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

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**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(aryloxyphosphazenes) showed ionic conductivities of $2.58 \times 10^{-1}$ S·cm$^{-1}$ at $25^\circ$C and $2.09 \times 10^{-3}$ S·cm$^{-1}$ at $80^\circ$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.,
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.  

Dye-sensitized solar cells (DSSCs) have been under intensive investigation as a low cost alternative to silicon solar cells. The most important factor affecting the practicality of DSSCs is the electrolyte, which usually consists of an $I^+ /I^-$ 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.

Polypophosphazenes 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. 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 $P=\text{N}$ 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. 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.

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. Organo- and organoamino-substituted cyclooligophosphazenes have been quaternized at the backbone nitrogen atoms to form phosphazeniun cations, but the quaternization of organoaminophosphazene high polymer has not been studied extensively.

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.
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. 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), cholestene (Aldrich), sodium thiosulfate pentahydrate (Aldrich), sodium bicarbonate (EMD), triethyloxonium tetrafluoroborate (EMD), sodium hydride (60% dispersion in oil, Aldrich), xylene (Aldrich), trichloroethylene (Aldrich), hexane (EMD), and polyethylene glycol (Aldrich) were all used as received.

### Attempted Quaternization of Hexa(phenoxy)cyclotriphosphazene (2) with Triethylammonium Tetrafluoroborate.
To a solution of hexa(phenoxy)cyclotriphosphazene (2) (0.347 g, 0.500 mmol) in 5 mL of DCM was added triethylammonium tetrafluoroborate (1 M in DCM) over 2 days. 31P NMR spectroscopy indicated that only 24% of trimer (2) had been quaternized. 1H NMR (145 MHz, crude reaction mixture with D2O capillary as external reference): δ = 4.08 (1 P), 1.28 (2 P), AB2, δ2pp = 77.1 Hz, 5.08 (broad, s, 76%). After quenching with saturated sodium bicarbonate solution, the singlet peak at 1.30 shifted back to 9.40, which could be assigned to trimer 2.

### Attempted Quaternization of Hexa(2-(2-methoxyethoxy)ethoxy)cyclotriphosphazene (4) as a colorless liquid (1.41 g, 2.46 mmol) in 25 mL of DCM was added tetrafluoroborate (1 M solution in DCM, 1.00 mL, 1.00 mmol) at room temperature dropwise, and the mixture was stirred at room temperature for 2 days. 31P NMR spectroscopy indicated that only 24% of trimer (2) had been quaternized.

### SyntheticAttempted Quaternization of Hexa(2,2,2-trifluoroethoxy)ethoxy)cyclotriphosphazene (5).
To a solution of hexa(phenoxy)cyclotriphosphazene (2) (1.01 g, 1.18 mmol) in 10 mL of DCM, which is sufficiently pure by 1H and 31P NMR spectra, was quaternized to yield trimer (8) as a colorless liquid (1.02 g, 1.10 mmol) by following a similar procedure to the one described for the synthesis of trimer (7). Yield: 86%.

### Treatment of N-Methyl Hexakis(2-(2-methoxyethoxy)ethoxy)cyclotriphosphazene (4).
To a solution of hexakis(2-(2-methoxyethoxy)ethoxy)cyclotriphosphazene (4) (0.365 g, 0.501 mmol) in 10 mL of DCM was added methyl trifluoromethanesulfonylate (0.113 mmol, 1.00 mL) at room temperature dropwise and the mixture. After stirring for 48 h at room temperature, no quaternization could be observed based on the 31P NMR spectra of the reaction mixture. The reaction mixture was then refluxed for 48 h. 31P 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.

