4486 *Chem. Mater.* **2006,** *18,* 4486−4492

# Lithium-Ion Conductive Polymers as Prospective Membranes for Lithium−Seawater Batteries

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*Received March 22, 2006. Revised Manuscript Received July 6, 2006*

Novel amphiphilic single-ion conductive polynorbornenes with pendent cyclotriphosphazenes have been studied as candidates for lithium-ion conductive membranes for lithium−seawater batteries. The cyclotriphosphazene components were linked to a 5-norbornene-2-methoxy substituent to provide a polymerizable unit. 2-(2-Phenoxyethoxy)ethoxy cosubstituents on the cyclotriphosphazene unit of the first comonomer were utilized to simultaneously facilitate lithium cation transport and introduce hydrophobicity into the polymer electrolyte. 4-(Lithiumcarboxalato)phenoxy side groups were linked to the rings of a second comonomer to provide tethered anions with mobile lithium cations and to increase the dimensional stability of the final polymers. The synthesis of norbornenemethoxy-based cyclotriphosphazene monomers, their ring-opening metathesis polymerization, deprotection and lithiation of the 4-(propylcarboxalato)phenoxy side groups, and the characterization of the polymers are discussed to illustrate the dependence of ion transport and hydrophobic properties on the polymer composition.

## Introduction

The objective of this work was the synthesis and characterization of new amphiphilic single-ion conductive polymers for possible applications as anode membranes in lithium−seawater batteries. Previous work has demonstrated the utility of organic-phosphazene hybrid polymers for electrolyte and membrane applications.[1−3] This class of polymers has the unique ability to combine two different competing properties by the utilization of various side groups linked to the polymer backbone. Polymeric electrolyte anode membranes when used in aqueous environments require the unusual combination of lithium ion conduction (which usually generates hydrophilicity) while simultaneously providing a hydrophobic barrier between water and the lithium metal anode.

Autonomous marine systems such as remote sea buoys, emergency signal beacons, underwater sensors, and navigation aids typically employ conventional primary batteries as their source of power.[4] However, primary battery systems are typically bulky, heavy, and expensive because of the protection required for operation in the harsh ocean environment.[5] Metal−seawater battery technology offers a solution to this problem by utilizing the ambient seawater as a battery component.[6,7]

Metal−seawater batteries use a metal anode and seawater as the electrolyte/oxidant solution.[8] For this reason and because it is an open system, this type of design can also be defined as a semifuel cell. The following electrochemical reactions take place in a metal−seawater primary cell.[4]

$$\text{anodic reaction: } \mathrm{M}^{\circ} \rightarrow \mathrm{M}^{n+} + ne^{-}$$

$$\text{cathodic reaction: } \mathrm{O_2} + 2\mathrm{H_2O} + 4e^{-} \rightarrow 4\mathrm{OH}^{-}$$

Utilization of seawater as an oxidant in the battery allows the size and weight to be drastically reduced because no protection from the ocean environment is required. In addition, metal−seawater batteries are stored dry, allowing them to be stored for long periods of time and subsequently activated by immersion in seawater.[6]

Lithium metal is a preferred anode material to increase the power density of the battery system. In addition, lithium metal has a high oxidation potential (−3.0 V) and high energy density, making it ideal for this application.[9,10] Despite, the advantages of metallic lithium, one major obstacle exists: a parasitic lithium−water reaction occurs when lithium metal and water come into contact.

$$\text{parasitic reaction: } 2\mathrm{Li}^{\circ} + {}^{1}\!/_{2}\mathrm{H_2O} \rightarrow \mathrm{H_2} + 2\mathrm{LiOH(s)}$$

As this reaction proceeds a layer of lithium hydroxide forms on the surface of the lithium anode inhibiting further oxidation of the lithium metal.[11] Eventually, the layer

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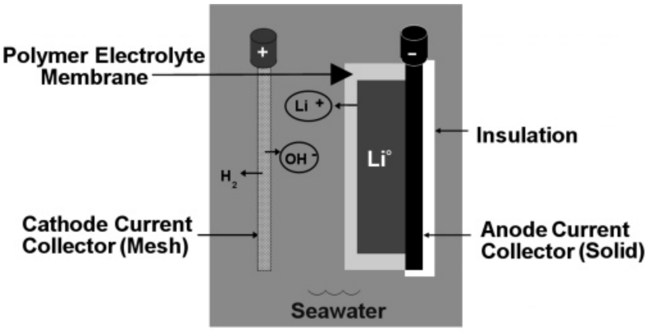

**Figure 1.** Schematic of a lithium−seawater battery.

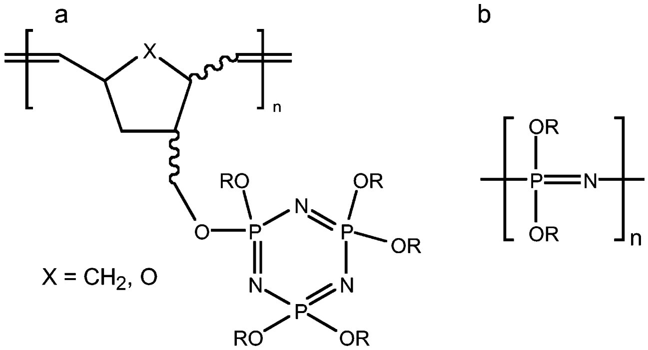

**Figure 2.** Structure of substituted (a) polynorbornenes/polyoxanorbornenes and (b) classical polyphosphazenes.

becomes so thick that the battery ceases to function. Thus, to eliminate the parasitic lithium−water reaction, all contact of the lithium anode surface with water must be prevented. In principle, this can be accomplished by the use of a highly selective polymeric membrane which acts as a barrier between the lithium metal anode and seawater but allows lithium ions to pass through. Figure 1 illustrates the general concept. There are four main components: (1) anode and cathode current collectors, (2) seawater electrolyte/oxidant, (3) lithium metal anode, and (4) polymer electrolyte anode membrane. The most important operational factor of a device of this type is the performance of the polymer electrolyte anode membrane.

