Synthesis and Characterization of Novel Solid Polymer Electrolytes Based on Poly(7-oxanorbornenes) with Pendent Oligoethyleneoxy-Functionalized Cyclotriphosphazenes

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ABSTRACT: The development of novel cyclotriphosphazene and oligoethyleneoxy-functionalized poly(7-oxanorbornenes) for possible use as solid polymer electrolytes in the electrolyte layer of rechargeable lithium batteries is described. The length of the oligoethyleneoxy group on the cyclotriphosphazene has been varied, and the effects on ion transport were studied. The synthesis of 5-[2-(2-methoxyethoxy)-ethoxymethyl]-7-oxanorbornene and 5-[2-(2-methoxyethoxy)ethoxymethyl]norbornene, their polymerization through ring-opening metathesis polymerization, and the characterization of the polymers are also discussed to illustrate the effect of oxygen atoms in the polymer backbone and in the cyclotriphosphazene side groups on the thermal and ion transport properties of these materials.

Introduction

The development of small, lightweight, powerful, safe, environmentally benign, and portable energy sources has received a great deal of attention during the past few decades.[1−5]

The rechargeable lithium battery is a system that has received considerable attention due to its low density and the low oxidation potential of lithium.[6] The development of liquid-free rechargeable lithium batteries that contain a polymeric electrolyte is a particular challenge. These could potentially yield batteries that are smaller, lighter, easier to manufacture, and contain less toxic compounds.[1] Numerous reports have been published on the advances in the field of solid-state lithium batteries.[1,3,6,7] Existing anode and cathode materials perform at acceptable levels.[8,9] However, the available solid polymer electrolytes do not yet possess the required combination of properties. Therefore, recent efforts have been focused on the design and synthesis of polymeric electrolytes in which the lithium ion transport is adequate for modern applications (10^{-3} S/cm).[1]

In 1973, poly(ethylene oxide) (PEO) (Figure 1), **1**, was shown to form complexes with metal salts,[10] and this suggested its use as a possible electrolyte for lithium batteries.[11] However, lithium cation transport in this polymer is hindered at temperatures below 80 °C due to the presence of crystalline domains.[1] Subsequently, research has emphasized the development of amorphous materials which provide facile lithium ion transport and show good chemical, mechanical, and thermal stability.[1]

Phosphazene-based electrolytes have received a great deal of attention.[12−20] The phosphazene system is a well-known hybrid inorganic−organic polymer platform with different properties generated by a variety of organic side groups.[21,22] Chemical stability and materials flexibility are imparted by the phosphazene skeleton, while the organic side groups can facilitate ion pair separation, lithium cation coordination, and ion transport.[12] The first phosphazene lithium cation conductor, poly[bis(2-(2′-methoxyethoxy)ethoxy)phosphazene] (MEEP), **2**, was developed nearly 20 years ago.[12] When **2** is complexed with a lithium salt, the ion transport is several orders of magnitude higher than that of materials based on poly(ethylene oxide). However, MEEP-based solid polymer electrolytes are amorphous gums at room temperature rather than solids, and recent efforts have been focused on the design and synthesis of polymers with both high ion transport and better dimensional stability.

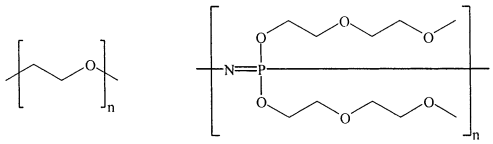

Figure 1. Polymer electrolytes.

Recently, we have published reports that describe the use of polynorbornenes with cyclophosphazene side groups as solid polymer electrolytes.[18,19] The cyclotriphosphazene units are designed to serve as a platform for multiple oligoethylene oxide substituents which themselves should promote ion transport.[23−25] Polynorbornenes often yield amorphous materials due to the many stereo- and regioisomers present. The earlier materials prepared by us had ion transport levels comparable to materials based on **2**, but with better mechanical properties.

Work by Grubbs et al. indicated that poly(7-oxanorbornenes) exist in a variety of microstructures which can interact with metal cations via the oxygen in the polymer backbone.[26,27] Thus, it was of interest to determine whether the poly(7-oxanorbornene) skeleton provides an advantage over the polynorbornene backbone in polymers with pendent oligoethyleneoxy side chains. Here we describe the synthesis, characterization, structure−property relationships, and ionic conductivity of polymer electrolytes based on (a) side chain oligoethyleneoxy-functionalized poly(7-oxanorbornenes) and (b) poly(7-oxanorbornenes) with pendent cyclotriphosphazene units that themselves bear five oligoethyleneoxy units per ring. The multiple oligoethyleneoxy pendent

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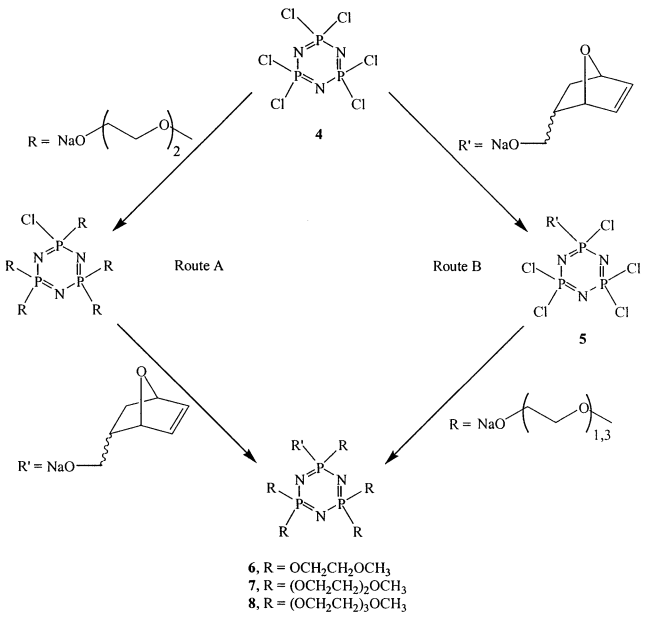
Scheme 1. Routes to Phosphazene-Based Monomers 6−8



groups should serve as a facile vehicle for cation transport. A second objective was to examine the role played by the oxygen atoms in the backbone as supplemental cation coordination sites. The behavior of these polymers was compared to that of the totally organic counterparts that lacked the phosphazene side groups but have linear oligoethyleneoxy side chains instead.

