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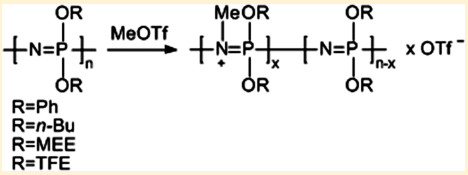
Synthesis of New Polyelectrolytes via Backbone Quaternization of Poly(aryloxy- and alkoxyphosphazenes) and their Small Molecule Counterparts

Chen Chen, Andrew R. Hess, Adam R. Jones, Xiao Liu, Greg D. Barber, Thomas E. Mallouk, and Harry R. Allcock*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

ABSTRACT: Novel polyelectrolytes were synthesized by quaternization of the backbone of poly(alkoxy- and aryloxyphosphazenes) with strong alkylation reagents. As models for the synthesis of these polymers, similar quaternization reactions were also carried out on small-molecule alkoxy and aryloxy cyclotriphosphazenes. The quaternized small molecules and high polymers were characterized by ^{1}H NMR, ^{31}P NMR, DSC, TGA, and AC impedance studies. The quaternized poly(alkoxyphosphazenes) showed ionic conductivities of 2.58×10^{-4} S·cm^{-1} at 25 °C and 2.09×10^{-3} S·cm^{-1} at 80 °C, which are among the highest values for known solvent-free ionically conducting polymers.



INTRODUCTION

Since the first report of a solid-state polymer electrolyte composed of poly(ethylene oxide)/salt complexes by Wright et al.[1] the development of polymeric solid-state electrolytes has drawn the attention of many researchers. Solid-state polymeric electrolytes have many advantages over conventional liquid electrolytes such as high dimensional stability, excellent processability, and improved safety, which make them ideal electrolytes for solid-state electrochemical devices such as high energy density rechargeable batteries, fuel cells, electric double-layer capacitors, and electrochromic displays.[2]

Dye-sensitized solar cells (DSSCs) have been under intensive investigation as a low cost alternative to silicon solar cells.[3,4] The most important factor affecting the practicality of DSSCs is the electrolyte, which usually consists of an I^-/I_3^- redox couple in a volatile liquid organic solvent. The serious drawbacks of organic solvent based liquid electrolytes are their volatility and the possibility of leakage during extended operation, especially at elevated temperatures, together with the necessary complexity of sealing the unit. Solid-state polymeric electrolytes are a logical solution to overcome both of the problems caused by liquid organic solvent.

Polyphosphazenes are long chain macromolecules that contain an inorganic backbone composed of alternating phosphorus and nitrogen atoms joined by unusual quasi-delocalized single−double bonds, and organic side groups attached to the backbone phosphorus atoms. Many different organic side groups can be linked to the polyphosphazene backbone in variable ratios, a feature that provides this polymer platform with versatile properties and applications.[5] With appropriate side groups attached to the backbone, polyphosphazenes are known to have low glass transition temperatures (T_g) and zero crystallinity: in other words, they remain highly flexible even at low temperatures due to the unusual torsional mobility of the P═N backbone. This flexibility, which is considerably higher than in most other ionic conducting polymers including poly(ethylene oxide), allows sufficient segmental motion for the facile migration of ions through the solid electrolyte medium. Polyphosphazenes with oligoethylene oxy side chains are among the most ionically conductive polymers.[6−8] One of the disadvantages of polymer/salt complexes as polymer electrolytes is that both cations and anions are mobile, which leads to concentration polarization which significantly reduces cell performance. In addition, the mobility of both anions and cations also hampers a fundamental understanding of the ion transport mechanisms in polymer electrolytes. A solution to these problems is to covalently link anions or cations to the polymer backbone, to yield polyelectrolytes. Side groups with both cations and anions have been tethered to the polyphosphazene backbones as side groups to form polycations and polyanions.[9−13]

Functionalization of the backbone nitrogen atoms of polyphosphazenes has received far less attention than the variation of side groups at the phosphorus centers. Backbone nitrogen atoms have been shown to play key role in coordination chemistry of oligo- and polyphosphazenes.[14−19] Organo- and organoamino-substituted cyclooligophosphazenes have been quaternized at the backbone nitrogen atoms to form phosphazenium cations,[20−25] but the quaternization of organoaminophosphazene high polymer has not been studied extensively.[26]

We report the first synthesis of novel polyelectrolytes via backbone quaternization of poly(aryloxy- and alkoxyphosphazenes), in which the charge carriers are located on skeletal nitrogen atoms . These new polyelectrolytes show good ionic conductivity without the presence of plasticizers or solvents.

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Although dealkylation reactions, which cause loss of charge carriers, were detected when these quaternized species were exposed to anions with strong nucleophilicity, the promising conductivity results reveal a new concept for the synthesis of highly conductive polyelectrolytes via backbone functionalization.

EXPERIMENTAL SECTION

Reagents and Equipment. All synthesis reactions were carried out under a dry argon atmosphere using standard Schlenk line techniques. Tetrahydrofuran (THF), 1,4-dioxane and dichloromethane (DCM) (EMD) were dried using a solvent purification system, in which the solvents pass through columns of molecular sieves under a dry argon atmosphere.[27] Di(ethylene glycol) methyl ether (Aldrich), 1-butanol (EMD), and 2,2,2-trifluoroethanol (Aldrich) were distilled over calcium hydride. Phenol was purified by sublimation under vacuum. Acetone (EMD), methanol (EMD), hexanes (EMD), *N,N*-dimethylformamide (EMD), sodium hydride (60% dispersion in mineral oil, Aldrich), sodium iodide (Aldrich), 1,2-dichloroethane (Aldrich), chorobenzene (Aldrich), sodium thiosulfate pentahydrate (Aldrich), sodium bicarbonate (EMD), triethyloxonium tetrafluoroborate (1 M solution in dichloromethane, Aldrich) and methyl trifluoromethanesulfonate (Aldrich) were used as received. Poly(dichlorophosphazene) was prepared via the thermal ring-opening polymerization of recrystallized and sublimed hexachlorocyclotriphosphazene (Fushimi Pharmaceutical Co., Japan or Ningbo Chemical Co., China) in evacuated Pyrex tubes at 250 °C.[28] Unpolymerized hexachlorocyclotriphosphazene was removed by vacuum sublimation. ^{31}P and ^{1}H NMR spectra were obtained with a Bruker 360 WM instrument operated at 145 and 360 MHz, respectively. ^{31}P NMR spectra were proton decoupled. ^{1}H shifts are reported in ppm relative to tetramethylsilane at 0 ppm. ^{31}P shifts are reported in ppm relative to 85% H_3PO_4 at 0 ppm. ^{31}P NMR spectra were simulated with SpinWorks (version 3.1.8.1). Glass transition temperatures were measured with a TA Instruments Q10 differential scanning calorimetry apparatus at a heating rate of 10 °C/min and a sample size of ca. 10 mg. Gel permeation chromatograms were obtained using a Hewlett-Packard HP 1100 gel permeation chromatograph equipped with two Phenomenex Phenogel linear 10 columns and a Hewlett-Packard 1047A refractive index detector. The samples were eluted at 1.0 mL/min with a 10 mM solution of tetra-*n*-butylammonium nitrate in THF, and the elution times were calibrated with polystyrene standards. Mass spectrometric analysis data were collected using the turbospray ionization technique with an Applied Biosystems API 150EX LC/MS mass spectrometer. Ionic conductivities were measured with a HP 4192A impedance analyzer in custom-made cells. All the ionic conductivity tests were carried out at a fixed AC level of 0.1 V, and the frequency was scanned from 5 to 6,000,000 Hz. Thermal decomposition traces were obtained using a Perkin−Elmer TGA 7 thermogravimetric analyzer. Heating occurred at a rate of 20 °C/min from 50 to 800 °C under a nitrogen atmosphere and a flow rate of 50 mL/min.