### Treatment of N-Methyl Hexa(2,2,2-trifluoroethoxy)ethoxy)cyclotriphosphazene (5) 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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Synthesis of 1,3,3,5,5-Pentakis(n-butoxy)1-o xo-2-methylcyclotriphosphazene (10). To a solution of N-methyl hexa(n-butoxy)-cyclotriphosphazene triluoromethanesulfonate (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%. 1H NMR (360 MHz, CDCl3): δ 8.58−1.00 (m, 15 H), 1.33−1.47 (m, 10 H), 1.58−1.75 (m, 10 H), 2.87 (dd, J_1/F2 = 9.8, 8.5 Hz, 3 H), 3.70−4.10 (m, 10 H). 31P NMR (145 MHz, CDCl3): δ 1.63 (dd, J_2/F3 = 58.0, 46.4 Hz, 1 P), 7.64 (dd, J_2/F3 = 75.4, 58.0 Hz, 1 P). 13C NMR (100 MHz, CDCl3): δ 35.08−38.68 (m, 10 H), J_1/F2 = 9.8−14.2 (m, 10 H). Polymerization of (10) with Sodium Iodide. To a solution of (10) (462 mg, 2.00 mmol) in 20 mL of DCM was added a solution of methyl trifluoromethanesulfonate (0.311 mL, 5.00 mmol), and the mixture was stirred at room temperature and the mixture was stirred for 2 days. 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%. 1H NMR (360 MHz, acetone-d_6); δ 0.87−1.05 (m, 6 H), 1.48−1.55 (m, 4 H), 1.58−1.65 (m, 4 H), 3.13−3.31 (m, 6.03 H), 3.95−4.43 (m, 4 H). 31P 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)_{0.87}[N+(CH3)(OTf)]_{0.13}][P(OCH3CH2CH2CH2CH2)_{0.13}][OTF] (19a). A solution of (19a) (640 mg, 2.04 mmol) in 25 mL of DCM was added a solution of methyl trifluoromethanesulfonate (82 μL, 0.725 mmol) to yield polymer 18a as a clear colorless gum (2.10 g, 7.19 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: 85%. 1H NMR (360 MHz, CDCl3): δ 3.00−3.16 (m, 0.58 H), 3.34−3.55 (m, 4 H), 3.48−4.55 (m, 4 H), 4.00−4.42 (m, 4 H). 31P NMR (145 MHz, CDCl3); δ −8.2 to −6.0 (m, 65.6%), 0.2−2.5 (m, 34.4%). Synthesis of [NP(OBu-n)_{0.87}[N+(CH3)(OTf)]_{0.13}][P(OCH3CH2CH2CH2CH2)_{0.13}][OTF] (19a). A solution of (19a) (2.40 g, 8.47 mmol) was quaternized to yield polymer 19a as a clear yellow gum (1.10 g, 3.63 mmol) by following a similar procedure to the one described for the synthesis of polymer 18a. Polymer 19a was soluble in acetone, methanol, DCM, and chloroform. Yield: 86%. 1H NMR (360 MHz, CDCl3); δ 3.00−3.12 (m, 0.37 H), 3.35−3.55 (m, 4 H), 3.48−4.54 (m, 4 H), 4.00−4.42 (m, 4 H). 31P NMR (145 MHz, CDCl3); δ −8.2 to −6.0 (m, 80.5%), 0.2−2.5 (m, 19.5%). Synthesis of [NP(OPh)_{0.50}[N+(CH3)(OTf)]_{0.19}][P(OBu-n)_{0.19}][OCH2CH2CH2CH2CH3]_{0.87} (18). A solution of (18) (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 1H NMR and 31P NMR spectra corresponded well to the unquaternized polymer 13. Synthesis of [NP(OBu-n)_{0.50}[N(CH3)P(O)(OBu-n)]_{0.19}][P(OBu-n)_{0.19}][OCH2CH2CH2CH2CH3]_{0.81} (17). To a solution of (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. 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%. 1H NMR (360 MHz, THF-d_4, 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). 31P NMR (145 MHz, THF-d_4, 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%).
**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 (MEO) 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 arlyloxide 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 $N_3P_3(NR_2)_6$ ($pK_a = 8.8–7.6$) > $N_3P_3(OR)_6$ ($pK_a = 6.4–1.5$) > $N_3P_3(OR)$ ($pK_a = 1.4–5.8$) > $N_3P_3Cl_6$ ($pK_a < -6.0$).