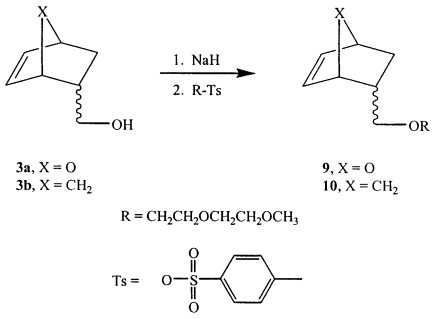
Results and Discussion

1. Principles Involved. Poly(7-oxanorbornenes) with pendent oligoethyleneoxy-functionalized cyclotriphosphazene side units (polymers **11**−**13**) have been prepared and studied for potential use in the electrolyte layer of solid-state rechargeable lithium batteries. Polymers **9** and **10**, which lack the cyclotriphosphazene side units, were investigated as controls to study the effect of the oxygen atoms in the polymer backbone and presence of the cyclotriphosphazene on ionic conductivity.

2. Monomer Synthesis. The synthesis of the monomers required the preparation of the precursor 7-oxa-5-norbornene-2-methanol, **3a**. A Diels−Alder reaction between furan and methyl acrylate in the presence of zinc iodide yielded methyl 7-oxa-5-norbornene-2-carboxylate (2:1 exo/endo).[28] The reduction of this compound with $LiAlH_4$ in diethyl ether yielded the desired precursor, **3a**, as a 2:1 mixture of exo/endo isomers[29] which was used in subsequent reactions without further purification.

Two different synthetic routes were employed to produce monomers **6**−**8**. The traditional method (route A, Scheme 1, used for the synthesis of **7**)[18,19] involved the reaction of hexachlorocyclotriphosphazene $(NPCl_2)_3$, **4**, with the oligoethyleneoxy nucleophile to give a mixture of penta- and hexa-substituted derivatives. Further treatment with the sodium salt of **3a** yields monomer **7** with a significant amount of the hexa-oligoethyleneoxy cyclotriphosphazene which was removed via column chromatography. In route B, treatment of $(NPCl_2)_3$ with the sodium salt of **3a** gave a mixture of mono- and unsubstituted $(NPCl_2)_3$. The $(NPCl_2)_3$ was removed by sublimation to give a purer monosubstituted product, **5**. Treatment of **5** with the oligoethyleneoxy nucleophiles afforded pure monomers **6** and **8**. Although route A suffered from the need for an extra purification step to remove the hexa-substituted product, all the monomers were obtained in satisfactory yields as transparent viscous oils.

Scheme 2. Synthesis of Phosphazene-Free Monomers 9 and 10



The syntheses of the totally organic monomers **9** and **10** are shown in Scheme 2. Similar monomers have been prepared and polymerized, although through a different synthetic approach.[30] First, the sodium salt of either **3a** or **3b** was prepared, followed by addition of 2-(2-methoxyethoxy)ethyl *p*-toluenesulfonate[14] at −78 °C. Following purification, the desired monomers (mixture of exo and endo isomers) were obtained in good yields as transparent oils.

3. Polymer Synthesis. Polymers **11**−**15** were prepared at ambient temperature, under inert atmosphere conditions, through ring-opening metathesis polymerization of the corresponding monomers using a monomer: catalyst ratio of 275:1 $[Cl_2(PCy_3)_2RuCHPh]$. Immediately following the addition of $[Cl_2(PCy_3)_2RuCHPh]$ in a minimal amount of dichloromethane, the solutions became progressively more viscous as the polymerization proceeded. All the polymerizations were terminated after 12 h by the addition of 0.5 mL of ethyl vinyl ether. The solutions were then diluted with tetrahydrofuran or methanol and were dialyzed against tetrahydrofuran and methanol. Following the removal of the solvent, polymers **11**−**13** were obtained in good yields as adhesive gums, whereas polymers **14** and **15** were obtained as solid elastomers. All the polymers were readily soluble in common organic solvents such as tetrahydrofuran, dichloromethane, methanol, and chloroform.

4. Solid Polymer Electrolytes. *(a) Thermal Analysis.* The morphological properties of the totally organic polymers and hybrid solid polymer electrolytes were examined by differential scanning calorimetry (DSC).

In the following discussion, species **16** is the polymer salt complex from polymer **11**, while **17** is from polymer **12**, **18** is from **13**, **19** is from the oxanorbornene−phosphazene-free system **14**, and **20** is from the norbornene−phosphazene-free system **15** (Table 1). All polymers and solid polymer electrolytes were amorphous over the entire temperature range studied (−100 to 50 °C). The presence of the phosphazene moiety depresses the glass transition temperature (T_g) significantly, as does an increase in the length of the oligoethyleneoxy side groups (compare **11**, **12**, **13**, and **14** in Table 1). As the length of the side groups increases, the polymers develop more free volume, macromolecular motion is increased, and the T_g is depressed. The presence of the oxygen unit in the backbone raises the T_g compared to the polynorbornene counterparts (compare **14** and **15** in Table 1). Presumably, the oxygen atoms in the main