Synthesis of Unquaternized Phosphazenes. Hexa(phenoxy)cyclotriphosphazene (**2**),[29] hexa(*n*-butoxy)cyclotriphosphazene (**3**),[30] hexakis(2-(2-methoxyethoxy)ethoxy)cyclotriphosphazene (**4**),[31] hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (**5**),[32] poly(diphenoxyphosphazene) (**13**),[28,33] poly[di(*n*-butoxy)phosphazene] (**14**),[34] poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (**15**)[7] and poly[bis(2,2,2-trifluoroethoxy)phosphazene] (**16**)[28,33] were synthesized by allowing sodium phenoxide or sodium alkoxides to react with hexachlorocyclotriphosphazene or poly(dichlorophosphazene) in THF or 1,4-dioxane at room temperature (25 °C) or reflux temperature. Cyclotriphosphazenes were purified by recrystallization or flash column chromatography, and polyphosphazenes were purified by reprecipitation or dialysis prior to being subjected to quaternization.

Synthesis of Cyclic Trimer Models. *Synthesis of N-Methyl Hexa(phenoxy)cyclotriphosphazenium Trifluoromethanesulfonate (**6**).* To a solution of hexa(phenoxy)cyclotriphosphazene (**2**) (2.10 g, 3.03 mmol) in 20 mL of DCM was added methyl trifluoromethanesulfonate (0.686 mL, 6.06 mmol) at room temperature dropwise, and the mixture was stirred at room temperature for 24 h. All volatiles were evaporated under vacuum and the resulting oil solidified slowly under high vacuum to yield the trimer (**6**) as a reddish waxy solid (2.42 g, 2.82 mmol), which is sufficiently pure by ^{1}H and ^{31}P NMR spectra. Yield: 93%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 3.77 (t, $^{3}J_{PH}$ = 10.8 Hz, 3 H), 6.59−6.65 (m, 4 H), 6.95−7.03 (m, 8 H), 7.15−7.25 (m, 6 H), 7.28−7.47 (m, 12 H). ^{31}P NMR (145 MHz, $CDCl_3$): δ −3.60 (1 P), 1.12 (2 P), AB_2, $^{2}J_{PP}$ = 78.4 Hz. ESIMS: *m/z* 708.2 $[M - OTf]^+$.

*Attempted Quaternization of Hexa(phenoxy)cyclotriphosphazene (**2**) with Triethyloxonium Tetrafluoroborate.* To a solution of hexa(phenoxy)cyclotriphosphazene (**2**) (0.347 g, 0.500 mmol) in 5 mL of DCM was added triethyloxonium tetrafluoroborate (1 M in DCM, 1.00 mL, 1.00 mmol) at room temperature dropwise, and the mixture was stirred at room temperature for 2 days. ^{31}P NMR spectroscopy indicated that only 24% of trimer (**2**) had been quaternized. ^{31}P NMR (145 MHz, crude reaction mixture with D_2O capillary as external reference: δ −4.08 (1 P), 1.28 (2 P), AB_2, $^{2}J_{PP}$ = 77.1 Hz, 5.08 (broad, s, 76%). After quenching with saturated sodium bicarbonate solution, the broad singlet peak at 1.30 shifted back to 9.40, which could be assigned to trimer **2**.

*Synthesis of N-Methyl Hexa(n-butoxy)cyclotriphosphazenium Trifluoromethanesulfonate (**7**).* To a solution of hexa(*n*-butoxy)cyclotriphosphazene (**3**) (1.41 g, 2.46 mmol) in 25 mL of DCM was added a solution of methyl trifluoromethanesulfonate (0.334 mL, 2.95 mmol) in 10 mL of DCM dropwise at −78 °C. The mixture was allowed to warm to room temperature gradually over 1 h. The resulting mixture was diluted with 30 mL of DCM, washed with 10% sodium bicarbonate solution, dried over anhydrous sodium sulfate, and concentrated under vacuum. The residue was purified on a Sephadex LH-20 column using THF/DCM (1/1, v/v) as eluent to yield trimer (**7**) as a colorless liquid (1.57 g, 2.13 mmol). Yield: 87%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 0.90−1.00 (m, 18 H), 1.35−1.50 (m, 12 H), 1.65−1.83 (m, 12 H), 2.96 (t, $^{3}J_{PH}$ = 9.3 Hz, 3 H), 3.96−4.05 (m, 4 H), 4.10−4.23 (m, 8 H). ^{31}P NMR (145 MHz, $CDCl_3$): δ 6.03 (1 P), 9.38 (2 P), AB_2, $^{2}J_{PP}$ = 72.3 Hz. ESIMS: *m/z* 588.4 $[M - OTf]^+$.

*Synthesis of N-Methyl Hexakis(2-(2-methoxyethoxy)ethoxy)cyclotriphosphazenium Trifluoromethanesulfonate (**8**).* Hexakis(2-(2-methoxyethoxy)ethoxy)cyclotriphosphazene (**4**) (1.01 g, 1.18 mmol) was quaternized to yield trimer (**8**) as a colorless liquid (1.02 g, 1.01 mmol) by following a similar procedure to the one described for the synthesis of trimer (**7**). Yield: 86%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 3.00 (t, $^{3}J_{PH}$ = 9.3 Hz, 3 H), 3.36 (s, 18 H), 3.50−3.57 (m, 12 H), 3.61−3.68 (m, 12 H), 3.70−3.80 (m, 12 H), 4.18−4.25 (m, 4 H), 4.29−4.37 (m, 8 H). ^{31}P NMR (145 MHz, $CDCl_3$): δ 6.55 (1 P), 9.79 (2 P), AB_2, $^{2}J_{PP}$ = 75.5 Hz. ESIMS: *m/z* 864.4 $[M - OTf]^+$.

