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Ring-Opening Metathesis Polymerization of Phosphazene-Functionalized Norbornenes

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ABSTRACT: Ring-opening metathesis polymerization (ROMP) of phosphazene-functionalized norbornenes was demonstrated with the use of $(PCy_3)_2Cl_2RuCHPh$ as catalyst (where Cy = cyclohexyl). This allowed the incorporation of alkoxy-, fluoroalkoxy-, and aryloxy-derived cyclic phosphazenes as side groups linked to the organic polymer backbone. The polymers were obtained in moderate yields with the properties being dependent on the side groups present and on the molecular weight. The polymers were characterized by multinuclear NMR, DSC, TGA, GPC, elemental analysis, and, in one case, contact angle measurements.

Introduction

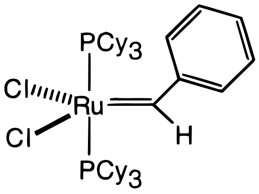
Polymers that contain phosphazene units fall into three categories. First and most numerous are macromolecules with a backbone of alternating phosphorus and nitrogen atoms and with two organic side groups attached to phosphorus.[1−4] Second are the cyclolinear and cyclomatrix polymers in which phosphazene ring units are linked by difunctional organic moieties.[1,2,5] The present work falls into the third group which consists of organic polymer chains to which are attached cyclic phosphazene side groups.[6−9]

Most of the research on organic polymers with cyclophosphazene side groups has been conducted by Allen and co-workers, who developed a series of vinyl- and allyl-substituted cyclophosphazenes which were then polymerized by addition reactions.[10−12] In this paper we report an alternative approach to polymers of this type which involves the ring-opening metathesis polymerization (ROMP) of norbornenes that bear cyclophosphazene pendent groups. From a mechanistic viewpoint a question existed about whether highly functionalized and bulky cyclophosphazene rings would allow ROMP polymerizations to occur and the effect that they might have on chain lengths and polydispersities. Apart from the fundamental interest in polymers of this type, an important need exists for the synthesis of polymers that resist burning. Fire resistance is a property that is often associated with the presence of phosphorus and nitrogen. Ring-opening metathesis polymerization (ROMP) of cyclic olefins was examined as a synthetic route because of the wide tolerance to polar functional groups that is characteristic of late transition metal ROMP initiators.[13,14] Norbornene-derived monomers and the ROMP method were chosen because they offered the prospect of an efficient way to produce polymers with a pendent phosphazene side unit on every repeating unit.[15−17] To our knowledge this work represents the first example of phosphazene functionalized polymers synthesized via ROMP.

Results and Discussion

The principal objective of this work was to examine the feasibility of synthesis of polymers with cyclic phosphazene side groups via the ROMP approach. The side units linked to the phosphazene (alkyloxy, or aryloxy) were selected to span the range of typical side groups normally found in cyclic and high polymeric phosphazenes. All these side units generate significant steric bulk and electronic effects, and it was of interest to determine whether these factors have an influence on the ROMP reaction.

The ruthenium-based metathesis initiator **1** developed by Grubbs and co-workers is tolerant of a wide variety of functional groups and appeared to be an appropriate starting point for this work.[18,19−22] Due to their increased atomic number and increased electronegativity relative to early transition metals, late transition metals are known to coordinate preferentially with relatively “soft” olefin groups rather than polar functional groups such as alcohols, aldehydes, ketones, esters, or ammonium salts.[20,23,24] The ability of **1** to initiate the ROMP of various cyclic olefins appeared to provide an excellent starting point for this work. This was confirmed by a few preliminary tests with classical ROMP initiators such as WCl_6/Bu_4Sn which yielded only low molecular weight oligomers. Although Schrock-type initiators are potentially good candidates for these polymerizations due to their high tolerance of functional groups, this initial study was based solely on polymerizations initiated by **1**, reactions which gave moderate polymer yields and conversions to high molecular weight species.



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Monomer Synthesis. The syntheses of pentasubstituted cyclotriphosphazenes were carried out on a multigram scale by treatment of hexachlorocyclotriphosphazene (**2**) with 5.7 mol equiv of the sodium salt of the appropriate alcohol or phenol. The pentasubstituted species were formed together with the hexa-

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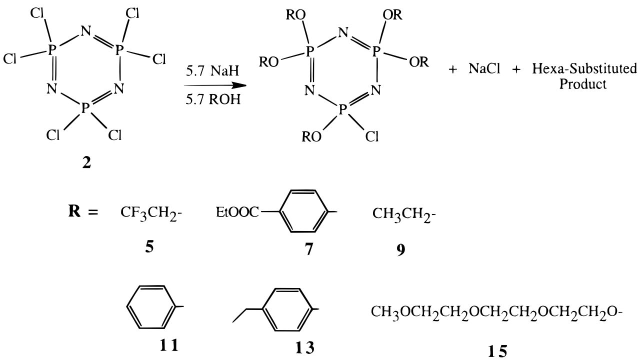
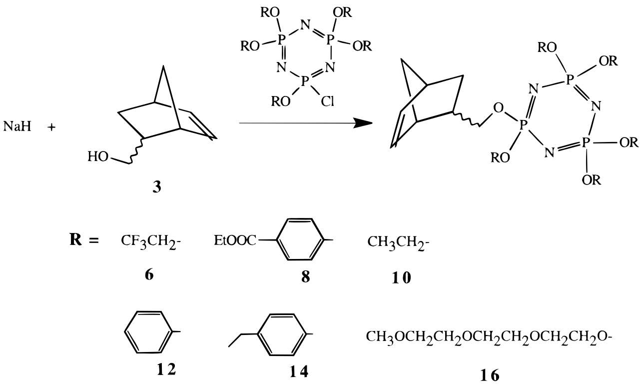
Scheme 1