In addition to preventing the ingress of water to the lithium metal anode, the other primary function of the polymeric membrane is to conduct lithium cations. The membrane must also protect the lithium anode surface from direct reaction with dissolved gases and ions in seawater such as $O_2$, $CO_2$, $N_2$, $Fe^{3+}$, and $HCO_3^-$. Moreover, it must maintain adherence to the lithium anode surface and retain structural, mechanical, and chemical integrity during storage and normal operation. Thus, a hybrid polymer system, which combines seemingly conflicting properties, is needed to meet all the requirements of an anode membrane material. This is a major challenge for both the design and synthesis of polymeric materials.

Previous work in our program utilized ring-opening metathesis polymerization methods to produce polynorbornenes[1] and poly(oxanorbornenes)[2] with pendent cyclotriphosphazenes as solid polymer electrolytes (Figure 2a). In these studies oligoethyleneoxy side chains of various lengths were linked to a cyclotriphosphazene unit, which was itself connected to the backbone of polynorbornene or poly(oxanorbornene). The cyclotriphosphazene units possess five sites per polymer repeat unit available for property tuning. The ability to utilize five side groups per repeat unit gives a higher density of functional side units than can be obtained for nearly all other polymers (Figure 2). Therefore, a wider variation in polymer properties can be generated by small compositional changes within the side group array. However, oligoethyleneoxy units are hydrophilic, which caused the earlier membranes to transmit water as well as lithium ions. In addition, when compared to linear polyphosphazenes, the polynorbornene backbone should increase the overall hydrophobicity of the polymer and could yield higher glass transition temperatures to improve the film-forming properties.

Other studies in our program utilized pendent-cyclotriphosphazene *polyoctenamers*.[3] Each of the cyclotriphosphazene groups bore both hydrophobic 2,2,2-trifluoroethoxy or 2,2,3,3,4,4,5,5-octafluoropentoxy and lithium ion conductive 2-(2-methoxyethoxy)ethoxy side chains. Polymers with these side groups conducted lithium cations at modest ionic conductivities ($10^{-6}$ S/cm) and showed good surface hydrophobicity (static water contact angle range, 95−112°). However, a disadvantage of these membranes proved to be the need for a free salt dissolved in the membrane to generate measurable ionic conductivities. The addition of a "mobile" salt to the polymer matrix provides an increased likelihood of diffusion-induced concentration gradients, which lead to increased resistance through the polymer electrolyte matrix. Leaching of the salt to the surface of the membrane is also possible over extended periods of storage time. An attractive alternative is the use of single-ion conductors, which incorporate an anion of a salt either into the polymer backbone (Figure 3a) or in a pendent group that is covalently linked to the polymer backbone (Figure 3b).[12−15] Immobilization of the anion should prevent diffusion and leaching. Thus, this class of materials could be promising anode membrane materials.

Here we report the synthesis, characterization, ionic conductivity, and hydrophobicity of prototype lithium-based amphiphilic single-ion conductive polymer electrolytes. Ring-opening metathesis polymerization (ROMP) techniques were used to copolymerize two different types of pendent cyclotriphosphazene norbornenemethoxy-based monomers. The cyclotriphosphazene unit of one comonomer bore 2-(2-phenoxyethoxy)ethoxy (PhEE) side groups. These groups were utilized because of their similarity to 2-(2-methoxyethoxy)ethoxy units, which are known to readily support ion transport.[16−19] However, the terminal phenyl group was expected to increase both the hydrophobicity and the glass

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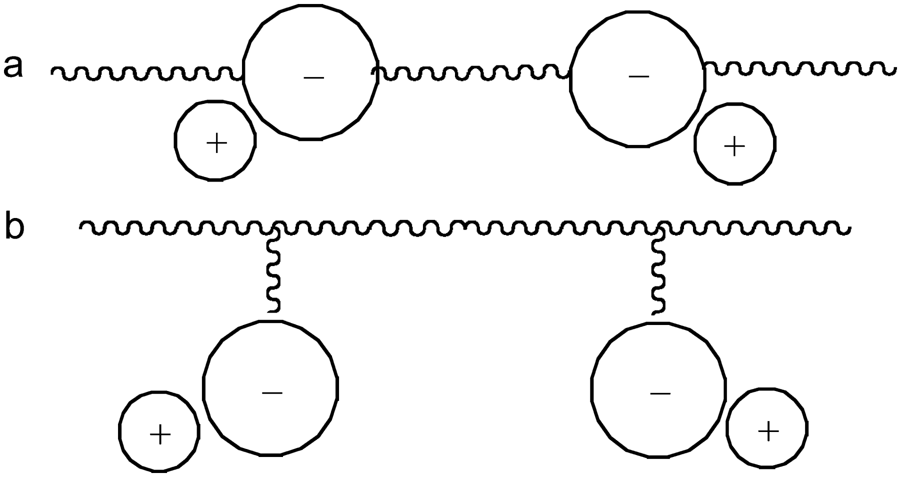

**Figure 3.** Schematic structures of (a) backbone-incorporated and (b) pendent-incorporated single-ion conductors.

transition temperature of the polymer to produce a more water-resistant and robust material. The second type of comonomer carried single-ion conductive side groups linked to the cyclotriphosphazene unit. These provided a lithium cation source. For this purpose, 4-(lithium carboxalato)-phenoxy (LiOOCPh) side groups were used because (1) the phenoxy unit should increase the polymer glass transition temperature[20] and (2) polymerization may be carried out with the use of the propylcarboxylato (protected) derivative to allow a more controlled polymerization due to the absence of the free carboxylic acid units. A free carboxylic acid group could coordinate with the polymerization catalyst and, thus, reduce its efficiency. Various ratios of the comonomers were copolymerized to investigate how the change in composition alters the thermal, ionic conductive, and hydrophobic properties.