*Attempted Quaternization of Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (**5**).* To a solution of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (**5**) (0.365 g, 0.501 mmol) in 10 mL of DCM was added methyl trifluoromethanesulfonate (0.113 mL, 1.00 mmol) at room temperature dropwise and the mixture. After stirring for 48 h at room temperature, no quaternization could be observed based on the ^{31}P NMR spectra of the reaction mixture. The reaction mixture was then refluxed for 48 h. ^{31}P NMR spectroscopy indicated that only 26% of trimer (**5**) had been quaternized, and the presence of quaternized species (**9**) could be detected in ESIMS spectrum as well. ^{31}P NMR (145 MHz, crude reaction mixture with D_2O capillary as external reference): δ 5.24 (1 P), 9.02 (2 P), AB_2, $^{2}J_{PP}$ = 82.3 Hz, 17.24 (s, 74.5%). ESIMS: *m/z* 864.4 $[M - OTf]^+$.

*Treatment of N-Methyl Hexa(phenoxy)cyclotriphosphazenium Trifluoromethanesulfonate (**6**) with Sodium Iodide.* To a solution of *N*-methyl hexa(phenoxy)cyclotriphosphazene trifluoromethanesulfonate (**6**) (429 mg, 0.500 mmol) in 10 mL of DCM was added sodium iodide (150 mg, 1.00 mmol) and the mixture was stirred at room temperature for 48 h. Then the reaction mixture was diluted with 10 mL of DCM, washed with 5% aqueous sodium thiosulfate and brine successively, dried over anhydrous sodium sulfate, and concentrated under vacuum to yield trimer (**2**) as a yellowish solid (309 mg, 0.446

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mmol). The yield was 89%. The ^{1}H NMR and ^{31}P NMR spectra correspond well with unquaternized trimer (**2**).

*Synthesis of 1,3,3,5,5-Pentakis(n-butoxy)-1-oxo-2-methylcyclotriphosphazadiene (**10**).* To a solution of *N*-methyl hexa(*n*-butoxy)cyclotriphosphazene trifluoromethanesulfonate (**7**) (2.02 g, 2.74 mmol) in 25 mL of DCM was added sodium iodide (821 mg, 5.48 mmol) and the mixture was stirred at room temperature for 24 h. The reaction mixture was then diluted with 25 mL of DCM, washed with 5% aqueous sodium thiosulfate and brine successively, dried over anhydrous sodium sulfate, and concentrated under vacuum. The residue was purified on a Sephadex LH-20 column using methanol/DCM (1/1) as an eluent to yield compound (**10**) as a pale yellow liquid (1.16 g, 2.18 mmol). Yield: 80%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 0.85−1.00 (m, 15 H), 1.33−1.47 (m, 10 H), 1.58−1.75 (m, 10 H), 2.87 (dd, $^3J_{PH}$ = 9.9, 8.2 Hz, 3 H), 3.70−4.10 (m, 10 H). ^{31}P NMR (145 MHz, $CDCl_3$): δ 1.63 (dd, $^2J_{PP}$ = 58.0, 46.4 Hz, 1 P), 7.64 (dd, $^2J_{PP}$ = 75.4, 58.0 Hz, 1 P), 15.02 (dd, $^2J_{PP}$ = 75.4, 46.4 Hz, 1 P). ESIMS: *m*/*z* 532.2 $[M + H]^+$.

*Synthesis of 1,3,3,5,5-Pentakis(2-(2-methoxyethoxy)ethoxy)-1-oxo-2-methylcyclotriphosphazadiene (**11**).* *N*-Methyl hexakis(2-(2-methoxyethoxy)ethoxy)cyclotriphosphazene trifluoromethanesulfonate (**8**) (1.90 g, 1.88 mmol) was treated with sodium iodide to form compound **11** as a colorless liquid (1.20 g, 1.58 mmol) by following a similar procedure to the one described in the synthesis of compound **10**. Yield: 84%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 2.91 (dd, $^3J_{PH}$ = 9.8, 8.5 Hz, 3 H), 3.33−3.42 (m, 15 H), 3.49−3.58 (m, 10 H), 3.62−3.68 (m, 10 H), 3.68−3.76 (m, 10H), 3.95−4.22 (m, 10 H). ^{31}P NMR (145 MHz, $CDCl_3$): δ 1.44 (dd, $^2J_{PP}$ = 60.9, 47.9 Hz, 1 P), 8.22 (dd, $^2J_{PP}$ = 75.4, 60.9 Hz, 1 P), 15.15 (dd, $^2J_{PP}$ = 75.4, 47.9 Hz, 1 P). ESIMS: *m*/*z* 762.3 $[M + H]^+$.

*Treatment of Hexa(phenoxy)cyclotriphosphazene (**2**) with Iodomethane.* To a solution of hexa(phenoxy)cyclotriphosphazene (**2**) (0.347 g, 0.500 mmol) in 5 mL pf chlorobenzene was added iodomethane (0.311 mL, 5.00 mmol), and the mixture was stirred at 100 °C for 2 days. No quaternization was detected according to ^{31}P NMR spectroscopy.

*Treatment of Hexakis(2-(2-methoxyethoxy)ethoxy)-cyclotriphosphazene (**4**) with Iodomethane.* To a solution of hexakis(2-(2-methoxyethoxy)ethoxy)cyclotriphosphazene (**4**) (0.425 g, 0.500 mmol) in 8 mL of 1,2-dichloroethane was added iodomethane (0.156 mL, 2.50 mmol). No quaternization could be detected after stirring at 40 °C for 24 h. The mixture was then stirred at 60 °C for 24 h, and ^{31}P NMR indicated that 37% of trimer **5** had been converted to compound **11**, which was further confirmed by ESIMS. Quaternization at 100 °C in chlorobenzene for 24 h resulted in a complex mixture with ^{31}P NMR signals ranging from −5 to +20 ppm. The yield of compound **11** in the mixture was 54% based on the integration in the ^{31}P NMR spectrum.

Synthesis of Polymers. *Synthesis of {[NP(OPh)$_2$]$_{0.50}$[N$^+$(CH$_3$)(OTf)$^-$P(OPh)$_2$]$_{0.50}$}$_n$ (**17**).* To a suspension of poly(diphenoxyphosphazene) (**13**) (462 mg, 2.00 mmol) in 20 mL of DCM was added a solution of methyl trifluoromethanesulfonate (0.226 mL, 2.00 mmol) in 10 mL of DCM dropwise at 0 °C. The mixture was allowed to warm to room temperature gradually and was stirred for 3 days until it turned into a clear solution. The reaction mixture was then precipitated into hexanes. The precipitation was repeated twice from THF into hexanes to yield polymer **17** as a white, fibrous solid (469 mg, 1.50 mmol), which was soluble in THF and was slightly soluble in DCM and chloroform. Yield: 75%. ^{1}H NMR (360 MHz, $CDCl_3$/THF-d_8 1/1 v/v): δ 4.00 (broad, s, 1.5 H), 6.30−7.00 (m, 10 H). ^{31}P NMR (145 MHz, $CDCl_3$/THF-d_8 1/1 v/v): δ −18.0 to −16.5 (m, 11.7%), −15.55 (broad, s, 75.8%), −11.2 to −10.2 (m, 12.5%).

