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Polynorbornenes Bearing Pendent Cyclotriphosphazenes with Oligoethyleneoxy Side Groups: Behavior as Solid Polymer Electrolytes

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ABSTRACT: Three different polynorbornenes (PNB) with pendent cyclotriphosphazene side units that bear different short-chain oligoethyleneoxy side groups were synthesized via ring-opening metathesis polymerization (ROMP). Polymers with methoxyethoxy ($-OCH_2CH_2)_nOCH_3$ ($n = 1$), di(ethylene glycol) methyl ether ($n = 2$), and tri(ethylene glycol) methyl ether ($n = 3$) were synthesized and characterized by multinuclear NMR, GPC, DSC, and elemental analysis. The solid polymers were complexed with $LiSO_3CF_3$ and $LiN(SO_2CF_3)_2$ (10−60% molar ratios), and the ionic conductivities were measured by impedance analysis as a function of temperature. The polymers with methoxyethoxy side units showed no detectable ambient temperature conductivities within the limitations of the impedance analyzer. The conductivities of the other polymer electrolytes increased as the concentration of salt was increased, with similar maximum conductivities found for the di(ethylene glycol) and tri(ethylene glycol) systems (2.1×10^{-5} S/cm at 30 °C with the use of 40 mol % $LiN(SO_2CF_3)_2$ in both cases). The conductivities showed non-Arrhenius temperature dependence. No melting or crystallization transitions were detected at temperatures above 25 °C for any of polymer−salt complexes tested. Modification of one polymer with $-O(CH_2CH_2O)_3CH_3$ side chains was carried out by epoxidation of the backbone C═C bonds.

Introduction

The development of the polymer−salt complex derived from poly(ethylene oxide) (PEO) and KSCN in 1973[1] led many research groups to pursue the development of polymer-based electrolytes that are both conductive and possess filmlike mechanical properties.[2] In 1984, a poly(organophosphazene) with oligoethyleneoxy side groups was shown by the combined research groups of Shriver and Allcock to produce polymer−salt systems with room-temperature conductivities 2−3 orders of magnitude higher than PEO (which is $\sim10^{-7}$ S/cm at 25 °C).[3] In particular, one of the earliest polymers in this class, poly[bis(2-(2′-methoxyethoxy)ethoxy)phosphazene] (MEEP), aroused considerable interest for its prospective use in rechargeable lithium batteries. The relatively high ionic conductivity of MEEP ($\sim5 \times 10^{-5}$ S/cm at 25 °C) can be attributed to (1) the unusually flexible backbone of poly(organophosphazenes), (2) the flexibility of the oligoethyleneoxy side groups, (3) the amorphous nature of the polymer microstructure, and (4) the ability of the ethyleneoxy-derived side groups to coordinate to metal ions.[4] Since that time, more than 30 counterparts of MEEP, with different oligoethyleneoxy side chains, have been synthesized and studied in our laboratory. These contain various linear, branched, and crown ether type side groups.[5−7] Ionically conductive small molecule additives comprised of small-molecule oligoethyleneoxy-functionalized cyclotriphosphazenes have also been used to increase the conductivity of the $MEEP/LiSO_3CF_3$ system.[8] The attributes of these poly(organophosphazene)−salt complexes prompted our investigation into an alternative comblike polymer system that not only is highly conductive but also possesses the dimensional stability needed for useful applications. These polymers have an organic polymer backbone which serves as a platform for cyclic phosphazene side groups which themselves bear oligoethyleneoxy side chains.

Most of the research on organic vinyl or allyl polymers with pendent cyclotriphosphazene rings has been conducted by Allen and co-workers,[9−12] but few studies exist on the use of these polymers as solid polymer electrolytes (SPEs). Moreover, this is the first type of organic polymer system bearing pendent cyclotriphosphazenes synthesized via ring-opening metathesis polymerization (ROMP). Other systems have been synthesized primarily via free radical addition chemistry, most notably with acrylic and styrene-based systems.[13−22]

Recently we have shown that polymers with a variety of functionalized pendent cyclotriphosphazene side groups can be synthesized readily via the ROMP of norbornene-based monomers.[23] ROMP-derived polymers have received considerable attention in recent years due to advances in the development of functional group tolerant catalysts. As a result, a wide range of organic monomer derivatives are available, many of which are made via Diels−Alder chemistry through the reaction of cyclopentadiene with various dienophiles.[24,25] One such derivative, 5-norbornene-2-methanol, yields monomers with a variety of isomers, including constitutional (exo and endo) isomers, along with the corresponding stereoisomers. Conversion of the alcohol to the sodium salt allows such monomers to be linked to halogenocyclotriphosphazenes, and the halogen atoms can then be replaced by organic groups. The resultant phosphazene-coupled norbornenes can then be polymerized by ROMP techniques to yield polynorbornenes with pendent cyclophosphazene side units. Thus, there are three components to these polymers: the norbornenyl backbone, the cyclophosphazene side groups, and the organic side chains linked to the cyclophosphazene units. Polymers synthesized by this method are noncrystalline, probably due to both the complex polymer stereochemistry and the presence of bulky cyclotriphosphazene side groups. The lack of crystallinity is advantageous for solid polymer electrolyte (SPE) studies because polycrystalline phases can reduce the ionic conductivity of polymers.[2] For example, although PEO has received the most attention as a host for electrolyte formation, at

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least 60% of the bulk material is crystalline at room temperature. This means that polymer–salt complexes must be heated above ~80 °C before useful ionic conductivities can be obtained.[2]

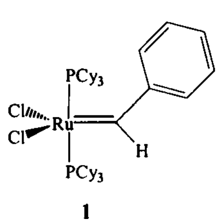
Research by Inoue and co-workers has shown that relatively high ionic conductivities can be obtained with polystyrenes that bear phosphazene rings with oligoethyleneoxy side groups.[14,16,17,26] However, crystalline phases and melting transitions occur in these systems above 30 °C in the presence of $LiClO_4$. Moreover, this salt has some disadvantages for solid polymer electrolyte battery applications.[27]