## Experimental Section

**Materials.** 5-Norbornene-2-methanol (95%) was obtained from City Chemicals LLC and was used as received. 2-(2-Chloroethoxy)-ethanol (99%), potassium carbonate (99+%), propyl 4-hydroxybenzoate (99+%), ethyl vinyl ether (99%), [bis(tricyclohexylphosphine)benzylidenyl]ruthenium(IV) dichloride (97%), sodium hydride (60%, mineral oil dispersion), magnesium sulfate (98%), and lithium hydroxide (98+%) were obtained from Sigma-Aldrich Co. and used as received. Phenol (99+%), lithium *tert*-butoxide (98+%), and potassium *tert*-butoxide (98+%) were obtained from Acros Organics and used as received. Hexachlorocyclotriphosphazene was obtained from Ethyl Corp./Nippon Fine Chemical and was recrystallized from heptane and sublimed at 0.1 mmHg at 30 °C before use. Polybis(2-(2-methoxyethoxy)ethoxy)phosphazene (MEEP) was synthesized according to literature procedures.[16] All solvents were anhydrous[21] and were obtained from EM Science unless otherwise noted.

**Equipment.** High-field $^1$H (360.14 MHz), $^{13}$C (90.56 MHz), and $^{31}$P (145.79 MHz) NMR spectra were recorded using a Bruker AMX-360 NMR spectrometer. $^1$H and $^{13}$C NMR spectra were referenced to external tetramethylsilane, while $^{31}$P NMR spectra were referenced to external 85% phosphoric acid. $^{13}$C and $^{31}$P NMR spectra were proton decoupled. Mass spectra were collected using a Micromass Quattro-II triple quadrupole mass spectrometer. Molecular weights and polydispersities were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, Phenomenex Phenogel 10 $\mu$m linear columns, and calibrated versus polystyrene standards. Sample elution was carried out at 40 °C with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Alfa Aesar) in stabilized tetrahydrofuran (THF; EMD) at a flow rate of 1.0 mL/min. Thermal transitions were determined through analysis via a TA Q10 differential scanning calorimeter. Calibration was accomplished with indium, water, and cyclohexane standards. All analyses were over a range of $-100$ to $+100$ °C at a heating rate of 10 °C/min. Static water contact angle measurements were obtained using a Rame-Hart, Inc., model 100-00 contact angle goniometer. Five static water contact angles were obtained at room temperature for each solid polymer electrolyte, and an average and standard deviation value was calculated. All reactions were carried out under an inert atmosphere of argon gas. Ionic conductivity measurements were obtained using a Hewlett-Packard 4192A LF impedance analyzer at a potential of 0.1 V with an alternating current frequency range of 5 Hz to 1 MHz. The samples were placed between platinum disk electrodes with a Teflon O-ring spacer, and the polymer electrolyte cell was compressed between aluminum blocks held in a Teflon fixture. Electrical leads were attached between the impedance analyzer, and the polymer electrolyte cell sample holder. All ionic conductivity measurements were carried out over a temperature range of 25−80 °C under an inert atmosphere of dry argon.

**Synthesis of 2-(2-Phenoxyethoxy)ethanol (2).** Potassium carbonate (216.4 g, 1.57 mol) was suspended in *N*,*N*-dimethylformamide (1.75 L). A solution of phenol (108.0 g, 1.15 mol) in *N*,*N*-dimethylformamide (250 mL) was added and stirred via mechanical means. 2-(2-Chloroethoxy)ethanol (130.0 g, 1.04 mol) was added dropwise, and the reaction mixture was heated to 140 °C for 24 h. The reaction solution was cooled to room temperature and filtered, and the solvent was distilled under reduced pressure (100 °C, 0.1 mmHg). The crude product was dissolved in diethyl ether (600 mL) and washed with a 0.5 M aqueous sodium hydroxide solution (3 × 150 mL). The aqueous layers were combined and washed with diethyl ether (600 mL). The diethyl ether layers were combined and dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure (slight heat, 0.1 mmHg) to yield 75.0 g of **2** (39% yield). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 7.18 (t, -CH$_2$O*Ar*, $J = 7.0$ Hz, 2H), 6.86 (t, -CH$_2$O*Ar*, $J = 7.1$ Hz, 1H), 6.83 (t, -OCH$_2$O*Ar*, $J = 7.0$ Hz, 2H), 4.01 (t, -OCH$_2$C*H*$_2$OAr, $J =$

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4.7 Hz, 2H), 3.73 (t, -OC$H_2$CH$_2$OAr, $J$ = 4.7 Hz, 2H), 3.64 (t, HOC$H_2$CH$_2$O-, $J$ = 4.5 Hz, 2H), 3.55 (t, HOCH$_2$C$H_2$O-, $J$ = 4.4 Hz, 2H), 2.76 (s, -O$H$, 1H). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 158.74 (C−Ar), 129.64 (C−Ar), 121.02 (C−Ar), 114.72 (C−Ar), 72.80 (C-2), 69.65 (C-4), 67.33 (C-3), 61.56 (C-1). MS = $m/z$ 183 (MH$^+$).

