# Synthesis of Pendent Functionalized Cyclotriphosphazene Polyoctenamers: Amphiphilic Lithium Ion Conductive Materials

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ABSTRACT: The synthesis of novel polyoctenamers with pendent functionalized cyclotriphosphazenes as amphiphilic lithium ion conductive membranes is described. Cyclotriphosphazene monomers were functionalized with one cycloocteneoxy substituent per ring. Two different types of monomer units, one with oligoethyleneoxy cation coordination side groups and the other with hydrophobic fluoroalkoxy side groups, were then prepared. The syntheses of these monomers, their ring-opening metathesis copolymerization, and the characteristics of the resultant polymers are discussed, with an emphasis on the dependence of ionic conductivity and hydrophobicity on polymer composition.

## Introduction

The purpose of this work was the synthesis and investigation of new polymers that are both hydrophobic and lithium ion conductive. A reason for the growing interest in polymers that have this unusual combination of properties is their possible use as lithium anode membranes in lithium/seawater batteries.<sup>1</sup> The hydrophobic character is needed to prevent water ingress to the lithium anode where parasitic lithium-water reactions may occur. An approach to solving this problem involves the utilization of a hydrophobic organic polymer to which is attached both hydrophobic and (hydrophilic) lithium ion conductive side units. Because of the ease with which different groups can be linked to cyclic sixmembered phosphazene rings, these units were chosen as the pendent side groups linked to a polyoctenamer main chain.

Numerous hybrid polymers that contain organic polymer components and either linear or cyclic phosphazenes are known,<sup>2-10</sup> and several polymers with phosphazene rings pendent to organic polymer chains have been described.<sup>11,12</sup> Allen and co-workers utilized addition reactions to polymerize vinyl- and allylsubstituted cyclotriphosphazenes.<sup>13</sup> Polystyrene with pendent oligo(ethyleneoxy)cyclotriphosphazenes, which have applications as polymer electrolytes, was synthesized by Inoue and co-workers using free-radical methods.<sup>12,14</sup> Van de Grampel and co-workers were able to introduce cyclotriphosphazenes into polysiloxanes via hydrosilation techniques.<sup>15</sup> In addition, cyclotriphosphazenes have been linked to polyurethanes by De Jaeger and Dez.<sup>16</sup>

Previous research in our program has demonstrated that ring-opening metathesis polymerization can be used to synthesize polynorbornenes with pendent cyclotriphosphazenes.<sup>17,18</sup> These polymers have the general structure shown in Figure 1. In that earlier work the pendent cyclotriphosphazene was functionalized with various types of oligoethyleneoxy units in order to produce lithium ion-based polymer electrolytes with better dimensional stability than the classical linear poly[bis-(2-(2-methoxyethoxy)phosphazene] (MEEP).

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Figure 1. Structure of pendent cyclotriphosphazene polynorbornenes.

Polyoctenamers are macromolecules prepared by the ring-opening metathesis polymerization (ROMP) of cyclooctene. These polymers have commercial uses in pure and blended elastomers.<sup>19,20</sup> The two stereoisomers associated with this system, cis-polyoctenamer and trans-polyoctenamer, have very different physical properties, as illustrated by their glass transition temperatures at -108 and -65 °C, respectively.<sup>21</sup> Polymers of this type are unique because the backbone can contain various structural repeat units, such as butadiene, ethylene, and substituted ethylene.<sup>19</sup> Although polyoctenamers have the potential to serve as an excellent platform for producing polymers with highly tailored properties, only a limited amount of research has been published on the ring-opening metathesis polymerization of cyclooctene-functionalized monomers.<sup>22-26</sup>

Here we describe the synthesis, characterization, structure-property relationships, and ionic conductivity of amphiphilic lithium-ion conductive solid polymer electrolytes synthesized via the ring-opening copolymerization of cyclooctene-based cyclotriphosphazene monomers. These monomers bear cyclotriphosphazenes units with either cation-solvating etheric or hydrophobic fluoroalkoxy side groups.

The monomers used for copolymerization differed with respect to the side groups linked to the cyclotriphosphazene rings. These side groups were (1) 2-(2methoxyethoxy)ethoxy substituents to provide a solvation source for lithium cations and (2) fluoroalkoxy chains with varying lengths and fluorine content to impart hydrophobicity. Two alternative hydrophobic monomers were utilized. The first bore five 2,2,2trifluoroethoxy substituents per cyclotriphosphazene





Scheme 2. Homopolymers from Monomers 5–7 (Polymers 8–10)



ring, while the second had five 2,2,3,3,4,4,5,5-octafluoropentoxy substituents. Differences in the ratios of the two comonomer types were investigated in an attempt to study the relationship of ionic conductivity and hydrophobicity with composition.

## **Results and Discussion**

**Monomer Synthesis.** The preparation of polyoctenamers with pendent functionalized cyclotriphosphazene rings required the synthesis of cycloocten-5-ol (3).<sup>22</sup> An epoxidation reaction was carried out on *cis*-1,5-cyclooctadiene in the presence of *m*-chloroperoxybenzoic acid. Cycloocten-5-epoxide (2) was then reduced with lithium aluminum hydride to yield compound 3.