Scheme 3. Polymerization of Monomers 6−10 to Polymers 11−15

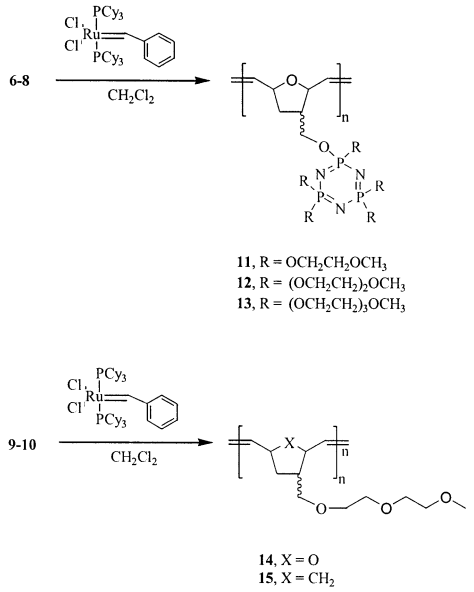


Table 1. Thermal Data and Salt Concentrations for Polymers 11−15 and Solid Polymer Electrolytes 16a−f to 20a−f

polymer	mol % $LiN(SO_2CF_3)_2$	solid polymer electrolyte	T_g (°C)
11	0		−47
11	10	**16a**	−50
11	20	**16b**	−37
11	30	**16c**	−33
11	40	**16d**	−33
11	50	**16e**	−30
11	60	**16f**	−25
12	0		−68
12	10	**17a**	−61
12	20	**17b**	−59
12	30	**17c**	−51
12	40	**17d**	−48
12	50	**17e**	−46
12	60	**17f**	−44
13	0		−70
13	10	**18a**	−70
13	20	**18b**	−67
13	30	**18c**	−63
13	40	**18d**	−61
13	50	**18e**	−57
13	60	**18f**	−54
14	0		−45
14	10	**19a**	−37
14	20	**19b**	−10
14	30	**19c**	−6
14	40	**19d**	−5
14	50	**19e**	−4
14	60	**19f**	−3
15	0		−54
15	10	**20a**	−29
15	20	**20b**	−14
15	30	**20c**	−6
15	40	**20d**	−6
15	50	**20e**	−4
15	60	**20f**	−4

chain increase the polarity of the polymer and enhance dipole−dipole interactions. Thus, the polymer becomes less flexible.

As shown in Table 1, the glass transition temperatures generally increase with increases in the concentration of added lithium salt. This is due to transient ionic cross-links formed between the lithium cations and the oxygen atoms in the polymer. However, this T_g increase did not occur for the materials based on **11** or **13**. In **11**, at low salt concentrations the short oligoethyleneoxy chains do not impart significant free volume to the system (compare **11**, **14**, and **15**, in Table 1.) Thus, the influence of the salt at low concentrations is that of a plasticizer rather than cross-linker. For **13**, a concentration of 10 mol % salt is too low for lithium cations to generate significant ionic cross-linking, to reduce the mobility of the polymer, or to raise the T_g. The T_g's for the phosphazene-free systems (**19a−f, 20a−f**) increased more dramatically as salt was added than did the values of the phosphazene-based solid polymer electrolytes (**16−18**). Fewer coordination sites are present in these phosphazene-free polymers. Hence, the formation of ionic cross-links has a more profound effect on the internal motion at lower salt concentrations in the phosphazene-free systems.

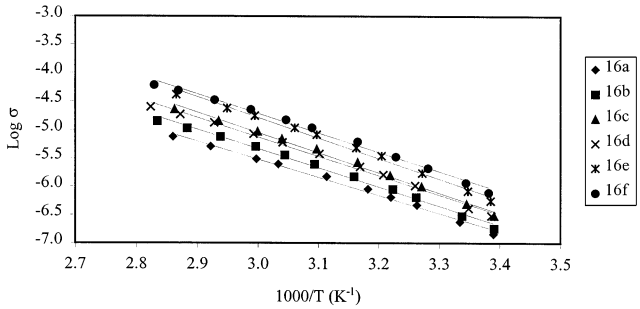


Figure 2. Temperature-dependent ionic conductivity for solid polymer electrolytes **16a−f**.

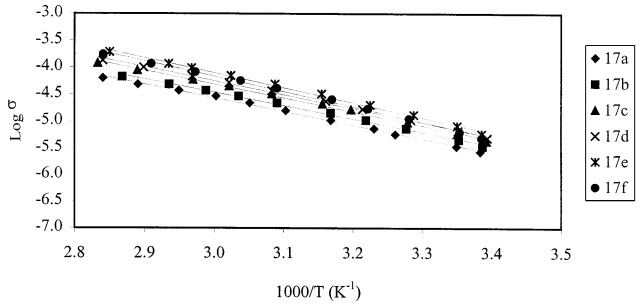


Figure 3. Temperature-dependent ionic conductivity for solid polymer electrolytes **17a−f**.

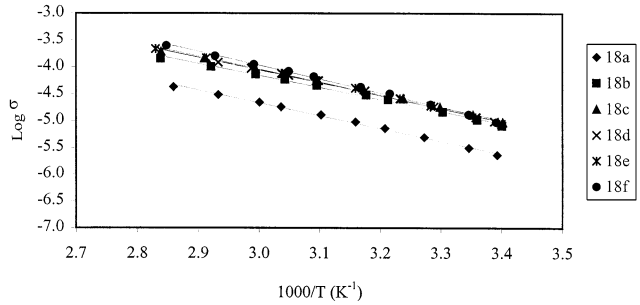


Figure 4. Temperature-dependent ionic conductivity for solid polymer electrolytes **18a−f**.