**Synthesis of 5-Norbornene-2-methoxypentachlorocyclotriphosphazene (Monomer 3).** The synthesis of **3** and subsequent substitution was adapted from a similar procedure.[9] 5-Norbornene-2-methanol (75.0 g, 604 mmol) was added to a solution of potassium *tert*-butoxide (72.6 g, 647 mmol) in THF (1.5 L), and the mixture was stirred at room temperature for 16 h. The potassium salt solution of 5-norbornene-2-methanol was cooled to −78 °C and added dropwise to a solution of hexachlorocyclotriphosphazene ((NPCl$_2$)$_3$; 300.0 g, 863 mmol) in THF (2.5 L) at −78 °C. The reaction mixture was then stirred and warmed to room temperature overnight. THF was removed via rotary evaporation, and the crude product was dissolved in diethyl ether (700 mL) and washed with water (2 × 500 mL). The aqueous layers were combined and washed with diethyl ether (700 mL). The diethyl ether layers were combined, dried over magnesium sulfate, and filtered. The solution was then concentrated via rotary evaporation, and excess hexachlorocyclotriphosphazene was removed by sublimation (0.1 mmHg at 40 °C for 24 h) to leave 163.3 g (77.8% yield) of a brown viscous oil. $^1$H NMR (CDCl$_3$, ppm): $\delta$ 6.01 (br m, -$H$C═C$H$-, 2H), 4.75 (br s, -OC$H_2$Nb, 2H), 1.04−3.28 (unresolvable, exo and endo isomers of norbornene, 7 H). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ (exo and endo isomers of norbornene) 137.56, 133.22, 131.18, 127.68, 66.76, 49.36, 44.56, 43.04, 42.13, 41.52, 39.01, 34.43 30.75, 28.72. $^{31}$P NMR (THF-$d_6$, ppm): $\delta$ 24.44 (d, $J$ = 55.2 Hz, 2P), 16.29 (t, $J$ = 55.3 Hz, 1P). MS = $m/z$ 434 (MH$^+$).

**Synthesis of 5-Norbornene-2-methoxypentakis(2-(2-phenoxyethoxy)ethoxy)cyclotriphosphazene (Monomer 4).** A solution of **2** (54.7 g, 350 mmol) in THF (300 mL) was added dropwise to a suspension of 60% sodium hydride (14.0 g, 344 mmol) in THF (300 mL) and stirred for 16 h. The solution of the sodium salt of **2** was then added dropwise to a solution of **3** (25.0 g, 57.4 mmol) in THF (750 mL) and stirred for 18 h. THF was then removed via rotary evaporation, and the crude product reaction mixture was dissolved in diethyl ether (1 L). The solution was washed with water (3 × 200 mL). The diethyl ether layers were combined, dried over magnesium sulfate, and filtered. The diethyl ether was removed via rotary evaporation, and the residual diethyl ether was removed under reduced pressure (room temperature, 0.1 mmHg) to leave 60.1 g (89.9% yield) of a yellow viscous oil. $^1$H NMR (CDCl$_3$ , ppm): $\delta$ 7.26 (m, -OCH$_2$CH$_2$O$Ar$, 2H), 6.93 (m, -OCH$_2$CH$_2$O$Ar$, 1H), 6.89 (m, -OCH$_2$CH$_2$O$Ar$, 2H), 6.04 (br m, -$H$C═C$H$-, 2H), 4.09 (m, -POC$H_2$CH$_2$OCH$_2$C$H_2$OAr, 4H), 3.82 (m, -OC$H_2$CH$_2$OAr, 2H), 3.74 (m, -POCH$_2$C$H_2$O-, 2H), 3.61 (br s, -OC$H_2$Nb, 2H), 0.71−2.12 (unresolvable, exo and endo isomers of norbornene, 7 H).$^{13}$C NMR (CDCl$_3$ , ppm): $\delta$ (exo and endo isomers) 160.01, 137.63, 136.96, 131.94, 129.64, 122.94, 114.87, 72.80, 69.65, 67.36, 67.33, 61.56, 49.80, 38.91, 38.82, 33.85, 30.78, 28.40. $^{31}$P NMR (CDCl$_3$ , ppm): $\delta$ 18.15 (m, 3P). MS = $m/z$ 1165 (MH$^+$).

**Synthesis of 5-Norbornene-2-methoxypentakis(4-propylcarboxalatophenoxy)cyclotriphosphazene (Monomer 5).** The same synthetic procedure was used as for monomer **4** to produce 45.6 g (86.0% yield) of a yellow viscous oil. Reagent quantities: propyl 4-hydroxybenzoate (50.5 g, 280 mmol), 60% sodium hydride (11.0 g, 275 mmol), and monomer **3** (20.0 g, 45.9 mmol). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 7.95 (m, -PO$Ar$COOPr, 2H), 7.18 (m, -PO$Ar$COOPr, 2H), 4.28 (t, -OC$H_2$CH$_2$CH$_3$, 2H), 6.05 (br m, -$H$C═C$H$-, 2H), 1.78 (q, -OCH$_2$C$H_2$CH$_3$, 2H), 1.05 (t, -OCH$_2$CH$_2$C$H_3$, 3H), 3.40 (br s, -OC$H_2$Nb, 2H), 0.79−1.98 (unresolvable, aliphatic-Nb, 7 H).$^{13}$C NMR (CDCl$_3$, ppm): $\delta$ (exo and endo isomers) 165.65, 137.56, 132.03, 131.92, 127.65, 120.72, 115.34, 66.79, 49.41, 45.27, 43.72, 42.35, 41.49, 38.91, 33.91, 30.98, 29.78, 28.57, 22.03, 10.50. $^{31}$P NMR (CDCl$_3$, ppm): $\delta$ 10.32 (m, 3P); MS = $m/z$ 1154 (MH$^+$).

