Synthesis of Cyclolinear Phosphazene-Containing Polymers via ADMET Polymerization

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Received January 16, 2001; Revised Manuscript Received May 14, 2001

ABSTRACT: We report here a new method for the synthesis of cyclolinear organic−inorganic polymers with phosphazene rings in the main chain structure by the use of ADMET polymerization. In this work, cyclic phosphazene trimers bearing two nongeminal alkene chains were prepared. Both of the alkene chains have a terminal double bond that together form the diene structure required for ADMET polymerizations. The remaining four substituents were varied to include phenoxy, benzyloxyphenoxy, methoxyethoxyethoxy, and dimethylamino groups. The resultant polymers are well-defined, low-polydispersity materials with phosphazene cyclic trimers uniformly incorporated into the backbone structure. The variation of substituents on the phosphazene ring affects both the polymerization and the properties of the resultant polymers.

Introduction

Phosphazenes are a unique class of inorganic−organic materials that offer a high degree of tailorability by variations in the synthesis procedures. Both linear polymers and cyclic small molecule phosphazenes can be functionalized with a broad range of organic substituents. The most widely studied phosphazene polymer systems have a linear backbone of alternating phosphorus and nitrogen atoms with two organic groups linked to each phosphorus atom. Several hundred different polymers of this type are known, with properties that range from tough hydrophobic elastomers to water-soluble and biodegradable polymers.[1−3] Despite the many attributes and potential uses of these materials, their relatively high cost has slowed their commercialization. An alternative promising area of research involves the incorporation of phosphazene units into organic polymers. The properties of organic polymers can be modified significantly to improve their fire retardance, ionic conductivity, biological compatibility, or other properties by the incorporation of a small amount of a specifically tailored phosphazene.[4−10]

A number of different strategies exist for the incorporation of phosphazenes into organic polymer systems.[2,3,11,12] The ambient temperature living cationic polymerization allows the synthesis of a wide variety of functionalized and telechelic polyphosphazenes.[13] These species can be combined with poly(ethylene oxide), poly(dimethylsiloxane), polystyrene, and polynorbornene as block and graft copolymers.[14−17] This work has allowed a variety of materials to be synthesized and studied, including amphiphilic systems with interesting solution behavior.[18]

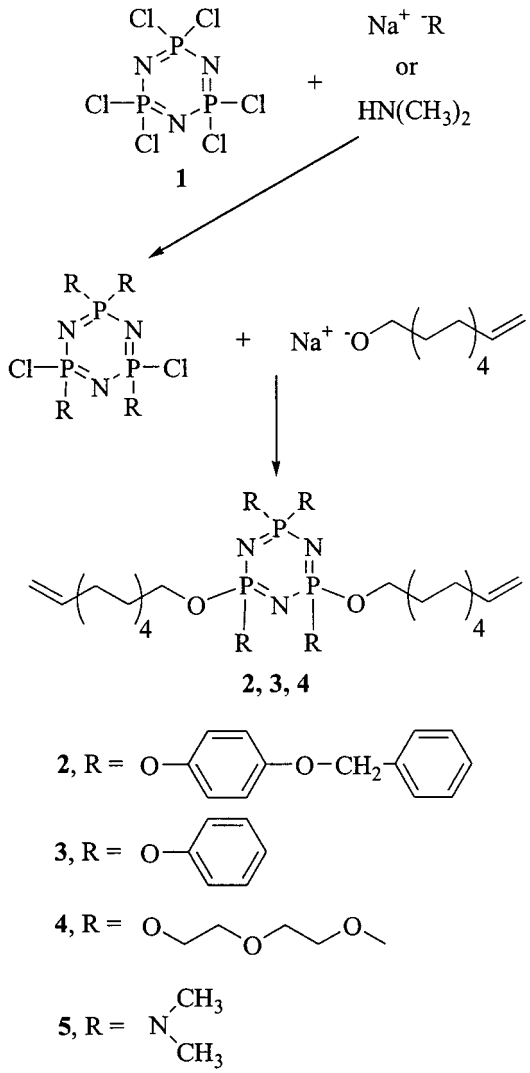
A second route used to introduce phosphazene moieties into organic polymer systems is to incorporate small-molecule cyclic phosphazene units as side groups pendent to an organic polymer chain. The overall properties of the polymer system can then be influenced both by the number of phosphazene units per chain and by the choice of side groups on the phosphazene ring. Most of these polymers have been synthesized via free radical polymerization of vinyl functionalized cyclic phosphazenes and have produced a wide variety of homopolymers and copolymers with polystyrene and poly(methyl methacrylate) backbones.[2,11,12,19] Recent work in our laboratory has yielded methyl methacrylate and styrene backbone polymers with pendent cyclic phosphazene trimers through nitrene insertion chemistry.[20] This work showed that the incorporation of a relatively small amount of functionalized phosphazene can markedly improve the properties of the base polymer. Moreover, it demonstrated the ease with which a wide range of functionalized phosphazenes can be incorporated into these organic systems. Another approach utilizing ROMP chemistry has yielded polynorbornenes with various phosphazene trimer units pendent to the main organic polymer chain.[21] The same flexibility of phosphazene structure seen in the nitrene insertion work is apparent, and this approach is currently being expanded to include oxynorbornene and octadiene monomers. Other research has shown that the incorporation of phosphazene trimers into silicon-containing polymers is also possible.[22,23]

