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MEMBRANE TRANSPORT BEHAVIOR AND THE LABILITY OF CHLORIDE ON POLYPHOSPHAZENES BEARING BULKY SUBSTITUENTS

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Introduction

The hydrolytic instability of chlorine-containing phosphazene polymers is well-documented and is a function of the lability of chlorine. Polyphosphazenes are hybrid organic-inorganic polymers that have a backbone comprised of phosphorus and nitrogen atoms with alternating double and single bonds. Phosphorus is pentalvalent leaving two points of substitution available for chemistry. The most commonly employed route to linear phosphazene polymers employs ring-opening polymerization of hexachlorocyclotriphosphazene to yield poly[bis-chlorophosphazene].[1] Phosphorus-chlorine linkages are hydrolytically unstable and susceptible to cleavage upon exposure to nucleophilic reagents as weak as water. Prompt substitution of poly[bis-chlorophosphazene] yields stable materials as long as the resulting nucleophile-phosphorus bond is stable. This chemistry was first realized and reported in the 1960's by the Allcock group.[2] Further development of this chemistry has led to rapid development of a multitude of phosphazene polymers that have been recently reviewed.[3] The disparate nature of these macromolecules, which includes glasses, semicrystalline materials, and rubbers, is unique in that they are all created with an identical backbone structure.

At the Idaho National Laboratory, we have sought to develop phosphazene chemistry to yield novel materials for membrane applications. Key advantages to phosphazene materials, beyond their rich and diverse chemistries, is the fact that they are non-flammable and have high decomposition temperatures ranging from 250-350 ºC, depending on the choice of pendant group.[4] In this paper we discuss several phosphazenes designed for gas transport and separation and the unprecedented synthesis of a phosphazene with hydrolytically stable chlorine occupying 48 % of the available sites on phosphorus.

Experimental

Materials. Phosphonitrilic chloride trimer was obtained from Esprit Chemicals and sublimed prior to use. 3,5-Di-*tert*-butylphenol, 4-*tert*-butylphenol, tetrahydrofuran (THF), diglyme, hexanes, and sodium hydride (as a 80% dispersion in mineral oil) were obtained from Aldrich Chemical Co and used as received. Toluene was purchased from Fisher Scientific and was azeotropically distilled to remove water prior to use. Methanol and reagent alcohol were obtained from Fisher Scientific and used as received.

Instrumentation. NMR analyses were performed on a Bruker DMX300WB operating at a magnetic field strength of 7.04 T. Thermal analyses were obtained using TA Instruments Model 2910 Differential Scanning Calorimeter (DSC). Density measurements were accomplished using a Micromeritics model Accupyc 1330 pycnometer using nitrogen as the analyte gas. Dilute solution techniques were used to characterize the macromolecular structure of the polymers. Tetrahydrofuran/0.1 % tetrabutylammonium bromide (TBABr) filtered through a 0.2 μm filter was used as solvent and all experiments were performed at 23 ºC. Solution refractive index increment, *dn/dc* values were obtained using a Wyatt Technologies OptiLab refractive index detector. High performance size exclusion chromatography (HPLC) was performed using a Waters Model 2690 solvent/sample delivery system with a column bank of two Styragel HR 5E (4.6 mm id. x 300 mm) solvent efficient columns. 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 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. Toluene was pre-filtered 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 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 of Poly[bis-(*tert*-butylphenoxy)phosphazene] (PTBPP). In a two-liter flask equipped with a mechanical stirrer and an N_2 purge was added 4-*tert*-butylphenol (108.3 g, 721 mmol) and THF (300 ml). To this mixture was added sodium hydride (27.4 g, 684 mmol) and the resulting solution was stirred at room temperature for one hour upon which the hydride was consumed. Poly[bis-chlorophosphazene] (20.9 g, 180 mmol) in toluene (150 ml) was added followed by diglyme (600 ml) and heating. At this point, a Dean-Stark trap was attached to the apparatus and the lower boiling solvents were removed until the reaction temperature reached 110 °C. The reaction was stirred for 22 hours at which point it was determined to be complete. Isolation and purification of the product was accomplished by repeated precipitations from THF solution into water and methanol to give a white fibrous solid in 84% yield. Characterization data: ^{1}H NMR ($CDCl_3$) δ (ppm) 1.08 (brs), 6.84 (brs). ^{31}P NMR ($CDCl_3$) δ (ppm) –17.1 (brs). T_d 386 °C. T_g 43 °C. Density = 1.160 g/ml. Molecular Weight (M_w) = $(1.15 \pm 0.01) \times 10^6$, PDI = 1.14 ± 0.018.