In the present work, norbornenyl–phosphazene monomers were ROMP polymerized and characterized, and the resultant polymers, when complexed with salts, yielded materials with good ionic conductivities. The fact that these polymerizations occur so readily can be attributed to the preferential coordination of the ruthenium-based initiator to C=C bonds instead of to the polar oligoethyleneoxy side groups. Advances in transition metal catalysts in recent years have facilitated the development of such highly functionalized polymers that were previously not possible with highly active early transition metal catalysts.[24,25,28–33]

Results and Discussion

Principles Involved. Polynorbornenes that bear cyclotriphosphazene rings with ethoxy, fluoroalkoxy, and aryloxy side groups have been synthesized previously in our program via ROMP techniques.[23] We have now synthesized via the ROMP method polynorbornenes with pendent cyclophosphazene units that bear various oligoethyleneoxy side groups. These are potential matrices for SPE applications. In this work we prepared polymers with short oligoethyleneoxy side groups of various lengths to study the influence of the side chain length on ionic conductivity and on mechanical and thermal properties. In addition, the effects of using two different salts, $LiSO_3CF_3$ and $LiN(SO_2CF_3)_2$, were also examined.

Monomer Synthesis. The syntheses of pentasubstituted cyclotriphosphazenes were carried out on a multigram scale by the treatment of hexachlorocyclotriphosphazene (**2**) with 5.7 mol equiv of the sodium salt of the appropriate alcohol as described previously.[23] The crude reaction mixtures were then treated with the sodium salt of 5-norbornene-2-methanol (**3**) (equimolar mixture of endo and exo isomers) to replace the remaining chlorine atoms. The overall synthetic sequence is illustrated in Scheme 1. Column chromatography with the use of ethyl acetate and methanol as cosolvents was used to isolate the pure monomers.



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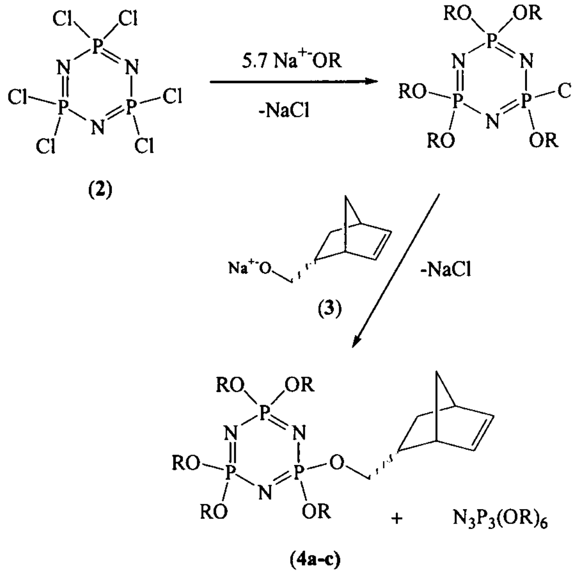
Polymerization Procedure. In a typical polymerization reaction, the initiator (**1**), dissolved in a minimum amount of CH_2Cl_2, was added to the monomer dissolved in CH_2Cl_2 (200 mg/mL) in a vial containing a magnetic stirrer bar. The reactions were carried out at room temperature. All the monomers polymerized without significant complications as illustrated in Scheme 2. Conversion to polymer was near 100% and was confirmed by ^1H NMR spectroscopy, which indicated the presence of polymer and lower molecular weight oligomers, but no detectable concentrations of monomer. However, monomers that had not been purified by column chromatography did not polymerize. This was attributed to the presence of excess 5-norbornene-2-methanol which presumably coordinates with and deactivates initiator **1**.[34] Broad polymer polydispersities were formed when the higher monomer-to-initiator ratios were employed, and the measured molecular weights were less than the calculated values, especially at high [M]/[**1**] values (Table 1, entries 6, 10, and 14). This is presumed to be a result of side reactions caused by active chain ends.

Scheme 1. Synthesis of Penta(oligo-ethyleneoxy) Mononorbornenyl Cyclotriphosphazenes

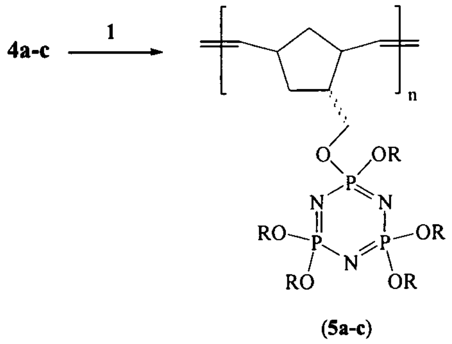


$R = CH_2CH_2OCH_3$ (**a**)

$= CH_2CH_2OCH_2CH_2OCH_3$ (**b**)

$= CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$ (**c**)

Scheme 2. ROMP of Penta(oligo-ethyleneoxy) Mononorbornenyl Cyclotriphosphazene Monomers



$R = -CH_2CH_2OCH_3$ (**a**)

$= -CH_2CH_2OCH_2CH_2OCH_3$ (**b**)

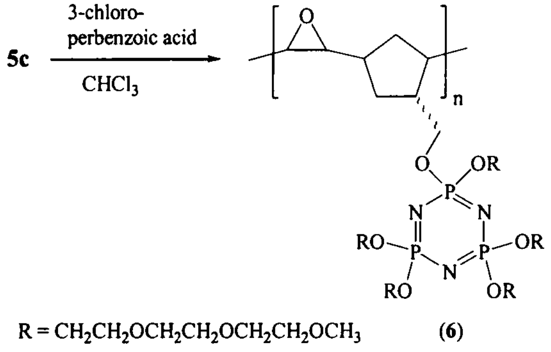
$= -CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$ (**c**)

Table 1. Characterization Data for Polymers 5a−c and Epoxide-Functionalized Polymer 6

entry	polymer	[M]/[**1**]	$10^{-3}M_n$^{a}	PDI	T_g^{b}(°C)
1	**5a**	25	16.1	1.32	−49.0
2		51	25.2	1.33	−49.2
3		100	38.5	1.27	−49.6
4		151	50.7	1.35	−48.2
5		341	101.1	1.44	−50.8
6		1000	139.3	2.49	−52.9
7	**5b**	50	23.4	1.44	−59.8
8		100	28.4	1.56	−60.5
9		526	38.3	1.76	−63.0
10		1000	50.0	4.35	−63.7
11	**5c**	48	21.3	1.48	−64.0
12		101	32.6	1.83	−64.3
13		179	38.1	1.96	−64.0
14		921	42.7	2.31	−66.5
15	**6**^{c}	1000^c	34.5^c	8.09^c	−51.1^c

^{a} Determined by GPC in THF using polystyrene standards. ^{b} Analysis by differential scanning calorimetry with a scan rate of 10 °C/min. ^{c} Polymer 14 was derived from 5c, entry 14, and was only partially soluble in THF.