A third, less common, strategy for the incorporation of phosphazene units into organic systems is by the synthesis of cyclolinear polymers. These polymers contain cyclic phosphazene units that are incorporated directly into an organic polymer backbone structure. The tailorability of the side groups in cyclic phosphazenes allows access to difunctional, polymerizeable species. In the late 1960s and early 1970s a great deal of research was reported on the formation of cyclolinear and cyclomatrix phosphazenes due to their excellent thermal resistance. Most of these materials were synthesized at relatively high temperatures (∼700 °C), and the products were frequently poorly characterized, densely cross-linked materials or low molecular weight oligomers.[2,12] The field of cyclolinear phosphazene polymers has been neglected in recent years except for a few examples of polyimides,[4,24,25] polyamides,[26] polyesters,[27] polyurethanes,[28,29] and polyketones[30] with cyclic phosphazenes incorporated into the backbone to improve thermal properties.

We report here a new method for the synthesis of cyclolinear polymers with phosphazene rings in the main chain structure. The polymers described in this work are well-defined, with moderate to high molecular weights and good solubility in common organic solvents.

10.1021/ma010084b CCC: $20.00
Published on Web 06/22/2001

Scheme 1. Synthesis of ADMET Monomers 2−5



The synthesis utilizes acyclic diene metathesis (ADMET) to polymerize cyclic phosphazene dienes. ADMET is a relatively new route to novel organic polymers that has been explored in detail, primarily by Wagener,[31−33] and made possible by the highly selective catalysts developed by Grubbs and Schrock.[34,35] This metathesis reaction is driven by the removal of ethylene and results in the condensation of highly pure dienes into linear polymers. ADMET chemistry allows the polymerization of many different monomers with a high degree of functionality and produces regular, well-defined, condensation polymers. However, little work in this area has been reported with monomers as large, or as complex, as those described here. The closest system described so far, with comparable sized monomers, is the polymerization of telechelic poly(tetrahydrofuran) oligomers to produce homopolymers and block copolymers.[36] The functionality and bulkiness of the monomers described here illustrate the versatility of the ADMET polymerization route.

Results and Discussion

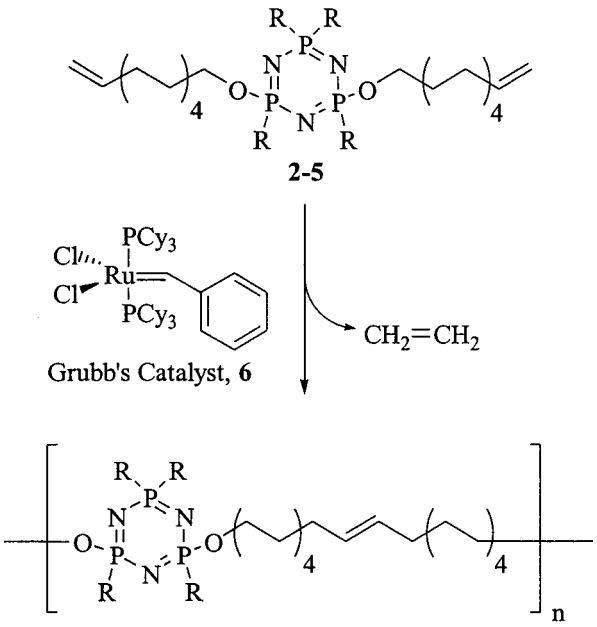
Monomer Synthesis. Four different small molecule cyclic phosphazene trimers bearing different organic groups were prepared with the diene structure required for ADMET monomers (Scheme 1). Each of the phosphazene monomers has two nongeminal undecenoxy substituents and four other organic side groups. The other organic groups utilized in this work demonstrate the range of structures that are possible. Two different types of aromatic side groups, phenoxy and benzyloxyphenoxy, as well as an oligoethyleneoxy chain and a secondary amine were linked to cyclic phosphazene trimers for metathesis polymerizations. The undecenoxy group was chosen as the bearer of double bonds due to its ready availability and the length of the carbon chain. The "negative neighboring group" effect has been described for ADMET polymerizations, and this inhibits polymerization when a functional group is too close to the active double bond.[37] The length of the undecenoxy substituent was designed to prevent the "negative neighboring group" effect from being a factor as well as to ensure that the reactive double bonds extend well beyond the bulky substituents on the phosphazene ring.