**Procedure for Ring-Opening Metathesis Polymerization.** Monomer **4** (9.01 g, 7.74 mmol, 0.90 equiv) and monomer **5** (0.99 g, 0.86 mmol, 0.10 equiv) were combined, degassed under reduced pressure (room temperature, 0.1 mmHg), and dissolved in THF (20 mL). A solution of initiator (bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (**1**); Grubbs' first generation catalyst;28 mg, 0.035 mmol; 300:1 monomer:initiator), in CH$_2$Cl$_2$ (1 mL) was added quickly to the monomer solution and stirred for 90 min. The reaction was then terminated with ethyl vinyl ether (1 mL). The polymer solution was concentrated under vacuum (room temperature, 0.1 mmHg) and dialyzed (12−14 K MWCO) against THF for 3 days. The polymer solution was then concentrated and precipitated into hexanes, where the product was collected and dried under reduced pressure (room temperature, 0.1 mmHg) to yield 4.80 g (48% yield) of polymer **6**. The average repeat unit composition was calculated from $^1$H NMR peak integration. Similar chemical shifts were observed for polymers **7**−**9**.

For **6**, average repeat unit composition: **4**, 89.1%; **5**, 10.9%). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 7.91 (br m, -PO$Ar$COOPr, 2H), 7.80 (br m, -PO$Ar$COOPr, 2H), 7.20 (br m, -CH$_2$O$Ar$, 2H), 7.93 (br m, -CH$_2$O$Ar$, 1H), 6.83 (br m, -CH$_2$O$Ar$, 2H), 5.24 (br m, -$H$C═C$H$-, 2H), 4.23 (br m, -OC$H_2$CH$_2$CH$_3$, 2H), 4.06 (br s, -OC$H_2$CH$_2$OAr, 2H), 3.97 (br s, -POC$H_2$CH$_2$O-, 2H), 3.82 (br m, -OC$H_2$Nb, 2H), 3.65 (br s, -POCH$_2$C$H_2$OC$H_2$CH$_2$OAr, 4H), 1.75 (br m, -OCH$_2$C$H_2$-CH$_3$, 2H), 1.03 (br m, -OCH$_2$CH$_2$C$H_3$, 3H), 0.87−2.61 (unresolvable, exo and endo isomers of norbornene, 7H). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 167.75, 158.71, 137.87, 137.21, 132.98, 131.94, 129.44, 123.12, 120.81, 115.12, 114.55, 70.21, 69.63, 67.27, 66.87, 65.08, 61.45, 49.84, 43.89, 40.69, 35.21, 30.01, 22.11, 11.05. $^{31}$P NMR (CDCl$_3$, ppm): $\delta$ 18.3 (s, 6P). $M_n$ = 106 kDa; $M_w$ = 123 kDa; PDI = 1.16.

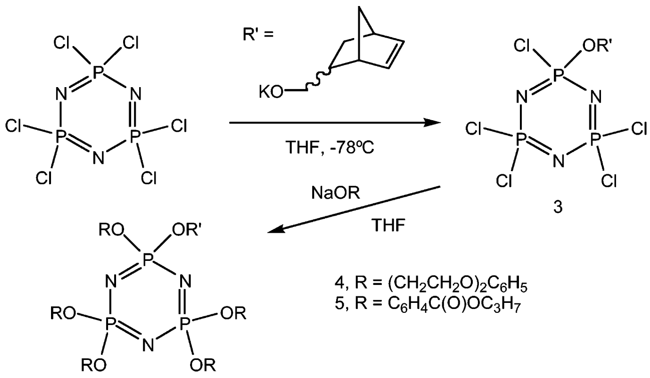
Polymer **7** was synthesized in a manner similar to that described for polymer **6** using monomer **4** (8.50 g, 7.30 mmol, 0.85 equiv) and monomer **5** (1.49 g, 1.29 mmol, 0.15 equiv) in a solution of THF (20 mL) and a solution of **1** (28 mg, 0.035 mmol) in CH$_2$Cl$_2$ (1 mL). After purification via dialysis, the THF was removed under reduced pressure (room temperature, 0.1 mmHg) to yield 3.3 g (33% yield) of polymer **7**. The average repeat unit composition: **4**, 86.3%; **5**, 13.7%. $M_n$ = 105 kDa. $M_w$ = 122 kDa. PDI = 1.16.

Polymer **8** was synthesized in a manner similar to that for polymer **6** using monomers **4** (8.01 g, 6.90 mmol, 0.80 equiv) and **5** (1.98 g, 1.72 mmol, 0.20 equiv) in a solution of THF (20 mL) and a solution of **1** (28 mg, 0.035 mmol) in CH$_2$Cl$_2$ (1 mL). After purification via dialysis, the THF was removed under reduced pressure (room temperature, 0.1 mmHg) to yield 4.5 g (45% yield) of polymer **8**. Average repeat unit composition: **4**, 81.2%; **5**, 18.8%. $M_n$ = 94 kDa. $M_w$ = 109 kDa. PDI = 1.16.

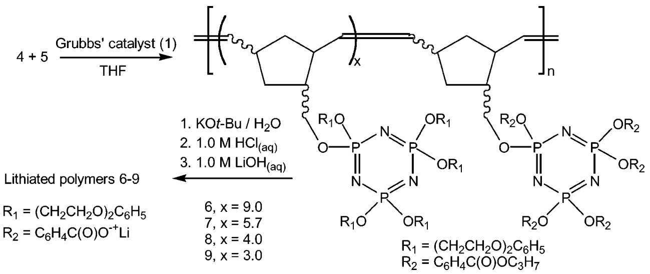
Polymer **9** was synthesized in a manner similar to that for polymer **6** using monomer **4** (7.52 g, 6.50 mmol, 0.75 equiv) and monomer 5 (2.48 g, 2.15 mmol, 0.25 equiv) in a solution of THF (20 mL) and a solution of **1** (28 mg, 0.035 mmol) in CH$_2$Cl$_2$ (1 mL). After purification via dialysis the THF was removed under reduced pressure (room temperature, 0.1 mmHg) to yield 4.9 g (49% yield) of polymer **9**. Average repeat unit composition: **4**, 78.0%; **5**, 22.0%. $M_n$ = 105 kDa. $M_w$ = 124 kDa. PDI = 1.18.