Scheme 3. Epoxidation of Polymer 5c with 3-Chloroperbenzoic Acid



At the end of each polymerization reaction, the resultant gels were dissolved in $CHCl_3$ that contained a trace amount of the antioxidant 2,6-di-*tert*-butyl-4-methylphenol and were then end-capped by the addition of ethyl vinyl ether. The products were soluble in alcohols, polar aprotic solvents, and water. Thus, the polymers could be purified by dialysis against methanol/THF solutions with the use of 5000 molecular weight cutoff dialysis tubing.

The mechanical properties of the polymers were influenced by both the length of the main chain (controlled by the monomer-to-initiator ratio) and the length of the oligoethyleneoxy side groups. The shortest oxyethylene side groups generated a solid. The triethyleneoxy side groups were responsible for the formation of highly viscous gums. Intermediate physical properties were generated by the diethyleneoxy derivative. Polymers produced with monomer-to-initiator ratios of less than 100:1 were mobile liquids, but polymers formed from ratios greater than 200:1 were solids or gums.

However, a subsequent epoxidation of the C=C backbone bonds of the polymer with $-O(CH_2CH_2O)_3CH_3$ side chains converted it from a gum to a solid. This was accomplished by treatment with 3-chloroperbenzoic acid to form polymer **6**. The reaction sequence is shown in Scheme 3. Unfortunately, the marked improvement in mechanical properties of the epoxidized polymer was accompanied by a decrease in solubility in the aforementioned solvents. Schrock et al.[35] have described similar findings with other epoxidized polynorbornene (PNB) derivatives.

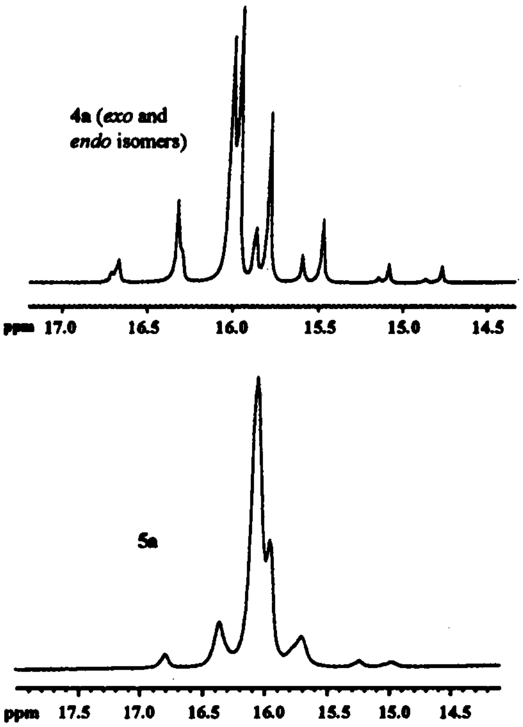


Figure 1. ^{31}P NMR spectra (146 MHz, $CDCl_3$) of monomer **4a** and polymer **5a**.

NMR Characterization. In the following discussion the acronym PNB refers to polynorbornene. $PNB-P_3N_3[O(CH_2CH_2O)_1CH_3]_5$ (**5a**), $PNB-P_3N_3[O(CH_2CH_2O)_2CH_3]_5$ (**5b**), and $PNB-P_3N_3[O(CH_2CH_2O)_3CH_3]_5$ (**5c**) were examined by multinuclear NMR, GPC, IR, DSC, and elemental analysis. Polymers complexed with $LiSO_3CF_3$ or $LiN(SO_2CF_3)_2$ were also characterized by DSC analysis and impedance analysis. Because of the mixture of isomers of 5-norbornene-2-methanol used for the synthesis of the monomers, the final polymers are presumed to be random copolymers with statistical distributions of isomers along the backbone. In addition, because norbornenes substituted at the 5-position are asymmetrical, a variety of repeat unit regioisomers are formed including head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT) repeat units.[36] Proton NMR spectra showed typical broad resonances at 4.9−5.4 ppm for the olefinic protons, and the cis contents could not be determined quantitatively at these monomer-to-initiator ratios, due to peak overlap. Broad resonances were also detected between 1 and 3.0 ppm, which are characteristic of PNB derivatives. The region between 3 and 4.2 was typical of the broad resonances ascribed to the oligoethyleneoxy groups on the phosphazene ring.

Because of similarities in the electronic effects of the different oligoethyleneoxy chains linked to phosphorus for monomers **4a**−**c** and polymers **5a**−**c**, the ^{31}P NMR shifts for the phosphorus ring atoms were similar for the monomers and the corresponding polymers. However, as with the proton resonances, broader phosphorus resonances were detected for the polymers. The ^{31}P NMR spectra of **4a** and corresponding polymer **5a** are shown in Figure 1. The ^{31}P NMR shifts (D_2O) are found in the region between 14.5 and 17.5 ppm, and the overlapped resonances of the different phosphorus atoms of the phosphazene ring are attributed to similar nuclear environments of the two types of atoms. This is in contrast to other phosphazene ring systems which

Table 2. T_g Values of Polymers 5a−c Complexed with $LiSO_3CF_3$

polymer	% $LiSO_3CF_3$	T_g (°C)	polymer	% $LiSO_3CF_3$	T_g (°C)
5a	10	−41.2	**5c**	20	−56.9
	20	−34.3		30	−45.8
	30	−28.7		40	−43.4
	40	−24.8		50	−33.9
	50	−19.4		60	−29.3
5b	5	−58.2			
	10	−56.4			
	20	−46.7			
	30	−39.8			
	40	−37.4			
	50	−29.8			

show more clearly defined A_2B splitting patterns when functionalized with fluoroalkoxy or aryloxy side groups.[23]

The ^{13}C NMR spectra of the epoxide-functionalized polymer **6** showed an absence of backbone C-olefin peaks in the region between 136 and 131 ppm. Vinyl protons were also absent in the region between 5.4 and 4.9 by ^1H NMR. The presence of epoxide groups and absence of olefin groups was further confirmed by FTIR (∼1250 and 1640 cm^{-1}, respectively). In addition, the C−O bands detected were attributed to the oxidation of the norbornene bridgehead carbons. Because of the low solubility of the epoxidized polymer in THF or chloroform, only the lower molecular weight extractables could be detected by GPC methods (Table 1, entry 16).