One of the limiting factors for efficient, high molecular weight condensation polymerizations is monomer purity. The synthesis of mixed substituent phosphazene cyclic trimers almost always results in a mixture of products. For ADMET polymerizations it is important to ensure that no monomer species are present that bear three or more terminal double bonds (this would yield cross-linked materials) or only one terminal double bond (which would end-cap the polymer chains). Three approaches were utilized for the synthesis of the monomers described in this work, all with hexachlorocyclotriphosphazene (**1**) as the starting material. The first strategy involved the synthesis and purification of a tetraorgano-substituted dichloro cyclic phosphazene trimer. This purified trimer was then treated with sodium undecenoxide to replace the remaining two chlorine atoms. This route was successful for monomers that bear benzyloxyphenoxy (**2**) and dimethylamino (**5**) cosubstituents and is shown in Scheme 1.

The synthesis of the other two monomers, with oligoethyleneoxy (**4**) and phenoxy (**3**) substituents, was attempted by the same route, but in each case there were purification difficulties. The tetrasubstituted oligoethyleneoxy dichloro derivative was difficult to purify by normal phase column chromatography due to its affinity for the silica gel. The analogous phenoxy species, when treated with sodium undecenoxide, gave a mixture of products due to the displacement of some phenoxy groups by undecenoxide groups. This mixture of tetra and tris species was also very difficult to separate, and the tetraphenoxy dichloro species could not be isolated pure. Thus, the tetraorgano dichloro compounds were not isolated, but the sodium undecenoxide was added to a mixture of tetra- and pentasubstituted phosphazene rings. The addition of the nonpolar aliphatic groups to the oligoethyleneoxy functionalized trimer then allowed separation by column chromatography. In the phenoxy-substituted derivative, the displacement reaction leading to trisubstituted phosphazene trimers was significantly lessened, and purification of the desired product was also successful through column chromatography. The third strategy was to synthesize and purify a tetrachloro cyclic phosphazene trimer with two undecenoxide substituents. This molecule could potentially serve as a good starting point for a wide range of phosphazene monomers. However, purification of this compound proved to be difficult.

Monomers **3**−**5** were obtained as pale yellow oils, and monomer **2** was obtained as a white crystalline solid.

Scheme 2. General Synthesis of ADMET Polymers



The structures were confirmed by ^{1}H,^{13}C, and ^{31}P NMR and mass spectrometry.

Polymerizations. It was known from previous ROMP work in our program that the catalysts necessary for ADMET polymerizations can normally tolerate the presence of phosphazene rings with various substituents. However, unlike ring-opening metathesis polymerizations, ADMET polymerizations are driven by the elimination of ethylene under reduced pressure, and they can be reversible if the ethylene is not removed.[33] Therefore, most polymerizations reported in the literature are carried out under solvent-free conditions with constant or intermittent vacuum.[31,38,39] Occasionally the reaction mixtures are heated to achieve higher conversions and higher molecular weights.[31,38,39]

In this work, literature-based polymerization procedures were followed for monomers **3**−**5**. However, the fact that monomer **2** is a crystalline solid at room temperature required the use of modified polymerization conditions. All the polymerizations were carried out with the addition of 1 equiv of the classical Grubbs catalyst (**6**) to 40 equiv of monomer (Scheme 2). The catalyst was weighed in an inert atmosphere drybox and added to the pure monomer in a 25 mL Schlenk flask. The flask was then removed from the drybox, and constant vacuum was applied at room temperature.

Monomers **3** and **4**, bearing phenoxy and oligoethyleneoxy substituents, respectively, condensed rapidly into polymers as evidenced by the immediate and rapid evolution of ethylene. The polymerizations proceeded until the magnetic stirrer bar could no longer rotate due to the increase in viscosity. At this point the temperature was gradually increased to 70 °C to reduce the viscosity and facilitate mixing of the polymer and to assist further condensation. Within 72 h the magnetic stirrer was again fully immobilized, and the color of the mixture had changed from purple to brown, which indicated deactivation of the catalyst. The polymers were dissolved in THF and precipitated into methanol before characterization.

The number-average molecular weights of these two polymers were 45 500 and 32 800 for the oligoethyleneoxy-functionalized monomer and the phenoxy-functionalized monomer, respectively. This corresponds to roughly 48 and 39 repeating units. The slightly higher molecular weight achieved for the oligoethyleneoxy-functionalized trimer is attributed to the lower viscosity of the polymerization mixture. This interpretation is supported by the DSC data which is discussed later. Moreover, the polydispersity is higher for the phenoxy-substituted species (3.3 vs 1.9) which is probably a result of less-thorough mixing of the reaction mixture and therefore a less uniform molecular weight distribution.

The polymerization of monomer **2**, bearing benzyloxyphenoxy substituents, was less straightforward due to the crystalline nature of the material at room temperature. Initial polymerizations were carried out in an inert atmosphere drybox with the addition of the catalyst in dichloromethane to the monomer, also in dichloromethane. The solvent was then removed under reduced pressure, and the mixture was heated to 65 °C, the approximate melting point of the monomer. The evolution of ethylene and an increase in viscosity of the melt indicated the onset of polymerization. The reaction temperature was gradually increased to 110 °C to lower the viscosity and facilitate stirring. Within 12 h at 110 °C ethylene evolution had ceased, and the catalyst had decomposed. The reaction mixture was then dissolved in THF, and the polymer was precipitated into methanol.