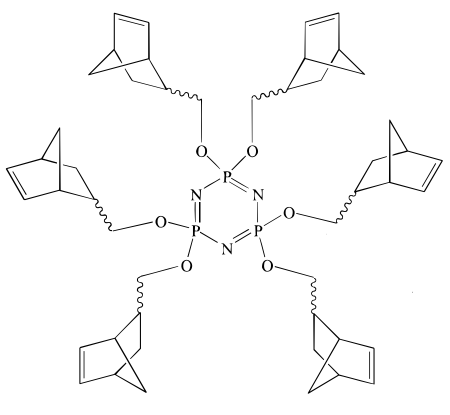


Scheme 2



substituted derivatives: hence, the overall yields were only 40−60%, with the highest conversions to the required product being associated with the aryloxy-derived trimers (**7**, **11**, and **13**). The reaction stoichiometry used (1:5.7 rather than 1:5) was employed to minimize the ultimate formation of monomers that contained more than one norbornene group, because such species, on polymerization, would generate branch points and cross-linking. The norbornene-derivatized species were prepared by treatment of the sodium salt of 5-norbornene-2-methanol (**3**) (equimolar mixture of endo and exo isomers) with the corresponding penta-organo monochlorocyclotriphosphazene (Scheme 2). Monomers **6** and **10** were clear, colorless liquids at room temperature, while species **8** and **14** were viscous, semicrystalline liquids. Monomer **12** was isolated as a crystalline solid and monomer **16** as a yellow liquid.

Polymerization Procedure. In preliminary experiments, a hexanorbornene-derived monomer (**4**) was synthesized and treated with various amounts of **1** in CH_2Cl_2. Immediate gelation was observed following the addition of **1** to **4** at all monomer-to-initiator ratios tested (60−600). The resultant materials were highly cross-linked as evidenced by the lack of solubility in organic solvents. Although in theory it might be possible to synthesize starlike cores by the slow addition of **4** to an excess of **1**, the preliminary experiments showed that cross-linking was strongly favored. Thus, subsequent work was focused on the polymerization of cyclophosphazenes with only one functional group.



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In a typical polymerization reaction the initiator (**1**), dissolved in a minimum amount of CH_2Cl_2, was added to the monofunctional monomer dissolved in CH_2Cl_2 in a small reaction vessel containing a magnetic stir bar. The amount of CH_2Cl_2 was optimized and varied for each monomer. Toluene, *o*-dichlorobenzene, and chlorobenzene were also used as solvents for reactions at higher temperatures and with shorter reaction times in an attempt to improve k_i/k_p ratios and lower the polydispersities. In general, the use of CH_2Cl_2 at room temperature (25 °C) gave the best results. ^1H NMR spectroscopy was used to confirm the progress of these reactions by following the upfield shift of the olefinic resonances caused by the opening of the norbornene ring. The resultant gels were dissolved in $CHCl_3$ that contained trace amounts of 2,6-di-*tert*-butyl-4-methylphenol and were then end-capped by the addition of ethyl vinyl ether. Finally, these polymers were isolated by precipitation into methanol. Because polymer **17** formed dispersions in methanol, a methanol−water solution was used to precipitate the polymer. When monomer-to-initiator ratios below 25:1 were employed, polymers **17** and **19** were isolated as gums. However, when the monomer-to-initiator ratios were higher than 50:1, the polymers were rubbery, adhesive solids. By contrast, polymers derived from monomers **8** and **12** were brittle solids when generated via low monomer-to-initiator ratios (10:1) but were flexible solids if produced using higher monomer-to-initiator ratios (>100:1). Polymers containing oligoethyleneoxy side groups (**22**) were liquids but became more viscous at higher monomer-to-initiator ratios.

Deprotection of the ester groups of polymer **18** was carried out by the addition of excess potassium *tert*-butoxide. Mild deprotection conditions (room temperature) were necessary to prevent cleavage of the cyclic trimer from the polymer backbone. This cleavage was detected by IR and ^{31}P NMR spectroscopy following prolonged exposure to the base at elevated temperatures (~60 °C). Deprotection was therefore carried out at room temperature (~25 °C) to preferentially cleave the ethyl carboxylate side groups rather than the phosphorus−alkoxide group linked to the polymer. After deprotection of the pendent ester groups, the polymer became soluble in aqueous sodium hydroxide. Subsequent addition of aqueous $CaCl_2$ to this solution resulted in gel formation due to ionic cross-linking. This behavior is similar to that of sodium alginate systems and of the polyelectrolyte phosphazenes synthesized previously in our laboratory.[25,26]

NMR Characterization. Polymers **17**, **18**, **19**, **20**, **21**, and **22** were examined by multinuclear NMR, GPC, and DSC analysis. Because of the stereochemical complexities that arise when a mixture of *exo*- and *endo*-5-norbornene-2-methanol (**3**) is used, it is presumed that a variety of repeat unit regioisomers are formed including head-to-head (HH), head-to-tail (HT), and tail-to-

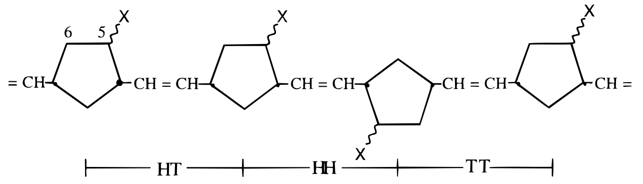


Figure 1. Possible repeat unit structures for the polymers of 5-substituted norbornenes. HH denotes head-to-head, HT denotes head-to-tail, and TT denotes tail-to-tail regioisomers.