The synthetic route employed to produce monomers **5**–**7** is shown in Scheme 1. The first step was the reaction of hexachlorocyclotriphosphazene,  $(NPCl_2)_3$ , with the potassium salt of **3** which yielded cycloocten-5-oxypentakis(chloro)cyclotriphosphazene (**4**). Nucleophilic replacement of the chlorine atoms by the appropriate sodium alkoxide was carried out to obtain singlesubstituent monomers **5**–**7** as transparent, viscous oils in yields of ~70%.

**Polymer Synthesis.** Polymers 8–16 were synthesized under an inert atmosphere of argon at 50 °C via ring-opening metathesis polymerization of the corresponding monomers (Schemes 2 and 3). Initially, polymerization reactions were attempted with Grubbs' first-generation catalyst (bis(tricyclohexylphosphine)-benzylideneruthenium(IV) dichloride). However, this produced extremely low molecular weight polymers which had insufficient dimensional stability to warrant further characterization. A possible reason is the low efficiency of this catalyst with substituted cyclooctene-based monomers.<sup>22</sup> Therefore, all subsequent polymerizations were carried out with tricyclohexylphosphine-

Scheme 3. Copolymers from Monomers 5 and 6 (Polymers 11–13) and from Monomers 5 and 7 (Polymers 14–16)



[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2ylidene][benzylidine]ruthenium(IV) dichloride (1) at a monomer-to-initiator ratio of 300:1 and were terminated after a specific time by the addition of ethyl vinyl ether. The polymer solutions were then concentrated and precipitated into hexanes to yield polymers 8-16 as adhesive gums in satisfactory yields. Each polymer was readily soluble in organic solvents such as tetrahydrofuran, methylene chloride, and chloroform.

The solid polymer electrolytes derived from polymers 8-16 are designated SPEs 17-25, respectively. The solid polymer electrolytes were fabricated by the addition of 10 mol % lithium tetrafluoroborate (LiBF<sub>4</sub>).

Polymer Characterization. Polymers 8-16 were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy. <sup>1</sup>H NMR peak integration of the aliphatic protons on the 2-(2-methoxyethoxy)ethoxy (MEE), 2,2,2-trifluoroethoxy (TFE), and 2,2,3,3,4,4,5,5-octafluoropentoxy (OFP) substituents was used to confirm their ratios on the cyclotriphosphazene units. Attempts to utilize <sup>13</sup>C NMR to examine the influence of the pendent cyclotriphosphazene on the regio- and stereospecificity of the polyoctenamer backbone were inconclusive due to unresolved peaks in the olefinic region. However, the <sup>13</sup>C NMR spectra of unsubstituted polyoctenamer showed two resonances in the olefinic region of the spectra, which correspond to the cis and trans isomers. Therefore, because of the asymmetric substitution of the cyclotriphosphazene-functionalized cyclooctene monomers, head-to-head, head-to-tail, and tail-to-tail repeat units are possible.<sup>22</sup> In addition, analysis of the alkyl region in the <sup>13</sup>C NMR spectra eliminated the possibility of a diblock structure, which suggests that the distribution of each type of cyclotriphosphazene unit is random. The <sup>31</sup>P NMR spectra for the monomers showed typical A<sub>2</sub>B splitting patterns, while the spectra of the polymers were inconclusive due to signal broadening and peak overlap.

Gel permeation chromatography was used to estimate the molecular weights of polymers **8–16**. For polymers **8–10**, the number-average molecular weight  $(M_n)$  values ranged from 89 to 455 kDa and the weight-average molecular weight  $(M_w)$  values ranged from 169 to 819 kDa. For polymers **11–13**, the  $M_n$  values ranged from 250 to 387 kDa and the  $M_w$  values were from 460 to 841 kDa. For polymers **14–16**, the  $M_n$  values ranged from 155 to 489 kDa and the  $M_w$  values were from 255 to 1129 kDa. The polydispersity index (PDI) values of polymer **8–16** were from 1.8 to 2.6. PDI values around 2.0 are typical for equilibrium-controlled polymerizations.<sup>27</sup>

Table 1. Thermal, Ionic Conductivity, and Static Water Contact Angle (sWCA) Data for Solid Polymer Electrolytes (SPEs) 17–25

SPE	$T_{\rm g}(^{\rm o}{\rm C})^a$	$T_{\rm g}(^{\rm o}{\rm C})$	$\begin{array}{c} \sigma  (10^{-5}  \mathrm{S/cm}) \\ (25   ^{\circ}\mathrm{C}) \end{array}$	$\begin{array}{c} \sigma  (10^{-5}  \mathrm{S/cm}) \\ (80   ^{\circ}\mathrm{C}) \end{array}$	sWCA (deg)
17 18 19 20 21 22	-68 -34 -58 -36 -31 -39	$-65 \\ -31 \\ -63 \\ -41 \\ -35 \\ -40 \\ 50$	$1.15 \\ 0.01 \\ 0.02 \\ 0.11 \\ 0.12 \\ 0.23 \\ 0.00$	$\begin{array}{c} 4.45\\ 0.04\\ 0.13\\ 1.32\\ 1.26\\ 2.92\\ 0.60\end{array}$	$\begin{array}{c} 31\pm 2\\ 105\pm 2\\ 113\pm 1\\ 104\pm 1\\ 99\pm 1\\ 95\pm 2\\ 111\pm 1\end{array}$
23 24 25	$^{-49}_{-51}$	$-50 \\ -48 \\ -47$	$0.08 \\ 0.07 \\ 0.08$	0.69 0.66 0.72	$111 \pm 1$ $112 \pm 1$ $111 \pm 1$

<sup>*a*</sup> Data for polymers 8-16 (with no LiBF<sub>4</sub>).