Because of the high viscosity and difficulty of stirring, the initial polymerizations of the benzyloxyphenoxy-functionalized monomer (**2**) achieved number-average molecular weights no higher than 10 000 (∼10 repeating units). More vigorous stirring gave increased molecular weights, (M_n = 32 000), but the polydispersities increased dramatically from 2 to near 5, with an apparent bimodal molecular weight distribution. This increase in polydispersity is attributed to incomplete mixing of the system as regions of the reaction mixture became too viscous to interact with the bulk material. However, the addition of small amounts of a high boiling solvent (diphenyl ether) allowed more complete mixing of the system and raised the number-average molecular weight to above 30 000 (∼30 repeating units) while the polydispersity remained near 2. These results are shown in Figure 1, which compares GPC traces of these three modified polymerization procedures for monomer **2**. The difficulty in obtaining high molecular weight polymer with low polydispersity is believed to be a function of the inability to stir the reaction mixture effectively. However, the steric bulk and purity of the monomer could also be factors.

Monomer **5**, with dimethylamino cosubstituents, also presented problems during polymerization. The initial evolution of ethylene was as rapid as with the other monomers. However, high molecular weight polymer was not obtained. After about 6 h the reaction mixture showed discoloration (indicative of catalyst decomposition or coordination), and ethylene evolution ceased. The viscosity of the mixture never reached a high level, and GPC traces showed evidence of only short oligomers, probably dimers, trimers, and tetramers. In an effort to obtain high molecular weight polymer, a second equivalent of catalyst was added to the reaction mixture after polymerization had ceased. This yielded only about 15 min of extended ethylene evolution and a negligible

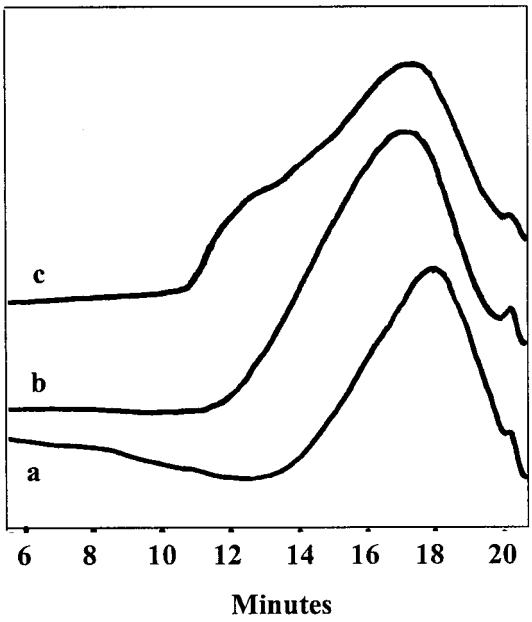


Figure 1. GPC traces of (a) polymer **2** synthesized neat with magnetic stirrer at 60 °C, M_n = 17 000, and PDI = 2.1; (b) polymer **2** synthesized in diphenyl ether at 60 °C, M_n = 30 000, and PDI = 2.5; and (c) polymer **2** synthesized with mechanical stirrer at 60 °C, M_n = 32 000, and PDI = 5.5.

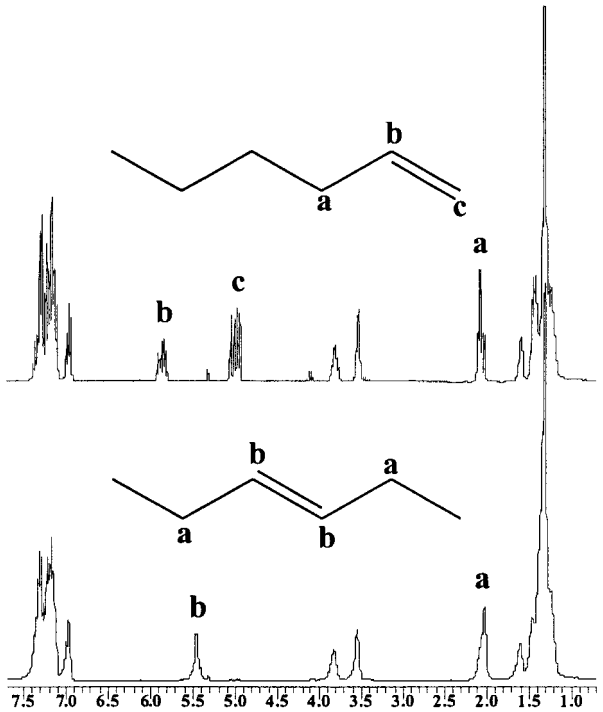


Figure 2. ^{1}H NMR comparison of ADMET monomer **3** (top spectrum) and polymer **3** (bottom spectrum).