*Synthesis of {[NP(OBu-n)$_2$]$_{0.79}$[N$^+$(CH$_3$)(OTf)$^-$P(OBu-n)$_2$]$_{0.21}$}$_n$ (**18**).* To a solution of poly[di(*n*-butoxy)phosphazene] (**14**) (2.00 g, 10.5 mmol) in 80 mL of DCM was added a solution of methyl trifluoromethanesulfonate (1.19 mL, 10.5 mmol) in 10 mL of DCM dropwise at −78 °C. The mixture was allowed to warm to room temperature gradually and was stirred for 2 days. The mixture was dialyzed versus acetone/methanol (1/1, v/v) for 3 days (MWCO 6000−8000) to yield polymer (**18**) as a clear colorless gum (1.90 g, 8.42 mmol), which was soluble in acetone and THF and was slightly soluble in DCM and chloroform. Yield: 80%. ^{1}H NMR (360 MHz, acetone-d_6): δ 0.87−1.05 (m, 6 H), 1.48−1.55 (m, 4 H), 1.58−1.85 (m, 4 H), 3.13−3.31 (m, 0.63 H), 3.95−4.43 (m, 4 H). ^{31}P NMR (145 MHz, acetone-d_6): δ −5.8 to −3.0 (m, 60.4%), 3.0 to 5.0 (m, 39.6%).

*Synthesis of {[NP(OBu-n)$_2$]$_{0.87}$[N$^+$(CH$_3$)(OTf)$^-$P(OBu-n)$_2$]$_{0.13}$}$_n$ (**18a**).* Poly[di(*n*-butoxy)phosphazene] (**14**) (1.15 g, 6.01 mmol) was quaternized with 0.12 equiv of methyl trifluoromethanesulfonate (82 μL, 0.725 mmol) to yield polymer **18a** as a clear colorless gum (1.01 g, 4.75 mmol) by following a similar procedure to the one described for the synthesis of polymer **18**. Polymer **18a** was soluble in acetone, methanol, DCM, and chloroform. Yield: 79%. ^{1}H NMR (360 MHz, acetone-d_6): δ 0.87−1.05 (m, 6 H), 1.48−1.55 (m, 4 H), 1.58−1.85 (m, 4 H), 3.13−3.25 (m, 0.40 H), 3.95−4.43 (m, 4 H). ^{31}P NMR (145 MHz, acetone-d_6): δ −5.8 to −3.0 (m, 72.7%), 3.0−5.0 (m, 27.3%).

*Synthesis of {[NP(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_2$]$_{0.81}$[N$^+$(CH$_3$)(OTf)$^-$P(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_2$]$_{0.19}$}$_n$ (**19**).* Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (**15**) (2.40 g, 8.47 mmol) was quaternized to yield polymer **19** as a clear yellow gum (2.26 g, 7.19 mmol) by following a similar procedure to the one described for the synthesis of polymer **18**. Polymer **19** was soluble in acetone, methanol, DCM, and chloroform. Yield: 85%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 3.00−3.16 (m, 0.58 H), 3.34 (s, 6 H), 3.48−3.55 (m, 4 H), 3.58−3.79 (m, 8 H), 4.00−4.42 (m 4 H); ^{31}P NMR (145 MHz, $CDCl_3$) δ −8.2 to −6.0 (m, 65.6%), 0−2.5 (m, 34.4%).

*Synthesis of {[NP(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_2$]$_{0.88}$[N$^+$(CH$_3$)(OTf)$^-$P(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_2$]$_{0.12}$}$_n$ (**19a**).* Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (**15**) (1.28 g, 4.52 mmol) was quaternized to yield polymer **19a** as a clear yellow gum (1.10 g, 3.63 mmol) by following a procedure similar to the one described for the synthesis of polymer **18a**. Polymer **19a** was soluble in acetone, methanol, DCM and chloroform. Yield: 80%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 3.00−3.12 (m, 0.37 H), 3.35 (s, 6 H), 3.46−3.54 (m, 4 H), 3.56−3.73 (m, 8 H), 3.97−4.38 (m 4 H); ^{31}P NMR (145 MHz, $CDCl_3$) δ −8.2 to −6.0 (m, 80.5%), 0−2.5 (m, 19.5%).

*Treatment of {[NP(OPh)$_2$]$_{0.50}$[N$^+$(CH$_3$)(OTf)$^-$P(OPh)$_2$]$_{0.50}$}$_n$ (**17**) with Sodium Iodide.* To a solution of {[NP(OPh)$_2$]$_{0.50}$[N$^+$(CH$_3$)(OTf)$^-$P(OPh)$_2$]$_{0.50}$}$_n$ (**17**) (332 mg, 1.06 mmol) in 25 mL of THF was added sodium iodide (0.159 g, 1.05 mmol) at room temperature, and the mixture was stirred for 2 days, and was concentrated and precipitated from THF into water four times to yield polymer **13** as a white fibrous solid (198 mg, 0.856 mmol). The yield was 81%. The ^{1}H NMR and ^{31}P NMR spectra corresponded well to the unquaternized polymer **13**.

*Synthesis of {[NP(OBu-n)$_2$]$_{0.81}$[N(CH$_3$)P(O)(OBu-n)]$_{0.19}$}$_n$ (**20**).* To a solution of {[NP(OBu-*n*)$_2$]$_{0.81}$[N$^+$(CH$_3$)(OTf)$^-$P(OBu-*n*)$_2$]$_{0.19}$}$_n$ (**18**) (332 mg, 1.06 mmol) in 25 mL of acetone was added sodium iodide (0.159 g, 1.05 mmol) at room temperature and the mixture was stirred for 2 days. The mixture was concentrated and precipitated from acetone into water once and from THF into water twice to yield polymer **20** as a gray elastomer (380 mg, 1.93 mmol). It was soluble in THF and was slightly soluble in DCM, acetone and chloroform. Yield: 90%. ^{1}H NMR (360 MHz, THF-d_8/acetone-d_6 1/1): δ 0.96 (br, s, 5.45 H), 1.38−1.55 (m, 3.61 H), 1.58−1.85 (m, 3.58 H), 2.94−3.08 (m, 0.57 H), 3.80−4.38 (m, 3.63 H). ^{31}P NMR (145 MHz, THF-d_8/acetone-d_6 1/1) δ −6.0 to −3.0 (m, 60.2%), −3.0 to 0.5 (m, 17.2%), 6.5 to 9.0 (m, 22.6%).