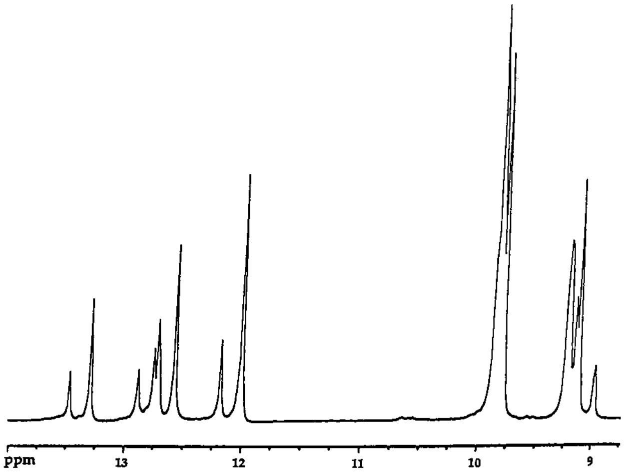


Figure 2. ^{31}P NMR spectrum (146 MHz, CDCl$_3$) of **12** (endo and exo isomers).

tail (TT) repeat units as shown in Figure 1.[27] ^{1}H NMR spectra of the polymers showed broad resonances at 5.0−5.5 ppm for the olefinic protons, and the cis content could not be quantitatively determined by ^{1}H NMR due to peak overlap in this region for all polymers. Broad resonances were also detected between 1.5 and 2.1 ppm and 2.5−3.1 ppm, and these are characteristic of polynorbornenes of this general type. The spectrum of polymer **19** was similar to that of **18** in the 5.0−5.5 and 2.4−3.0 ppm regions, but the region between 1.5 and 2.0 ppm could not be analyzed in detail for **19** because of the broad resonances ascribed to the ethoxy groups on the phosphazene ring.

A broadening effect of the ^{31}P NMR signal was also anticipated for all polymers due to the immobilized phosphazene rings along the polymer chain and the increased number of resonances that are possible as a result of the complex stereochemistry. Figure 2 shows the ^{31}P NMR spectrum of monomer **12** and the typical A$_2$B splitting pattern for the mononorbornene-substituted cyclotriphosphazene containing endo and exo isomers. Polymerization of monomer **12** resulted in a broadening of the phosphorus signals, together with a slight downfield shift. The formation of polymers **17**, **20**, and **21** was also accompanied by signal broadening. However, the splitting behavior in the aryloxy systems was reversed for the different phosphorus atoms due to differences in the electronic effects of trifluoroethoxy side groups and phenoxy side units when the groups are linked to phosphazenes. The phosphorus splitting patterns for polymers **17** and **20** are shown in Figures 3 and 4, respectively. Phosphorus splitting patterns were not as clearly defined for polymers bearing ethoxy and oligoethyleneoxy groups (**19** and **22**, respectively). In both cases, the phosphazene ring atoms showed overlapped resonances between 17.1 and 20.4.

Molecular Weights and Polydispersities. Molecular weights and polydispersities, as determined by gel permeation chromatography, were in the range (8.8−101.3) × 10^3, while the polydispersities (PDIs) ranged from 1.4 to 2.2 (Table 1). Control of the molecular weight of polymer **20** was possible by varying the monomer-to-initiator ratio. Because the total number of chains in the reaction mixture should be determined by the initiator concentration and should remain constant during the reaction, the number-average molecular weight of the polymer should ideally be a linear function with respect to the monomer-to-initiator ratio. In all cases, an increase in molecular weight (M_n) was detected with increasing monomer-to-initiator ratios (Table 1). The measured molecular weights for the polymers were higher than calculated. This discrepancy is between theoretical and experimentally obtained molecular weights is thought to be because of an overestimation by gel permeation chromatography versus polystyrene standards.

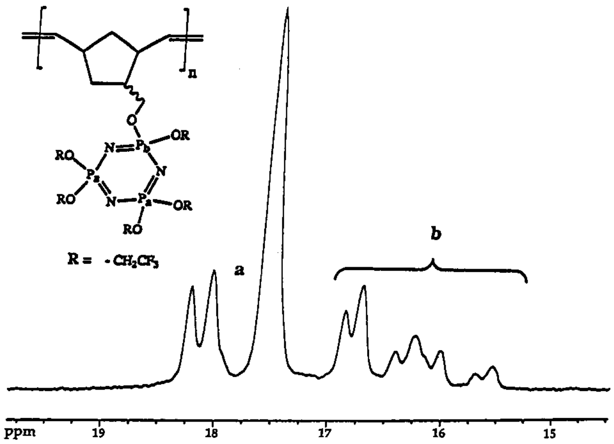


Figure 3. ^{31}P NMR spectrum (146 MHz, CDCl$_3$) of **17** ([**M**]/[**1**] = 89).

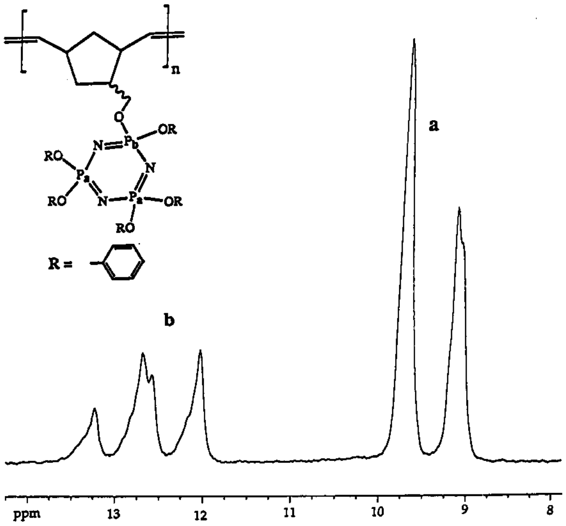


Figure 4. ^{31}P NMR spectrum (146 MHz, CDCl$_3$) of **20** ([**M**]/[**1**] = 77).

The significantly higher PDI values of 1.4−2.2 for all the polymers prepared in this work, compared to PDI values of polynorbornenes produced by “living” systems, were first thought to be a consequence of coordination of the nitrogen ring atoms to the Ru center. Evidence exists in the literature that pyridine and other nitrogen-containing groups, when linked to norbornenes, may drastically affect the metal center of Schrock-type initiators.[28] However, the Ru initiator used in this work