increase in molecular weight detected by GPC. The most likely explanation for the lack of polymer formation is the coordination of nitrogen lone pair electrons to the electron-deficient metal center of the catalyst. It is well-known that sites with lone pair electrons can coordinate to metathesis catalysts.[40−42] Work by Portmess and co-workers demonstrated the ability of the nitrogen lone pair of diallylamine to inhibit metathesis polymerizations using the Schrock catalyst.[42] In that work the problem was circumvented by the preparation of a series of *N*-phenylamines to decrease the nucleophilicity of the lone pair. In the monomers used here, the methyl substituents on the amine serve to increase the nucleophilicity of the lone pair and increase the coordinating ability. Moreover, the concentration of amine functionality present in the monomer is very high relative to the double-bond concentration. It is possible that, when the catalyst is added to the monomer, there is a high enough concentration of double bonds to promote metathesis but that, as the reaction proceeds, the ratio of amine groups to double bonds increases dramatically, and thus the metal centers are more likely to coordinate to a nitrogen lone pair than to find a free terminal double bond. This could also explain why a second catalyst addition was only marginally successful in promoting further condensation.

Polymer Characterization. The polymers obtained range from gums (polymer **4**) to tough leathery materials (polymer **2**) readily soluble in common organic solvents such as THF and CH_2Cl_2. For monomers **2**−**4** the polymerization reaction proceeds very cleanly despite the bulk and functionality of the monomers, with almost complete conversion and very little residual unreacted monomer. The resultant polymers were characterized via multinuclear NMR, GPC, and DSC. The efficiency of these reactions is seen in the ^{1}H NMR spectra of the phenoxy-substituted monomer (**3**) and polymer superimposed in Figure 2. The monomer peaks corresponding to the reactive allyl groups are designated as protons a, b, and c in the top spectrum. The terminal olefinic protons, labeled c, are present in the monomer but disappear in the polymer spectrum. Moreover, the large shift of peak b and slight shift of peak a is indicative of reaction at this site to form the polymer and release ethylene. Similar changes are also evident in the ^{13}C NMR spectra, and these too support a condensation polymerization.

Thermal characterization showed some interesting trends and also illustrates the range of properties possible in this system due to the variation in the phosphazene cosubstituent groups. The effect of side groups on the glass transition temperature is significant. The flexible oligoethyleneoxy units of monomer **4** yield a polymer with a T_g of −75 °C. Because of the low glass transition temperature, this polymer is adhesive and flows under minimal pressure. These properties could make this polymer an ideal candidate for ionic conduction applications. The presence of aromatic substituents on the phosphazene ring decreases the free volume and flexibility of the system, and the T_g is increased by 40 °C to −35 °C for polymer **3**. The final polymer, with cyclic phosphazene rings bearing benzyloxyphenoxy cosubstituents, has a significantly higher T_g of 28 °C. Presumably the steric bulk of the benzyloxyphenoxy groups permits only restricted chain motion.

Melting transitions were detected in two of the three systems. The oligoethyleneoxy polymer shows a T_m at −55 °C. This is in good agreement with polymers that bear pendent oligoethyleneoxy-substituted cyclic phosphazenes and is attributed to crystallization of the oligoethyleneoxy units.[6,7] The benzyloxyphenoxy polymer has a T_m of 47 °C, which is slightly lower than that of the corresponding monomer.

Conclusions

A series of cyclic phosphazene trimers have been synthesized with the diene structure required for ADMET polymerizations. Three of the four monomers

polymerized to give moderate molecular weight cyclolinear phosphazenes with properties influenced by the cosubstituents on the phosphazene rings. These monomers are among the largest and most complex known to undergo ADMET polymerization, and they illustrate the potential versatility of this polymerization route. The amine-functionalized phosphazene monomer did not undergo condensation to high polymer, probably due to an interaction of the catalyst metal center with the lone pair electrons on the nitrogen atoms. The ADMET approach provides opportunities for the synthesis of a wide range of phosphazene cyclolinear polymers as well as copolymers with other dienes. Moreover, the continuing development of more highly active catalysts offers the promise of higher molecular weights and a higher incorporation of functionality into future polymer systems.

Experimental Section

Materials. All chemicals and reagents were obtained from Aldrich and used as received unless described otherwise. Hexachlorocyclotriphosphazene, **1** (Ethyl Corp./Nippon Fine Chemical Co.), was recrystallized from heptane and sublimed at 40 °C (0.05 mmHg). Sodium hydride (Fluka, 60% suspension in mineral oil) was used as received. Tetrahydrofuran was obtained from EM Science and distilled from sodium benzophenone ketyl prior to use.

Equipment. High-field ^{1}H (360 MHz), ^{13}C (90 MHz), and ^{31}P (146 MHz) NMR spectra were obtained using a Bruker AMX-360 spectrometer. The ^{31}P and ^{13}C spectra were proton decoupled. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 with positive shifts recorded downfield from the reference. ^{1}H and ^{13}C were referenced to external tetramethylsilane. 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 samples were eluted with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate in THF. The GPC column was calibrated with polystyrene standards. Thermal transition temperatures were determined by DSC using a Perkin-Elmer-7 thermal analysis system. Polymer samples were heated from −120 to +100 °C under an atmosphere of dry nitrogen. The heating rates used were 10, 20, and 40 °C/min. The glass transition temperatures were determined by extrapolating to zero degrees heating rate.

