Articles

Incorporation of Cyclic Phosphazene Trimers into Saturated and Unsaturated Ethylene-like Polymer Backbones

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ABSTRACT: The synthesis of well-defined cyclolinear phosphazene polymers via acyclic diene metathesis (ADMET) has been demonstrated. This work extends the range of properties achievable in cyclolinear phosphazenes synthesized via ADMET and provides an assessment of the synthetic limitations. A series of tetraphenoxy and tetramethoxyethoxyethoxy functionalized phosphazene trimers have been synthesized that bear two alkene side chains, which together form the diene structure necessary for ADMET. The alkene chains vary in length from three carbons to 11 carbons. This has allowed the influence of the negative neighboring group effect to be examined as well as steric factors as they apply to the metathesis of phosphazene monomers. Moreover, the role of different catalysts is discussed together with the influence of the nonolefinic phosphazene substituents on the reactivity of the monomers. The influence on bulk polymer properties of the incorporation of different amounts of cyclic phosphazene per average polymer chain, through copolymerization studies with decadiene, is also discussed.

Introduction

Olefin metathesis has significantly broadened the scope of polymer chemistry in the past 10 years together with the advent of highly specialized catalysts that initiate the ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) of a wide variety of functionalized monomers.[1] Polymer structures that were difficult, or even impossible, to synthesize less than 20 years ago can now be produced efficiently via ROMP techniques, and the commercialization of a number of materials has been made possible.[1] ADMET is a related polymerization route, in which terminal dienes condense to form polymer chains with the release of ethylene.[1−3] The versatility of this polymerization route has made it possible to polymerize numerous terminal dienes, provided ethylene is removed from the system to move the equilibrium toward polymer formation. This has led to the synthesis of well-defined macromolecules, such as perfectly linear polyethylene.[4,5] It has also allowed the study of regularly spaced functional groups introduced into polymer backbone structures of unsaturated polyethylene and other unsaturated systems.[1,3]

Cyclic phosphazene compounds have recently been incorporated into polymer systems based on both ROMP[6] and ADMET[7] chemistry. In each case, the size and functionality of the cyclic phosphazene trimer do not significantly inhibit the performance of the catalyst. These extensions of olefin metathesis chemistry now make it possible to incorporate the versatile phosphazene platform into a wide range of organic polymers. The most widely studied phosphazene polymers are linear macromolecules with alternating phosphorus and nitrogen atoms in the skeleton and with two substituents on each phosphorus atom. By contrast, in this paper we discuss the use of small-molecule cyclic trimers as components in the main chain of hybrid organic−inorganic polymers.[8] The degree of tailorability possible in phosphazenes is unique because the reactive phosphorus−chlorine bonds present in the precursors to both the cyclic and high polymer species can be replaced by a wide range of different side groups. For the linear high polymers this has generated properties appropriate for fuel cell membranes, lithium ion transport layers, biodegradable polymers, biologically inert polymers, noncombustible materials, and high-performance elastomers.[9−14] The incorporation of functionalized cyclic phosphazene moieties into commodity organic polymer structures could substantially alter the physical properties and resistance to combustion through careful tailoring of the phosphazene component. In this work we describe the synthesis of cyclolinear polymers in which cyclic phosphazene trimer units are incorporated into the polymer backbone of saturated and unsaturated polyethylene-like systems.

The synthesis of cyclolinear phosphazene polymers has been an important topic of research for many years because of the high thermal stability and fire resistance of polymers that contain cyclic phosphazene moieties.[15,16] In the late 1960s and early 1970s a great deal of research was reported on the formation of cyclolinear and cyclomatrix phosphazenes via condensation processes. Most of these materials were synthesized at relatively high temperatures (∼700 °C), and the products were frequently poorly characterized, densely crosslinked materials, or low molecular weight oligomers.[15,16] More recently, cyclolinear phosphazene-containing polymers have been developed for a range of backbone systems including polyimides,[17−19] polyamides,[20] poly-

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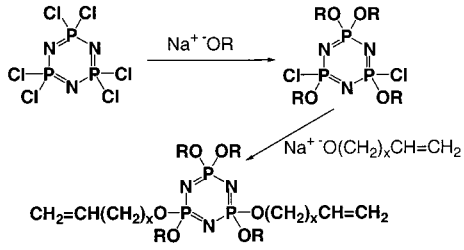
Scheme 1. Synthesis of Phosphazene Monomers 3−8 and 10−13



OR = OPh		OR = $OCH_2CH_2OCH_2CH_2OCH_3$	
x	Monomer	x	Monomer
1	**3**	1	**10**
2	**4**	2	**11**
3	**5**	3	**12**
4	**6**	9	**13**
8	**7**		
9	**8**		

esters,[21] polyurethanes,[22,23] and polyketones[24] in order to improve the properties of the organic polymer.