*Synthesis of {[NP(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_2$]$_{0.81}$[N(CH$_3$)P(O)(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)]$_{0.19}$}$_n$ (**21**).* To a solution of {[NP(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_2$]$_{0.81}$[N$^+$(CH$_3$)(OTf)$^-$P(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_2$]$_{0.19}$}$_n$ (**19**) (640 mg, 2.04 mmol) in 25 mL of acetone was added sodium iodide (306 mg, 2.04 mmol) at room temperature and the mixture was stirred for 4 days. The mixture was dialyzed versus methanol for 3 days (MWCO 6000−8000) to yield polymer **21** as a clear yellow gum (500 mg, 1.88 mmol), which is soluble in acetone and THF, DCM and chloroform. Yield: 92%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 2.86−2.95 (m, 0.58 H), 3.34 (s, 5.65 H), 3.45−3.53 (m, 3.94 H), 3.55−3.74 (m, 7.48), 3.95−4.35 (m, 3.6 H).

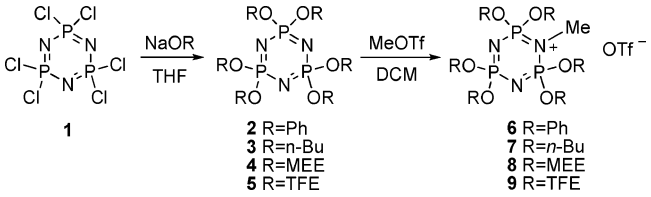
^{31}P NMR (145 MHz, $CDCl_3$) δ −7.0 to −5.0 (m, 66.9%), −4.0 to 2.5 (m, 16.4%), 4.5 to 6.2 (m, 16.7%).

*Treatment of Poly[bis(2-(2-methoxyethoxy)ethoxy)-phosphazene] (**15**) with Iodomethane.* To a solution of poly[bis-(2-(2-methoxyethoxy)ethoxy)phosphazene] (**15**) (567 g, 2.00 mmol) in 8 mL of 1,2-dichloroethane was added iodomethane (0.623 mL, 10.0 mmol) at room temperature. The mixture was stirred at 40 °C for 17 h and at 60 °C for 27 h. Then the solution was concentrated and dried under vacuum to yield a brown gum (608 mg), which is insoluble in common solvents.

RESULTS AND DISCUSSION

Quaternization of Cyclic Trimer Models. To our knowledge, the skeletal quaternization of organophosphazenes that bear P−O linked side groups has not been reported. Thus, phenoxy, *n*-butoxy, 2-(2-methoxyethoxy)ethoxy (MEEO) and 2,2,2-trifluoroethoxy (TFEO) were chosen as side groups to cover the spectrum of P−OR linked species. Reactions carried out on high polymeric phosphazenes are always more challenging than their small-molecule counterparts, especially for purification and characterization and, for this reason, small-molecule cyclic phosphazenes have played a major role as models for the development of polyphosphazene chemistry.[35] In this field, cyclotriphosphazenes (usually referred to as "trimers") are the most readily available models, and are favored for their ease of synthesis. Model reactions are shown in Scheme 1.

Scheme 1. Quaternization of Trimer Models



The syntheses of the small-molecule unquaternized trimers were carried out by the treatment of hexachlorocyclotriphosphazene **1** with an excess amount of the corresponding sodium aryloxide or alkoxides. The yields of all four trimers were over 80%. The susceptibility of the backbone nitrogen atoms in phosphazenes in the presence of alkylation reagents is controlled by their electron densities, which are ultimately determined by the substituents bonded to the neighboring phosphorus atoms. Basicity studies with small molecule cyclic phosphazenes show the ring nitrogen atoms to be the centers of greatest electron density in these molecules.[36] It is noteworthy that the basicity of a compound will not necessarily be in the same order as its nucleophilicity or electron density, because the nucleophilicity is influenced by other factors such as steric hindrance. However, the basicity of cyclotriphosphazenes with similar structures may serve as a preliminary indicator of nucleophilicity. The basicities of cyclotriphosphazenes with various substituents are reported to decrease in the order: $N_3P_3(NHR)_6$ or $N_3P_3(NR_2)_6$ (pK_a = 8.8−7.6) > $N_3P_3R_6$ (pK_a = 6.4−1.5) > $N_3P_3(OR)_6$ (pK_a = 1.4∼-5.8) > $N_3P_3Cl_6$ (pK_a < −6.0).[37−39] Fairly basic organoamino-substituted cyclooligophosphazenes are readily quaternized at the ring nitrogen atoms to form phosphazenium cations using simple alkyl halides or stronger alkylating reagents such as methyl trifluoromethanesulfonate or trimethyloxonium fluoroborate.[20−22,26] Because of the relatively lower electron densities at the ring nitrogen atoms, alkoxy or aryloxy-substituted phosphazenes are inert to iodomethane at room temperature,[26] or they undergo rearrangement of the alkoxyphosphazene to the *N*-alkyloxophosphazane at higher temperatures.[36] In this study, methyl trifluoromethanesulfonate and triethyloxonium tetrafluoroborate, two of the most aggressive alkylation reagents, were used for methyl or ethyl quaternization respectively. Dichloromethane (DCM) was chosen as the solvent because of its ability to solubilize all the trimers and its resistance to aggressive alkylation reagents. The reactions were monitored using ^{31}P NMR spectroscopy. Monoquaternization of trimer **2** was achieved at room temperature with methyl trifluoromethanesulfonate. Further quaternization did not occur even after prolonged reaction times in the presence of excess amounts of methyl trifluoromethanesulfonate. Triethyloxonium tetrafluoroborate was less reactive to trimer **2** than was methyl trifluoromethanesulfonate (see Experimental Section). Thus, only methyl trifluoromethanesulfonate was utilized for the remaining quaternization studies. For the quaternization of trimers **3** and **4**, methyl trifluoromethanesulfonate was added at −78 °C. Meanwhile, the reaction temperatures, reaction times, and the stoichiometries were carefully controlled to avoid the formation of byproduct. Only 26% of trimer **5** had been monoquaternized to form compound **9** after 48 h of refluxing. Prolonged reaction times or elevated temperatures led to the formation of a complex mixture of products. Quaternized trimer **6** could be heated at 60 °C under vacuum for drying for 1 day or stored at room temperature unsealed for a few months without detectable decomposition. Quaternized trimers **7** and **8** were found to be unstable at 60 °C while drying under vacuum. The reactivity of the trimers with different substituents corresponded well with the basicities of their skeletal nitrogen