Table 1. ROMP Results for Polymers 17−22

entry	polymer	[**M**]/[**2**]	$10^{-3}M_n$^{a}	PDI^a	T_g^{b}(°C)
1	**17**	10	16.3	1.7	−45.8
2	**17**	13	28.6	1.7	−44.1
3	**17**	25	44.0	1.7	−36.5
4	**17**	29	44.9	1.7	−36.3
5	**17**	50	66.4	1.9	−28.6
6	**17**	89	44.0^c	1.5	−18.6
7	**17**	205	*c*	*c*	−11.1
8	**18**	9	13.0	1.6	36.3
9	**18**	23	21.0	1.8	32.2
10	**18**	57	27.8	1.6	28.3
11	**18**	105	44.0^c	*c*	6.6
12	**19**	25	15.8	1.5	*d*
13	**19**	100	34.3	2.2	−15.7
14	**20**	11	8.8	1.5	25.6
15	**20**	14	9.8	1.5	25.8
16	**20**	25	14.4	1.6	25.7
17	**20**	31	21.7	1.7	25.4
18	**20**	55	33.7	1.7	24.8
19	**20**	69	47.2	1.8	23.6
20	**20**	150	72.2	1.5	23.0
21	**20**	217	101.3	1.7	21.9
22	**21**	5	11.6	1.4	−29.5
23	**21**	10	16.0	1.4	−19.8
24	**21**	25	19.7	1.4	−15.2
25	**21**	51	39.5	1.6	−11.5
26	**21**	77	97.1	2.2	−4.2
27	**22**	10	8.7	1.4	−65.9
28	**22**	55	47.1	2.0	−64.0

[a] Determined by GPC in THF using polystyrene standards. [b] Analysis by differential scanning calorimetry with a scan rate of 10 °C/min. [c] Polymers were mostly insoluble in THF. [d] No thermal transitions were observed.

was chosen specifically to minimize the coordination by the phosphazene nitrogen atoms, which are even less basic than groups such as pyridine. ^{31}P NMR studies of mixtures of equimolar amounts of **1** with hexakis(trifluoroethoxy)cyclotriphosphazene or hexakis(phenoxy)cyclotriphosphazene in either CH_2Cl_2 or toluene showed no significant phosphorus shifts in either the initiator or the phosphazene. Similarly, the presumably more reactive hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) when mixed with **1** induced no significant change in ^{31}P nuclei environments in either the initiator or the phosphazene, and this indicates a high tolerance of **1** to both phosphazene P−Cl bonds and nitrogen ring atoms. Although polymerizations initiated by **1** have been reported to occur by a living mechanism to give polymers with low polydispersities,[19,20,29] optimization of the reaction conditions for the polymerization of monomer **8** resulted in only slight improvements in polydispersities at the various concentrations examined. The PDI values increased only marginally when the reactions times were extended from 20 min to 24 h, and in the majority of cases, the GPC trace signals remained monomodal. Only a few reaction mixtures showed evidence of slightly higher molecular weight GPC shoulders when longer reaction times were employed, and these are attributed to side reactions at longer reaction times. Although the polymerization of norbornenes with bulky side groups can occur via a living process, examples in the literature suggest that this is not always the case.[28,31,32] Indeed, this appears to be consistent with the results of this study.

Thermal Behavior. The thermal behavior of the polymers was analyzed by DSC techniques, and the T_g values are reported in Table 1. The T_g values were all below room temperature for polymers **17**, **19**, **21**, and **22** and ranged from −65.9 to −4.2 °C. Polymers **17** and **19** also showed an abrupt decline in heat flow between 190 and 200 °C which was attributed to decomposition. A lack of crystallinity in **17** and **19** was inferred by the absence of melting transitions, and this is probably due to the irregular microstructures of the polymers. For polymers **18** and **20** the T_g values were all above room temperature. However, unlike polymers **17** and **19**, no decomposition was detected by DSC below 200 °C. Thermogravimetric analysis of the polymers (Figures 5 and 6) showed that none of the new polymers were as stable as polynorbornene in terms of the loss of weight between 25 and 400 °C, but all gave higher char yields above 450 °C, a factor that can favor fire resistance.

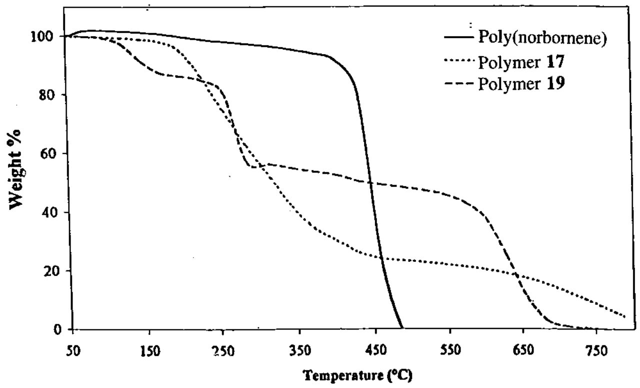


Figure 5. Percent weight loss vs temperature for polynorbornene ([**M**]/[**1**] = 200) and polymers **17** and **19**.

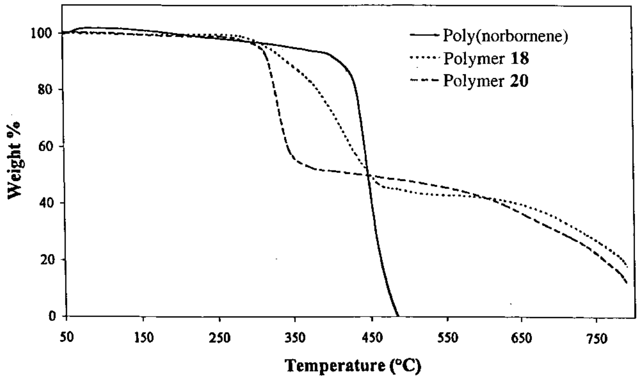


Figure 6. Percent weight loss vs temperature for polynorbornene ([**M**]/[**1**] = 200) and polymers **18** and **20**.

Ionic Conduction. Polymer **22** and analogues that bear longer oligoethyleneoxy side groups are solid solvents for salts such as lithium triflate. Preliminary results have shown ionic conductivities above 10^{-5} S/cm at 25 °C for polymers of type **22** with $LiN(SO_2CF_3)_2$. No crystalline type thermal transitions have been detected above room temperature, a factor that is important for SPE applications. Thus, polymers of this type are of interest in a variety of solid polymer electrolyte applications.

