higher values. Addressed separately, the phosphorus and nitrogen backbone is highly flexible. Although the backbone is conventionally drawn with alternating double and single bonds, the p -d bonding between phosphorus and nitrogen leaves nodes at each phosphorus through which electrons cannot pass. Electrons are delocalized between each phosphorus, but not through them. Thus, the rotational energy barrier for the backbone is low resulting in a flexible structure with a low T_g. This behavior differs strongly from corresponding organic systems. For example, poly[acetylene] has p -p bonding between carbons that allows for electron delocalization down the carbon skeleton. Orbital overlap between carbons creates a rotational barrier resulting in a less flexible structure, which would be expected to yield higher T_g values. With an inherently flexible P-N backbone, pendant groups can either support this flexibility by introducing little steric encumbrance into the polymer, or the pendant groups can stiffen the polymer by restricting backbone motion.

Table 2. Gas Permeability Data (Barrers).

Polymer	H_2	Ar	N_2	O_2	CH_4	CO_2
1	11.0	3.5	1.4	3.3	1.5	12.0
2	30.9	8.8	3.5	10.1	7.9	45.0
3	38.8	14.7	6.6	17.5	18.5	130.8
4	27.7	9.5	4.7	13.0	15.6	157.3
5	53.2	29.8	14.0	32.7	34.7	274.6
6	6.3	1.3	0.6	1.3	1.1	8.3
7	62.1	44.1	21.0	46.2	67.3	386.4
PNCl2	83.9	-	-	-	91.7	543.0

Gas permeabilities were determined on thin films (~150 μm) of polymers **1**-**7** and poly[bis-(chloro)phosphazene] (PNCl2) at 30 °C using H_2, Ar, N_2, O_2, CH_4, and CO_2 as the analyte gases, see Table 2. PNCl2 was added into this study due to the relatively small size of chlorine, which is reflected in a T_g of –66 °C.

The CO_2 permeability data for **1**-**7** was interpreted in terms of a previous study where it was found to have a positive correlation with the polyether content.[4] In that study, polyether groups and aromatic groups were each individually attached to phosphorus and NMR integration yielded relative amounts of each pendant group as a percentage of the total pendant group attachments. This method proved

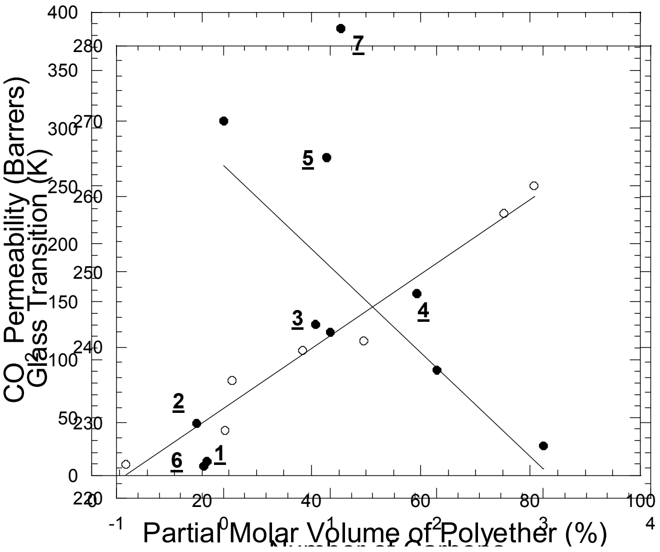


Figure 2. Plot of CO_2 permeability vs. partial molar volume of polyether for selected polymers.

the phenyl ring as a relative measure of the effect of adding steric bulk to a pendant group.

inadequate for polymers **1**-**7** since both components were incorporated into each pendant group. To address this shortcoming, a volumetric approach was taken where the molar volumes of the polyether regions and the total polymer were calculated using group contribution theory.[10] From group contribution molar volume values, an estimation of the partial molar volume of polyether in each polymer was made. A plot of this data is shown in Figure 2 where the open circles refer to literature data[4] that provides a high degree of correlation (r^2 = 0.984). However, the data derived from this new work shows little correlation suggesting that the polyether content alone does not dictate CO_2 permeability. Furthermore, PNCl2 with no polyether content shows high CO_2 permeability, suggesting a mechanism for transport other than a molecular interaction between the polyether and CO_2.