Molecular Weights. The average molecular weights of all the polymers, as determined by gel permeation chromatography, were in the range (1.6−14) × 10^4 (∼100 repeating units), while the polydispersities (PDIs) ranged from 1.3 to 4.4 (Table 1). Regulation of the molecular weight of polymer PNB−$P_3N_3[O(CH_2CH_2O)_1CH_3]_5$ (**5a**) was investigated by varying the monomer-to-initiator ratio by 2 orders of magnitude. An increase in molecular weight (M_n) occurred with increased monomer-to-initiator ratios, but the linear relationship between [M]/[**1**] and M_n was not maintained at higher monomer-to-initiator ratios. This is attributed to backbiting, chain transfer, and termination reactions due to the small number of active chain ends relative to the number of available C═C bonds that are formed during the polymerization process. This discrepancy can be seen with polymer **5a**, in which a 3-fold increase in [M]/[**1**] leads to only a marginal increase in molecular weight (Table 1, entries 5 and 6). The increased polydispersity with an increase in [M]/[**1**] is also shown in Table 1 for all the polymers: PNB−$P_3N_3[O(CH_2CH_2O)_1CH_3]_5$ (**5a**), PNB−$P_3N_3[O(CH_2CH_2O)_2CH_3]_5$ (**5b**), and PNB−$P_3N_3[O(CH_2CH_2O)_3CH_3]_5$ (**5c**).

Glass Transition Temperatures. The thermal properties of PNB−$P_3N_3[O(CH_2CH_2O)_1CH_3]_5$ (**5a**), PNB−$P_3N_3[O(CH_2CH_2O)_2CH_3]_5$ (**5b**), PNB−$P_3N_3[O(CH_2CH_2O)_3CH_3]_5$ (**5c**), and the epoxide-functionalized polymer **6** were studied by DSC analysis. The T_g values are reported in Table 1. These values are well below room temperature for all the polymers examined, and the low values reflect the high flexibility of the oligoethyleneoxy side groups. The decrease in T_g values with longer oxyethylene units per side chain is attributed to the greater free volume imparted by the longer side chains.

Polymers **5a**−**c** were complexed with 5−60% $LiCF_3SO_3$. All the polymers showed increases in T_g values with increases in salt concentration, presumably due to coordinative cross-linking. The T_g values of the polymer−salt complexes are shown in Table 2. These values were higher with **5b**−salt than with **5c**−salt complexes. However, at higher salt concentrations, the T_g values of **5c**−salt complexes increased more rapidly than the corresponding **5b**−salt complexes. This is attributed to the larger number of available coordination sites present in the longer side chains of **5c** which permit a higher loading of ions and more ionic cross-links per chain. Thus, the effect on T_g values would be greater for polymer **5c** at higher salt concentrations because the saturation point, where ionic cross-linking becomes a factor, is higher.

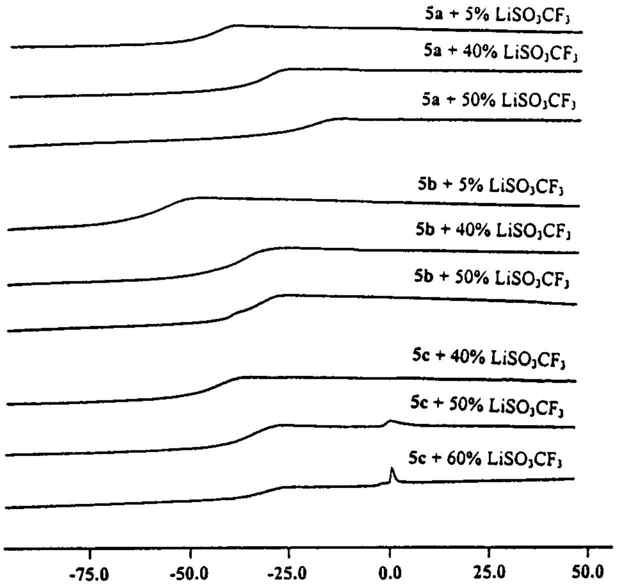


Figure 2. DSC curves for $C_8H_{11}O-P_3N_3[O(CH_2CH_2O)_n, n = 2)]_5-LiSO_3CF_3$ complexes (40−60 mol % $LiSO_3CF_3$) and $C_8H_{11}O-P_3N_3[O(CH_2CH_2O)_n, n = 3)]_5-LiSO_3CF_3$ complexes (0−60 mol % $LiSO_3CF_3$).

The same polymers were complexed with 30 and 40 mol % $LiN(SO_2CF_3)_2$ and showed similar trends in T_g values to those found for $LiSO_3CF_3$. However, the increase in T_g was less pronounced, and this is attributed to the greater ability of the larger anion to increase the free volume.[37] For example, the T_g of uncomplexed polymer **5c** (T_g = −64.0 °C) increased to −43.4 °C when complexed with 40 mol % $LiSO_3CF_3$, yet increased to only −51.0 °C when complexed with 40 mol % $LiN(SO_2CF_3)_2$. In Figure 2 is shown representative DSC curves of polymer−salt complexes of **5a**−**c** with various amounts of $LiSO_3CF_3$. Crystallization or melting transitions of polymers **5a**−**c** were not detected at any concentration of $LiN(SO_2CF_3)_2$. However, polymer **5c** had a weak melting transition when complexed with 50 mol % $LiSO_3CF_3$, and the transition became more pronounced at 60 mol % $LiSO_3CF_3$. This is a direct result of the ionic cross-linking discussed previously.