4. Solid Polymer Electrolytes. *(b) Temperature-Dependent Ionic Conductivity.* The results of the temperature-dependent ionic conductivity studies of solid polymer electrolytes **16a−f** to **20a−f** are shown in Figures 2−6. The conductivities increase with increasing temperature in a nonlinear manner that is typical of solid polymer electrolytes.[31] The ionic conductivities are higher when the cyclotriphosphazene moiety is present and increase with increased length of oligo-

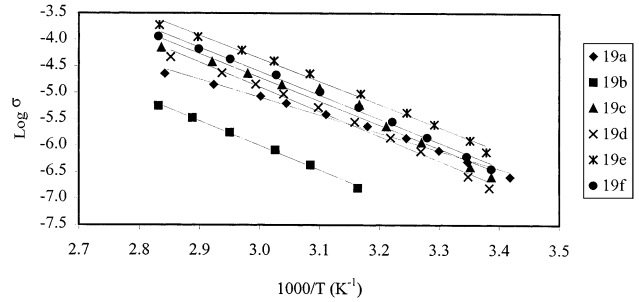


Figure 5. Temperature-dependent ionic conductivity for solid polymer electrolytes **19a**−**f**.

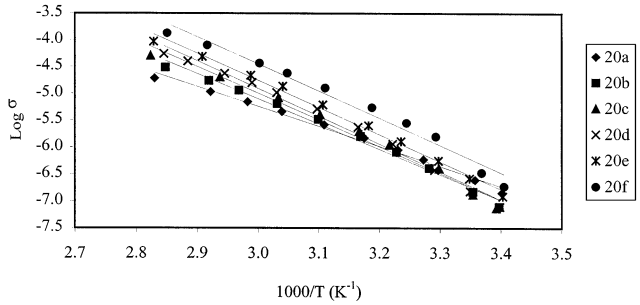


Figure 6. Temperature-dependent ionic conductivity for solid polymer electrolytes **20a**−**f**.

ethyleneoxy unit (compare Figures 2−5). The conductivities are similar to those of the norbornene-based materials.[18,19] As the side groups become longer (depressing T_g and increasing macromolecular motion) and as the number of coordination sites increases, the lithium cations can be transported more efficiently. For the phosphazene-based systems, the T_g data correlate well with the ionic conductivity data. However, the presence of oxygen in the backbone of the phosphazene-free polymers increases both the glass transition temperature (see above) and the ionic conductivity (compare Figures 5 and 6). Presumably, the oxygen in the backbone provides coordination sites in addition to those in the side chains, and these sites can aid the transport of lithium cations as is evident from the conductivity results (Figures 5 and 6). Solid-state lithium-7 NMR spectroscopy of both the phosphazene-containing and phosphazene-free systems (**18c**, **19c**, **20c**) confirmed the interaction of lithium cations with the oxygen units in backbone through broadening of the ^{7}Li peaks.

Further examination of the solid polymer electrolytes revealed some unique features. The conductivities increase with increased amounts of salt for **16a**−**f** and **17a**−**f** due to the increased number of charge carriers present in the system. However, the effect of increasing salt concentration in SPEs (**18b**−**f**) comprised of the longer ethyleneoxy containing polymer **13** is not as distinct at lower temperatures but begins to display a more profound effect at higher temperatures. These data suggest that the extended length of the oligoethyleneoxy chain of polymer **13** results in partial ionically cross-linking of SPEs **18b**−**f** at low temperatures and moderate to high salt concentrations, which can be overcome at high temperatures when more chain mobility is imparted in the system. Phosphazene-free solid polymer electrolytes **19a**−**f** and **20a**−**f** have significantly fewer coordination sites. Therefore, ambient temperature conductivities will be higher at lower salt loadings, but the material will be ionically cross-linked at higher salt concentrations. However, at increased temperatures the ionic cross-links may be disrupted, and ion transport is increased. The absence of oxygen in the backbone of phosphazene-free systems **20a**−**f** limits the ion solvation by the polymer to the oxygen atoms in the pendent oligoethylene oxide chains. Consequently, at lower temperatures, low concentrations of salt generate the best conductivities because high concentrations of salt will induce ionic cross-linking of the system under these conditions.

Conclusions

The synthesis of poly(7-oxanorbornenes) with pendent oligoethyleneoxy-functionalized cyclotriphosphazenes has been achieved via ROMP techniques to yield organic-soluble, high molecular weight polymers in good yields. These polymers have some of the highest molecular weights and are among the most polar molecules to be produced via ROMP, and this illustrates the compatibility of the heteroatom-rich, oligoethyleneoxy-functionalized cyclotriphosphazenes with olefin metathesis catalysts. Lithium ion transport in these materials is similar to that in norbornene-based materials.[18,19] The introduction of the oxygen atoms into the backbone of polynorbornenes raises the glass transition temperature which often lowers ionic conductivity, but the skeletal oxygen atoms also facilitate lithium ion transport. The linkage of the pendent cyclotriphosphazene ring to poly(7-oxanorbornenes) depresses the glass transition temperature and also introduces more coordination sites, thereby improving lithium ion transport significantly. The highest conductivities found for these polymer−salt systems suggest that gel electrolytes with a minimal amount of coordinative organic solvent present may provide property combinations that are superior to those of existing gel systems.

Experimental Section

1. General. Syntheses were carried out under an argon atmosphere using standard Schlenk techniques or use of an argon-filled glovebox (MBraun).