Table 1. NMR Data for Small-Molecule Models

side group	trimer	^{31}P NMR	^{1}H NMR[a]
OPh	**2**	9.35 (s)	–
	6	−3.60 (1 P), 1.12 (2 P), AB_2, $^2J_{PP}$ = 78.4 Hz	3.77 (t, $^3J_{PH}$ = 10.8 Hz, 3 H)
	2[b]	9.34 (s)	–
OBn-*n*	**3**	18.90 (s)	–
	7	6.03 (1 P), 9.38 (2 P), AB_2, $^2J_{PP}$ = 72.3 Hz	2.96 (t, $^3J_{PH}$ = 10.8 Hz, 3 H)
	10	1.63 (dd, $^2J_{PP}$ = 58.0, 46.4 Hz, 1 P), 7.64 (dd, $^2J_{PP}$ = 75.4, 58.0 Hz, 1 P), 15.02 (dd, $^2J_{PP}$ = 75.4, 46.4 Hz, 1 P)	2.87 (dd, $^3J_{PH}$ = 9.9, 8.2 Hz, 3 H)
OMEE	**4**	19.05 (s)	–
	8	6.55 (1 P), 9.79 (2 P), AB_2, $^2J_{PP}$ = 75.5 Hz	3.00 (t, $^3J_{PH}$ = 10.8 Hz, 3 H)
	11	1.44 (dd, $^2J_{PP}$ = 60.9, 47.9 Hz, 1 P), 8.22 (dd, $^2J_{PP}$ = 75.4, 60.9 Hz, 1 P), 15.15 (dd, $^2J_{PP}$ = 75.4, 47.9 Hz, 1 P)	2.91 (dd, $^3J_{PH}$ = 9.8, 8.5 Hz, 3 H)

[a]Only the methyl groups attached to backbones are shown here. [b]Trimer **2** recovered from treatment of compound **17** with sodium iodide.

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atoms. The pK_a values of trimers **2**, **3**, **4**, and **5** are −5.8, 0.1, ∼−1 (estimated), and −6.0 respectively. The higher stability of trimer **6** than those of trimers **7** and **8** might result from a shielding effect by bulky phenoxy groups to stabilize the quaternization site, and from the resistance of the sp^2 carbons to migration and rearrangement reactions.

Because of the lack of hydrogen bonding sites and the asymmetric geometries of the quaternized trimers, quaternized trimer **6** is an amorphous solid at room temperature, whereas **7** and **8** are liquids. Thus, no X-ray crystallography data were available. The NMR spectra of unquaternized and quaternized trimers are shown in Table 1. Triplet signals at 3.77, 2.96, and 3.00 in ^{1}H NMR spectra clearly indicate the methyl groups attached to backbone nitrogen atoms in quaternized trimers **6**, **7**, and **8**. The two adjacent phosphorus atoms split the methyl groups with formally identical coupling constants ($^3J_{PH}$). The

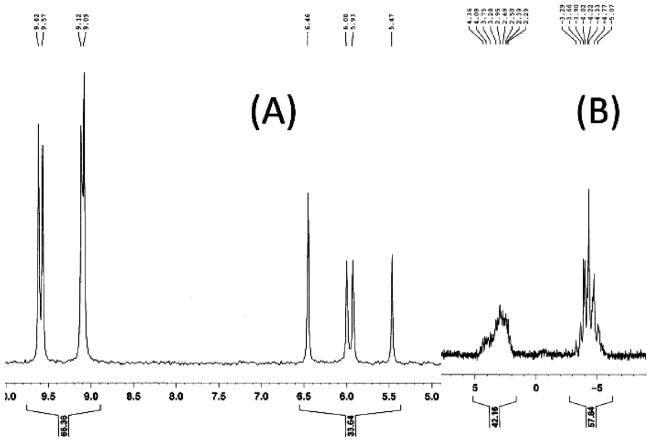
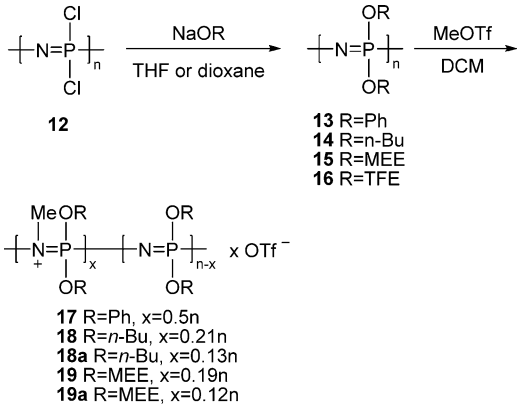


Figure 1. ^{31}P NMR spectra of quaternized phosphazenes: (A) trimer **7** and (B) polymer **18**.

^{31}P NMR spectrum of trimer **7** is shown in Figure 1A. ^{31}P NMR signals of quaternized trimers are shifted upfield compared to the singlet signals of the parent phosphazenes. Software simulation indicated that the spin systems are AB_2, similar to the reported quaternized amino-substituted trimers.[20] However, the extra splittings might be the result of the large coupling constants. Mass spectra also provide evidence for the formation of phosphazenium cations. (See Experimental Section)

Quaternization of Polymers. Following similar synthesis procedures to those employed for the small molecule models, the quaternization of polymers **13**−**16** were carried out as shown in Scheme 2. Unquaternized polymers were synthesized by replacement of the chlorine atoms in poly(dichlorophosphazene) using sodium salts of the corresponding aryloxide or alkoxide. Quaternization of the backbone nitrogen atoms of polymers **13**−**16** was attempted using methyl trifluoromethanesulfonate in dichloromethane (DCM) solutions. In all cases except for polymer **16**, the quaternization of the polymers followed the same pattern as for the small-molecule models. Quaternization of polymer **16** was unsuccessful because of its poor solubility in DCM and in other solvents which are inert to methyl trifluoromethanesulfonate and the low electron density on the backbone nitrogen atoms. The physical data for polymers **17**−**19** are shown in Table 2. Little structural information could be obtained from

Scheme 2. Quaternization of Polymers



the ^{31}P NMR data due to the inherent structural complexity of the polymers compared to those of their small-molecule models as well as the random distribution of quaternization sites along the backbone. The ^{31}P NMR spectrum of polymer **18**, as a representative, is shown in Figure 1B. Broadened peaks with ambiguous coupling in ^{1}H NMR spectra were also detected, which is also quite common for polyphosphazenes and some other polymers. These phenomena further emphasized the key role of model reactions in this chemistry. With the presence of 1 equiv of quaternization reagent per repeating unit, the percentages of quaternized backbone nitrogen atoms in polymers **17**, **18**, and **19** were 50%, 21%, and 19% respectively, with 1−2% variation from batch to batch. The surprisingly high degree of quaternization for polymer **17** can be attributed to the shielding effect of bulky phenoxy substituents as observed in the quaternization of trimer **2**. Lower degrees of quaternization were achieved by controlling the stoichiometry of the quaternization reagent. Thermogravimetric analysis (TGA) showed that the thermal stability of quaternized polymers is lower than their unquaternized counterparts, but they are considerably more stable than the small-molecule models.

Molecular weight data for quaternized polymers **17**−**19** could not be obtained by gel permeation chromatography (GPC) although they are completely soluble in THF, the mobile phase used. This is a common problem for polyelectrolytes in the absence of additional salting.[40] Because of the large quantity of alkali trifluoromethanesulfonate required to saturate the mobile phase and the solubility and possible instability of these polymers in aqueous media, we did not attempt to measure the molecular weights with the use of additional salting.

Elimination Reactions of Quaternized Phosphazenes. In order to expand the possible uses of these new materials, further attempts were conducted with the quaternized polyphosphazenes to exchange the anions from the stable trifluoromethanesulfonate ion to other anions. A motivation for this aspect was the need for an I^-/I_3^- redox couple for use in DSSC electrolytes.