For the terpolymers, the correlation between polyether content and the CO_2 permeability can be thought of more as a correlation with the more permeable region of the polymer. Aromatic groups directly attached to polyphosphazenes tend to lower gas permeability. For example, the CO_2 permeability of PPOP is only 4.8 Barrers,[3] which is substantially lower than the permeability of MEEP at 250 Barrers.[4] Thus, using the partial molar volumes of polyether in each polymer; the permeability of only the polyether region can be calculated assuming little permeation through the "non-polyether" regions. For polymers **1**-**7**, correlation of this calculated CO_2 permeability with the polyether chain length gave good correspondence with all polymers except **7**, Figure 3. Polymer **7** has a much higher permeability than would be expected with this analysis suggesting that other regions of the polymer may also be responsible of CO_2 permeation.

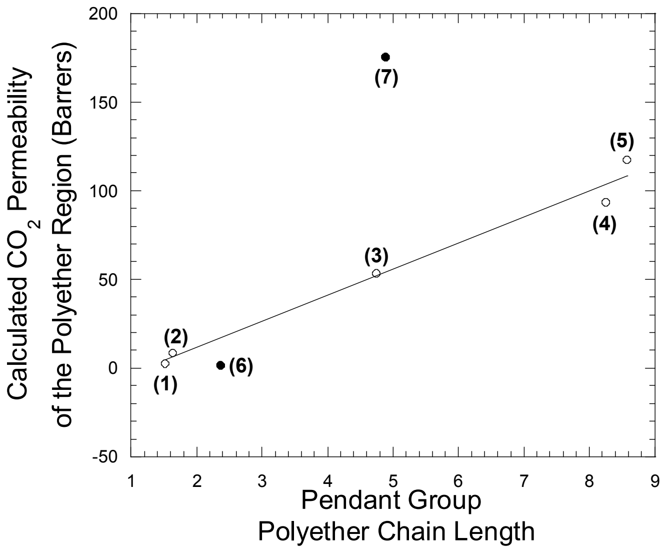


Figure 3. Calculated permeability of the polyether region vs. pendant group chain length for polymers **1**-**7**.

The location of the aromatic ring is more important than its presence. Aromatic rings displaced from the phosphazene backbone yield polymers with substantially higher CO_2 permeabilities than ones with the aromatic ring directly on the backbone. The location of the aromatic ring also has a large effect on the observed T_g. Aromatic rings close to the backbone hinder backbone motions, thus increasing T_g. As the aromatic ring is displaced from the backbone, its influence on T_g subsides. For example, in a series of phosphazene homopolymers synthesized from phenol (PPOP), benzyl alcohol, 2-phenyl-1-ethanol, and 3-phenyl-1-propanol, "bridges" between the aromatic ring and the backbone of 0,1,2,and 3 carbons, respectively, are created. This results in decreasing T_g with increasing "bridge" length, Figure 4. For polymers **1**-**7**, the aromatic rings are displaced by at least an average of 1.5 ethyleneoxy units, which equates to approximately four sp^3-hybridized atoms of carbon and oxygen. The hybridization of the bridging atoms is important for molecular flexibility. Carbons that are sp^3 hybridized have a greater degree of motional freedom (degrees of freedom) than either sp^2 or sp hybridized carbons. Aromatic rings, formed from aromatized sp^2 carbons have less degrees of freedom than the sp^3-hybridized analog, cyclohexane. Lower motional freedom creates energy barriers to free molecular motion that are reflected in lower T_g values.

Relatively subtle changes in molecular structure, as shown in polymers **1**-**7**, can have significant changes in T_g, as shown in Table 1. From an analysis of the gas permeability data with respect to T_g, it appears that as T_g decreases, CO_2 permeability increases, see Figure 5. All the polymers in this set plus PNCl2 appear to follow this trend, except for polymer **6**. However, polymer **6** has a melt transition at 22 °C, and at the temperature at which the gas permeability experiments were conducted, 30 °C, the polymer was not completely in a melt phase, which would be expected to significantly lower the gas permeability with respect to the phase above T_m. Thus, polymer **6**, under the conditions of the permeability test, is in a differing phase than the other amorphous polymers and polymer **7**, who's T_m is substantially lower at -5 °C.