Conclusions

We have demonstrated the feasibility of the ring-opening metathesis polymerization of norbornenes that bear bulky cyclophosphazene side units. The polymerization of a hexakis(5-norbornene-2-methoxy)cyclotriphosphazene (**4**) resulted in a highly cross-linked material. Polymerization of mononorbornenyl phosphazene monomers yielded un-cross-linked polymers. The success of these polymerizations is ascribed to the preferential coordination of initiator **1** with olefins, even in the presence of the potentially coordinative cyclotriphosphazene units. However, the bulky phosphazene side units have a marked influence on the polymerization by increasing the polydispersity. Predictable molecular weight control was demonstrated at relatively low [**M**]/[**1**] ratios for polymer **20**. Only slight increases in PDI and NMR signal broadening were detected when reaction times were increased from 20 min to 24 h at room temperature. The polymers were generally soluble in polar aprotic solvents such as THF, dimethylacetamide, and $CHCl_3$ and, in the case of **22**, in alcohols. Deprotection of polymer **18** under basic conditions yielded a novel water-soluble polyelectrolyte material which can be cross-linked under mild conditions by divalent cations. Polymer **22** shows promise for use as a solid polymeric electrolyte.

Finally, the contact angle to water for fluorinated polymer **17** was measured following literature methods.[33] On the basis of an average of eight trials the contact angle was calculated to be 105°, which confirmed that this material has a highly hydrophobic surface.

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 WM360 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 chromatographs 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. Heating rates of 10−40 °C/min and sample sizes of 20−30 mg were used. Thermal weight loss measurements were made using a SSC 5200 Haak-Buchner thermogravimetric analyzer equipped with a HP model 712/60 Power Risk Station under an atmosphere of compressed air at a flow rate of 30 cm^3/min using a heating rate of 10 °C/min. Elemental analysis was performed by Quantitative Technologies, Inc. Mass spectral data were collected using a Voyager DESTR (+FAB) spectrometer.

Materials. Hexachlorocyclotriphosphazene was isolated from a cyclic trimer−tetramer mixture by sublimation (30 ^{o}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, *p*-ethylphenol, potassium *tert*-butoxide, 4-ethylhydroxy benzoate, and tri(ethylene glycol) monomethyl ether were purchased from Aldrich Chemical Co. Sodium hydride was purchased from Fluka, absolute ethanol from Pharmco, and α,α,α-trifluoroethanol from Acros. All were used without further purification with the exception of ethanol and tri(ethylene glycol) monomethyl ether, which were doubly distilled. The benzylidene catalyst was purchased from Strem Chemicals, Inc.

Preparation of Hexakis[(5-norbornene-2-methoxy)]-cyclotriphosphazene (4). The sodium salt of **3** was prepared by the reaction of **3** (38 mmol, 1.5 g) with NaH (38 mmol, 1.5 g, 60% dispersion in mineral oil) in THF. The mixture was added dropwise to **2** and then refluxed for 48 h. The mixture was washed with 5% HCl, H_2O, and brine solutions. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure to yield a yellow oil which was dissolved in boiling hexanes. Slow evaporation of the solvent afforded 4 g (80%) of an off-white solid (exo and endo product). ^1H NMR ($CDCl_3$) (exo and endo isomers): δ 6.05 (bs, 1H), 6.01 (bs, 1H), 5.91 (bs, 1H), 3.86 (m, 2H), 3.73 (m, 1H), 3.61 (bs, 1H), 3.40 (m, 1H), 3.25 (bs, 1H), 3.04 (m, 1H), 2.87 (m, 1H), 2.74 (m, 1H), 2.51 (bs, 1H), 2.43 (bs, 1H), 2.36 (bs, 1H), 1.73 (m, 1H), 1.36 (m, 1H), 1.23 (m, 1H), 1.19 (m, 1H), 1.08 (m, 1H), 0.73 (m, 1H), 0.43 (m, 1H); ^{13}C NMR ($CDCl_3$) exo and endo isomers: δ 137.1, 136.7, 136.3, 132.4, 68.9, 66.1, 51.0, 49.2, 44.8, 43.6, 43.3, 42.1, 41.5, 41.1, 39.1, 29.5, 29.2. ^{31}P NMR ($CDCl_3$) exo and endo isomers: δ 17.5 (m, 3P); *m/e* 874 MH^+.

General Method for the Preparation of Pentasubstituted (Monochloro)cyclotriphosphazenes 5, 7, 9, 11, 13, and 15. A solution of 428 mmol of the appropriate alcohol or substituted phenol in 200 mL of dry THF was added dropwise to a stirred suspension of of NaH (428 mmol, 60% dispersion in mineral oil) in 100 mL of dry THF at room temperature (∼23 °C). The mixture was stirred under ambient conditions for 20 h and was then added dropwise to a stirred solution of of **2** (75 mmol) in 150 mL of dry THF at −30 °C. The mixture was allowed to warm to room temperature, refluxed overnight, and cooled to room temperature. The trifluoroethoxy, ethoxy, and tri(ethylene glycol) monomethyl ether containing trimers were concentrated and used without further purification in the subsequent syntheses of **6**, **10**, and **16**. However, for trimers **7**, **11**, and **13** the organic layer was concentrated and purified by column chromatography (silica gel, 70/30 hexanes/ethyl acetate for **7** and 55/45 CH_2Cl_2/hexanes for **11** and **13**).

Pentakis[(α,α,α-trifluoroethoxy)(monochloro)]cyclotriphosphazene **(5)**: ^{31}P NMR (D_2O) δ 27.3 (t, 1P), 17.8 (s, 3P) (hexa), 15.3 (d, 2P).

Pentakis[(4-ethylcarboxylatophenoxy)(monochloro)]cyclotriphosphazene **(7)**: 49% of a noncrystallizable oil. ^1H NMR ($CDCl_3$): δ 7.91 (m, 10H), 7.05 (m, 10H), 4.32 (q, 10H), 1.33 (t, 15H). ^{31}P NMR ($CDCl_3$): δ 21.39 (t, 1P), 5.86 (d, 2P).