$N_3P_3(OC_6H_4OCH_2C_6H_5)_4Cl_2$. Hexachlorocyclotriphosphazene, **1** (118.32 g, 0.34 mol), was dissolved in 500 mL of THF. Benzyloxyphenol (238 g, 1.19 mol) was dissolved in 400 mL of THF and added dropwise to a suspension of sodium hydride (52.4 g, 1.19 mol) in 200 mL of THF. The resultant sodium aryloxide of benzyloxyphenol was added dropwise to the stirring solution of **1** at −78 °C. The reaction warmed to room temperature overnight and was checked by ^{31}P NMR to show 71% tris substitution and 29% tetra substitution. Solvent was removed by reduced pressure rotary evaporation, and the resultant wax was dissolved in 1 L of diethyl ether. This solution was washed four times with 1 L of 3% aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated by rotary evaporation. Column chromatography was performed in an 80% CH_2Cl_2/20% hexanes mixture to separate the tetra- and tris-substituted products. The desired product was recrystallized from hot hexanes three times to yield a white powder (16.8 g, 5% yield). ^{1}H NMR (d_8-THF): δ (ppm) 4.9 (s, 2H) and 6.7−7.3 (m, 9H). ^{13}C NMR (d_6-acetone): δ (ppm) 71.3, 116.9, 123.0−123.8 (m), 128.8−129.8 (m), 138.4, 157.8−158.1 (m). ^{31}P NMR (d_8-THF): δ (ppm) 23.9 (d, 2P) and 8.9 (t, 1P). FAB(+)-MS: m/z 1004 MH^+ base peak.

$N_3P_3(OC_6H_4OCH_2C_6H_5)_4(OC_{11}H_{21})_2$ (2). ω-Undecenyl alcohol (6.00 g, 35.24 mmol) was added to sodium metal (0.83 g, 36.08 mmol) in 150 mL of hexanes and refluxed for 24 h. The solution was cooled to room temperature and added dropwise to a solution of **2** (16.83 g, 16.78 mmol) in 200 mL of THF cooled to −78 °C. The reaction mix was monitored by ^{31}P NMR and after 48 h at room temperature was heated to reflux. After 48 h at reflux the reaction was still incomplete. One extra equivalent of the sodium alkoxide was prepared as above (0.40 g of Na metal, 2.86 g of ω-undecenyl alcohol, 16.78 mmol) and added to the reaction; 24 h of further reflux yielded the desired product. The solvent was removed from the reaction mix by rotary evaporation; the residue was dissolved in CH_2Cl_2 and washed with water, followed by three recrystallizations from hexanes to yield a white solid (17.4 g, 81.6% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.1−1.5 (m, 28H), 1.9 (4H), 3.4 (2H), 3.7 (2H), 4.8 (m, 12H), 5.7 (m, 2H), and 6.6−7.2 (m, 36H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.4, 28.9−30.2 (m), 33.8, 66.5, 70.3, 114.1, 115.2, 121.7−122.1 (m), 127.3−128.5 (m), 136.8, 139.1, 144.6, 155.5−155.7 (m). ^{31}P NMR (d_8-THF): δ (ppm) 11.8 (d, 2P) and 8.8 (t, 1P). Elemental analysis found: C, 69.24; H, 6.78; N, 3.21; P, 7.42. Requires: C, 70.0; H, 6.8; N, 3.3; P, 7.3. MALDI: $MH^+ = 1270.6$.

$N_3P_3(OC_6H_5)_4(OC_{11}H_{21})_2$ (3). Hexachlorocyclotriphosphazene, **1** (25 g, 71.84 mmol), was dissolved in 400 mL of THF. Phenol (28.6 g, 0.301 mol) was dissolved in 150 mL of THF and added dropwise to a suspension of sodium hydride (12.07 g, 0.301 mol) in 200 mL of THF. The resultant sodium aryloxide was added dropwise to the stirring solution of **1** at 0 °C. The reaction warmed to room temperature overnight and was checked by ^{31}P NMR to show 78% tetra substitution and 22% penta substitution. ω-Undecenyl alcohol (24.4 g, 0.144 mol) was added to sodium hydride (5.75 g, 0.144 mol) in 200 mL of THF and refluxed for 24 h. The solution was cooled to room temperature and added dropwise to the trimer reaction mix. The reaction mix was monitored by ^{31}P NMR, and after 48 h at room temperature was heated to reflux. After 24 h at reflux the solvent was removed from the reaction mix by rotary evaporation; the residue was dissolved in diethyl ether and washed with water. The final product was purified by column chromatography in an 80%/20% v/v mixture of hexanes and diethyl ether (9.2 g, 15% yield). ^{1}H NMR (CD_2Cl_2): δ (ppm) 1.2−1.6 (m, 28H), 2.1 (quad, 4H), 3.5 and 3.8 (4H), 5.0 (quad, 4H), 5.9 (m, 2H), 6.9 (tr 4H), 7.1−7.3 (m 16H). ^{13}C NMR (CD_2Cl_2): δ (ppm) 26.0 (d), 29.5, 29.7, 30.0−30.1 (m), 30.5−30.7 (m), 34.4, 67.2 (d), 114.5, 121.5 (d), 121.6, 121.7, 121.8 (d), 122.0 (d), 125.0−125.6 (m), 130.0 (d), 139.9, 151.5 (d). ^{31}P NMR (CD_2Cl_2): δ (ppm) 13.5 (d, 2P), 10.3 (t, 1P). Elemental analysis found: C, 65.43; H, 7.40; N, 4.96; P, 10.89. Requires: C, 65.3; H, 7.4; N, 5.0; P, 11.0. APCI: $MH^+ = 846.3$.