**General Procedure for Deprotection and Lithiation of Polymers 6−9.** Deprotection of the propyl ester groups in polymers **6**−**9** was carried out by treating a given amount of polymer in THF with 7 equiv of potassium *tert*-butoxide and 2 equiv of water for 48 h. The polymer was then acidified by precipitation into 1.0 M HCl(aq), collected, and dried under reduced pressure (60 °C, 0.1

**Scheme 1. Synthesis of Norbornene-Based Cyclotriphosphazene Monomers 4 and 5**



**Scheme 2. Copolymerization of Monomers 4 and 5 To Yield Polymers 6−9**



mmHg). Acidification could not be confirmed because the carboxylic acid peak in the $^1$H NMR could not be resolved. However, the disappearance of the propyl peaks in the $^1$H NMR [$(CDCl_3$, ppm) $\delta$ 1.03 (br m, $-OCH_2CH_2CH_3$, 3H), 1.75 (br m, $-OCH_2CH_2CH_3$, 2H), 4.22 (br m, $-OCH_2CH_2CH_3$, 2H)] and $^{13}$C NMR [$(CDCl_3$, ppm) $\delta$ 65.08 ($OCH_2CH_2CH_3$), 22.11 ($OCH_2CH_2CH_3$), 11.05 ($OCH_2CH_2CH_3$)] indicated full deprotection.

Lithiation of polymers **6**−**9** was accomplished by multiple precipitations of the deprotected polymer into 1.0 M LiOH(aq). Once the polymer was collected, it was washed with water and dried under reduced pressure (60 °C, 0.1 mmHg). The polymer was then dissolved in methanol and dialyzed (1 K MWCO) against methanol for 5 days to remove any residual ions. The methanol was then removed under reduced pressure (40 °C, 0.1 mmHg). The lithiated derivatives for polymers **6**−**9** were transparent light brown tough rubbery solids and were recovered in quantitative yields to their propyl ester counterpart.

**Preparation of Polymer Electrolyte Samples for Impedance Analysis.** Lithiated polymers **6**−**9** were dried under vacuum at 40 °C for 1 week before fabrication. Each polymer (0.3 g) was dissolved in dry methanol and poured into a 2 cm × 2 cm mold. The methanol was then air-evaporated in a dry environment, and the samples were subjected to reduced pressure (40 °C, 0.1 mmHg, 72 h) to remove any residual methanol. Once dried, the appropriate size sample was cut from each film, and a small amount of a 10% MEEP−10 mol % $LiBF_4$ (w/v) in THF solution was painted lightly onto each side of the electrolyte sample. The polymer electrolyte cell was then assembled and exposed to vacuum (room temperature, 0.1 mmHg, 12 h) to remove residual solvent. Following the exposure to vacuum, the impedance analysis sample holder was assembled and measurements were carried out.

**Preparation of Films for Static Water Contact Angle Measurements.** Lithiated polymers **6**−**9** were dried under vacuum at 40 °C for 1 week before fabrication. Each polymer was dissolved in methanol (30% (w/v)). The polymer solution was poured onto a glass substrate, and the methanol was air-evaporated in a dry environment and dried under a reduced pressure (room temperature for 24 h, 40 °C for 72 h, 0.1 mmHg) to remove any residual methanol.

## Results and Discussion

**Synthesis of Monomers.** The synthetic route employed to produce monomers **4** and **5** is shown in Scheme 1. The first step was the reaction of $(NPCl_2)_3$ with the potassium salt of 5-norbornene-2-methanol, which yielded a brown viscous oil, 5-norbornene-2-methoxypentachlorocyclotriphosphazene (**3**). Nucleophilic replacement of the remaining chlorine atoms on the cyclotriphosphazene by the appropriate sodium alkoxide was carried out to obtain single-substituent monomers **4** and **5** as transparent, yellow viscous oils in yields of approximately 86−90%.

**Synthesis of Polymers.** Polymers **6**−**9** were synthesized under an inert atmosphere of argon at ambient temperature via ROMP of the corresponding monomers (Scheme 2). Copolymerization reactions were attempted with Grubbs' first-generation catalyst ([bis(tricyclohexylphosphine)benzylidenyl]ruthenium(IV) dichloride (**1**) at a monomer-to-initiator ratio of 300:1 and were terminated after 90 min by the addition of ethyl vinyl ether. The polymer solutions were then dialyzed against THF, concentrated, and precipitated into hexanes to yield polymers **6**−**9** in satisfactory yields (33−49%) as transparent brown tough rubbery solids. Each polymer was readily soluble in organic solvents such as tetrahydrofuran, methylene chloride, and chloroform. The ester groups of polymers **6**−**9** were deprotected under basic conditions and then acidified by multiple precipitations into 1.0 M HCl(aq). Lithiation was then performed by multiple precipitations into 1.0 M LiOH(aq). Following purification via dialysis the lithiated derivatives of polymers **6**−**9** were obtained in quantitative yields, on the basis of their propyl ester counterparts, as transparent light brown tough rubbery solids.