Pentakis(ethoxy)(monochloro)cyclotriphosphazene **(9)**. ^{31}P NMR (D_2O): δ 27.8 (t, 1P), 18.8 (s, 3P) (hexa), 15.8 (d, 2P).

Pentakis(phenoxy)(monochloro)cyclotriphosphazene **(11)**: 47% of a white solid. ^1H NMR ($CDCl_3$): δ 6.96 (m, 25H, aromatic). ^{13}C NMR ($CDCl_3$): δ 147.1, 140.0, 127.8, 119.6. ^{31}P NMR ($CDCl_3$): δ 22.88 (t, 1P), 7.6 (d, 2P); *m/e* 636 MH^+.

Pentakis[(*p*-ethylphenoxy)(monochloro)]cyclotriphosphazene **(13)**. 50% of a viscous semicrystalline liquid. ^1H NMR ($CDCl_3$): δ 7.88 (m, 20H, aromatic), 2.57 (d, 10H), 1.11 (t, 15H). ^{13}C NMR ($CDCl_3$): δ 148.4, 141.0, 128.7, 121.0, 28.2, 15.6. ^{31}P NMR (D_2O): δ 23.0 (t, 1P), 7.9 (d, 2P); *m/e* 760 MH^+.

Pentakis[(2-(2-(2-methoxyethoxyethoxy)ethoxy)(monochloro)]-cyclotriphosphazene (**15**): ^{31}P NMR (D_2O): δ 27.9 (t, 1P), 19.2 (s, 3P), 16.1 (d, 2P).

General Procedure for the Preparation of (5-Norbornene-2-methoxy) Pentasubstituted Cyclotriphosphazenes 6, 8, 10, 12, 14, and 16. A solution of 66 mmol (8.1 g) of **3** in 20 mL of dry THF was added dropwise to a stirred suspension of NaH (66 mmol, 2.6 g, 60% dispersion in mineral oil) in 80 mL of dry THF at room temperature (∼23 °C). The mixture was stirred under ambient conditions for 20 h and was then added dropwise to a stirred solution of the appropriate monochloro trimer (66 mmol) in 300 mL of dry THF at room temperature. The mixture was allowed to warm to room temperature and was then refluxed gently overnight, cooled to room temperature, and quenched with water.

[(5-Norbornene-2-methoxy)pentakis(α,α,α-trifluoroethoxy)]cyclotriphosphazene (6). The organic layer was concentrated and the crude product purified by column chromatography (silica gel, 50/50 hexanes/ ethyl acetate). The resultant oil was fractionally distilled twice under reduced pressure to yield a clear colorless oil containing both endo and exo isomers (58%). ^1H NMR ($CDCl_3$) (exo and endo isomers): δ 6.08 (dd, 1H), 6.06 (dd, 1H), 6.00 (dd, 1H), 5.90 (dd, 1H), 4.19 (m, 10H), 3.97 (m, 1H), 3.79 (m, 1H), 3.64 (m, 1H), 3.51 (m, 1H), 2.82−2.66 (m, 2H), 2.36 (m, 1H), 2.00 (m, 1H), 1.73 (m, 1H), 1.41 (m, 1H), 1.29 (m, 1H), 1.19 (m, 1H), 1.06 (m, 1H), 0.79 (m, 1H), 0.42 m, 1H). ^{13}C NMR ($CDCl_3$): δ 137.9, 136.0, 131.8, 71.0, 70.9, 63.7−62.3, 49.2, 44.6, 43.7, 39.2, 29.1.

^{31}P NMR (CDCl$_3$): δ 18.3−17.6 (m, 2P), 16.8−15.5 (m, 1P); *m*/*e* 753 MH$^+$.

[(5-Norbornene-2-methoxy)pentakis(4-ethylcarboxylatophenoxy)]cyclotriphosphazene (8). The organic layer was concentrated and the product dried under high vacuum with gentle heating for 72 h to yield a viscous noncrystallizable oil containing both endo and exo isomers (71%). ^{1}H NMR (CDCl$_3$) (exo and endo isomers): δ 7.85 (d, 10H), 7.01 (d, 10H), 6.10 (dd, 1H), 5.92 (dd, 1H), 4.29 (m, 10H), 4.16−4.02 (m, 1H), 3.82−3.71 (m, 1H), 2.85 (m, 1H), 2.74 (m, 1H), 2.68 (m, 1H), 2.62 (m, 1H), 2.44 (m, 1H), 2.04 (m, 1H), 1.81 (m, 1H), 1.37 (m, 1H), 1.26 (m, 15H), 1.17 (m, 1H), 1.09 (m, 1H), 0.78 (m, 1H), 0.56 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 165.4, 153.8, 137.6, 132.1, 131.0, 126.6, 120.4, 68.4, 63.3, 61.0, 49.3, 43.9, 42.1, 37.8, 28.9, 15.6, 14.2. ^{31}P NMR (CDCl$_3$): δ 11.0−12.3 (m, 1P), 8.0−8.6 (m, 2P); *m*/*e* 1084 MH$^+$.

[(5-Norbornene-2-methoxy)pentakis(ethoxy)]cyclotriphosphazene (10). The organic layer was concentrated and the resultant oil purified by column chromatography (silica gel, 70/30 hexanes/ethyl acetate) to yield a clear colorless oil containing both endo and exo isomers (53%). ^{1}H NMR (CDCl$_3$) (exo and endo isomers): δ 6.07 (dd, 1H), 6.06 (dd, 1H), 6.02 (d, 1H), 5.93 (d, 1H), 3.93 (m, 10H), 3.73 (m, 1H), 3.62 (m, 1H), 3.42 (m, 1H), 2.90 (m, 1H), 2.72 (m, 1H), 2.39 (m, 1H), 1.99 (m, 1H), 1.72 (m, 1H), 1.33 (m, 1H), 1.23 (m, 1H), 1.22 (m, 15H), 1.21 (m, 1H), 1.18 (m, 1H), 1.09 (m, 1H), 0.46 (m, 1H). ^{31}P NMR (D$_2$O): δ 27.8 (t, 1P), 18.8 (s, 3P), 15.8 (d, 2P); *m*/*e* 484 MH$^+$.