Solution-state NMR spectra were obtained at 298 K using a Bruker AMX 360 NMR spectrometer resonating at 360.24 MHz for ^{1}H, 145.81 MHz for ^{31}P, and 90.56 MHz for ^{13}C. For ^{1}H and ^{13}C NMR spectra, the chemical shifts were referenced to internal $CDCl_3$ unless otherwise noted. For ^{31}P spectra, the chemical shifts were referenced to external 85% phosphoric acid. Solid-state lithium-7 NMR experiments were obtained using a Varian/Chemagnetics Infinity-500 NMR spectrometer operated in quadrature mode at ambient temperature and 194.2 MHz. The quadrupole echo pulse sequence was used with an echo delay of 30 μs, a relaxation delay of 60 s, a spectral width of 1 MHz, and a $\pi/2$ pulse width of 2.55 μs. Gel permeation chromatography results were obtained by means of a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with two Phenomenex Phenogel linear 10μ columns and a Hewlett-Packard 1047A refractive index detector calibrated vs monodisperse polystyrene standards. Elemental analyses were obtained by Quantitative Technologies Inc. Complex impedance analysis was performed in a constant-flow, argon-atmosphere glovebox. The solid polymer electrolyte was placed between two platinum electrodes and was supported by a Teflon spacer. The platinum electrode−solid polymer electrolyte sandwich was held in place in a Teflon fixture by aluminum blocks. Leads were connected from the aluminum blocks to a Hewlett-Packard 4192A LF impedance analyzer, controlled by a desktop computer, and tested with an AC frequency range of 5 Hz−13 MHz and an amplitude of 0.1 V. Thermal data were obtained through differential scanning calorimetry (DSC) using a Perkin-Elmer-7 thermal analysis system equipped with a desktop computer. Polymer samples

were heated from −100 to 50 °C under an atmosphere of dry nitrogen. An approximately 30 mg sample was hermetically sealed in aluminum pans and heated at rates of 10, 20, and 40 °C/min. The final T_g values were determined through extrapolation to 0 °C/min heating rate. Mass spectra were collected using a Micromass Quattro-II triple quadrupole mass spectrometer.

2. Materials. Furan (99+%), methyl acrylate (99%), 5-norbornene-2-methanol (mixture of endo and exo isomers, **3b**), zinc iodide (98+%), sodium hydride (95%, 60% dispersion in mineral oil), lithium aluminum hydride (95%), lithium bis(trifluoromethylsulfonyl)imide (3M), $[Cl_2(PCy_3)_2RuCHPh]$ (Strem), *p*-toluenesulfonyl chloride (98%), ethyl vinyl ether (99%), ethyl acetate, heptane, and methanol were used as received. Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) (Ethyl Corp./Nippon Fine Chemical) was recrystallized from heptane and sublimed at 0.2 mmHg at 30 °C before use. 2-Methoxyethanol (99%), 2-(2-methoxyethoxy)ethanol (99%), 2-(2-(2-methoxyethoxy)ethoxy)ethanol (95%), dichloromethane, and diethyl ether were distilled from calcium hydride prior to use. THF was distilled from sodium benzophenone ketyl before use.

Solid polymer electrolytes **16a**−**f** to **20a**−**f** were prepared by the dissolution of the polymer and the salt in anhydrous THF, followed by slow evaporation of the solvent and subsequent vacuum-drying (40 °C at 0.1 mmHg) for 5 days. The solid polymer electrolytes were then transferred to a glovebox under an atmosphere of argon.

3. Preparation of Cyclotriphosphazene-Functionalized Monomers. *(a) Route A.* Preparation of [(7-oxa-5-norbornene-2-methoxy)pentakis(2-(2-methoxyethoxy)ethoxy)]-cyclotriphosphazene, **7**. A solution of 2-(2-methoxyethoxy)ethanol (22.4 g, 0.1864 mol) in 50 mL of THF was added dropwise to a suspension of sodium hydride (8.28 g, 0.207 mol) in 350 mL of THF. The reaction mixture was stirred under argon at room temperature for 10 h and was added to a solution of hexachlorocyclotriphosphazene (12.00 g, 0.0345 mol) in 300 mL of THF at 0 °C. The reaction mixture was allowed to warm to room temperature with continued stirring for 12 h. The resultant suspension was centrifuged to remove sodium chloride, and the remaining solution was decanted and concentrated under reduced pressure to yield 25.2 g (95%) of an oil containing 54% pentakis[(2-(2-methoxyethoxy)ethoxy)(monochloro)]cyclotriphosphazene (^{31}P NMR (D_2O): δ 27.8 (t, 1P), 15.61 (d, 2P)) and 46% hexakis[(2-(2-methoxyethoxy)ethoxy)]cyclotriphosphazene (^{31}P NMR (D_2O): δ 18.99 (s, 3P)) which was used without further purification. A solution of this oil (19.82 g, 0.0259 mol) in 200 mL of THF was treated with potassium 7-oxa-5-norbornene-2-methoxide, itself synthesized via the reaction of 7-oxa-5-norbornene-2-methanol (3.59 g, 0.0285 mol) with potassium *tert*-butoxide (4.36 g, 0.0388 mol) in 200 mL of THF. The solution was stirred for 24 h at room temperature, concentrated under reduced pressure, and purified by column chromatography (silica gel, 85:15 ethyl acetate:methanol) to afford 7.2 g (65% based on pentakis[(2-(2-methoxyethoxy)-ethoxy)(monochloro)]cyclotriphosphazene) of colorless oil, **7**.

For **7**, ^{1}H NMR: δ 0.77 (dd,1H, endo), 1.22 (m, 1H, exo), 1.34 (m, 1H, exo), 1.75 (m, 1H, exo), 1.95 (m, 1H, endo), 2.42 (m, 1H, endo), 3.33 (m, 2H, exo), 3.46 (s, 15H), 3.55 (m, 2H, endo), 3.62 (m, 10H), 3.73 (m, 10H), 3.78 (m, 10H), 4.17 (m, 10H), 4.91 (m,1H, endo), 4.93 (m,1H, exo), 4.98 (m,1H, exo), 5.03 (m, 1H, exo), 6.35 (dd, 1H, endo), 6.40 (s, 2H, exo), 6.45 (dd, 1H, endo). ^{13}C NMR: δ 26.49, 27.05, 36.90, 37.2, 57.72, 63.80, 67.14, 66.91, 68.80, 69.27, 70.46, 75.62, 75.97, 76.49, 131.25, 133.48, 134.75. ^{31}P NMR: δ 18.1 (m, 3P). MS = *m*/*e* 856 (MH^+). Elemental analysis: calcd % C, 44.91; % H, 7.54; % N, 4.91; % O, 31.78; % P, 10.86. Found: % C, 43.59; % H, 7.68; % N, 4.96; % P, 10.38.