Synthesis of Poly[bis-(3,5-di-*tert*-butylphenoxy)phosphazene] (PDTBPP). An apparatus for preparation of the aryloxide and polymer was assembled consisting of a two-liter three neck round bottom flask, mechanical stirrer, and nitrogen purge. The aryloxide was prepared in THF (500 ml) solution from 3,5-di-*tert*-butylphenol (127.5 g, 618 mmol) and sodium hydride (18.5 g, 617 mmol). The resulting solution was stirred for 1.5 hours under nitrogen to assure consumption of the hydride. To this solution was added poly[bis-chlorophosphazene] (23.9 g, 206 mmol) as a solution in toluene (150 ml). Additional toluene was added to bring the total volume to approximately 1000 ml. The resulting mixture was heated to reflux for 48 hours upon which the mother liquor was poured into 2 liters of water. The precipitated product was collected and dried. Further purification was accomplished through repeated precipitation of the product from THF into water, methanol, and reagent alcohol. Drying afforded a white solid in 56% yield. Characterization data: ^{1}H NMR ($CDCl_3$) δ (ppm) 1.07 (brs), 6.98 (brs). ^{31}P NMR ($CDCl_3$) δ (ppm) –16.6 (brs), -21.0 (brs). ^{13}C NMR ($CDCl_3$) δ (ppm) 32.2, 35.5, 116.0, 116.6, 118.0, 152.2. Tg 55 °C. Density = 1.098 g/ml. T_g 55 °C. Molecular weight (M_w) = $(1.11 \pm 0.01) \times 10^6$, PDI = 1.16 ± 0.020.

Results and Discussion

Poly[bis-(*tert*-butylphenoxy)phosphazene] (PTBPP). In general, polyphosphazenes containing aromatic rings directly attached to the phosphorus-bound oxygen are materials with a T_g around 0 ºC.[5] This differs from both alkyl and alkoxy substituted phosphazenes in which the T_g can be as low as -60 ºC.[4] Differences in T_g are a function of the polymer chain, and more specifically the backbone flexibility. Aromatic rings in close proximity to the polymer backbone tend to restrict motions, thus driving up T_g. A positive ramification of aromatic substitution is greatly increased thermal stability as compared to alkyl or alkoxy phosphazenes, which suggests that they should be good candidates for gas separation membranes in harsh chemical environments.

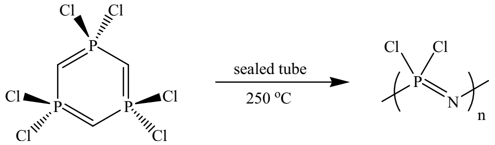

Figure 1. Ring Opening Polymerization of Phosphonitrilic Chloride.

Formation of PTBPP is achieved in a multi-step synthesis beginning with the ring opening polymerization of phosphonitrilic chloride trimer yielding poly[bis-chlorophosphazene] using literature procedures, see **Figure 1.**[6] Poly[bis-chlorophosphazene] is hydrolytically unstable and readily will react with nucleophiles. In fact, water will react with the polymer to generate phosphates, cleaving the backbone along the way. To maintain the macromolecular nature of the phosphazene, this lability of chlorine is exploited to yield organo-phosphorus moieties that are stable to hydrolysis.

Substitution of poly[bis-chlorophosphazene] with the sodium salt of 4-*tert*-butylphenol, formed by deprotonation of the phenol with sodium or sodium hydride, was found to yield PTBPP, see **Figure 2**.[5] Purified PTBPP is a white fibrous polymer that is readily soluble in solvents such as THF and toluene.

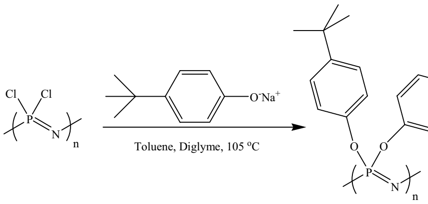

Figure 2. Synthesis of PTBPP.

^{31}P NMR spectroscopy of the isolated product gave a single resonance at -17.1 ppm corresponding to a homogenously substituted material. From DSC, only one feature was observed, a T_g at 43 ºC. This value is nearly 50 ºC higher than what is observed for poly[bis-phenoxyphosphazene] that is lacking the tert-butyl groups. Thus, the addition of tert-butyl substituents far from the polymer backbone can significantly influence polymer chain mobility through steric interactions.