**Thermal Analysis.** The morphological properties of polymers **8–16** and of the corresponding solid polymer electrolytes (SPEs) with lithium tetrafluoroborate **17–25** were examined by differential scanning calorimetry (Table 1).

Polymers 8–16 and SPEs 17–25 were amorphous over the temperature range of -100 to 100 °C. The linkage of the cyclotriphosphazene units to the polyoctenamer backbone led to  $T_{\rm g}$  values similar to or higher than unsubstituted *trans*-polyoctenamer ( $T_{\rm g} = -65$  °C) for all polymers. This suggests that the polyoctenamer backbone is predominately trans. In addition, the bulky cyclotriphosphazene units probably caused a reduction in backbone mobility which contributed to the increase in  $T_{\rm g}$  values for polymers 8–16 compared to unsubstituted *trans*-polyoctenamer.

The glass transition temperature  $(T_g)$  values of polymers 14–16 and SPEs 23–25 were lower than those of polymers 11–13 and SPEs 20–22. A similar decrease in the  $T_g$  values is observed when comparing homopolymer 9 to 10. The  $T_g$  decrease is attributed to the increase in free volume of the system induced by the presence of longer OFP substituents linked to the cyclotriphosphazene rings.

Surprisingly, the  $T_{\rm g}$  values for these polymers showed no change following addition of LiBF<sub>4</sub>. Typically, the addition of a salt to a coordinative polymer causes an increase in the  $T_{\rm g}$  due to transient cross-link formation between lithium cations and coordination sites in the polymer. However, in the systems studied, the MEE substituents, which are capable of coordination to lithium cations, are sufficiently distanced from the polyoctenamer backbone that any transient cross-links that form may not significantly affect the segmental motion of the polymer backbone.

**Ionic Conductivity and Hydrophobicity.** Ionic conductivity and static water contact angle values for SPEs **17–25** are shown in Table 1. The highest ambient temperature ionic conductivity was found for SPE **17** ( $1.15 \times 10^{-5}$  S/cm), which was the most hydrophilic polymer. This SPE contained the highest concentration of MEE-functionalized cyclotriphosphazene units, and these facilitated lithium ion transport. By contrast, SPE's **18** and **19**, which contained only the hydrophobic TFE or OFP-functionalized cyclotriphosphazene units, had the lowest ionic conductivities ((1-2) ×  $10^{-7}$  S/cm).

The temperature-dependent ionic conductivity studies carried out on SPEs 20-25 are shown in Figure 2. A nonlinear increase in ionic conductivity was detected for each SPE as the temperature was raised. This type of temperature-dependent behavior is typical of solid polymer electrolytes.<sup>28</sup> The ionic conductivity values for



Figure 2. Temperature-dependent ionic conductivity for solid polymer electrolytes 20–25.



Figure 3. Ambient temperature ionic conductivity and static water contact angle relationship to composition for solid polymer electrolytes 20–22.

SPEs 20-22 were lower than SPE 17 because they contained a smaller amount of MEE-functionalized cyclotriphosphazene units and were higher than SPE 18, which contained only TFE-functionalized cyclotriphosphazene units (Table 1). In addition, the ambient temperature ionic conductivity values increased from SPE 20 to 22 (Figure 3) as the content of MEE-functionalized cyclotriphosphazene units was increased. This increase is presumably due to a larger number of lithium cation coordination sites provided by the MEE groups, which generated more efficient conductive pathways.

Again, SPEs 23-25 had lower ionic conductivities than SPE 17 but higher than SPE 19 (Table 1). In addition, they had lower ionic conductivities than SPEs 20-22. Moreover, no increase in ambient temperature ionic conductivity was detected as the MEE-functionalized cyclotriphosphazene content in the polymer was increased from SPE 23 to 25 (Figure 4). This is presumably due to the long OFP substituents, which served to disrupt conductive pathways at all ratios.

Static water contact angle (sWCA) values were measured to evaluate the hydrophobicity of SPEs 17–25 (Table 1). Figures 3 and 4 illustrate the relationship between static water contact angle and polymer composition for SPEs 20–22 and 23–25. As shown in Figure 3, the sWCA values for SPEs 20–22 increased as the content of the hydrophobic TFE-functionalized cyclotriphosphazene in the system was increased. By comparison, the sWCA value for SPE 17, which contained all MEE-functionalized cyclotriphosphazene units showed



Figure 4. Ambient temperature ionic conductivity and static water contact angle relationship to composition for solid polymer electrolytes 23–25.

the lowest value. The sWCA value for SPE 18, which contained all TFE-functionalized cyclotriphosphazene units, was similar to that of SPE 20, which contained  $\sim$ 90% TFE-functionalized cyclotriphosphazene units.

SPEs 23–25, with OFP instead of TFE side groups as the hydrophobic substituents, had similar sWCA values (111° to 112°), despite the variation in the OFPfunctionalized cyclotriphosphazene content. Presumably, the extents of phase separation in these three SPEs are similar, so that the hydrophobicity of the surface remained the same, even though the overall fluorine content of the polymer varied over a broad range. This premise is supported by the sWCA value for SPE 19, which contained all OFP-functionalized cyclotriphosphazene units. Here, the sWCA was similar to the values observed for SPE 23–25. This leads us to believe that the surfaces of these SPEs are dominated by hydrophobic OFP units.