Parallel syntheses of each 5-norbornene-2-methoxy monomer was carried out with *cyclooctene-5-oxy* units in place of the 5-norbornene-2-methoxy units in order to examine the influence of backbone architecture on the polymer's physical, thermal, conductive, and hydrophobic properties. However, when the cyclooctene-5-oxy monomers were copolymerized with Grubbs' second-generation catalyst, the molecular weights obtained were insufficient to warrant further characterization. Despite the use of this catalyst, which is significantly more active than its first-generation predecessor,[22−24] the steric constraints of the cyclooctenеoxy-based monomers probably reduced the accessibility of the monomers to the propagating chain end. This, in combination with the low ring strain of cyclooctene and low reactivity of its propagating metal−carbene complex,[25,26] led to limited

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**Table 1. Glass Transition Temperature ($T_g$), Ionic Conductivity ($\sigma$), and Static Water Contact Angle (sWCA) Data for Polymers 6−9**

| polymer | $T_g$ (°C) | $T_g$ (°C) (Li)[a] | $\sigma^a$ ($10^{-5}$ S/cm) at 25 °C | at 80 °C | sWCA[a] (deg) |
|---|---|---|---|---|---|
| **6** | −16 | −8 | 0.59 | 3.1 | 76 ± 2 |
| **7** | −15 | −7 | 0.35 | 2.1 | 80 ± 3 |
| **8** | −15 | −7 | 0.20 | 1.6 | 76 ± 3 |
| **9** | −14 | −5 | 0.07 | 0.39 | 80 ± 4 |

[a] Analyses performed on the lithiated derivatives.

degrees of polymerization and low molecular weights for each polymer. Thus, all the work described here involved the norbornene-based monomers.

**Polymer Characterization.** Polymers **6−9** were characterized by $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopies. $^1$H NMR peak integration of the aromatic protons on the 2-(2-phenoxyethoxy)ethoxy (PhEE) and 4-propylcarboxalatophenoxy (PrOOCPh) substituents was used to confirm their ratios on the cyclotriphosphazene units. $^1$H and $^{13}$C NMR spectroscopies were utilized to examine the effectiveness of the deprotection protocol. Disappearance of the propyl ester $^1$H and $^{13}$C NMR peaks indicated complete deprotection.

Gel permeation chromatography of the propyl ester polymer derivatives was used to estimate the molecular weights of protected polymers **6−9**, which had number average molecular weight ($M_n$) values from 94 to 105 kDa and weight average molecular weight ($M_w$) values from 109 to 125 kDa. Typically polydispersity index (PDI) values for equilibrium controlled polymerizations of this type are approximately 2.0;[27] however, the PDI values for polymers **6−9** were significantly lower at 1.16−1.18. A possible explanation for the lower PDI values is that these polymerizations were terminated before they reached a high degree of polymerization (average DP = 96). At higher degrees of polymerization branching and chain recombination can occur, which can lead to higher PDI values.

**Morphological Properties.** The morphological properties of polymers **6−9** and their lithiated derivatives were examined by differential scanning calorimetry. The glass transition temperature ($T_g$) values are summarized in Table 1. Each polymer gave a single $T_g$ and no melting transition, which suggest that the polymers are completely amorphous. The $T_g$ values of polymers **6−9** ranged from −16 (**6**) to −14 °C (**9**). The lithiated derivatives of polymers **6−9** had slightly higher $T_g$ values compared to their propyl ester counterparts. The $T_g$ values ranged from −8 (**6**) to −5 °C (**9**).

**Temperature-Dependent Ionic Conductivity.** Initial attempts to measure the ionic conductivities of lithiated polymers **6−9** were unsuccessful due to poor contact between the electrolyte sample and the platinum disk electrodes. To achieve good contact between the electrolyte samples and the electrodes, a layered electrolyte sample was fabricated. This was accomplished by utilizing a second polymer, poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene], as an adhesive between each platinum disk electrode and the electrolyte sample. This polymer is a well-studied solid polymer electrolyte with known ionic conductivity data.[16−19] Urquidi-Macdonald and co-workers have shown that MEEP has good adhesion to lithium metal.[28] In that work MEEP was utilized as an adhesion layer between lithium metal and a hydrophobic cosubstituted polyphosphazene. The MEEP−lithium metal interface was shown to be stable via cyclic voltammetry and hydrogen gas evolution measurements.

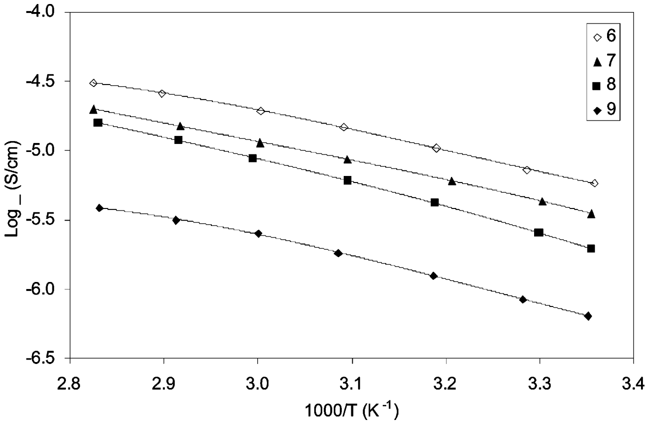

**Figure 4.** Temperature-dependent ionic conductivities of polymers **6−9**.

A control experiment was carried out to ascertain if such a layered electrolyte assembly would affect the ionic conductivity measurements of lithiated polymers **6−9**. This experiment consisted of measuring the ionic conductivity of a poly(ethylene oxide)−lithium tetrafluoroborate (PEO−LiBF$_4$) sample and comparing that value to a layered electrolyte sample with PEO and MEEP. PEO was used because it is one of the most widely studied solid polymer electrolytes which typically shows ionic conductivities around $10^{-8}$ S/cm.[29,30] The ionic conductivity was initially measured without the MEEP−LiBF$_4$ adhesive layers and then subsequently with the MEEP−LiBF$_4$ layer. The difference in ionic conductivities between the control samples was only $6.0 \times 10^{-8}$ S/cm. This small variation in ionic conductivity, when compared to the orders of magnitude higher ionic conductivities for polymers **6−9**, indicated that the layered electrolyte sample technique is an effective means for measuring the ionic conductivity of lithiated polymers **6−9** without causing significant discrepancies.