Rationale. Recent work in our laboratory utilized olefin metathesis catalysts and ADMET chemistry to synthesize a variety of cyclolinear phosphazene polymers.[7] These polymers are of moderate molecular weight, with good solubility in organic solvents, and low polydispersities. Moreover, it was found that the physical properties of these polymers could be varied through alteration of the substituents on the phosphazene rings. The present work extends ADMET chemistry as it applies to cyclic phosphazene systems. New monomers have been synthesized that bear four nonpolymerizable phenoxy or alkyl ether cosubstituents and two reactive terminal olefin sites. The olefins units were linked to the phosphazene trimer by nucleophilic substitution using alkoxides derived from a series of commercially available alkenols that ranged from allyl alcohol to 10-undecen-1-ol. It is well-known that the number of carbon atoms between an active olefin group and a potential second catalyst coordination site has a strong influence on ADMET polymerizations. Because the nitrogen atoms in the phosphazene ring and the oxygen atoms between the ring and the double bond are potential coordination sites, it was of interest to examine monomer reactivity in terms of separation between the olefinic sites and these electron-donating groups. In addition, the properties of each polymer were modified slightly by varying the spacing between the phosphazene units along the polymer backbone through copolymerization of the phosphazene monomers with 1,9-decadiene. The copolymerizations yielded a series of polymers that contained from 1 to 20 mol % phosphazene repeating units. Additional treatment of the resultant copolymers with *p*-toluenesulfonhydrazide (TSH) gave a fully saturated backbone with polyethylene-like structures between the cyclic phosphazene residues that were spaced intermittently along the polymer backbone. These variations allowed the effect of the phosphazene rings on a variety of polymer properties to be studied.

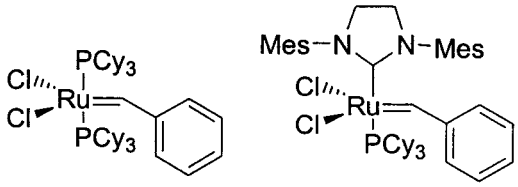
Results and Discussion

Monomer Synthesis. All the monomers for this work were synthesized in a similar fashion (Scheme 1). The starting material, hexachlorocyclotriphosphazene (**1**), was treated with 4.7 equiv of either sodium phenoxide or sodium methoxyethoxyethoxide to yield a mixture of cyclic phosphazenes with four or five substituents. The cyclic phosphazene trimers with phenoxy substituents were separated via column chromatography in a 45/55 mixture of hexanes/CH_2Cl_2. The oligoethyleneoxy-substituted trimers were also separated via column chromatography, but because of the higher polarity of these side groups, a solvent mixture of 90/10 ethyl acetate/methanol was used. The tetrasubstituted trimers thus isolated were then treated with the various sodium alkenoxides to complete the substitution and yield a diene structure. If complete chlorine replacement does not occur during treatment with the alkenoxide, the resultant cyclic phosphazene could bear only one olefin group and therefore end-cap a growing polymer chain. Similarly, if displacement of one organic side group by another occurs, the possibility exists for three or more olefin groups to be present on a single cyclic phosphazene trimer. This would lead to cross-linking of the polymer chains due to the larger number of possible propagation sites.