## Conclusions

The development of polyoctenamer copolymers with pendent functionalized cyclotriphosphazenes was accomplished via the ring-opening metathesis copolymerization of cyclooctene-based cyclotriphosphazene monomers with 2-(2-methoxyethoxy)ethoxy (MEE) and 2,2,2trifluoroethoxy (TFE) or 2,2,3,3,4,4,5,5-octafluoropentoxy (OFP) substituents. Dimensionally stable high molecular weight polymers were obtained in satisfactory yields. The linkage of the pendent cyclotriphosphazene units to the polyoctenamer backbone resulted in glass transition temperatures similar to or slightly higher than unsubstituted *trans*-polyoctenamer. In addition, the cyclotriphosphazene units allowed both lithium cation solvation and hydrophobicity to be imparted to the final polymers. The temperature-dependent ionic conductivities were typical of solid polymer electrolyte behavior. Different effects on the ionic conductivity and static water contact angle were detected depending on the type of hydrophobic substituent present. The 2,2,2trifluoroethoxy-containing solid polymer electrolytes (20-22) showed decreased ambient temperature ionic conductivity and increased static water contact angle as the amount of the fluorinated unit was increased. Those polymers with 90-60% 2,2,2-trifluoroethoxy groups and 10-40% 2-(2-methoxyethoxy)ethoxy groups showed the best compromise between ionic conductivity and hydrophobicity with values in the range of  $(1-2) \times 10^{-6}$ S/cm and static water contact angles of 95°-104°.

However, the 2,2,3,3,4,4,5,5-octafluoropentoxy-containing solid polymer electrolytes (23-25) underwent no significant change in ambient temperature ionic conductivity ((7–8) ×  $10^{-7}$  S/cm) or static water contact angle (111°-112°) as the amount of this longer fluoroalkoxy group was changed. This is attributed to the ability of the 2,2,3,3,4,4,5,5-octafluoropentoxy substituents to disrupt lithium cation conductive pathways in the polymer matrix by phase separation and to the concentration of the fluorinated units at the polymer surface. Polymers of the types discussed here are prototype candidates for lithium anode membranes in lithium/seawater batteries. Further optimization of the property balances is anticipated with the use of mixed substituent monomers in which each pendent cyclotriphosphazene ring contains both lithium ion solvating and hydrophobic side groups. In addition, alternative ion transport and hydrophobic side groups are being investigated.

#### **Experimental Section**

General. High-field <sup>1</sup>H (360.14 MHz), <sup>13</sup>C (90.56 MHz), and <sup>31</sup>P (145.79 MHz) NMR spectra were recorded using a Bruker AMX-360 NMR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to external tetramethylsilane, while <sup>31</sup>P NMR spectra were referenced to external 85% phosphoric acid. <sup>13</sup>C and <sup>31</sup>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 vs polystyrene standards. Sample elution was carried out at 40 °C with a 0.1 wt % solution of tetra-nbutylammonium nitrate (Alfa Aesar) in THF (EMD). 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 performed over a range of -100 to 100 °C at a heating rate of 10 °C/min. 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-1 MHz. The samples were placed between platinum 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 20-80 °C under an inert atmosphere of dry argon. 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 for each solid polymer electrolyte, and an average and standard deviation value was calculated. All reactions were performed under an inert atmosphere of argon gas.

Materials. cis-1,5-Cyclooctadiene (99+%), m-chloroperoxybenzoic acid (77%), lithium aluminum hydride (95%), 2-(2methoxyethoxy)ethanol (99%), 2,2,2-trifluoroethanol (99%), ethyl vinyl ether (99%), (bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride) (97%), tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2ylidene][benzylidine]ruthenium(IV) dichloride (97%), sodium hydrogen carbonate (99%), sodium hydrogen sulfate (99%), magnesium sulfate (98%), and sodium hydride (95%) were obtained from Sigma-Aldrich Co. and used as received. Potassium tert-butoxide (98+%) was obtained from Acros Organics and used as received. 2,2,3,3,4,4,5,5-Octafluoropentanol (99%) was obtained from TCI, Inc., and used as received. Lithium tetrafluoroborate (99.9985%) was obtained from Alfa Aesar 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. All solvents were anhydrous and were obtained from EM Science and used as received unless otherwise noted. Polyoctenamer was synthesized according to the literature procedure.<sup>22</sup>

**Preparation of Cyclotriphosphazene-Functionalized Monomers.** Synthesis of cycloocten-5-epoxide (2). The synthesis of cycloocten-5-epoxide was carried out as described previously.<sup>22</sup> A solution of *m*-chloroperoxybenzoic acid (357 g, 2.07 mol) in chloroform (4 L) was added dropwise to a solution of *cis*-1,5-cycloctadiene (280 g, 2.59 mol) in tetrahydrofuran (THF) (400 mL) with stirring. The reaction mixture was stirred at room temperature for 18 h, and the resultant 3-chlorobenzoic acid was filtered off. The organic layer was washed with an aqueous solution of 20% (w/v) NaHSO<sub>3</sub>, 10% (w/v) NaHCO<sub>3</sub>, and brine solution. The organic layer was then concentrated via rotary evaporation and purified via column chromatography (silica, 70/30 hexanes/ethyl acetate) to yield 257 g (90% yield) of a colorless oil (2).