The epoxide-functionalized polymer **6** showed an approximate 15 °C increase in T_g value (polymer 6, Table 1, entry 15) compared to the unepoxidized polymer. The higher T_g values for this material are attributed to cross-linking reactions due to the ring-opening of epoxide groups. This also resulted in a decrease in solubility.

Ionic Conductivity Results. Previous work suggests[17,37] that ion transport in comblike polymer systems results from the segmental motion of oligoethyleneoxy side chains and is essentially independent of the nature of the polymer backbone. However, the structure of the backbone does influence conductivity to some degree, as demonstrated by comparisons between polystyryl and

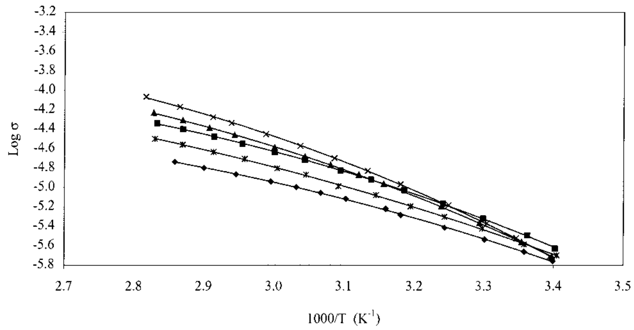


Figure 3. Conductivity dependence on temperature for PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_n$CH$_3$, $n = 2$)]$_5-$LiSO$_3$CF$_3$: ◆, 10% LiSO$_3$CF$_3$; *, 20% LiSO$_3$CF$_3$; ■, 30% LiSO$_3$CF$_3$; ▲, 40% LiSO$_3$CF$_3$; ×, 50% LiSO$_3$CF$_3$.

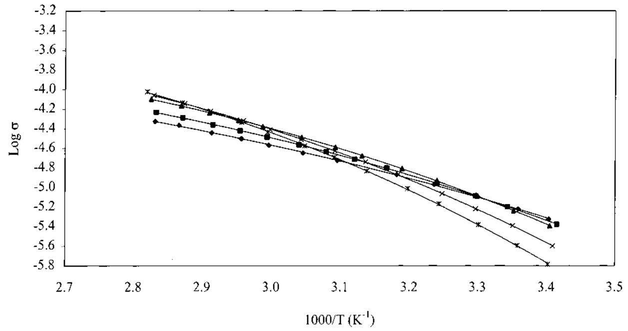


Figure 4. Conductivity dependence on temperature for PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_n$CH$_3$, $n = 3$)]$_5-$LiSO$_3$CF$_3$: ◆, 20% LiSO$_3$CF$_3$; ■, 30% LiSO$_3$CF$_3$; ▲, 40% LiSO$_3$CF$_3$; ×, 50% LiSO$_3$CF$_3$; *, 60% LiSO$_3$CF$_3$.

Table 3. Ionic Conductivities of Polymers 5b and 5c Complexed with LiSO$_3$CF$_3$

		10^{-5} S/cm		
polymer	% LiSO$_3$CF$_3$	30 °C	60 °C	80 °C
5b	10	0.3	1.2	1.8
	20	0.4	1.6	3.2
	30	0.5	2.3	4.6
	40	0.4	2.6	5.9
	50	0.4	3.5	8.6
5c	20	0.8	2.7	4.7
	30	0.8	3.3	5.9
	40	0.8	4.2	8.0
	50	0.9	3.9	8.8
	60	0.4	3.7	9.5

the more rigid poly(vinyl biphenyl) systems.[17,26] In general, the conductivities of the polymer$-$salt complexes discussed here increased as the number of oxyethylene units in each side chain was increased. Polymer **5a** showed no detectable ionic conductivity within the limits of the impedance analyzer at any of the LiSO$_3$CF$_3$ salt concentrations. This is attributed to the relatively small number of oxygen coordination sites available, as well as to the low segmental mobility expected for the methoxyethoxy side groups. The temperature dependence of the ionic conductivities of PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_2$CH$_3$]$_5-$LiSO$_3$CF$_3$ and PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_3$CH$_3$]$_5-$LiSO$_3$CF$_3$ is shown in Figures 3 and 4, respectively, and the data are summarized in Table 3. The type of ion transport, suggested by all the plots, can be described by the WLF equation or the VTF equation.[2,38,39]

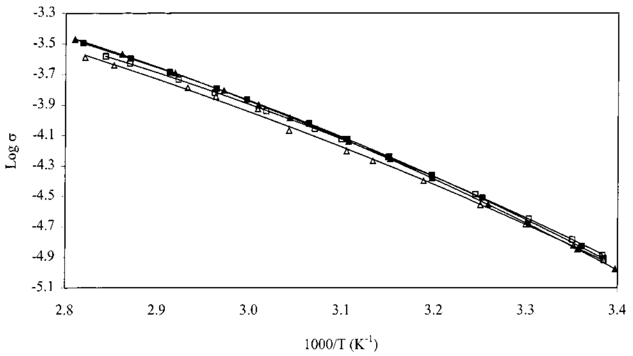


Figure 5. Conductivity dependence on temperature for PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_n$CH$_3$, $n = 2$)]$_5-$LiN(SO$_2$CF$_3$)$_2$, and PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_n$CH$_3$, $n = 3$)]$_5-$LiN(SO$_2$CF$_3$)$_2$: □, 30% LiN(SO$_2$CF$_3$)$_2$ in PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_n$CH$_3$, $n = 2$)]$_5-$LiN(SO$_2$CF$_3$)$_2$; ■, 40% LiN(SO$_2$CF$_3$)$_2$ in PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_n$CH$_3$, $n = 2$)]$_5-$LiN(SO$_2$CF$_3$)$_2$; △, 30% LiN(SO$_2$CF$_3$)$_2$ in PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_n$CH$_3$, $n = 3$)]$_5-$LiN(SO$_2$CF$_3$)$_2$; ▲, 40% LiN(SO$_2$CF$_3$)$_2$ in PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_n$CH$_3$, $n = 3$)]$_5-$LiN(SO$_2$CF$_3$)$_2$.