$N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_4(OC_{11}H_{21})_2$ (4). Hexachlorocyclotriphosphazene, **1** (25 g, 71.84 mmol), was dissolved in 400 mL of THF. 2-(2-Methoxyethoxy)ethanol was distilled from CaH_2 and then added via syringe (36.2 g, 0.302 mol) to a suspension of sodium hydride (12.07 g, 0.302 mol) in 200 mL of THF. The resultant sodium alkoxide was added dropwise to the stirring solution of **1** at 0 °C. The reaction warmed to room temperature overnight and was checked by ^{31}P NMR to show 62% tetra substitution and 38% penta substitution. ω-Undecenyl alcohol (24.4 g, 0.144 mol) was added to sodium hydride (5.75 g, 0.144 mol) in 200 mL of THF and refluxed for 24 h. The solution was cooled to room temperature and added dropwise to the trimer reaction mix. The reaction mix was monitored by ^{31}P NMR and after 48 h at room temperature was heated to reflux. After 24 h at reflux the solvent was removed from the reaction mix by rotary evaporation; the residue was dissolved in diethyl ether and washed with water. The final product was purified by column chromatography in a 70%/30% v/v mixture of diethyl ether/THF (14.4 g, 21% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.1−1.5 (m, 28H), 1.9 (4H), 3.4 (2H), 3.7 (2H), 4.8 (m, 12H), 5.7 (m, 2H), and 6.6−7.2 (m, 36H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.4, 28.9−30.2 (m), 33.8, 66.5, 70.3, 114.1, 115.2, 121.7−122.1 (m), 127.3−128.5 (m), 136.8, 139.1, 144.6, 155.5−155.7 (m) ^{31}P NMR (d_8-THF): δ (ppm) 11.8 (d, 2P) and 8.8 (t, 1P). Elemental analysis found: C, 53.28; H, 8.85; N, 4.54; P, 10.40. Requires: C, 53.1; H, 9.1; N, 4.4; P, 9.8. MALDI: $MH^+ = 950.8$.

$N_3P_3(N(CH_3)_2)_4(OC_{11}H_{21})_2$ (5). Hexachlorocyclotriphosphazene, **1** (25 g, 71.84 mmol), was dissolved in 1250 mL of diethyl ether. Dimethylamine was bubbled into the solution at 0 °C for 4 h. As reported previously, the dimethylamine serves as its own HCl acceptor, and the trimer substitutes nongeminally to yield the tetrasubstituted species.[43] The salts were filtered, and the solvent was removed to yield a white crystalline material. This was further purified by three recrystallizations from hexanes (23.0 g, 84%). A portion of this product (11.5 g, 0.0299 mol) was then dissolved in 250 mL of THF. ω-Undecenyl alcohol (11.71 g, 0.0689 mol) was added to sodium hydride (2.76 g, 0.0689 mol) in 150 mL of THF and refluxed for 24 h. The sodium alkoxide solution was cooled to room temperature and added dropwise to the trimer solution. The reaction mix was monitored by ^{31}P NMR, and after 24 h at room temperature and 24 h at reflux almost no reaction was evident. The THF was removed by distillation and gradually replaced with dioxane. This was then refluxed for 72 h before another equivalent of sodium alkoxide was prepared and added. An additional 24 h of reflux completed the reaction. The solvent was removed from the reaction mix by rotary evaporation; the residue was dissolved in diethyl ether and washed with water. The excess ω-undecenyl alcohol was distilled away from the final product (12.7 g, 65% yield). ^{1}H NMR (CD_2Cl_2): δ (ppm) 1.2−1.6 (m, 28H), 2.0 (quad, 4H), 2.4−2.5 (m, 24H), 3.5 and 3.7 (4H), 4.9 (quad, 4H), and 5.7 (m, 2H). ^{13}C NMR (CD_2Cl_2): δ (ppm) 26.7 (d), 29.7−30.4 (m), 31.2, 34.5, 37.0 (d), 64.9, 114.7, and 139.5 ^{31}P NMR (CD_2Cl_2): δ (ppm) 24.4 (d, 2P) and 27.1 (t, 1P). Elemental analysis found: C, 56.0; H, 9.91; N, 15.33; P, 14.98. Requires: C, 55.5; H, 10.2; N, 15.1; P, 14.3. APCI: $MH^+ = 650.4$.