3. Preparation of Cyclotriphosphazene-Functionalized Monomers. *(b) Route B.* Preparation of pentachloromono(7-oxa-5-norbornene-2-methoxy)cyclotriphosphazene, **5**. Hexachlorocyclotriphosphazene $(NPCl_2)_3$ (30 g, 0.863 mol) was dissolved in 300 mL of THF in a 2 L flask. A 1 L flask was charged with 95% sodium hydride (1.57 g, 0.052 mol) and 200 mL of THF. 7-Oxa-5-norbornene-2-methanol (**3a**) (6.53 g, 0.062 mol) was added dropwise to a sodium hydride suspension and stirred overnight. Sodium 7-oxa-5-norbornene-2-methoxide solution was added dropwise to the $(NPCl_2)_3$ solution at −78 °C. The mixture was then stirred and warmed slowly overnight to ambient temperature. THF was removed by rotary evaporation to leave a viscous oil. The oil was dissolved in diethyl ether (500 mL) and was washed with water (3 × 250 mL). The diethyl ether layer was dried over $MgSO_4$ and filtered. The solution was then concentrated, and the crude product was sublimed (0.1 mmHg at 40 °C for 12 h) to leave the product (**5**) as a viscous oil.

For **5**, ^{1}H NMR: δ 0.68 (dd, 1H, endo), 1.22 (m, 1H, exo), 1.39 (m, 1H, exo), 1.87−1.99 (br m, 2H, endo + exo), 2.55 (m, 1H, endo), 4.03 (m, 2H, exo), 4.16 (m, 2H, endo), 4.81 (s, 1H, exo), 4.91 (m, 2H, endo + exo), 4.97 (m, 1H, endo), 6.24 (s, 2H, exo), 6.33 (dd, 1H, endo), 6.38, (dd, 1H, endo). ^{13}C NMR: δ 28.30, 28.90, 38.30, 71.97, 72.30, 78.50, 79.00, 79.30, 79.60, 132.4, 134.90, 137.00, 137.90. ^{31}P NMR: δ 14.87 (td, 1 P), 22.89 (d, 2 P). MS = *m*/*e* 438 (MH^+).

Preparation of [(7-oxa-5-norbornene-2-methoxy)pentakis(2-methoxyethoxy)]cyclotriphosphazene (monomer **6**). A 1 L flask was charged with 95% sodium hydride (4.68 g, 0.185 mol) and 500 mL of THF. 2-Methoxyethanol (15 g, 0.185 mol) was added dropwise to the sodium hydride suspension. The mixture was stirred overnight. Compound **5** (13.5 g, 0.031 mol) was dissolved in 500 mL of THF in a 2 L flask. The sodium 2-methoxyethoxide solution was added dropwise to the solution of **5** at −78 °C. The mixture was then stirred and warmed slowly to room temperature overnight. The THF was then removed by rotary evaporation, and the crude reaction mixture was dissolved in ether and centrifuged. The ether was removed, and the product was purified by column chromatography (silica gel, 95:5 ethyl acetate: methanol). The solvent was removed, and the residue was dried overnight (room temperature 0.1 mmHg) to leave 10.0 g (51%) of viscous oil (**6**).

For **6**, ^{1}H NMR: δ 0.59 (dd, 1H, endo), 1.18 (m, 1H, exo), 1.30 (m, 1H, exo), 1.77−1.91 (m, 2H, endo + exo), 2.45 (m, 1H, endo), 3.21 (s, 15H), 3.35 (m, 2H, exo), 3.45 (m, 10H), 3.61 (m, 2H, endo), 3.87 (m, 10H), 4.73 (s, 1H, exo), 4.76 (m, 2H, endo + exo), 4.87 (d,1H, endo), 6.14 (s, 2H, exo), 6.26 (dd, 1H, endo), 6.31 (dd, 1H, endo). ^{13}C NMR: δ 28.10, 28.60, 38.50, 38.80, 57.09, 59.30, 61.40, 65.30, 67.40, 68.50, 68.70, 71.70, 78.10, 78.70, 79.40, 79.80, 132.90, 135.10, 136.4. ^{31}P NMR: δ 18.20 (m, 3 P). MS = *m*/*e* 636 (MH^+). Elemental analysis: calcd % C, 41.60; % H, 7.00; % N, 6.60; % P, 14.60. Found: % C, 41.50; % H, 7.20; % N, 6.60; % P, 14.90.

Preparation of [(7-oxa-5-norbornene-2-methoxy)pentakis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)]cyclotriphosphazene, (monomer **8**). The procedure to prepare monomer **8** was the same as for monomer **6**. The quantities used are as follows: 95% sodium hydride (3.88 g, 0.162 mol) and 200 mL of THF, 2-(2-(2-methoxyethoxy)ethoxy)ethanol (26.00 g, 0.158 mol), **5** (11.2 g, 0.026 mol), and 100 mL of THF. The product was purfied through column chromatography (silica gel, 85:15 ethyl acetate:methanol) to afford 10.1 g (37%) of monomer **8**.