Table 4. Ionic Conductivities of Polymers 5b and 5c Complexed with LiN(SO$_2$CF$_3$)$_2$

		10^{-5} S/cm		
polymer	% LiN(CF$_2$SO$_3$)$_2$	30 °C	60 °C	80 °C
5b	30	2.2	11.5	26.3
	40	2.1	13.6	32.0
5c	30	2.1	11.8	25.7
	40	2.1	12.6	33.9

On the basis of previous work,[5-8] typical trends formed for other SPEs were seen for the systems studied here. First, an increase in temperature results in higher conductivities, presumably due to the greater segmental mobility of the oligoethyleneoxy side chains and the backbone and to the increased mobility of the ions. Second, as the salt concentration is increased, the conductivity increases as a result of the larger number of charge carriers present. However, above a certain concentration, ionic cross-links restrict polymer motion, thereby decreasing the conductivity.

The conductivity behavior was also influenced by the type of anion in the metal salt. Larger anions induce better ion-pair separation, in addition to generating a larger free volume. Thus, Li ions become more mobile when large anions are present, and this results in improved conductivities. This effect was detected for PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_2$CH$_3$]$_5$ (**5b**) and PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_3$CH$_3$]$_5$ (**5c**), where the conductivities were higher with the use of LiN(SO$_2$CF$_3$)$_2$ than with LiSO$_3$CF$_3$. The temperature dependence of the ionic conductivities of PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_2$CH$_3$]$_5-$LiN(SO$_2$CF$_3$)$_2$ and PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_3$CH$_3$]$_5-$LiN(SO$_2$CF$_3$)$_2$ is shown in Figure 5. The maximum conductivity for PNB$-$P$_3$N$_3$[O(CH$_2$CH$_2$O)$_n$CH$_3$, $n = 2$ or 3)]$_5-$LiN(SO$_2$CF$_3$)$_2$ reached 2.1×10^{-5} S/cm at 30 °C when complexed with 40 mol % LiN(SO$_2$CF$_3$)$_2$. The conductivity results for polymers complexed with LiN(SO$_2$CF$_3$)$_2$ are summarized in Table 4.

In addition to the trends discussed above, the variable temperature impedance analyses showed interesting behavior in the intersection of the curves representing different salt concentrations. At higher salt concentrations (above 30 mol %), polymers **5b** and **5c** showed decreased conductivities until the temperature was raised to 40 °C (**5b**) and 60 °C (**5c**). This can be explained by the presence of crystalline phases associated with the systems that contain the highest salt concentrations. As shown by DSC analysis, crystalline transitions appear in the polymer$-$salt complexes at the highest salt concentrations. Although the points of intersection of the curves do not coincide perfectly with T_c and T_m values, it is well established that polycrystalline phases will hinder ion transport and conductivity.[2] Therefore, in samples with large amounts of salt, the temperature must be increased high enough to disrupt any residual ordering of polymer chains.

Conclusions

A series of three poly(norbornenes) bearing side-chain cyclotriphosphazenes with oligoethyleneoxy side groups have been synthesized via ring-opening metathesis polymerization with the use of initiator **1**. The length of the oligoethyleneoxy side units ranged from 1 to 3 in the general formula: $-O(CH_2CH_2O)_nCH_3$. The polymers are soluble in polar organic solvents, water, and alcohols. Monomer-to-initiator ratios below 100:1 yielded polymers that were viscous oils. Monomer-to-initiator ratios higher than 200:1 gave polymers that were adhesive solids.

The ionic conductivities of these polymers were generally in the same 10^{-5} S/cm range as the best phosphazene backbone polymers studied earlier in our program (2.7×10^{-5} S/cm at 25 °C for MEEP).[6] The conductivities of the polymer−salt complexes generally increased as the lengths of the oligoethyleneoxy side groups were increased and reached 2.1×10^{-5} S/cm at 30 °C for polymers $PNB-P_3N_3[O(CH_2CH_2O)_2CH_3]_5$ (**5b**) and $PNB-P_3N_3[O(CH_2CH_2O)_3CH_3]_5$ (**5c**) complexed with 40 mol % $LiN(SO_2CF_3)_2$. No crystalline or melting transition phases were detected above room temperature for the polymers in this study, at any salt concentration tested. We are currently exploring other related polymers with longer-chain oligoethyleneoxy side units, together with their behavior as gel polymer electrolytes.

Experimental Section

General. All manipulations were carried out under an atmosphere of dry argon using standard Schlenk line techniques. ^{31}P, ^{13}C, and ^{1}H NMR spectra were recorded on a Bruker AMX360 spectrometer operated at 146, 90.27, and 360 MHz, respectively. Chemical shifts are reported in ppm relative to the deuterated solvent resonances. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gel permeation chromatograms were obtained using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with two Phenomenex Phenogel linear 10 columns and a Hewlett-Packard 1047A refractive index detector. Data collection and calculations were accomplished with use of a Hewlett-Packard Chemstation equipped with Hewlett-Packard and Polymer Laboratories software. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Differential scanning calorimetry was performed using a Perkin-Elmer DSC-7 differential scanning calorimeter controlled by a PE7500 computer. Polymer samples were heated from −100 to 80 °C under an atmosphere of dry nitrogen. Heating rates of 5−100 °C/min and sample sizes of 20−30 mg were used. Conductivity measurements were made using a Hewlett-Packard 4192A LF impedance analyzer at a potential of 0.1 V with an alternating frequency range of 800 Hz to 1 MHz. The samples were placed between platinum electrodes separated by a Teflon spacer. The platinum electrode polymer−salt complexed cell was compressed between aluminum blocks held in a Teflon fixture. Electrical leads were attached between the impedance analyzer and aluminum blocks. All conductivity measurements were carried out at variable temperatures under an atmosphere of argon. Elemental analysis was performed by Quantitative Technologies, Inc.

Materials. Hexachlorocyclotriphosphazene was purified by recrystallization from heptane followed by sublimation (30 °C/0.2 mmHg). The methylene chloride used in the polymerization was distilled from CaH_2. All other solvents and common reagents were reagent grade and were used without further purification. 5-Norbornene-2-methanol, 2-methoxyethanol, di(ethylene glycol) methyl ether, tri(ethylene glycol) methyl ether, and 3-chloroperbenzoic acid were purchased from Aldrich Chemical Co. Sodium hydride was purchased from Fluka. All alcohols were distilled from CaH_2. The benzylidene catalyst was obtained from Strem Chemicals, Inc.