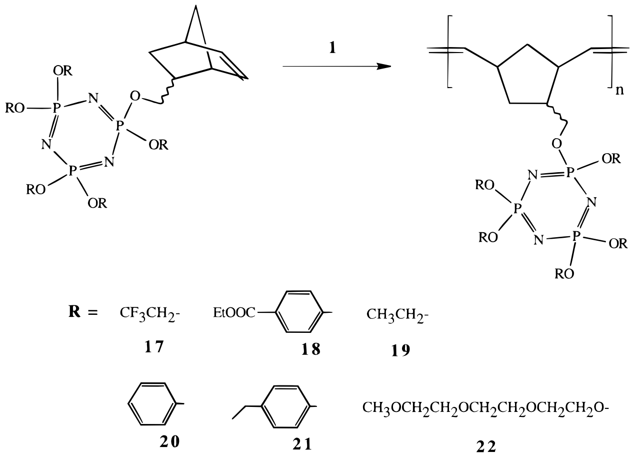
[(5-Norbornene-2-methoxy)pentakis(phenoxy)]cyclotriphosphazene (12). The organic layer was concentrated and the product recrystallized in hexanes to yield a crystalline solid containing both endo and exo isomers (89%). ^{1}H NMR (CDCl$_3$) (exo and endo isomers): δ 7.17−6.85 (m, 25H), 5.95 (dd, 1H), 5.72 (dd, 1H), 3.45−3.30 (m, 1H), 3.20−3.05 (m, 1H), 2.70−2.66 (m, 2H), 2.10 (m, 1H), 1.54 (m, 1H), 1.44 (m, 1H), 1.30 (m, 1H), 1.15 (m, 1H), 1.06 (m, 1H), 0.98 (m, 1H), 0.82 (m, 1H), 0.20 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 151.2, 137.3, 132.8, 129.9, 125.3, 121.6, 70.0, 49.7, 45.3, 44.0, 42.0, 39.3, 28.9. ^{31}P NMR (CDCl$_3$): δ 13.4−11.9 (m, 1P), 9.9−9.3 (m, 2P); *m*/*e* 724 MH$^+$.

[(5-Norbornene-2-methoxy)pentakis(*p*-ethylphenoxy)]cyclotriphosphazene (14). The organic layer was concentrated and then dried for 24 h to yield a viscous noncrystallizable oil containing both endo and exo isomers (67%). ^{1}H NMR (CDCl$_3$) (exo and endo isomers): δ 6.94−6.70 (m, 20H), 5.93 (dd, 1H), 5.67 (dd, 1H), 3.43−3.30 (m, 1H), 3.24−2.98 (m, 1H), 2.68−2.64 (m, 2H), 2.50 (d, 10H), 2.08 (m, 1H), 1.53 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 147.8, 139.5, 136.0, 131.4, 127.5, 119.9, 68.4, 48.2, 43.1, 40.8, 37.9, 33.7, 30.6, 27.4, 21.6, 14.6, 13.1. ^{31}P NMR (CDCl$_3$): δ 11.9−10.1 (m, 1P), 8.1−7.3 (m, 2P); *m*/*e* 864 MH$^+$.

[(5-Norbornene-2-methoxy)pentakis(2-(2-(2-methoxyethoxyethoxy)ethoxy)]cyclotriphosphazene (16). The organic layer was concentrated and the resultant oil purified by column chromatography (silica gel, 80/20 ethyl acetate/methanol) to yield a clear yellow oil containing both exo and endo isomers (55%). ^{1}H NMR (CDCl$_3$) (exo and endo isomers): δ 5.81 (dd, 1H), 5.76 (d, 1H), 5.75 (d, 1H), 5.67 (d, 1H), 3.74 (m, 10H), 3.38−3.31 (m, 40H), 3.22 (m, 10H), 3.05 (bs, 15 H), 2.64 (m, 1H), 2.49 (m, 1H), 1.00 (m, 1H), 0.96 (m, 1H), 0.92 (m, 1H), 0.84 (m, 1H), 0.20 (m, 1H). ^{13}C NMR (CDCl$_3$) (exo and endo isomers): δ 136.2, 135.9, 135.8, 135.3, 131.5, 70.9, 69.6, 69.5, 69.0, 64.7, 64.0, 59.1, 57.9, 48.3, 43.9, 42.6, 42.4, 41.2, 40.6, 38.2, 28.5, 19.9, 13.1. ^{31}P NMR (D$_2$O): δ 19.8−18.6 (m, 1P), 19.1 (m, 2P); *m*/*e* 1074 MH$^+$.

General Polymerization Procedure. An example of the polymerization procedure is described for the polymerization of **6**. Under an inert atmosphere, a 20 mL vial containing a magnetic stir bar was charged with 4.75 g of degassed **6** (3.64 mmol). A solution of 15 mg of **1** (0.018 mmol) ([**M**]/[**1**] = 200) in 5 mL of methylene chloride was added to the vial via a pipet. The vial was capped, and the contents were stirred at room temperature (∼23 °C). Within 2 min the dark red solution became progressively more viscous, and after 10 min the contents of the vial were solid. After 2 h the polymer gel was transferred to a separate container, and 0.5 mL of ethyl vinyl ether and 50 mL of chloroform were added. The polymer solution was poured into 500 mL of a 50/50 methanol/H$_2$O mixture and stirred. The rubbery solid that precipitated was collected and dried overnight under vacuum to yield 2.4 g (50%).