The temperature-dependent ionic conductivity of lithiated polymers **6−9** is shown in Figure 4. Room-temperature ionic conductivities ranged from $5.9 \times 10^{-6}$ (**6**) to $7.0 \times 10^{-7}$ S/cm (**9**) and the 80 °C ionic conductivities ranged from $3.1 \times 10^{-5}$ (**6**) to $3.9 \times 10^{-6}$ S/cm (**9**). The ionic conductivities of each polymer increased in a nonlinear manner as the temperature was increased, which is typical of solid polymer electrolytes.[31] In addition, the ionic conductivities of lithiated polymers **6−9** increased as the content of LiOOCPh-substituted cyclotriphosphazene was decreased. This decrease is attributed to the deficiency of lithium cations available for transport because of inter- and intrachain transient cross-links which utilize lithium cations as a bridge between

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polymer chains. It should be noted that the presence of transient cross-links did not cause a significant change in the $T_g$ values for polymers **6**−**9** (Table 1). This phenomenon, which had previously been observed in polyoctenamer pendent−cyclotriphosphazenes,[3] occurs because the cation coordinative side groups, PhEE, are adequately separated from the polynorbornene backbone and, therefore, have little or no influence on the $T_g$ of the polymer even if they participate in transient cross-links.

**Hydrophobic Properties.** Static water contact angle (sWCA) measurements were utilized to investigate the hydrophobicity of each lithiated polymer. Values for lithiated polymers **6**−**9** are shown in Table 1. The sWCA values ranged from 76 (**6**) to 80° (**9**). Curiously, there were no significant differences in the sWCA values for polymers **6**−**9** on the basis of the measurements and their standard deviations. This suggested that the surface of each polymer film is chemically similar, despite the compositional variations.

The sWCA values generated by these polymers are probably 10−15° lower than those required for a practical device, although the ionic conductivities may be adequate.[32,33] There are two main approaches to improving the hydrophobicity of the polymers. The first requires a modification of the amphiphilic side group (PhEE) in order to make the phenyl moiety more hydrophobic. In principle, this can be accomplished by utilizing fluorinated or trifluoromethylated phenol in the synthesis of the PhEE side group. This approach is being investigated. The second strategy employs more of an engineering approach by using a second, more hydrophobic polymer, as part of a layered membrane. The hydrophobic polymer would be located on the seawater-exposed side of the anode membrane, while the other side of the membrane would be cemented to the lithium mental anode by an ionic conductive membrane such as MEEP.

**Comparison with Classical Polyphosphazene Electrolytes.** The polynorbornene-based amphiphilic single-ion conductive polymer electrolytes have several advantages over existing classical linear polyphosphazene electrolytes for lithium−seawater batteries. Thus, although MEEP with dissolved lithium triflate gives higher ionic conductivities, in the range of $10^{-4}$ S/cm at room temperature, it is a very hydrophilic polymer with $T_g = -83$ °C and a tendency to undergo liquidlike viscous flow.[34] MEEP-based linear *co*-polymers designed to increase both dimensional stability and hydrophobicity include systems that contain 2,2,2-trifluoroethoxy (TFE) cosubstituents.[35] These require the addition of 30% propylene carbonate to generate ionic conductivities in the range of $10^{-5}$ to $10^{-4}$ S/cm, which is acceptable for a lithium secondary battery but unacceptable for a lithium−seawater system. Polymers with lithium sulfonamide (LiSI)[36] and MEEP cosubstituents are hydrophilic single-ion conductive polymer electrolytes with low ambient temperature ionic conductivities in the range of $10^{-6}$ to $10^{-7}$ S/cm. The low conductivity and tendency for water absorption make them unacceptable for a primary seawater battery. However, the classical polyphosphazenes such as MEEP are exceedingly adhesive, and this points to their use as the adhesive layer between a metallic lithium anode and a hydrophobic single-ion conductive membrane in contact with water.

## Conclusions

The membranes synthesized in this work provide encouragement for the view that polymers can be designed that combine the seemingly opposing properties of lithium ion conduction and water repellency. Two types of 5-norbornene-2-methanoxy monomers were copolymerized, (a) 4-(propylcarboxyalato)phenoxy-containing (PrOOCPh), which was subsequently lithiated to yield 4-(lithium carboxyalato)-phenoxy (LiOOCPh), and (b) 2-(2-phenoxyethoxy)ethoxy-containing (PhEE). The LiOOCPh-containing cyclotriphosphazenes provided a source for lithium cations, while the PhEE-containing cyclotriphosphazenes functioned as lithium ion solvating and hydrophobic groups. The polymers showed ionic conductivities near $10^{-6}$ S/cm at room temperature and $10^{-5}$ S/cm at elevated temperatures, with static water contact angles around 80°. Polymer **6**, which contained 10% LiOOCPh and 90% PhEE, gave the highest ionic conductivity ($5.9 \times 10^{-6}$ S/cm) with a modest static water contact angle of 76°. Although adequate ionic conductivities were obtained for lithium metal anode membrane applications, and the glass transition temperatures are below 0 °C, the hydrophobic properties of the polymers need to be improved. This aspect is currently being investigated through two different strategies: (1) modification of the amphiphilic side groups with fluoro−organic units and (2) use of a hydrophobic polymer in a layered membrane assembly. In addition, alternative single-ion conductive groups, which allow increased dissociation of the lithium cation, are being examined.

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