General Method for the Preparation of Pentasubstituted(monochloro) Cyclotriphosphazenes. A solution of 428 mmol of the appropriate alcohol in 200 mL of dry THF was added dropwise to a stirred suspension of NaH (428 mmol, 60% dispersion in mineral oil) in 100 mL of dry THF at room temperature. The mixture was at room temperature for 20 h and was then added dropwise to a stirred solution of **2** (75 mmol) in 150 mL of dry THF at room temperature. The mixture was refluxed overnight, and then cooled to room temperature. The trimers were concentrated and used without further purification for the subsequent syntheses of monomers **4a**−**c**.

Penta[(2-methoxyethoxy)(monochloro)]cyclotriphosphazene. ^{31}P NMR (D_2O) δ 28.0 (t, 1P), 19.2 (s, 3P) (hexa), 16,1 (d, 2P).

Penta[(2-(2-methoxyethoxy)ethoxy)(monochloro)]cyclotriphosphazene: ^{31}P NMR ($CDCl_3$) δ 27.9 (t, 1P), 19.2 (s, 3P)(hexa), 16.1 (d, 2P).

Penta[(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)(monochloro)]cyclotriphosphazene. ^{31}P NMR (D_2O) δ 28.0 (t, 1P), 19.2 (s, 3P) (hexa), 16.1 (d, 2P).

General Procedure for the Preparation of (5-Norbornene-2-methoxy)-Pentasubstituted Cyclotriphosphazenes 4a−c. A solution of 5-norbornene-2-methanol (66 mmol, 8.1 g) in 100 mL of dry THF was added dropwise to a stirred suspension of NaH (66 mmol, 2.6 g, 60% dispersion in mineral oil) in 100 mL of dry THF at room temperature. The mixture was heated at 50 °C for 20 h, and the resultant alkoxide (**3**) was then added dropwise to a stirred solution of the appropriate monochlorophosphazene trimer (66 mmol) in 300 mL of dry THF at room temperature. The mixture was then refluxed gently overnight, cooled to room temperature, and quenched with water.

[(5-Norbornene-2-methoxy)penta(2-methoxyethoxy)]cyclotriphosphazene **(*4a*).** The organic layer was concentrated and the crude product purified by column chromatography (silica gel, 90/10 ethyl acetate/methanol) to yield a clear yellow oil containing both endo and exo isomers (65%). ^{1}H NMR ($CDCl_3$) (exo and endo isomers): δ 5.94 (dd, 1H), 5.89 (d, 1H), 5.88 (d, 1H), 5.80 (dd, 1H), 4.07 (m, 1H), 3.87 (m, 10H), 3.64 (m, 1H), 3.51 (m, 1H), 3.40 (m, 10H), 3.31 (m, 1H), 3.18 (m, 1H), 2.75 (s, 1H), 2.60 (s, 1H), 2.40 (m, 1H), 2.25 (m, 1H), 1.60 (m, 1H), 1.22 (m, 1H), 1.11 (m, 1H), 1.05 (m, 1H), 0.95 (m, 1H), 0.31 (m, 1H). ^{13}C NMR ($CDCl_3$) (exo and endo isomers): δ 136.8, 136.6, 135.9, 132.0, 70.7, 68.8, 64.4, 58.4, 48.8, 44.4, 43.3, 41.8, 38.9, 28.8. ^{31}P NMR ($CDCl_3$): δ 16.7−14.8 (m, 3P); *m*/*e* 634 MH^+.

[(5-Norbornene-2-methoxy)penta((2-(2-methoxyethoxy)ethoxy))]cyclotriphosphazene **(*4b*).** The organic layer was concentrated and the crude product purified by column chromatography (silica gel, 80/20 ethyl acetate/methanol) to yield a yellow oil containing both endo and exo isomers (60%). ^{1}H NMR ($CDCl_3$) (exo and endo isomers): δ 5.77 (dd, 1H), 5.72 (d, 1H), 5.71 (d, 1H), 5.64 (dd, 1H), 4.47 (m, 2H), 4.14 (m, 1H), 3.71 (m, 10H), 3.34 (m, 10H), 3.29 (m, 10H), 3.16 (m, 10H), 3.01 (m, 15H), 2.59 (m, 1H), 2.45 (m, 1H), 2.29 (m, 1H), 2.09 (m, 1H), 1.08 (m, 1H), 0.96 (m, 1H), 0.92 (m, 1H), 0.89 (m, 1H), 0.80 (m, 1H), 0.16 (m, 1H). ^{13}C NMR ($CDCl_3$) (exo and endo isomers): δ 136.2, 135.8, 135.3, 131.5, 70.9, 69.5, 69.0, 64.4, 57.8, 48.2, 43.9, 42.7, 42.5, 40.9, 27.7. ^{31}P NMR ($CDCl_3$): δ 18.3−16.3 (m, 3P); *m*/*e* 854 MH^+.

[(5-norbornene-2-methoxy)penta((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)]cyclotriphosphazene **(*4c*).** The organic layer was concentrated and the resultant oil purified by column chromatography (silica gel, 80/20 ethyl acetate/methanol) to yield a yellow oil containing both endo and exo isomers (60%). ^{1}H NMR ($CDCl_3$) (exo and endo isomers): δ 5.81 (dd, 1H), 5.76 (d, 1H), 5.75 (d, 1H), 5.68 (dd, 1H), 3.74 (m, 10H), 3.38 (m,

10H), 3.32 (m, 30H), 3.22 (m, 10H), 3.05 (s, 15H), 2.64 (m, 1H), 2.49 (m, 1H), 2.32 (m, 1H), 2.12 (m, 1H), 1.45 (m, 1H), 1.12 (m, 1H), 1.00 (m, 1H), 0.94 (m, 1H), 0.84 (m, 1H), 0.20 (m, 1H). ^{13}C NMR ($CDCl_3$) (exo and endo isomers): δ 136.3, 135.9, 135.4, 131.6, 71.0, 69.7, 69.6, 68.9, 68.2, 64.1, 58.0 48.4, 44.0, 42.8, 42.5, 41.3, 40.7, 38.3, 28.4, 27.8. ^{31}P NMR ($CDCl_3$): δ 18.7−16.8 (m, 3P); *m/e* 1074 MH$^+$.