For **8**, ^{1}H NMR: δ 0.55 (dd, 1H, endo), 1.03 (m, 1H, exo), 1.19 (m, 1H, exo), 1.74−1.89 (br m, 2H, exo + endo), 2.36 (m, 1H, endo), 3.16 (s, 15H), 3.26 (m, 2H, exo), 3.35 (m, 10H), 3.45 (m, 40H), 3.61 (m, 2H, endo), 3.79 (m, 10H), 4.66 (s, 1H, exo), 4.69 (m, 2H, endo + exo), 4.81 (d, 1H, endo), 6.13 (s, 2H, exo), 6.17 (dd, 1H, endo), 6.28 (dd, 1H, endo). ^{13}C NMR: δ 27.60, 28.20, 38.10, 38.30, 50.20, 58.80, 64.90, 68.00, 68.30, 69.80, 70.40, 71.80, 73.90, 78.20, 78.80, 79.20, 132.30, 134.60, 135.90, 136.30. ^{31}P NMR: δ 17.90 (m, 3 P). MS = *m*/*e* 1077 (MH^+). Elemental analysis: calcd % C, 46.91; % H, 7.92; % N, 3.95; % P, 8.62. Found: % C, 47.11; % H, 8.11; % N, 3.91; % P, 8.67.

4. Preparation of Oligoethyleneoxy-Functionalized Norbornene and 7-Oxanorbornene Monomers. Preparation of 5-[2-(2-methoxyethoxy)ethoxymethyl]-7-oxanorbornene (monomer **9**). 7-Oxa-5-norbornene-2-methanol (**3a**) (10.0 g, 0.0793 mol) was added slowly to a suspension of NaH (95%) (2.00 g, 0.0793 mol) in 165 mL of THF. After the mixture was stirred at room temperature for 10 h, it was cooled to −78 °C, and to the mixture was added 2-(2-methoxyethoxy)ethyl *p*-toluenesulfonate (22.83 g, 0.0832 mol). Following the complete

addition of 2-(2-methoxyethoxy)ethyl *p*-toluenesulfonate the reaction mixture was warmed to room temperature and stirred for 12 h. The resultant suspension was filtered and washed with ethyl acetate, and the remaining ethyl acetate solution was extracted with deionized water. The ethyl acetate layer was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield an oil which was further purified through column chromatography (silica gel, 90:10 EtOAc:hexanes) to afford 9.9 g (55%) of colorless oil (**9**) (mixture of endo and exo isomers).

For **9**, ^{1}H NMR: δ 0.66 (dd, 1H, endo), 1.20 (m, 1H, exo), 1.35 (m, 1H, exo), 1.75 (m, 1H, exo), 1.89 (m, 1H, endo), 2.35 (m, 1H, endo), 3.29−3.35 (m, 4H, endo + exo), 3.51 (s, 3H), 3.53−3.63 (br m, 8H), 4.84 (s, 1H, exo), 4.90 (d, 2H, exo + endo), 4.97 (d, 1H, endo), 6.23 (dd, 1H, endo), 6.30 (s, 2H, exo), 6.35 (dd, 1H, endo). ^{13}C NMR: δ 26.39, 26.51, 36.29, 36.38, 57.43, 68.82, 68.86, 68.95, 68.98, 70.42, 72.26, 72.61, 75.63, 75,99, 76.20, 76.70, 78.1, 130.92, 133.42, 134.23. MS = *m/e* 228 (M^+). Elemental analysis: calcd % C, 63.14; % H, 8.83; % O, 28.03. Found: % C, 62.51; % H, 8.68; % O, 28.56.

Preparation of 5-[2-(2-methoxyethoxy)ethoxymethyl]norbornene (monomer **10**). Monomer **10** was synthesized in a manner similar to monomer **9**. 5-Norbornene-2-methanol, **3b** (10.0 g, 0.0805 mol), was added slowly to a suspension of NaH (95%) (2.03 g, 0.0805 mol) in 165 mL of THF. After being stirred at room temperature for 10 h the reaction mixture was cooled to −78 °C, and to the mixture was added 2-(2-methoxyethoxy)ethyl *p*-toluenesulfonate (23.19 g, 0.0846 mol). Following the addition the reaction mixture was allowed to warm to room temperature and stirred for 12 h. The resultant suspension was filtered and washed with diethyl ether, and the remaining diethyl ether solution was extracted with deionized water. The diethyl ether layer was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield a dark oil which was further purified through column chromatography (silica gel, 80:20 hexanes:ethyl acetate) to afford 9.0 g (50%) of colorless oil, **10** (mixture of endo and exo isomers).

For **10**, ^{1}H NMR: δ 0.55 (dd, 1H), 1.05−1.45 (m, 4H), 1.5−1.9 (m, 2H), 2.30 (m, 1H), 2.70−2.91 (br m, 2H), 3.38 (s, 3H), 3.55 (m, 4H), 3.65 (m, 6H), 5.92 (dd, 1H), 6.11 (dd, 1H). ^{13}C NMR: δ 29.15, 29.70, 38.71, 38.79, 41.53, 42.19, 43.64, 43.95, 44.99, 49.40, 59.02, 70.26, 70.29, 70.56, 70.63, 72.00, 75.07, 76.05, 132.48, 136.62, 137.06. MS = *m/e* 226 (M^+). Elemental analysis: calcd % C, 68.99; % H, 9.80; % O, 21.21. Found: % C, 67.90; % H, 9.69; % O, 22.29.

5. General Preparation of Polymers. Preparation of polymer **11**. Monomer **6** (5 g, 8 mmol) was degassed under vacuum in 50 mL three-neck flask and then dissolved in 25 mL of anhydrous dichloromethane. The initiator [$Cl_2(PCy_3)_2$-RuCHPh] (0.026 g, 0.03 mmol) in 1 mL of dichloromethane was added to the monomer quickly. The solution was stirred overnight, and then 0.5 mL of ethyl vinyl ether was added to terminate the reaction. The polymer solution was dialyzed against THF, 50:50 THF:methanol, and methanol. The solvent was removed to yield 2.6 g (52%) of a rubbery gum.