The previous syntheses of phosphazene trimers with similar structures showed evidence of side group displacement. Therefore, further purification by column chromatography of the final monomers was necessary before successful polymerizations could be carried out.[7] The use of shorter chain alkenols avoided this problem. The tendency for side group displacement is increased in the presence of large excesses of the salt of the alkenol, with long reaction times, and at elevated temperatures. However, complete substitution by the undecenoxide species requires high reaction temperatures (refluxing dioxane), a large excess of sodium salt (from 4 to 10 excess equivalents), and long reaction times (up to 1 week). This is attributed to the low solubility of long chain sodium alkenoxides in organic solvents. As the length of the alkenol is decreased, the solubility of the corresponding sodium salt is increased, and therefore lower reaction temperatures, shorter reaction times, and smaller excesses are required for complete reaction. Problems of side group displacement were still encountered for the introduction of the decenol derivative. This resulted in the need to perform additional column chromatography for monomer purification.

The cyclic phosphazene dienes were characterized by ^{31}P, ^{1}H, and ^{13}C NMR as well as by mass spectrometry. The ^{31}P NMR spectra indicate tetra-/di-substitution through the characteristic A_2B splitting pattern.[15] This splitting is not as clear for cyclic trimers that bear chemically similar groups as, for example, with the oligoethyleneoxy derivatives, and the spectra degenerate into a singlet with several smaller surrounding peaks.[25] ^{1}H and ^{13}C NMR provided further structural confirmation, and integration of the ^{1}H NMR spectra together with the mass spectra confirmed the identity and purity of the monomers.

Polymer Synthesis and Characterization. The monomers were polymerized with both the bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride (**A**) and the tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]ruthenium(IV) dichloride (**B**) Grubbs catalysts (Figure 1). The polymerizations were carried out initially with the addition of 1 equiv of catalyst (**A** or **B**) to 100 equiv of monomer. The stirred reaction mixtures were monitored for ethylene evolution, and, after gas evolution had



A B

Figure 1. Grubbs catalysts used for ADMET reactions.

Table 1. Characterization Data for Polymerization of Monomers 4–8 and 11–13

polymer	M_n(cat **A**)	PDI(cat **A**)	M_n(cat **B**)	PDI(cat **B**)	T_g
4	1230	1.2	1120	1.1	−29
5	1350	1.1	1440	1.1	−34
6	21700	4.4	16300	3.3	−33
7	26300	2.1	28400	2.4	−36
8	33300	2.6	29500	2.0	−35
11	1470	1.1	1520	1.1	−72
12	8700	1.6	11800	1.8	−74
13	45400	1.9	29200	1.7	−75

ceased, another equivalent of catalyst was added. Approximately 24 h after the second catalyst addition the reaction mixture was heated, and the temperature was gradually increased to promote further polymerization.

The results of these polymerizations are shown in Table 1. One point of interest is the lack of difference seen between the two catalyst systems. The newer catalyst (**B**) shows higher reactivities in metathesis reactions for a variety of other systems,[26–28] but this behavior was not observed consistently for any of the monomers studied in this work. The molecular weights obtained using these two catalysts were very similar. However, in some cases, polymers produced using catalyst **A** had higher molecular weights. The rates of reaction were also very similar for the two catalysts, typically requiring more than 48 h for complete reaction. A possible explanation for this behavior is the low concentration of olefin sites. Even at relatively high catalyst-to-monomer ratios, the formation of a productive metallocyclobutane complex[3] with an olefinic end group is unlikely because of the large phosphazene structure. Moreover, the phosphazene ring and its substituents could interfere through steric interactions with coordination of the catalyst to the olefin unit. These factors would account for the small difference in activity found for the two catalysts, the relatively slow reaction, and the smaller number of repeating units detected in these polymers compared to simpler olefin systems.