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 trimethylxonium tetrafluoroborate.20–22,26 Because of the relatively lower electron densities at the ring nitrogen atoms, alkoxo or arlyloxy-substituted phosphazenes are inert to iodomethane at room temperature,26 or they undergo rearrangement of the alkoxyphosphazene to the N-alkyloxophosphazene at higher temperatures.36 In this study, methyl trifluoromethanesulfonate and trimethylxonium 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. Triethylxonium 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>
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<th>side group</th>
<th>trimer</th>
<th>$^{31}P$ NMR</th>
<th>$^1H$ NMR$^a$</th>
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<tr>
<td>OPh</td>
<td>2</td>
<td>9.35 (s)</td>
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<tr>
<td></td>
<td>6</td>
<td>−3.60 (1 P), 1.12 (2 P), $J_{PP} = 78.4$ Hz</td>
<td>3.77 (t, $J_{PH} = 10.8$ Hz, 3 H)</td>
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<tr>
<td></td>
<td>2$^a$</td>
<td>9.34 (s)</td>
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<tr>
<td>OBu-n</td>
<td>3</td>
<td>18.90 (s)</td>
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<tr>
<td></td>
<td>7</td>
<td>6.03 (1 P), 9.38 (2 P), $J_{PP} = 72.3$ Hz</td>
<td>2.96 (t, $J_{PH} = 10.8$ Hz, 3 H)</td>
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<tr>
<td></td>
<td>10</td>
<td>1.63 (dd, $J_{PP} = 58.0$, 46.4 Hz, 1 P), 7.64 (dd, $J_{PP} = 75.4$, 58.0 Hz, 1 H), 15.02 (dd, $J_{PP} = 75.4$, 46.4 Hz, 1 P)</td>
<td>2.87 (dd, $J_{PH} = 9.9$, 8.2 Hz, 3 H)</td>
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<td>OME</td>
<td>4</td>
<td>19.05 (s)</td>
<td></td>
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<tr>
<td></td>
<td>8</td>
<td>6.55 (1 P), 9.79 (2 P), $J_{PP} = 75.5$ Hz</td>
<td>3.00 (t, $J_{PH} = 10.8$ Hz, 3 H)</td>
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<td>11</td>
<td>1.44 (dd, $J_{PP} = 60.9$, 47.9 Hz, 1 P), 8.22 (dd, $J_{PP} = 75.4$, 60.9 Hz, 1 P), 15.15 (dd, $J_{PP} = 75.4$, 47.9 Hz, 1 P)</td>
<td>2.91 (dd, $J_{PH} = 9.8$, 8.5 Hz, 3 H)</td>
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$^a$Only the methyl groups attached to backbones are shown here. $^b$Trimer 2 recovered from treatment of compound 17 with sodium iodide.
atoms. The pKₐ values of trimers 2, 3, 4, and 5 are −5.8, 0.1, −1, and −6.0 respectively. The higher stability of trimer 6 than that 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 sp² 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 ¹H 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 (JPH). The ³¹P NMR spectrum of trimer 7 is shown in Figure 1A. ³¹P 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 AB₂, similar to the reported quaternized amino-substituted trimers. The NMR signals of quaternized trimers are shifted upfield asymmetric geometries of the quaternized trimers, quaternized and the resistance of the sp² carbons to migration and rearrangement reactions.