Scheme 3



The polymerization procedure was modified slightly for monomers bearing aromatic side groups. For monomers **8**, **12**, and **14** it was necessary to dilute the system to 8−10 mL of solvent per 1 g of monomer to allow sufficient stirring.[29] All the monomers polymerized without complications as illustrated in Scheme 3. Polymers **18**, **20**, and **21** were recovered as off-white solids, and polymer **17** was recovered as a brown gum. Polymer **19** was recovered as a yellow rubbery solid and polymer **22** as a highly viscous oil. Because of the soluble nature of polymer **22**, dialysis tubing with a 6−8000 molecular weight cutoff was used for its purification. All polymers were soluble in common polar organic solvents such as THF, dimethylacetamide, or chloroform. In addition, polymer **22** was soluble in alcohols and hydrocarbons such as hexanes and toluene. The reactions were carried out under argon at room temperature for a period of 15 min to 24 h with varying monomer-to-initiator ratios (Table 1). At higher concentrations and monomer-to-catalyst ratios of 50:1 or higher, the polymerizations occurred rapidly as indicated by short gelation times (typically less than 10 min). Deprotection of the ester groups of polymer **18** was carried out by the addition of excess potassium *tert*-butoxide (10 equiv per ester) in THF, and the mixture was stirred at room temperature for 3 days.[25]

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

Polymer **17**: ^{1}H NMR (CDCl$_3$): δ 5.54−5.03 (bd, 2H), 4.25 (bs, 10H), 4.00 (bm, 1H), 3.81 (bm, 1H), 3.70 (m, 1H), 2.92 (bm, 1H), 2.73 (bm, 1H), 2.33 (m, 1H), 1.95 (bs, 1H), 1.48 (bm, 1H), 1.17 (m, 1H), 0.75 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 137.8, 136.0, 137.3−133.6 (backbone C-olefin), 123.9, 70.7, 62.8, 48.8−43.4 (backbone C-alkyl), 43.3, 39.3, 29.1. ^{31}P NMR (CDCl$_3$): δ 18.3−17.5 (m, 2P), 16.8−15.6 (m, 1P). Anal. Calcd for $C_{18}H_{21}O_6N_3P_3F_{15}$: C, 28.70; H, 2.81; N, 5.58. Found: C, 28.02; H, 2.47; N, 5.31.

Polymer **18**: ^{1}H NMR (CDCl$_3$): δ 7.82 (d, 10H), 7.00 (d, 10H), 5.52−5.01 (bd, 2H), 4.31 (m, 10H), 4.02−3.88 (bm, 2H), 3.70 (m, 1H), 3.01 (bm, 1H), 2.62 (bm, 1H), 2.40 (bs, 1H), 1.91 (bs, 1H), 1.50 (bm, 1H), 1.28 (m, 15H), 1.12 (m, 1H), 1.02 (m, 1H), 0.72 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 165.8, 154.1, 135.6−132.5 (backbone C-olefin), 131.6, 128.1, 120.9, 67.6, 63.8, 61.5, 45.4−36.2 (backbone C-alkyl), 14.7. ^{31}P NMR (CDCl$_3$): δ 18.3−17.6 (m, 2P), 16.9−15.6 (m, 1P). Anal. Calcd for $C_{53}H_{56}O_6N_3P_3$: C, 58.73; H, 5.21; N, 3.88. Found: C, 59.14; H, 5.21; N, 3.60.

Polymer **19**: ^{1}H NMR (CDCl$_3$): δ 5.51−5.02 (bd, 2H), 3.87 (bs, 10H), 2.90 (bm, 1H), 2.66 (bm, 1H), 2.31 (bs, 1H), 1.88 (bs, 1H), 1.78 (bm, 1H), 1.62−0.20 (bm, 15H); ^{13}C NMR

($CDCl_3$): δ 135.7−130.6 (backbone C-olefin), 123.9, 71.8, 70.4, 64.9, 61.7, 47.2−37.8, 34.8, 30.2, 16.1. ^{31}P NMR (D_2O): δ 20.4−17.5 (bm, penta + hexa-substituted). Anal. Calcd for $C_{18}H_{36}O_6N_3P_3$: C, 44.72; H, 7.51; N, 8.69. Found: C, 46.10; H, 7.17; N, 7.67.

Polymer **20**: ^{1}H NMR ($CDCl_3$): δ 7.18−6.85 (m, 25H), 5.47−4.98 (bd, 2H), 3.62−3.01 (bm, 4H), 2.98 (bm, 1H), 2.71 (bm, 1H), 2.68 (bm, 1H), 2.12 (bs, 1H), 1.95 (bs, 1H), 1.55 (bm, 1H), 1.29 (bm, 1H), 1.17 (m, 1H), 1.03 (m, 1H), 0.98 (m, 1H), 0.80 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 151.1, 137.4−132.6 (backbone C-olefin), 130.0, 124.9, 121.7, 69.2, 49.8, 45.4−39.1 (backbone C-alkyl), 29.1. ^{31}P NMR ($CDCl_3$): δ 13.2−12.1 (t, 1P), 9.7−9.1 (d, 2P). Anal. Calcd for $C_{38}H_{36}O_6N_3P_3$: C, 63.07; H, 5.01; N, 5.81. Found: C, 63.18; H, 5.10; N, 5.65.

Polymer **21**: ^{1}H NMR ($CDCl_3$): δ 6.98−6.74 (m, 20H), 5.32−4.88 (bd, 2H), 3.68−3.23 (bm, 4H), 2.75 (bm, 1H), 2.62 (bm, 1H), 2.46 (bs, 10H), 2.21 (bs, 1H), 1.97 (bs, 1H), 1.68 (bm, 1H), 1.55 (bm, 1H), 1.22 (m, 1H), 1.16 (m, 15H), 0.93 (m, 1H), 0.86 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 148.8, 137.4−133.0 (backbone C-olefin), 128.6, 120.9, 67.8, 48.0, 45.6−35.6 (backbone C-alkyl), 31.6, 28.2, 22.8, 15.6, 14.1. ^{31}P NMR ($CDCl_3$): δ 13.6−12.4 (t, 1P), 10.0−9.4 (d, 2P). Anal. Calcd for $C_{38}H_{36}O_6N_3P_3$: C, 66.74; H, 6.53; N, 4.86. Found: C, 66.38; H, 6.22; N, 4.63.

Polymer **22**: ^{1}H NMR ($CDCl_3$): δ 5.36−5.00 (bd, 2H), 3.95 (m, 15H), 3.75 (bm, 1H), 3.61 (m, 1H), 3.59−3.51 (m, 40H), 3.45 (m, 10H), 3.43 (m, 1H), 3.28 (m, 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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