The synthesis of different phosphazene monomers with olefinic side groups of different lengths was designed to test the limits of polymerization of cyclic phosphazenes via ADMET as well as to compare properties of cyclolinear polymers with different spacer groups between the phosphazene rings. In the phenoxy series (monomers **3**–**8**) the polymerizations were largely unsuccessful unless the alkenoxy group was at least six carbon atoms in length or had a four-carbon spacer unit between the olefin and the phosphazene ring (monomer **6**). The phosphazene trimer with allyloxy groups (**3**) underwent almost no polymerization reaction, and the NMR spectra of the reaction mixture showed evidence of numerous side reactions. This could be a result of steric hindrance that prevents the formation of a metallocyclobutane ring as well as possible complexation of the catalyst with the oxygen atom of the allyloxy group. Coordination of the catalyst to oxygen is supported by the complexity of the ^{31}P and ^{1}H NMR spectra, and similar results have been found for other ADMET monomers with functional groups adjacent to the active site.[29,30] This has been termed the negative neighboring group effect. Monomers **4** and **5**, bearing butenoxy and pentenoxy side groups, respectively, showed evidence of oligomerization based on ^{1}H NMR spectra and had low molecular weights as monitored by GPC. If the hindrance to polymerization of these monomers was entirely a result of the negative neighboring group effect, then slow oligomerization of the butenoxy species (monomer **4**) would be expected (based on comparisons to the polymerization of monomers with an etheric functionality).[31] Moreover, normal polymerization of the phosphazene trimer that bears pentenoxy groups (monomer **5**) might be anticipated. This does not occur. Therefore, it is unlikely that the failure of monomers **4** and **5** to polymerize is entirely a result of the negative neighboring group effect. Steric factors can also inhibit ADMET polymerizations if the formation of the metallocyclobutane species is hindered, and this has been reported when pendent methyl groups are located too close to the reactive olefin.[32–34]

To determine whether the lack of polymerization is a result of the negative neighboring group effect or steric factors, a series of monomers were prepared with flexible methoxyethoxyethoxy side groups. Trimers cofunctionalized with methoxyethoxyethoxy and allyloxy, butenoxy, or pentenoxy were prepared (monomers **10**, **11**, and **12**). The polymerization of the allyl species (**10**) yielded products with complex NMR spectra, similar to those seen for the phenoxy/allyloxy monomer (**3**). This suggested catalyst coordination to the oxygen atoms of the allyloxy groups had occurred. Attempted polymerization of the butenoxy derivative (**11**) resulted in some oligomer formation, as in the case of the similar phenoxy trimer (**4**). The pentenoxy functionalized trimer (**12**) polymerized to give moderate molecular weight macromolecules. This suggests that, for the phenoxy-substituted counterpart (**5**), steric hindrance inhibits the polymerization rather than possible catalyst coordination. The formation of the metallocyclobutane intermediate is crucial for ADMET polymerization to occur, and it is likely that steric hindrance from bulky phosphazene substituents can slow or prevent this formation.

The glass transition temperatures of the new homopolymers were measured using DSC analysis. Slight changes in the polymer repeat unit had little effect on the glass transition temperature. The increase from 10 carbon atoms between phosphazene units (polymer **6**) to 20 carbon atoms between phosphazene units (polymer **8**) results in a change in T_g of only 2 °C. The T_g values are similar for all of the cyclolinear polymers and oligomers functionalized with phenoxy groups. If the measured T_g for oligomers produced from monomers **4** and **5** (six and eight carbons between phosphazene units, respectively) are compared with those for polymers from monomers **6**–**8**, then a slight lowering of glass transition temperature from −29 to −35 °C can be detected. This is attributed to the increased flexibility of the polymer chain as the separation between phosphazene units increases. The polymers that contain oligoethyleneoxy functionalized cyclic trimers show similar trends. The overall difference in glass transition temperature is rather small, but a slight decrease can be accounted for by increased molecular motion as the phosphazene rings become more separated along the polymer backbone.

Scheme 2. Synthesis of Copolymers of 1,9-Decadiene and Monomer 8

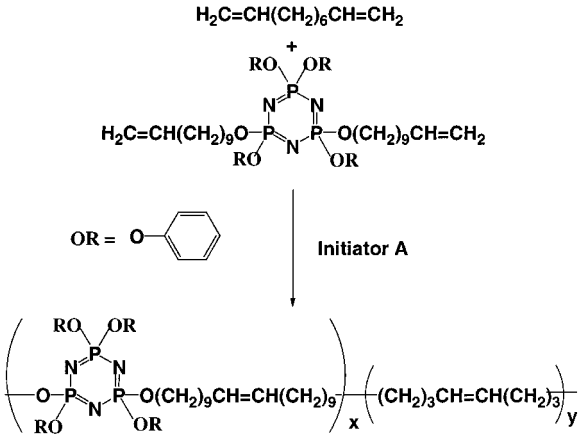


Table 2. Characterization Data for Copolymers of 1,9-Decadiene and Monomer 8

mol % **8**	wt % **8**	M_n	PDI	% **8** (NMR)	T_m	$T_m(H_2)$
0	0	8 300	2.0	0	55	119
1	5.8	10 200	1.4	1.3	56	123
2.5	13.5	13 300	1.4	2.6	58	115
5	24.3	33 400	1.7	4.4	65	100
10	40.4	24 000	1.8	11.3	40	99
20	60.4	25 000	2.0	22.5	34	91
100	100	33 300	2.6	100		