However, the extra splittings might be the result of the large coupling constants. Mass spectra also provide evidence for the formation of phosphazenido 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 aryl 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 the ³¹P 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 ³¹P NMR spectrum of polymer 18, as a representative, is shown in Figure 1B. Broadened peaks with ambiguous coupling in ¹H 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. 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⁻ 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 phosphazenes 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...
nucleophiles. For alkoxy substituted quaternized species iodomethane, trimer equiv of iodomethane at 100 °C underwent rearrangement to form oxophosphazanes. To further investigate the mechanism of the reactions, unquaternized phosphazenes were treated with sodium iodide. This is due to the inertness of sp² carbon atoms to regenerate unquaternized trimer or polymer.

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

Figure 2. ³¹P NMR spectra of dealkylization products: (A) trimer and (B) polymer.

Table 2. Structural and Physical Properties for Polymers

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<tr>
<th>side group</th>
<th>polymer</th>
<th>³¹P NMR</th>
<th>³¹H NMRa</th>
<th>Mw (x10⁵)</th>
<th>T onset (°C)</th>
<th>Tg (°C)</th>
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<tbody>
<tr>
<td>OPh</td>
<td>13</td>
<td>−18.75</td>
<td>211.0 242.5</td>
<td>1596.2</td>
<td>426.6</td>
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<tr>
<td>OBu-n</td>
<td>14</td>
<td>7.32</td>
<td>345.5 372.8</td>
<td>351.6</td>
<td>−18.1</td>
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<tr>
<td>17</td>
<td>18</td>
<td>5.30 to 3.0 (m, 57.8%), 3.0 to 3.5 (m, 42.2%)</td>
<td>3.13−3.32 (m)</td>
<td>157.1</td>
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<tr>
<td>18a</td>
<td>20</td>
<td>8.5 to 5.5 (m, 59.1%), 4.7 to 3.0 (m, 17.7%), 3.8 to 6.2 (m, 23.3%)</td>
<td>2.85−3.01</td>
<td>176.1</td>
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<tr>
<td>OMEE</td>
<td>15</td>
<td>5.74</td>
<td>778.0 268.7</td>
<td>268.7</td>
<td>−79.2</td>
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<tr>
<td>19</td>
<td>19a</td>
<td>8.2 to 6.0 (m, 65.6%), 0 to 2.5 (m, 34.4%)</td>
<td>3.00−3.16 (m)</td>
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<td>20</td>
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<td>8.5 to 5.0 (m, 66.9%), 4.0 to 2.5 (m, 16.4%), 4.3 to 6.2 (m, 23.3%)</td>
<td>2.85−2.95 (m)</td>
<td>242.5</td>
<td>−73.9</td>
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</table>

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 ³¹P 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 sp² 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 ³¹P 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 solvent-free quaternized trimer 6, 7, and 8 are 3.36 × 10⁻³ S·cm⁻¹, 9.46 × 10⁻³ S·cm⁻¹ and 6.21 × 10⁻⁴ S·cm⁻¹ at 25 °C, values that are lower than imidazolium based ionic liquids with trifluoromethanesulfonate counterion, which usually show conductivities above 10⁻³ S·cm⁻¹. 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 × 10⁻³ S·cm⁻¹, due to its high Tg. No further research was carried out on these compounds.

The ionic conductivities of solvent-free quaternized poly-alkoxyphosphazenes 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 groups.
dependent conductivities of polymers in Figure 3. The highest conductivities of polymer lithium trifluoromethanesulfonate complex (2.8 applied to polymers of a polyelectrolyte and a salt under vacuum. Additional salt lytes. To further compare the effect of backbone-quaternization unplasticized solid-state polymer electrolytes or polyelectro-

<table>
<thead>
<tr>
<th>entry</th>
<th>polymer</th>
<th>salt (mol %)</th>
<th>OTF/ m²</th>
<th>conductivity (S·cm⁻¹)</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18a</td>
<td>–</td>
<td>0.13</td>
<td>1.72 × 10⁻⁴</td>
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<tr>
<td>2</td>
<td>–</td>
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<td>7.45 × 10⁻⁴</td>
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<td>3</td>
<td>–</td>
<td>AgOTf (8%)</td>
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<td>9.88 × 10⁻⁴</td>
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</tr>
<tr>
<td>4</td>
<td>18</td>
<td>–</td>
<td>0.21</td>
<td>2.14 × 10⁻⁴</td>
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</tr>
<tr>
<td>5</td>
<td>–</td>
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<tr>
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<td>–</td>
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<tr>
<td>7</td>
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<td>0.26</td>
<td>9.59 × 10⁻⁴</td>
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</tr>
<tr>
<td>8</td>
<td>–</td>
<td>AgOTf (10%)</td>
<td>0.31</td>
<td>5.34 × 10⁻⁴</td>
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</tr>
<tr>
<td>9</td>
<td>19a</td>
<td>–</td>
<td>0.12</td>
<td>1.55 × 10⁻⁴</td>
<td>−74.2</td>
</tr>
<tr>
<td>10</td>
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<td>LiOTf (7%)</td>
<td>0.19</td>
<td>1.23 × 10⁻⁴</td>
<td>−69.9</td>
</tr>
<tr>
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<td>0.19</td>
<td>2.09 × 10⁻⁴</td>
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</tr>
<tr>
<td>12</td>
<td>19</td>
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<td>2.58 × 10⁻⁴</td>
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<tr>
<td>13</td>
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<td>1.92 × 10⁻⁴</td>
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<tr>
<td>14</td>
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<td>15</td>
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<tr>
<td>16</td>
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<td>0.29</td>
<td>1.49 × 10⁻⁴</td>
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</tr>
</tbody>
</table>

*Repeating unit.

The quaternization of poly(alkoxyphosphazenes) and poly-

The higher conductivity and lower T_g of backbone quaternized polyelectrolytes compared to conventional poly-

The quaternization of poly(alkoxyphosphazenes) and poly-

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Notes

The authors declare no competing financial interest.
REFERENCES