General Polymerization Procedure. An example of the polymerization procedure is described for the polymerization of **4a**. Under an inert atmosphere, a 50 mL round-bottom flask containing a magnetic stirrer bar was charged with 1.44 g of degassed **4a** (2.27 mmol) and 5 mL of CH_2Cl_2. A solution of 37 mg of **1** (0.045 mmol) ([**M**]/[**1**] = 50) in 5 mL of methylene chloride was added rapidly to the round-bottom flask via pipet. The flask was capped, and the contents were stirred at room temperature. Within 10 min the pink solution became progressively more viscous, and after 24 h the reaction products were noticeably more viscous. The polymer solution was transferred to a separate container, and 0.5 mL of ethyl vinyl ether, 10 mg of 2,6-di-*tert*-butyl-4-methylphenol, and 50 mL of chloroform were added. The mixture was stirred for 1 h and poured into 500 mL of methanol, and finally, the dissolved contents were poured into dialysis tubing (5000 MWCO). The contents were dialyzed against THF/methanol (50/50) for 2−4 weeks. The solvent was removed by rotary evaporation to yield 0.8 g of a clear yellow sticky rubber.

All monomers polymerized without complications as illustrated in Scheme 2. However, improper removal of excess 5-norbornene-2-methanol by column chromatography resulted in a lack of polymerization. The polymers were recovered as yellow adhesive materials that were soluble in polar solvents such as THF, dimethylacetamide, chloroform, alcohols, and water. The polymers also became more adhesive with the incorporation of longer oligoethyleneoxy side chains. The reactions were carried out under argon at room temperature for a period of 1−24 h with varying monomer-to-initiator ratios (Table 1). As expected, at higher monomer-to-initiator ratios, the measured molecular weights were much less than calculated.

As a general procedure for the epoxidation of polymer **5c**, 3 equiv of 3-chloroperbenzoic acid was added to a polymer solution of **5c** in chloroform (50 mg/mL), and the mixture was stirred under ambient conditions for 48−72 h. The polymer solution was poured into methanol and then dialyzed as mentioned previously. The resultant polymer showed a marked improvement in film-forming properties with an approximate 15 °C increase in T_g (Table 1). However, the new material was only partially soluble in THF or chloroform, and only the lower molecular weight extractables could be detected by GPC. This is attributed to cross-linking reactions caused by the ring-opening of epoxide groups. No conductivity measurements were carried out on this material.

Polymer Characterization. The polymers were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies and by C, H, and N analyses. The data are presented below.

Polymer ***5a***. ^{1}H NMR ($CDCl_3$): δ 5.45−4.98 (bm, 2H), 4.15 (bm, 1H), 4.02 (bs, 10H), 3.83 (bm, 1H), 3.52 (bs, 10H), 3.28 (bs, 15H), 2.89 (bm, 1H), 2.68 (bm, 1H), 2.57 (bm, 1H), 2.35 (bm, 1H), 2.27 (bm, 1H), 2.09 (bm, 1H), 1.88 (bm, 1H), 1.74 (bm, 1H), 1.45 (bm, 1H), 1.12 (bm, 1H). ^{13}C NMR ($CDCl_3$): δ 135.4−129.0 (backbone C-olefin), 128.2, 125.7, 71.1, 67.8, 64.6, 58.7, 44.4−35.2 (backbone C-alkyl), 27.3, 26.0. ^{31}P NMR ($CDCl_3$): δ 19.0−17.1 (m, 1P), 18.2 (m, 2P). Anal. Calcd for $C_{23}H_{46}O_{11}N_3P_3$: C, 43.60; H, 7.32; N, 6.63. Found: C, 43.63; H, 7.24; N, 6.58.

Polymer ***5b***. ^{1}H NMR ($CDCl_3$): δ 5.47−5.00 (bm, 2H), 4.10 (bm, 1H), 3.98 (bs, 10H), 3.81 (bm, 1H), 3.50 (bs, 20H), 3.38 (bs, 10H), 3.26 (bs, 15H), 2.89 (bm, 1H), 2.69 (bm, 1H), 2.55 (bm, 1H), 2.33 (bm, 1H), 2.25 (bm, 1H), 2.09 (bm, 1H), 1.87 (bm, 1H), 1.71 (bm, 1H), 1.44 (bm, 1H), 1.10 (bm, 1H). ^{13}C NMR ($CDCl_3$): δ 135.6−130.5 (backbone C-olefin), 128.1, 125.6, 71.6, 70.3, 69.5, 64.8, 58.7, 43.3−33.2 (backbone C-alkyl), 27.2, 25.9. ^{31}P NMR ($CDCl_3$): δ 18.8−16.8 (m, 1P), 18.1 (m, 2P). Anal. Calcd for $C_{33}H_{66}O_{16}N_3P_3$: C, 46.42; H, 7.79; N, 4.92. Found: C, 47.03; H, 7.10; N, 4.51.

Polymer ***5c***. ^{1}H NMR ($CDCl_3$): δ 5.36−5.00 (bd, 2H), 3.95 (bm, 15H), 3.61 (bm, 1H), 3.59−3.51 (bm, 40H), 3.45 (bm, 10H), 3.43 (bm, 1H), 3.28 (bm, 10H), 2.87 (bm, 1H), 2.68 (bm, 1H), 2.55 (bm, 1H), 2.28 (bm, 1H), 2.05 (bm, 1H), 1.87 (bm, 1H), 1.71 (bm, 1H), 1.43 (bm, 1H), 1.07 (bm, 1H). ^{13}C NMR ($CDCl_3$): δ 136.3−131.5 (backbone C-olefin), 127.5, 125.0, 71.0, 69.6, 69.5, 69.1, 64.0, 58.0, 48.3, 43.6−38.2 (backbone C-alkyl), 28.7, 26.9. ^{31}P NMR ($CDCl_3$): δ 18.9−17.1 (m, 1P), 18.2 (m, 2P). Anal. Calcd for $C_{43}H_{86}O_{21}N_3P_3$: C, 48.08; H, 8.07; N, 3.91. Found: C, 48.16; H, 8.21; N, 3.80.

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