Synthesis of cycloocten-5-ol (3). The synthesis of cycloocten-5-ol was carried out as described previously.<sup>22</sup> A solution of **2** (257 g, 2.07 mol) in THF (2.5 L) at 0 °C was added dropwise to a solution of lithium aluminum hydride (39.3 g, 1.04 mol) in THF (1 L) at room temperature. The reaction mixture was stirred for 24 h at room temperature under argon, cooled to 0 °C, and quenched with 30 mL of water. The reaction mixture was allowed to warm to room temperature and filtered. The resultant solution was concentrated via rotary evaporation, and residual THF and water were removed under reduced pressure (room temperature, 0.1 mmHg). Purification via vacuum distillation was performed to yield 240 g (89% yield) of a colorless oil (3).

For **3**, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 5.74 (q, J = 7.8 Hz, -CH=CH–, 1H), 5.63 (q, J = 7.8 Hz, -CH=CH–, 1H) 3.81 (dt,  $-CH_2CH(OH)CH_2-$ , J = 8.1, 5.1 Hz, 1H), 2.29 (s, -OH, 1H), 1.58–2.35 (br m,  $-CH_2-$ , 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 130.14 (C-2), 129.51 (C-1), 72.86 (C-5), 37.63 (C-4), 36.51 (C-6), 25.66 (C-3), 24.91 C-8), 22.80 (C-7). MS = m/z 127 (MH<sup>+</sup>).

Synthesis of cycloocten-5-oxypentakis(chloro)cyclotriphosphazene (monomer 4). The synthesis of 4 and subsequent substitution were adapted from a similar procedure.<sup>18</sup> Compound 3 (59.0 g, 469 mmol) was added to a solution of potassium tert-butoxide (49.4 g, 431 mmol) in THF (2.25 L), and the mixture was stirred at room temperature for 18 h. A solution of hexachlorocyclotriphosphazene (NPCl<sub>2</sub>)<sub>3</sub> (250.0 g, 720 mol) in THF (2.75 L) at -78 °C was added dropwise to the solution of the potassium salt of **3** cooled to -78 °C. The reaction mixture was stirred and allowed to warm to room temperature overnight. THF was removed via rotary evaporation, and the crude product was dissolved in diethyl ether (1 L) and washed with water  $(2 \times 200 \text{ mL})$ . The aqueous layers were combined and washed with diethyl ether (600 mL). The diethyl ether layers were then combined, dried over MgSO<sub>4</sub> overnight, and filtered. The solution was concentrated via rotary evaporation, and the crude product was sublimed (0.1 mmHg at 40 °C for 24 h) to leave the product (4) as a viscous oil (163.7 g, 87% yield).

For 4, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 5.64 (m, -CH=CH-, 2H), 4.69 (m,  $-CH_2CH(O-)CH_2-$ , 1H), 1.56–2.43 (br m,  $-CH_2-$ , 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 130.23 (C-2), 129.78 (C-1), 80.75 (C-5), 34.76 (C-4), 33.84 (C-6), 25.61 (C-3), 24.63 (C-8), 22.46 (C-7). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 22.42 (d, J = 61.5 Hz, 2P), 13.45 (t, J = 61.7 Hz, 1P). MS = m/z 436 (MH<sup>+</sup>).

Synthesis of cyclooctene-5-oxypentakis (2-(2-methoxyethoxy)-ethoxy)cyclotriphosphazene (monomer 5). 2-(2-Methoxyethoxy-)ethanol (51.43 g, 428 mmol) was added dropwise to a suspension of sodium hydride (9.86 g, 411 mmol) in THF (500 mL), and the mixture was stirred for 5 h. The sodium 2-(2-methoxyethoxy)ethoxide solution was then added dropwise to a solution of 4 (30.0 g, 68.5 mmol) in THF (500 mL), and the reaction mixture was stirred overnight under low heat. THF was then removed via rotary evaporation, and the crude product reaction mixture was dissolved in methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) (500 mL). The CH<sub>2</sub>Cl<sub>2</sub> solution was washed with water (3  $\times$  100 mL). The aqueous layers were combined and washed with  $CH_2Cl_2$  (700 mL). The  $CH_2Cl_2$  layers were combined, dried over MgSO<sub>4</sub> overnight, and filtered. The  $CH_2$ - $Cl_2$  was removed via rotary evaporation and under reduced pressure (room temperature, 0.1 mmHg) to produce 26.4 g (68% yield) of viscous oil (5).

For **5**, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 5.61 (m, -CH=CH-, 2H), 4.39 (m,  $-CH_2CH(O-)CH_2-$ , 1H), 4.06 (m,  $OCH_2CH_2O-$ , 10H), 3.69 (m,  $-OCH_2CH_2O-$ , 10H), 3.63 (m,  $-OCH_2CH_2-$ OCH<sub>3</sub>, 10H), 3.52 (m,  $-OCH_2CH_2OCH_3$ , 10H), 3.36 (s,  $-OCH_3$ , 15H), 1.49–2.35 (br m,  $-CH_2-$ , 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 129.71 (C-2), 129.46 (C-1), 78.56 (C-5), 71.90 ( $-OCH_2-CH_2O-$ ), 70.52 ( $-OCH_2CH_2OCH_3$ ), 70.05 ( $-OCH_2CH_2OCH_3$ ), 64.91 ( $-OCH_2CH_2O-$ ), 58.99 ( $-OCH_3$ ), 35.37 (C-4), 34.36 (C-6), 25.54 (C-3), 24.66 (C-8), 22.32 (C-7). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 17.5 (m, 3P); MS = m/z 856 (MH<sup>+</sup>).