Copolymerizations. Monomer **8**, substituted with four phenoxy groups and two undecenoxy groups, was copolymerized with 1,9-decadiene in five molar ratios from 1% to 20% incorporation (Scheme 2). This phosphazene monomer was chosen because of its encouraging behavior in homopolymerization. Decadiene was selected as a comonomer because of its known ease of polymerization by ADMET and its relatively low volatility. The data for these polymers are summarized in Table 2. These copolymerizations were carried out in the absence of a solvent, as with all the above reactions, and the combined monomer-to-initiator ratio was held constant at 500:1 for each polymerization. Initially, the decadiene monomer covolatilized from the system along with the ethylene under vacuum as the polymerization progressed, and this prevented good control over the ratio of the monomers. A modified polymerization apparatus that allows control of the pressure was designed to prevent the volatilization of monomer. Moreover, this equipment allowed the addition of solvent in the later stages of the polymerizations, while maintaining enough vacuum to constantly remove ethylene. With this arrangement, slightly different polymerization conditions were used than for the homopolymerizations. When the second aliquot of catalyst was added, a few milliliters of *o*-dichlorobenzene was also added to help solubilize the polymer and continue polymerization.

In these copolymerizations initial concerns existed that the phosphazene monomers would be excluded from the reaction due to the relatively low concentration of olefin sites attached to a phosphazene ring. However, the incorporation of phosphazenes into the polymer chains is confirmed by multinuclear NMR spectroscopy, which revealed the presence of both the phosphorus atoms and the aryloxy protons. In those copolymers with relatively high loadings of phosphazene monomer it was also possible to detect the resonances for the protons adjacent to the oxygen atoms. These signals did not arise from monomer trapped in the polymer structure because the polymer had been purified by precipitation into cold CH_2Cl_2 in which the monomers are highly soluble. The GPC traces showed only one polymer peak, with no evidence of a second, cyclic phosphazene trimer, peak. Further evidence that the phosphazene is covalently incorporated into the backbone structure is the solubility of the resultant polymers. Polyethylenes and similar polymers typically have low solubility in most solvents at room temperature. All the homopolymers derived from the cyclotriphosphazene monomers are readily soluble in a variety of solvents at and below room temperature. Only the polymer produced from the homopolymerization of decadiene was completely insoluble in CH_2Cl_2 at room temperature. As the amount of phosphazene monomer incorporated into the copolymerization was increased, the solubility of the resultant copolymers improved until the copolymer with 20% phosphazene is fully soluble in CH_2Cl_2 at room temperature.

A ^{1}H NMR analysis of these polymers showed that the experimental incorporation of phosphazene units matches the theoretical values fairly well. On the basis of these data, it is assumed that random copolymers were formed with no preferential reactivity between different monomers. Moreover, the long alkyl chain separating the active double bond from the phosphazene ring should minimize any difference that could cause preferential polymerization. The relatively low molar incorporation of phosphazene monomer, however, will still result in a polymer with a blocky structure of isolated phosphazene units surrounded by long segments of poly(decadiene).

The theoretical and experimental incorporation as estimated from ^{1}H NMR integration is reported in Table 2. A melting transition for the pure poly(decadiene) is detected at 55 °C. The copolymers with 1%, 2.5%, and 5% phosphazene monomer have very similar melting transitions, but all at slightly higher temperatures than the value for poly(decadiene). Phosphazene residues would be expected to destabilize crystalline regions within the polymer matrix due to their irregular size and location relative to the decadiene monomers. Thus, in theory they should lower the T_m. This was not detected in these three copolymers possibly because of the low molecular weights of the materials. The molecular weight increases gradually for each of these polymers, perhaps allowing the formation of more highly ordered crystalline domains. However, beyond the point at which 10% of the phosphazene monomer is incorporated, the T_m begins to decrease, and for materials with 100% phosphazene monomer, no crystalline transition was detected, presumably because the proximity of phosphazene rings interrupts any crystallite formation.