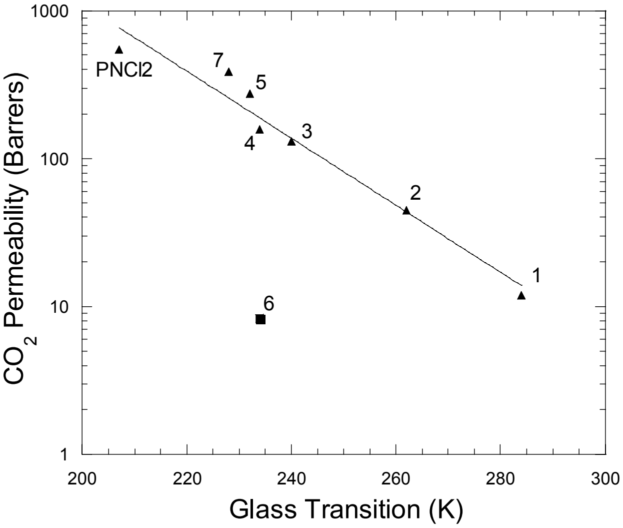


Figure 5. Plot of CO_2 permeability vs. T_g for selected polymers.

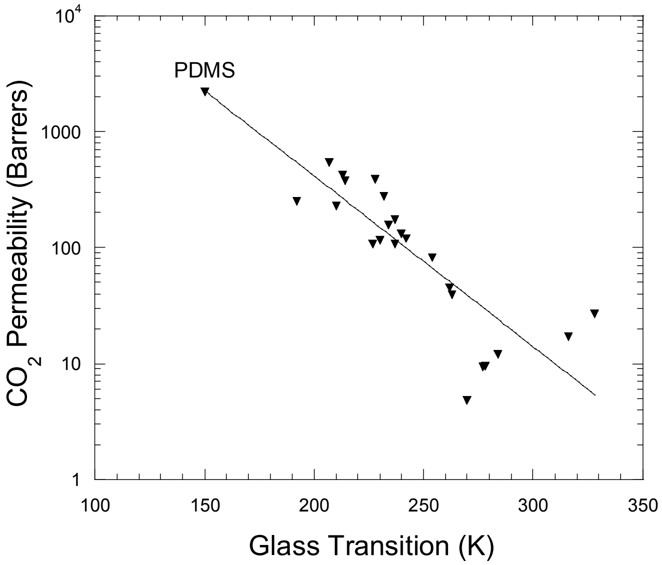


Figure 6. CO$_2$ permeability vs. T$_g$ for selected polyphosphazenes and PDMS.

The inclusion of PNCl2 into this study is intriguing because its gas permeability correlated well with the other polymers that are also amorphous rubbers, however, its chemical affinity is different. For example, PNCl2 will not swell in water, although it is slowly reactive with water. Polymers **1**-**7** rapidly swell in water. This observation suggests that CO$_2$ permeability is not a function of the chemical affinity of the polymer as it is more of a function of the T$_g$. To further study this observation, a general correlation plot was made using available CO$_2$ permeability and T$_g$ data from a large variety of poly-phosphazenes including perfluorinated, aromatic, and all of the polymers discussed in this work, see Figure 6. The data showed good linearity, although at higher T$_g$ values, the data appears to correlate less well. Four polymers below the trend line with T$_g$ values between 260-290 K are phenoxy-containing phosphazenes that are semi-crystalline, so their permeabilities are lower than what is obtained for 100% amorphous phase polymers. Furthermore, the two polymers with the highest T$_g$'s (310-330 K) are poly[bis-(tert-butylphenoxy)phosphazene] and poly[bis-(3,5-di-*tert*-butylphenoxy)$_{1.2}$(chloro)$_{0.8}$phosphazene] that have groups which serve to increase the fractional free volume of the polymers, resulting in higher permeabilities due to a higher contribution to transport from diffusion. Poly[dimethylsiloxane] (PDMS) was also added to this analysis due to its highly flexible silicon-oxygen backbone that is homologous to the phosphazene phosphorus-nitrogen backbone. The degree of linearity of this data is remarkable with an r^2 of 0.968.

Conclusion

In this work, it has been shown that for a series of phosphazene polymers that shares the same backbone structure but have differing pendant groups, the CO$_2$ permeability is a function of the polymer T$_g$ and that the chemical affinity plays a small role. This differs significantly from what has been determined for liquid transport.[11] Thus, gas and liquid transport have been decoupled so that either hydrophilic or hydrophobic membranes can be made for relatively high CO$_2$ transport through depression of the T$_g$. Lower T$_g$ materials then can be formed from groups that incorporate sp^3 hybridized atoms that embody the highest degrees of motional freedom. High flexibility hydrophobic pendant groups will form hydrophobic polymer membranes with relatively high CO$_2$ permeability. Likewise, a low flexibility hydrophobic pendant group incorporating groups such as aromatics will yield polymers that are both hydrophobic and have relatively low CO$_2$ permeability. Thus, chemical transport can be controlled to a high degree through chemical synthesis and adroit selection of pendant groups.

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