For **11**, ^{1}H NMR: δ 1.81−2.45 (br m, 3H), 3.31 (br s, 17H), 3.52 (br s, 10H), 3.99 (br s, 10H), 4.26 (br m, 1H), 4.65 (br m, 1H), 5.50 (br s, 1H), 5.56 (br s, 1H). ^{13}C NMR: δ 29.70, 35.80, 45.80, 46.50, 56.80, 59.00, 61.20, 65.00, 65.90, 71.40, 74.4, 81.3, 132.90. ^{31}P NMR: δ 18.20 (s, 3 P); M_n = 176 977, M_w = 394 718, PDI = 2.23. Elemental analysis: calcd % C, 41.61; % H, 7.03; % N, 6.62; % P, 14.62. Found: % C, 41.72; % H, 6.97; % N, 6.54; % P, 14.74.

Preparation of polymer **12**. Polymer **12** was prepared in a manner similar to polymer **11** using monomer **7** (5.0 g, 0.0058 mol) in 5 mL of dichloromethane and a solution of [$Cl_2(PCy_3)_2$-RuCHPh] (0.017 g, 0.0212 mmol) in 1 mL of dichloromethane. After purification by dialysis, the solvent was removed under reduced pressure to yield 3.5 g (70%) of polymer **12**.

For **12**, ^{1}H NMR: δ 1.77−2.41 (br m, 3H), 3.32 (s, 17H), 3.48 (m, 10H), 3.55 (m, 20H), 4.02 (m, 10H), 4.25 (br m, 1H), 4.62 (br m, 1H), 5.42 (br s, 1H), 5.67 (br s, 1H). ^{13}C NMR: δ 35.83, 45.83, 46.55, 59.12, 65.17, 65.95, 70.17, 70.65, 72.07, 74.36, 81.29, 133.22, 133.51. ^{31}P NMR: δ 18.12 (s, 3P); M_n = 132 000, M_w = 172 000, PDI = 1.3. Elemental analysis: calcd % C, 44.91; % H, 7.54; % N, 4.91; % P, 10.86. Found: % C, 44.95; % H, 7.66; % N, 4.70; % P, 10.85.

Preparation of polymer **13**. Polymer **13** was prepared in a manner similar to polymer **11** using monomer **8** (3.97 g, 3.7 mmol) in 8 mL of dichloromethane and a solution of [$Cl_2(PCy_3)_2$-RuCHPh] (0.011 g, 0.01 mmol) in 1 mL of dichloromethane. After purification by dialysis, the solvent was removed under reduced pressure to yield 2.2 g (51%) of polymer **13**.

For **13**, ^{1}H NMR: δ 1.82−2.5 (br m, 3H), 3.30 (s, 17H), 3.33 (m, 10H), 3.36−3.45 (br m, 40H), 3.89 (br s, 10H), 4.15 (br m, 1H), 4.55 (br m, 1H), 5.42−5.67 (br m, 2H). ^{13}C NMR: δ 25.50, 29.60, 30.8, 58.90, 65.10, 67.90, 70.00, 70.5, 71.8, 132.3. ^{31}P NMR: δ 18.1 (m, 3 P); M_n = 132 000, M_w = 168 000, PDI = 1.27. Elemental analysis: calcd % C, 46.91; % H, 7.93; % N, 3.94; % P, 8.63. Found: % C, 47.12; % H, 8.03; % N, 3.87; % P, 8.56.

Preparation of polymer **14**. Under inert atmosphere, a solution of [$Cl_2(PCy_3)_2$RuCHPh] (0.047 g, 0.057 mmol) in 5 mL of dichloromethane was added to a solution degassed monomer **9** (3.6 g, 0.0158 mol) in 14 mL of dichloromethane. After addition of the catalyst, the solution became increasingly viscous, and the polymerization was continued for 10 h at room temperature, at which time 0.5 mL of ethyl vinyl ether was added to the reaction mixture. The polymer solution was then precipitated into hexanes to yield a rubbery polymer. This was further purified by precipitations into hexane and pentane and was dried under vacuum to yield 2.5 g (69%) of polymer **14**.

For **14**, ^{1}H NMR: δ 1.65−2.41 (br m, 3H), 3.38 (s, 5H), 3.54−3.63 (br m, 8H), 4.36 (br m, 1H), 4.69 (br m, 1H), 5.53 (br s, 1H), 5.72 (br s, 1H). ^{13}C NMR: δ 36.81, 37.24, 44.82, 46.41, 46.59, 47.01, 59.42, 71.21, 71.99, 72.73, 75.12, 78.15, 79.35, 82.75, 133.54, 133.32. M_n = 109 000, M_w = 300 000, PDI = 2.8. Elemental analysis: calcd % C, 63.14; % H, 8.83; % O, 28.03. Found: % C, 63.10; % H, 8.68; % O, 28.27.

Preparation of polymer **15**. Polymer **15** was prepared in a manner similar to polymer **14** using monomer **10** (4.0 g, 0.0177 mol) in 15 mL of dichloromethane and a solution of [$Cl_2(PCy_3)_2$-RuCHPh] (0.0529 g, 0.064 mmol) in 5 mL of dichloromethane. Polymer **15** was purified through precipitations into methanol/water and hexanes to yield 3.0 g (60%) of polymer **15**.

For **15**, ^{1}H NMR: δ 0.86 (br m, 1H), 1.54 (br m, 1H), 1.17 (br m, 1H), 1.85 (br m, 1H), 2.20 (br m, 1H), 2.73 (br m, 1H), 2.93 (br m, 1H), 3.34 (br s, 5H), 3.51 (br m, 4H), 3.59 (br m, 4H), 5.48 (br m, 2H). ^{13}C NMR: δ 29.81, 36.50, 37.34, 39.20, 39.91, 41.65, 42.53, 44.59, 46.50, 59.18, 70.49, 70.67, 72.12, 73.54, 74.84, 129.99, 131.25, 133.26, 134.59. M_n = 94 000, M_w = 107 000, PDI = 1.1 Elemental analysis: calcd % C, 68.99; % H, 9.80; % O, 21.21. Found: % C, 68.87; % H, 9.90; % O, 21.60.

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