Hydrogenations. Each of the copolymers was hydrogenated via a method developed by Hahn to saturate polymer backbones in solution without the use of high pressure and without significant molecular weight decline.[35] A sample of each polymer was heated with *p*-toluenesulfonhydrazide and tripropylamine in *o*-xylene. During reflux, the toluenesulfonhydrazide decomposes to yield a diimide, which serves as the hydrogenating agent, and the tripropylamine quenches side reactions that can lead to polymer chain cleavage.[35] These reactions provided 100% hydrogenation as evidenced by the complete disappearance of olefin peaks in the ^{1}H NMR

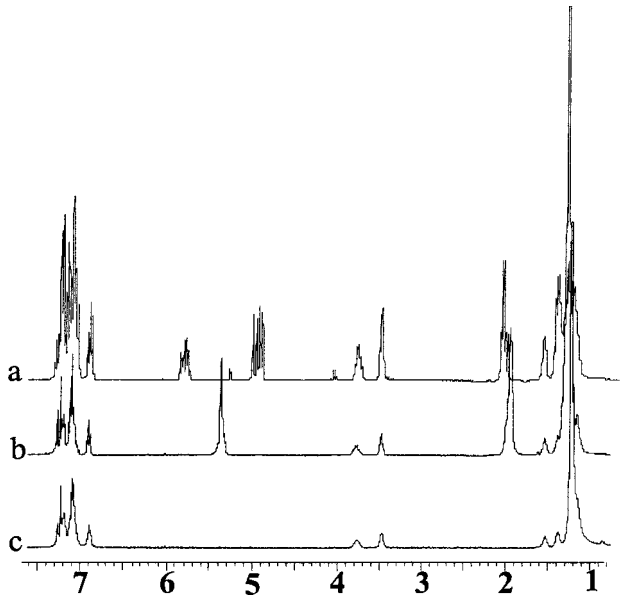


Figure 2. ^{1}H NMR of monomer **8** (a), a copolymer of 80% 1,9-decadiene and 20% monomer **8** (b), and the same polymer after hydrogenation (c).

spectra. The resultant materials were significantly more brittle than the original unsaturated copolymers. Moreover, the solubility was decreased dramatically, so much so that the NMR analyses had to be carried out in d_5-chlorobenzene at 100 °C. Figure 2 shows ^{1}H NMR spectra of the phosphazene monomer, the resultant copolymer, and the hydrogenated copolymer for 20% cyclic phosphazene monomer incorporation. During polymerization, the olefin peaks initially shift to indicate the formation of internal olefins and the loss of all terminal double bonds. After hydrogenation, the internal olefin peaks disappear completely, and the remaining spectrum shows only the aryloxy protons from the phosphazene and the protons on the carbon atom closest to the phosphazene ring.

The marked decrease in solubility of the hydrogenated species is a direct result of the increased stability of the crystalline regions of these materials. In each case, the T_m is increased by approximately 50 °C. The T_m is similar for the first three polymers in the series (1%, 2.5%, and 5% phosphazene monomer) and then decreases significantly for higher percentages. Again this can be linked to the increasing molecular weight of the materials, which initially offsets the crystallinity-decreasing influence of the phosphazene units. However, eventually enough phosphazene exists in the system to disrupt the crystallinity and decrease the T_m. This behavior has been reported in the past by Wagener for other pendent groups, and larger, bulkier groups lead to a larger decrease in T_m.[36] Glass transitions were not detected for any of the hydrogenated polymers over the temperature range scanned under any conditions and is attributed to the generally weak and poorly defined transition of polyethylene.

The homopolymer from monomer **8** was also hydrogenated. However, complete reduction did not occur under the same conditions. The double bonds may be sterically protected by the bulky phosphazene substituents. This product did remain soluble at room temperature, and GPC analyses suggested that there had been no significant molecular weight decline. Moreover, the T_g of the homopolymer was affected only moderately by hydrogenation, with a slight decrease from −35 to −39 °C, as would be expected for a slight increase in freedom of molecular motion due to decreased double-bond character in the backbone.