Synthesis of cycloocten-5-oxy*pentakis*(2,2,2-trifluoroethoxy)cyclotriphosphazene (monomer **6**). The same synthetic procedure used for monomer **5** was used to produce 48.3 g of monomer **6** (72% yield). Reagent quantities: 2,2,2-trifluoroethanol (55.71 g, 557 mmol), sodium hydride (13.15 g, 548 mmol), monomer **4** (40.0 g, 91.3 mmol).

For **6**, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 5.66 (m, -CH=CH-, 2H), 4.44 (m,  $-CH_2CH(O-)CH_2-$ , 1H), 4.27 (s,  $OCH_2CF_3$ , 10H), 1.43–2.41 (m,  $-CH_2-$ , 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 129.92 (C-2), 129.15 (C-1), 122.45 (q,  $J = 271.7, -CH_2CF_3$ ), 81.22 (C-5), 62.85 (m,  $-OCH_2CF_3$ ), 35.14 (C-4), 34.67 (C-6), 25.56 (C-3), 24.57 (C-8), 21.96 (C-7). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 17.1 (m, 3P); MS = m/z 756 (MH<sup>+</sup>).

Synthesis of cycloocten-5-oxypentakis(2,2,3,3,4,4,5,5-octafluoro-1-pentoxy)cyclotriphosphazene (monomer 7). The same synthetic procedure used for monomer 5 was used to produce 47.2gofmonomer7(73% yield). Reagent quantities: 2,2,3,3,4,4,5,5octafluoro-1-pentanol (64.75 g, 279 mmol), sodium hydride (6.58 g, 274 mmol), monomer 4 (20.0 g, 45.7 mmol).

For **7**, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 6.05 (m,  $-CF_2CF_2H$ , 5H), 5.65 (m, -CH=CH-, 2H), 4.44 (m,  $-CH_2CH(O-)CH_2-$ , 1H), 4.42 (s,  $OCH_2CF_2-$ , 10H), 1.25–2.50 (m,  $-CH_2-$ , 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 129.74 (C-2), 129.19 (C-1), 110.43 (m,  $-CF_2-$ ), 81.40 (C-5), 67.97 ( $-CF_2CF_2H$ ), 62.23 (m,  $-OCH_2-CF_2-$ ), 35.05 (C-4), 34.41 (C-6), 25.41 (C-3), 24.41 (C-8), 21.93 (C-7). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 17.3 (m, 3P); MS = m/z 1416 (MH<sup>+</sup>).

General Procedure for Ring-Opening Metathesis Polymerization. Synthesis of polymer 8. Monomer 5 (5.00 g, 5.8 mmol) was degassed under reduced pressure (room temperature, 0.1 mmHg), dissolved in  $CH_2Cl_2$  (7 mL), and heated to 50 °C. A solution of initiator, tricyclohexylphosphine[1,3bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidine]ruthenium(IV) dichloride (1) (17.0 mg, 0.020 mmol), in  $CH_2Cl_2$  (1 mL) was added quickly to the monomer solution, and the mixture was stirred for 10 min. The reaction was terminated with ethyl vinyl ether (1 mL). The polymer solution was cooled to room temperature, concentrated under vacuum (room temperature, 0.1 mmHg), and precipitated into hexanes three times. The polymer was collected and dried under reduced pressure (room temperature, 0.1 mmHg) to yield 1.70 g (34% yield) of a rubbery gum.

For 8, <sup>1</sup>H NMR ( $d_6$ -THF):  $\delta$  (ppm) 5.46 (br m, -CH=CH-, 2H), 4.29 (br m,  $-CH_2CH(O-)CH_2-$ , 1H), 4.00 (br m,  $-OCH_2$ -CH<sub>2</sub>O-, 10H), 3.65 (br m,  $-OCH_2CH_2O-$ , 10H), 3.58 (br m,  $-OCH_2CH_2OCH_3$ , 10H), 3.47 (br m,  $-OCH_2CH_2OCH_3$ , 10H), 3.29 (s,  $-OCH_3$ , 15H), 1.45–2.06 (br m,  $-CH_2-$ , 10H). <sup>13</sup>C NMR ( $d_6$ -THF):  $\delta$  (ppm) 130.08 (C-2), 127.48 (C-1), 77.67 (C-5), 71.90 ( $-OCH_2CH_2O-$ ), 70.60 ( $-OCH_2CH_2OCH_3$ ), 70.02 ( $-OCH_2CH_2OCH_3$ ), 64.82 ( $-OCH_2CH_2O-$ ), 58.03 ( $-OCH_3$ ), 35.23 (C-4), 35.07 (C-6), 32.77 (C-3), 28.29 (C-8), 27.31 (C-7). <sup>31</sup>P NMR ( $d_6$ -THF):  $\delta$  (ppm) 18.06 (m, 3P);  $M_n = 89$  kDa,  $M_w = 169$  kDa, PDI = 1.9.