Ion exchange was first studied by dialyzing polymer **19** versus 2% sodium iodide solution in methanol. The resultant polymer showed a much lower ionic conductivity. This prompted a study of the chemistry that occurs during the anion exchange. All the quaternized phophazenes were subjected to treatment with excess sodium iodide in DCM, THF, or acetone at room temperature, as shown in Scheme 3. All were found to be

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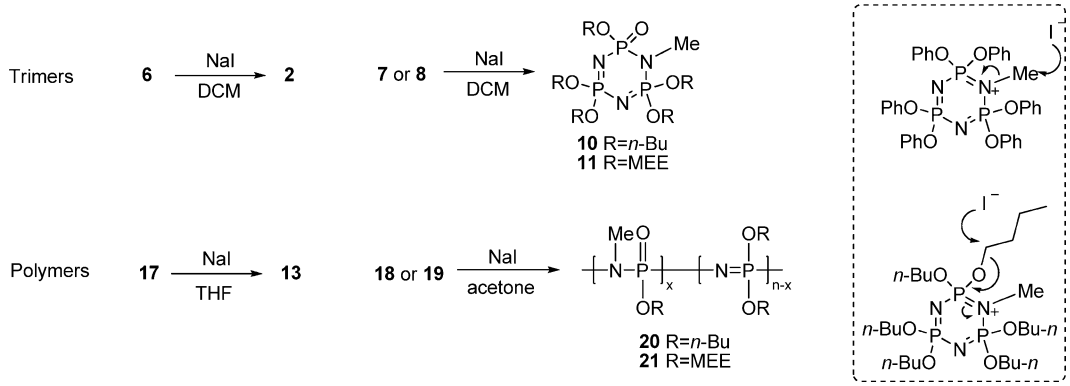
Table 2. Structural and Physical Properties for Polymers

side group	polymer	^{31}P NMR	^{1}H NMR[a]	M_w (×10^3)	T_{onset} (°C)	T_g (°C)
OPh	**13**	−18.75 (s)	–	1596.2	426.6	−4.5
	17	−18.0 to −16.5 (m, 11.7%), −15.55 (br, s, 75.8%), −11.2 to −10.2 (m, 12.5%)	4.00 (br, s)	–	351.6	10.3
	13[b]	−18.81 (s)	–	345.5	372.8	−1.7
OBu-*n*	**14**	−7.32 (s)	–	2242.3	260.0	−108.7
	18	−5.8 to −3.0 (m, 57.8%), 3.0 to 5.0 (m, 42.2%)	3.13−3.32 (m)	–	157.1	−81.8
	18a	−6.0 to −3.5 (m, 72.7%), 2.2 to 4.5 (m, 27.3%)	3.13−3.24 (m)	–	192.7	−93.2
	20	−8.5 to −5.5 (m, 59.1%), −4.7 to −3.0 (m, 17.7%), 3.8 to 6.2 (m, 23.3%)	2.85−3.01	659.2	176.1	−87.7
OMEE	**15**	−7.74 (s)	–	778.0	268.7	−79.2
	19	−8.2 to −6.0 (m, 65.6%), 0 to 2.5 (m, 34.4%)	3.00−3.16 (m)	–	173.9	−70.6
	19a	−7.2 to −6.8 (m, 80.5%), 0 to 2.5 (m, 19.5%)	3.00−3.16 (m)	–	211.1	−74.2
	21	−8.5 to −5.0 (m, 66.9%), −4.0 to −2.5 (m, 16.4%), 4.3 to 6.2 (m, 23.3%)	2.85−2.95 (m)	211.0	242.5	−73.9

[a]Only the methyl groups attached to backbones are shown here. [b]Polymer **13** recovered from treatment of polymer **17** with sodium iodide.

Scheme 3. Treatment of Quaternized Phosphazenes with Sodium Iodide



susceptible to the strong nucleophilicity of iodide ion. Depending on the structures of the side groups, dealkylation of the quaternary nitrogen atoms or of the side-chain alkyl groups was detected. The progress of the elimination reactions was monitored with ^{31}P NMR spectra. For the phenoxy substituted quaternized trimer **6** or polymer **17** iodide ion attacks the methyl groups attached to the skeletal nitrogen atoms to regenerate unquaternized trimer **2** or polymer **13.** This is due to the inertness of sp^2 carbon atoms to nucleophiles. For alkoxy substituted quaternized species **7**, **8**, **18**, and **19**, iodide ion attacks the α-carbon atoms of the side groups to form oxophosphazanes **10**, **11**, **20**, and **21**, by following the mechanism proposed in Scheme 3. (see Table 1 and Table 2 for structural and physical properties and Figure 2 for ^{31}P NMR spectra) The molecular weights of the resultant polymers **13** (product by elimination), **20** and **21** were lower than the corresponding unquaternized parent polymers **13**, **14**, and **15**. This suggests that scission of the polymer backbone occurred during either the quaternization or the elimination reactions. To further investigate the mechanism of the rearrangements, unquaternized phosphazenes were treated with iodomethane. Trimer **2** was stable in the presence of 10 equiv of iodomethane at 100 °C for 2 days. In the presence of iodomethane, trimer **4** underwent rearrangement to form oxophosphazane **11** in 37% yield after being stirred at 60 °C for 24 h. Polymer **15** became an insoluble elastomer after treatment with iodomethane at 60 °C, probably due to cross-linking induced by the elevated temperature.

Ionic Conductivity and Thermal Analysis. The ionic conductivities of quaternized trimers **6**, **7**, and **8** are 3.36 × 10^{-5} S·cm^{-1}, 9.46 × 10^{-4} S·cm^{-1} and 6.21 × 10^{-4} S·cm^{-1} at 25 °C,

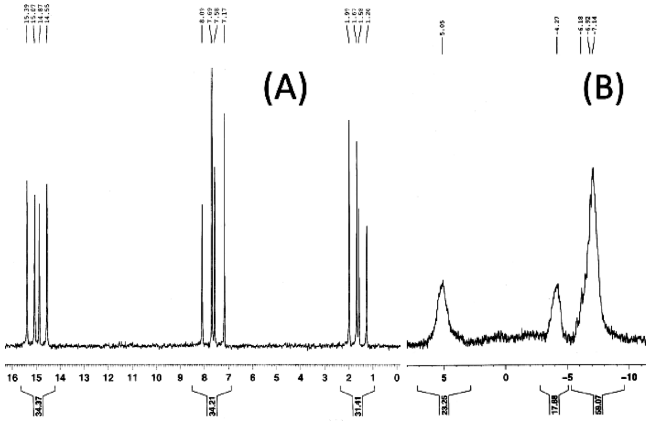


Figure 2. ^{31}P NMR spectra of dealkylization products: (A) trimer **10** and (B) polymer **20**.

values that are lower than imidazolium based ionic liquids with trifluoromethanesulfonate counterion, which usually show conductivities above 10^{-3} S·cm^{-1}.[41] This can be explained by the large sizes of the cations and the high viscosity. Polymer **17** has a low ionic conductivity of 2.53 × 10^{-9} S·cm^{-1}, due to its high T_g. No further research was carried out on these compounds.