Conclusions

A series of cyclic phosphazene trimers were prepared, each with two olefinic side groups, to give a diene structure capable of undergoing metathesis polymerizations. These monomers were polymerized using two different ruthenium catalysts. The molecular weights of the materials ranged from about 10 000 to 45 000 and are comparable to molecular weights seen previously for the ADMET polymerization of other phosphazene monomers.[37] The chemistry of ADMET requires the formation of a metallocyclobutane intermediate in order for polymerization to occur. Previous studies have shown that the formation of this intermediate can be retarded by both electronic (preferential catalyst coordination to a functional group) and steric effects. The polymerization of phosphazene-containing dienes is affected significantly by both of these factors, and the steric effects may extend beyond those observed with other systems due to the size of the phosphazene ring and the size and steric bulk of substituents on that ring. This was illustrated by the polymerization of a monomer functionalized with flexible oligoethyleneoxy groups compared with the failure to polymerize a similar monomer with phenoxy cosubstituents.

Copolymerizations were carried out between one of the cyclophosphazenes and 1,9-decadiene to illustrate further the versatility of this approach. Levels of phosphazene incorporation from 1% to 20% had a significant effect on polymer properties, most notably on the melting transition temperature. Subsequent hydrogenation of these polymers illustrated the stability of the cyclolinear structure to these reaction conditions. The hydrogenated polymers had significantly higher melting temperatures, but this was affected directly by the amount of phosphazene present in the polymer. The phosphazene components serve to disrupt the crystallinity of the polyethylene-like structure once present in high enough amounts. They also lower the melting transition temperature. This is in agreement with other studies that have incorporated functional groups into a polyethylene backbone. The use of this chemistry to generate polymers and polymer blends that resist combustion is being investigated.

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). 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. Elevated temperature ^{1}H NMR spectroscopy was performed at 100 °C using a Bruker DPX-300 spectrometer for hydrogenated polymer samples. 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 −150 to +150 °C under an atmosphere of dry nitrogen at a heating rate of 20 °C/min.

Synthesis of $N_3P_3(OC_6H_5)_4Cl_2$ (2). Hexachlorocyclotriphosphazene, **1** (100.0 g, 0.287 mol), was dissolved in 2000 mL of THF. Phenol (124 g, 1.32 mol) was dissolved in 150 mL of THF and added dropwise to a suspension of sodium metal (30.73 g, 1.33 mol) in 500 mL of THF. This reaction mixture was stirred at room temperature for 24 h to allow all the sodium to react. The resultant sodium phenoxide solution was added dropwise to the stirred solution of **1** at −78 °C. The reaction mixture was allowed to warm to room temperature overnight and was monitored by ^{31}P NMR spectroscopy to show 57% tetra-substitution and 43% penta-substitution. Solvent was removed by reduced pressure rotary evaporation, and the resultant oil was dissolved in 250 mL of diethyl ether. This solution was washed three times with 250 mL of water, dried over $MgSO_4$, and concentrated by rotary evaporation. Column chromatography was carried out in a 55% CH_2Cl_2/45% hexanes mixture to separate the tetra- and pentasubstituted products. The desired product was recrystallized at −55 °C from hexanes to yield an off-white oil (36.2 g, 25.8%). ^{31}P NMR ($CDCl_3$): δ (ppm) 5.2 (t, 1P) and 20.4 (d, 2P).