Synthesis of polymer **9**. Polymer **9** was synthesized in a manner similar to polymer **8** using monomer **6** (5.00 g, 2.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL) and a solution of **1** (9.4 mg, 0.011 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) to yield 1.20 g (48% yield) of polymer **9**. <sup>1</sup>H NMR ( $d_6$ -THF):  $\delta$  (ppm) 5.43 (br m, -CH=CH-, 2H), 4.65 (br m,  $-CH_2CH(O-)CH_2-$ , 1H), 4.43 (br m,  $-CH_2CF_3$ ,

10H), 1.32–2.23 (br m,  $-{\rm CH_2-}$  10H).  $^{13}{\rm C}$  NMR ( $d_6{\rm -THF}$ ):  $\delta$  (ppm) 129.87 (C-2), 128.65 (C-1), 122.88 (m,  $-{\rm CF_2-}$ ), 80.10 (C-5), 62.89 (m,  $-{\rm CH_2CF_3}$ ), 34.33 (C-4), 32.35 (C-6), 28.06 (C-3), 26.99 (C-8), 25.23 (C-7).  $^{31}{\rm P}$  NMR ( $d_6{\rm -THF}$ ):  $\delta$  (ppm) 17.31 (m, 3P);  $M_{\rm n}=$  397 kDa,  $M_{\rm w}=$  866 kDa, PDI = 2.2.

Synthesis of polymer **10**. Polymer **10** was synthesized in a manner similar to polymer **8** using monomer **7** (2.59 g, 1.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL) and a solution of **1** (5.2 mg, 0.006 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) to yield 0.30 g (12% yield) of polymer **10**. <sup>1</sup>H NMR ( $d_6$ -THF):  $\delta$  (ppm) 6.54 (br m,  $-CF_2CF_2H$ , 5H), 5.42 (br m, -CH=CH-, 2H), 4.53 (br s,  $-CH_2CF_2-$ , 10H), 4.02 (br m,  $-CH_2CH(O-)CH_2-$ , 1H), 1.04–2.14 (br m,  $-CH_2-$ , 10H). <sup>13</sup>C NMR ( $d_6$ -THF):  $\delta$  (ppm) 131.23 (C-2), 128.89 (C-1), 111.14 (m,  $-CF_2-$ ), 73.15 (C-5), 64.23 ( $-CF_2$ H), 57.45 (m,  $-OCH_2CF_2-$ ), 36.23 (C-4), 32.14 (C-6), 31.98 (C-3), 28.12 (C-8), 26.67 (C-7). <sup>31</sup>P NMR ( $d_6$ -THF):  $\delta$  (ppm) 17.22 (m, 3P);  $M_n = 455$  kDa,  $M_w = 819$  kDa, PDI = 1.8.

Synthesis of polymer **11**. Polymer **11** was synthesized in a manner similar to polymer **8** using monomer **5** (0.28 g, 0.33 mmol, 0.10 equiv) and monomer **6** (2.19 g, 3.0 mmol, 0.90 equiv) in  $CH_2Cl_2$  (5.5 mL) and a solution of **1** (9.3 mg, 0.011 mmol) in  $CH_2Cl_2$  (1 mL) to yield 0.88 g (35% yield) of a rubbery gum. The average repeat unit composition was calculated from <sup>1</sup>H NMR peak integration. Similar <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P chemical shifts were observed for polymers **12** and **13**.

For **11**, average repeat unit composition (**5**, 11.2%; **6**, 88.8%). <sup>1</sup>H NMR ( $d_6$ -THF):  $\delta$  (ppm) 5.41 (br m, -CH=CH-, 4H), 4.48 (br s,  $-CH_2CF_3-$ , 18H), 4.41 (m,  $-CH_2CH(O-)CH_2-$ , 2H), 4.01 (br m,  $-OCH_2CH_2O-$ , 2H), 3.63 (br m,  $-OCH_2CH_2O-$ , 2H), 3.59 (br m,  $-OCH_2CH_2OCH_3$ , 2H), 3.48 (br m,  $-OCH_2CH_2-$ OCH<sub>3</sub>, 2H), 3.28 (s,  $-OCH_3$ , 3H), 1.35–2.62 (br m,  $-CH_2-$ , 20H). <sup>13</sup>C NMR ( $d_6$ -THF):  $\delta$  (ppm) 129.49 (C-2), 129.23 (C-1), 123.46 (m,  $-CH_2CF_3$ ), 80.06 (C-5), 71.94 ( $-OCH_2CH_2O-$ ), 70.36 ( $-OCH_2CH_2OCH_3$ ), 70.03 ( $-OCH_2CH_2OCH_3$ ), 65.94 ( $-OCH_2CH_2O-$ ), 62.49 ( $-CH_2CF_3$ ), 57.97 ( $-OCH_3$ ), 34.69 (C-4), 34.30 (C-6), 32.45 (C-3), 27.95 (C-8), 27.01 (C-7). <sup>31</sup>P NMR ( $d_6$ -THF):  $\delta$  (ppm) 18.12 (m, 6P);  $M_n = 387$  kDa,  $M_w = 841$ kDa, PDI = 2.2.