The ionic conductivities of solvent-free quaternized polyalkoxyphosphazenes and their salt complexes with lithium trifluoromethanesulfonate and silver trifluoromethanesulfonate are shown in Table 3. For the pure quaternized polymers, a similar trend in conductivity with increasing degree of quaternization was found for all the polymers with same side

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Table 3. Conductivities and T_g's of Quaternized Polyphosphazenes

entry	polymer	salt (mol %)	OTf⁻/ru[a]	conductivity (S·cm^{-1})	T_g (°C)
1	**18a**	–	0.13	1.72×10^{-4}	−93.2
2		LiOTf (8%)	0.21	7.45×10^{-5}	−90.7
3		AgOTf (8%)	0.21	9.88×10^{-5}	−75.8
4	**18**	–	0.21	2.14×10^{-4}	−81.8
5		LiOTf (5%)	0.26	8.21×10^{-5}	−77.4
6		LiOTf (10%)	0.31	4.44×10^{-5}	−74.8
7		AgOTf (5%)	0.26	9.59×10^{-5}	−71.0
8		AgOTf (10%)	0.31	5.34×10^{-5}	−67.0
9	**19a**	–	0.12	1.55×10^{-4}	−74.2
10		LiOTf (7%)	0.19	1.23×10^{-4}	−69.9
11		AgOTf (7%)	0.19	2.09×10^{-4}	−70.7
12	**19**	-	0.19	2.58×10^{-4}	−70.8
13		LiOTf (5%)	0.24	1.92×10^{-4}	−67.6
14		LiOTf (10%)	0.29	1.28×10^{-4}	−63.1
15		AgOTf (5%)	0.24	2.04×10^{-4}	−66.9
16		AgOTf (10%)	0.29	1.49×10^{-4}	−61.9

[a]Repeating unit.

group. Even if only the anions are mobile, the conductivities of solvent-free quaternized polymers **18** (entry 4) and **19** (entry 12) are higher than that of a MEEP/silver trifluoromethanesulfonate complex (1.68×10^{-4} S·cm^{-1}, 12 mol %), or a MEEP/lithium trifluoromethanesulfonate complex (2.8×10^{-5} S·cm^{-1}, 17 mol %) at similar temperature.[42] The temperature dependent conductivities of polymers **18** and **19** are illustrated in Figure 3. The highest conductivities of polymer **19** of 2.58×10^{-4} S·cm^{-1} at 25 °C and 2.09×10^{-3} S·cm^{-1} at 80 °C were achieved, which are among the highest conductivities of unplasticized solid-state polymer electrolytes or polyelectrolytes. To further compare the effect of backbone-quaternization versus simple salt-complexing on conductivity, polyelectrolyte/salt complexes were formulated by drying an acetone solution of a polyelectrolyte and a salt under vacuum. Additional salt applied to polymers **18** or **19** resulted in decreased ionic conductivities (entry 5−8 and entry 13−16). Polyelectrolyte/salt complexes formulated with polymer **18a** and **19a** had lower ionic conductivities, compared to pure polymers **18** and **19** which have same ion concentrations, and even compared to polymers **18a** and **19a** which have lower ion concentrations. (entry 2−4 and entry 10−12).

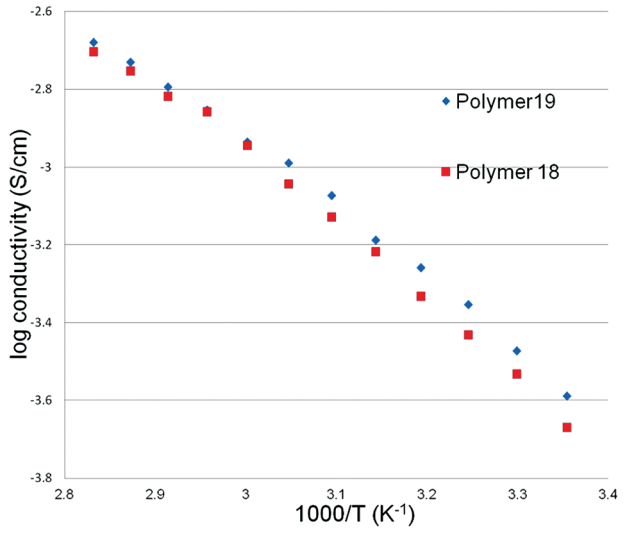

Figure 3. Arrhenius plots for the conductivity of solvent/salt-free polymers **18** and **19**.

T_g's for polyelectroytes and polyelectrolyte/salt complexes were measured by differential scanning calorimetry (DSC). All the salt/polyelectrolyte complexes underwent increases in T_g. (See Table 3.) Metal ions coordinate to the polymers to form ionic cross-links. These cross-links hinder the motion of the polymer side chains, and this is reflected in the T_g's. The elevated T_g's conform to the trend of lower conductivity of polyelectrolyte/salt complexes.

The higher conductivity and lower T_g of backbone quaternized polyelectrolytes compared to conventional polymer electrolytes can be attributed to the following factors. First, the shielding effect by side chains linked to the backbone immobilizes cations and hinders ion pairing, whereas cations and anions are more likely to pair with each other in conventional polymer electrolytes. Second, Coulombic repulsion between side-chain shielded cations is weaker compared to that in polymer electrolytes, which could help to maintain high segmental flexibility. Furthermore, ionic cross-linking is avoided or minimized in backbone quaternized polymers as there are no metal ions in the backbone quaternized species.

SUMMARY

The quaternization of poly(alkoxyphosphazenes) and poly[(bisphenoxy)phosphazene] has been accomplished. Because of the lower electron donating ability of alkoxy and aryloxy side groups than in the case of alkylamino side groups, efficient quaternization could only be achieved with methyl trifluomethanesulfonate as the reagent. This is the first report of backbone functionalization of phosphazenes that bear P−O linked side groups at both the small molecule and high polymer levels. However, the quaternized poly(alkoxyphosphazenes) are sensitive to dealkylation in the presence of nucleophilic iodide anions.

These new backbone quaternized poly(alkoxyphosphazenes) have high ionic conductivity without plasticizers or additional salts. This offers the potential for insight into the mechanism of ion transport and for the applications of polymers in solid-state electrochemical devices. The new concept of immobilizing ions onto or near to a polymer backbone may have several advantages over conventional polymer/salt complexes or side chain functionalized polyelectrolytes. The corresponding quaternization of poly(alkylaminophosphazenes) to improve the stability of polyelectrolytes is currently ongoing.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hra@chem.psu.edu.

Notes

The authors declare no competing financial interest.

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