Polymerization of 2. Conditions were varied slightly with each polymerization in an attempt to increase the molecular weight, but the following procedure is typical. A solution of the Grubbs catalyst, **4** (0.015 g, 0.018 22 mmol), in 1 mL of CH_2Cl_2 was added to **3** (0.926 g, 0.7291 mmol) in a 25 mL Schlenk flask in an inert atmosphere drybox. The reaction flask was then removed from the glovebox, and the contents were stirred under reduced pressure while heating to 60 °C. After removal of all CH_2Cl_2, the molten trimer was stirred with the catalyst and ethylene was evolved. Temperature was gradually increased to a maximum of 110 °C until the reaction mixture turned brown, an indication of inactivity of the catalyst. Immobilization of the stirrer bar and discoloration of the catalyst occurred within 12 h. The polymer was then dissolved in THF and was precipitated into methanol. In some cases 1 mL of dry diphenyl ether was added to the polymerizations before addition of catalyst to the phosphazene trimer. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.1−1.6 (m, 28H), 1.8 (4H), 3.4 (2H), 3.7 (2H), 4.9 (m, 8H), 5.3 (m, 4H), and 6.7−7.3 (m, 36H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.2−33.5 (m), 66.0, 69.9, 114.9, 121.6−122.0 (m), 127.0−128.2 (m), 130.0, 136.5, 144.4, 155.2−155.6 (m). ^{31}P NMR ($CDCl_3$): δ (ppm) 11.8 (d, 2P) and 8.8 (t, 1P). GPC data discussed in text.

Polymerization of 3. Grubbs' catalyst, **7** (0.012 g, 0.015 mmol), was added to **4** (0.5 g, 0.592 mmol) in a 25 mL Schlenk flask in an inert atmosphere drybox. The reaction flask was then removed from the glovebox, and the reaction mixture was stirred under reduced pressure. The temperature was gradually increased to 70 °C after 24 h to maintain fluidity and facilitate magnetic stirring. Immobilization of the stirrer bar and discoloration of the catalyst occurred within an additional 24 h. The polymer was dissolved in THF and precipitated into methanol. ^{1}H NMR (CD_2Cl_2): δ (ppm) 0.9−1.7 (m, 28H), 2.1 (4H), 3.5 and 3.8 (4H), 5.4 (2H), and 6.7−7.3 (m, 20H). ^{13}C NMR ($CDCl_3$): δ (ppm) 26.1 (d), 27.8, 29.8−30.6 (m), 33.2, 67.2 (d), 121.5 (d), 121.6, 121.7, 122.0 (d) 125.1−125.8 (m) 130.0 (d), 131.0, 151.5 (d). ^{31}P NMR ($CDCl_3$): δ (ppm) 13.3 (d, 2P) and 10.0 (t, 1P). $M_n = 33\,000$, $M_w = 108\,000$, and PDI = 3.3.

Polymerization of 4. Polymer **4** was prepared as described for polymer **3**. The following reagents and quantities were used: Grubbs' catalyst, **7** (0.011 g, 0.013 mmol), and **5** (0.5 g, 0.527 mmol). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.2 (24H), 1.6 (4H), 1.9 (4H), 3.3 (12H), 3.5 (8H), 3.6−3.7 (m, 16H), 3.9 (4H), 4.0 (8H), 5.3−5.4 (2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.6, 29.0−29.6, 30.2, 32.6, 58.9, 64.9, 66.1, 70.0, 70.5, 71.9, 129.7, 130.2 ^{31}P NMR ($CDCl_3$): δ (ppm) 18.1 (3P). $M_n = 45\,500$, $M_w = 86\,000$, and PDI = 1.9.

Polymerization of 5. Polymer **5** was prepared as described for polymer **3**. The following reagents and quantities were used: Grubbs' catalyst, **7** (0.013 g, 0.015 mmol), was added to **6** (0.5 g, 0.770 mmol). ^{1}H NMR (CD_2Cl_2): δ (ppm) 1.1−1.6 (b, 28H), 1.9 (4H), 2.4−2.6 (24H), 3.5 and 3.7 (4H), 5.2−5.4 (2H). ^{13}C NMR (CD_2Cl_2): δ (ppm) 26.5, 29.7−30.3, 31.1, 33.2, 37.0, 64.9, 130.3, 130.8. ^{31}P NMR (CD_2Cl_2): δ (ppm) 24.4 (d, 2P) and 27.1 (t, 1P).

Acknowledgment. This work was funded by the Federal Aviation Administration and the National Science Foundation Polymer program.

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MA010084B