Synthesis of polymer **12**. Polymer **12** was synthesized in a manner similar to polymer **8** using monomer **5** (0.68 g, 0.8 mmol, 0.25 equiv) and monomer **6** (2.22 g, 2.5 mmol, 0.75 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (5.5 mL) and a solution of **1** (9.3 mg, 0.011 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) to yield 0.90 g (36% yield) of polymer **12**. Average repeat unit composition (**5**, 31.5%; **6**, 68.5%);  $M_n = 250$  kDa,  $M_w = 463$  kDa, PDI = 1.9.

Synthesis of polymer **13**. Polymer **13** was synthesized in a manner similar to polymer **8** using monomer **5** (1.11 g, 1.3 mmol, 0.40 equiv) and monomer **6** (1.40 g, 1.9 mmol, 0.60 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (5.5 mL) and a solution of **1** (9.3 mg, 0.011 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) to yield 1.09 g (44% yield) of polymer **13**. Average repeat unit composition (**5**, 44.0%; **6**, 56.0%);  $M_n = 279$  kDa,  $M_w = 632$  kDa, PDI = 2.3.

Synthesis of polymer 14. Polymer 14 was synthesized in a manner similar to polymer 8 using monomer 5 (0.32 g, 0.37 mmol, 0.10 equiv) and monomer 7 (4.67 g, 3.3 mmol, 0.90 equiv) in  $CH_2Cl_2$  (12 mL) and a solution of 1 (10.5 mg, 0.012 mmol) in  $CH_2Cl_2$  (1 mL) to yield 1.51 g (30% yield) of polymer 14. Similar chemical shifts were observed for polymers 15 and 16.

For 14, average repeat unit composition (5, 8.3%; 7, 91.7%). <sup>1</sup>H NMR ( $d_6$ -THF):  $\delta$  (ppm) 6.36–6.67 (br m,  $-CF_2CF_2H$ , 9H), 5.43 (br m, -CH=CH-, 4H), 4.56 (br m,  $-CH_2CF_2-$ , 18H), 4.43 (br m,  $-CH_2CH(O-)CH_2-$ , 2H), 4.02 (br m,  $-OCH_2-CH_2O-$  2H), 3.64 (br m,  $-OCH_2CH_2O-$ , 2H), 3.57 (br m,  $-OCH_2CH_2OCH_3$ , 2H), 3.45 (br m,  $-OCH_2CH_2OCH_3$ , 2H), 3.28 (s,  $-OCH_3$ , 3H), 1.37–2.31 (br m,  $-CH_2-$ , 20H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 133.45 (C-2), 130.11 (C-1), 110.48 (m,  $-CF_2-$ ), 80.98 (C-5), 71.94 ( $-OCH_2CH_2O-$ ), 70.34 ( $-OCH_2CH_2O-$ ), 0CH<sub>3</sub>), 70.02 ( $-OCH_2CH_2OH_3$ ), 64.71 ( $-OCH_2CH_2O-$ ), 62.14 ( $-CF_2CF_2H$ ), 62.06 ( $-CH_2CF_2-$ ), 57.96 ( $-OCH_3$ ), 37.45 (C-4), 34.69 (C-6), 32.57 (C-3), 27.98 (C-8), 26.74 (C-7). <sup>31</sup>P NMR ( $d_6-$ THF):  $\delta$  (ppm) 17.2 (m, 6P);  $M_n = 489$  kDa,  $M_w = 1129$  kDa, PDI = 2.3.

Synthesis of polymer 15. Polymer 15 was synthesized in a manner similar to polymer 8 using monomer 5 (0.83 g, 0.98

mmol, 0.25 equiv) and monomer **7** (4.11 g, 2.9 mmol, 0.74 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (12 mL) and a solution of **1** (10.5 mg, 0.013 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) to yield 2.25 g (45% yield) of polymer **15**. Average repeat unit composition (**5**, 27.1%; **7**, 72.9%);  $M_n$  = 376 kDa,  $M_w$  = 964 kDa, PDI = 2.6.

Synthesis of polymer **16**. Polymer **16** was synthesized in a manner similar to polymer **8** using monomer **5** (1.45 g, 1.7 mmol, 0.40 equiv) and monomer **7** (3.54 g, 2.5 mmol, 0.60 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) and a solution of **1** (11.9 mg, 0.014 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) to yield 1.87 g (37% yield) of polymer **16**. Average repeat unit composition (**5**, 39.4%; **7**, 60.6%);  $M_n = 155$  kDa,  $M_w = 255$  kDa, PDI = 1.7.

**Preparation of Solid Polymer Electrolytes.** Polymers **8–16** were dried under vacuum at 40 °C for 1 week before fabrication. Each polymer (0.3 g) was combined with 10 mol % lithium tetrafluoroborate (LiBF<sub>4</sub>) and was dissolved in THF. The THF was removed by air evaporation in a dry environment, and the samples were subjected to a reduced pressure (40 °C, 0.1 mmHg, 72 h) to remove any residual THF to yield solid polymer electrolytes (SPEs) **17–25**.

**Preparation of Films for Static Water Contact Angle Measurements.** Polymers 8–16 were dried under vacuum at 40 °C for 1 week before fabrication. Each polymer was combined with 10 mol % LiBF<sub>4</sub> and was dissolved in THF (30% (w/v)). The polymer solutions were poured onto a glass substrate, and the THF was air-evaporated in a dry environment. Residual THF was removed under a reduced pressure (room temperature for 24 h, 40 °C for 72 h, 0.1 mmHg).

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#### **References and Notes**

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