Poly[bis-(3,5-di-*tert*-butylphenoxy)phosphazene] (PDTBPP). A dramatic exploitation of the theme was provided by studying the chemistry of even bulkier pendant groups, such as 3,5-di-*tert*-butylphenol. The polymer synthesis was conducted similarly to PTBPP; however the ^{31}P signals obtained from reaction samples never coalesced into the expected single resonance. Two peaks were observed at -16.6 and -21 ppm. Two peaks in a homogenous synthesis generally indicates unreacted chlorine. To probe this conclusion, a reactive, sterically small nucleophile, sodium methoxyethoxyethoxide, was added to the reaction solution and stirred at reflux for 24 hours. No change was observed in the NMR data. Purification of the polymer yielded a white fibrous material (PDTBPP), reminiscent of PTBPP and poly[bis-phenoxyphosphazene], suggesting a completely substituted polymer. The product was demonstrated to be hydrolytically stable using soxhlet extraction with water over 10 days.

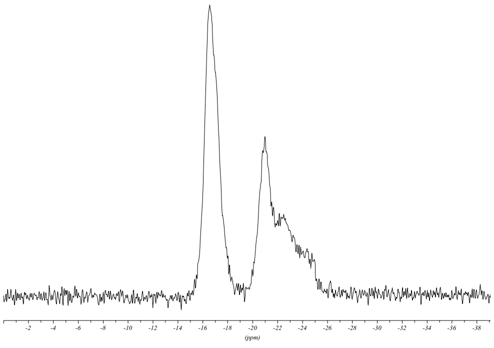

Figure 3. ^{31}P NMR spectrum of polymer product (PDTBPP) from the reaction of poly[bis-chlorophosphazene] with 3,5-di-tert-butylphenol.

To ascertain the presence of unreacted chlorine, the polymer product, PDTBPP, was subjected to elemental analysis, **Table 1**. A comparison of the calculated and found numbers reveals complete disagreement. The most striking find was the chlorine amount. By manipulating the percentages of chlorine with respect to the phenol amount, a composition of 39 % is proposed, which is in good agreement with the data giving the structure shown in **Figure 4**.

Table 1. Elemental analysis for PDTBPP.

Result	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Chlorine (%)
Calculated	73.81	9.29	3.07	0
Found	63.58	8.05	4.31	8.52
Assume 39 % chlorine	63.49	7.99	4.33	8.56

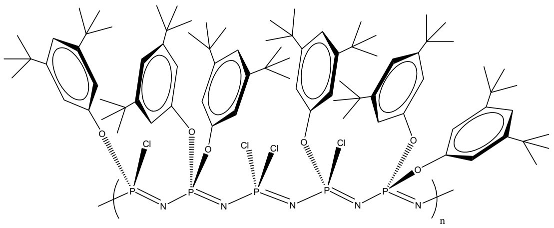

Figure 4. Proposed structure of PDTBPP with 40% of the sites occupied by chlorine.

Pure Gas Permeation Studies. A method for observation of the morphological effects introduced into a phosphazene by pendant group choice is gas permeation. In our labs, we have designed and constructed a gas permeation system that has been discussed earlier.[7] This system employs a barometric method for measuring gas permeability through flat sheet membranes. Both polymers discussed in this work were effective film formers, meaning that defect free films ranging from 100 to 200 µm in thickness could easily be cast from solution.

Table 2 shows pure gas permeabilities and ideal separation factors for selected gases. The increase in steric bulk posed by the additional tert-butyl group increases both the permeability of gases such as hydrogen and oxygen, and the ideal separation factors calculated for the H_2/CH_4, O_2/N_2, and CO_2/N_2 gas pairs.

Table 2. Permeability separation factor data for selected gases.

Polymer	H_2 (Barrers)	O_2 (Barrers)	H_2/CH_4	O_2/N_2	CO_2/N_2
PTBPP	23	8.2	13.5	3.4	7.1
PDTBPP	75	11	15.0	3.7	9.0

Conclusions

In this work, an unusual circumstance is described where a hydrolytically stable polyphosphazene was characterized to have 39 % of the available sites occupied by chlorine. This observation is a ramification of the selection of a sterically hindered pendant group that serves to sheath the polymer backbone preventing both complete substitution and subsequent hydrolysis. This polymer has been shown to be stable in the presence of excess nucleophile (base) and water over long periods of time. Gas transport data suggests that the increase in steric bulk of the pendant groups serves to increase both the permeability and the ideal separation factor for small permanent gases.

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