Synthesis of $N_3P_3(OC_6H_5)_4(OCH_2CH{=}CH_2)_2$ (3). Allyl alcohol (1.69 g, 29.06 mmol) was added to 95% sodium hydride (0.77 g, 30.45 mmol) in 100 mL of freshly distilled THF, and the mixture was refluxed for 24 h. The solution was cooled to room temperature and added dropwise to a solution of **2** (8.00 g, 13.84 mmol) in 75 mL of THF. After 24 h at room temperature the reaction mixture was heated to reflux. After 48 h at reflux the reaction was complete on the basis of the ^{31}P NMR spectra. The solvent was removed from the reaction mixture by rotary evaporation, the residue was dissolved in CH_2Cl_2, and the solution was washed with water to remove NaCl. The organic layer was dried over $MgSO_4$, and the solvent was removed by rotary evaporation to yield a yellow oil (7.25 g, 84.4% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 3.9 (m, 2H), 4.2 (m, 2H), 5.0−5.2 (m, 4H), 5.5−5.7 (m, 2H), 6.8 (t, 4H), 7.0−7.2 (m, 16H). ^{13}C NMR ($CDCl_3$): δ (ppm) 66.3, 116.8, 120.9, 124.5, 129.1, 132.4, 150.5. ^{31}P NMR ($CDCl_3$): δ (ppm) 13.2 (d, 2P) and 9.8 (t, 1P). APCI, $MH^+ = 622.2$.

Synthesis of $N_3P_3(OC_6H_5)_4(O(CH_2)_2CH{=}CH_2)_2$ (4). This compound was synthesized as described for **3**. The following reagents and quantities were used: 3-buten-1-ol (2.09 g, 29.07 mmol), 95% NaH (0.77 g, 30.45 mmol), **2** (8.00 g, 13.84 mmol), freshly distilled THF (200 mL) (7.43 g, 82.7% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.1 (quad, 2H), 2.2 (quad, 2H), 3.5 and 3.8 (4H), 4.9 (quint, 4H), 5.6 (m, 2H), 6.9(tr, 4H), 7.0−7.2 (m 16H). ^{13}C NMR ($CDCl_3$): δ (ppm) 34.1, 65.3, 117.0, 120.9, 124.6, 129.2, 133.4, 150.7. ^{31}P NMR ($CDCl_3$): δ (ppm) 13.2 (d, 2P), 9.9 (t, 1P). APCI, $MH^+ = 650.2$

Synthesis of $N_3P_3(OC_6H_5)_4(O(CH_2)_3CH{=}CH_2)_2$ (5). This compound was synthesized as described for **3**. The following reagents and quantities were used: 4-penten-1-ol (2.62 g, 30.45 mmol), 95% NaH (0.76 g, 33.22 mmol), **2** (8.00 g, 13.84 mmol), freshly distilled THF (200 mL) (7.16 g, 76.4% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.3 and 1.5 (quints, 4H), 1.8 and 1.9 (quads, 4H), 3.4 and 3.7 (4H), 4.8 (quint, 4H), 5.6 (m, 2H), 6.8 (tr, 4H), 6.9−7.1 (m, 16H). ^{13}C NMR ($CDCl_3$): δ (ppm) 28.9, 29.1, 65.6, 115.1, 121.1, 124.7, 129.2, 137.3, 150.8. ^{31}P NMR ($CDCl_3$): δ (ppm) 13.3 (d, 2P), 10.0 (t, 1P). APCI, $MH^+ = 678.3$.

Synthesis of $N_3P_3(OC_6H_5)_4(O(CH_2)_4CH{=}CH_2)_2$ (6). This compound was synthesized as described for **3**. The following reagents and quantities were used: 5-hexen-1-ol (1.96 g, 19.60 mmol), 95% NaH (0.49 g, 20.49 mmol), **2** (5.15 g, 8.91 mmol), freshly distilled THF (200 mL) (5.75 g, 91.5% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.0−1.4 (m, 8H), 1.7−1.8 (quad, 4H), 3.3 and 3.6 (4H), 4.8 (m, 4H), 5.5 (m, 2H), 6.8(tr, 4H), 6.9−7.1 (m 16H). ^{13}C NMR ($CDCl_3$): δ (ppm) 24.5, 29.1, 32.9, 66.0, 114.5, 120.9, 124.6, 129.0, 138.0, 150.6. ^{31}P NMR ($CDCl_3$): δ (ppm) 13.4 (d, 2P), 10.1 (t, 1P). APCI, $MH^+ = 706.2$.

Synthesis of $N_3P_3(OC_6H_5)_4(O(CH_2)_8CH{=}CH_2)_2$ (7). This compound was synthesized as described for **3**. The following reagents and quantities were used: 9-decen-1-ol (2.40 g, 15.33 mmol), 95% NaH (0.37 g, 15.33 mmol), **2** (4.22 g, 7.30 mmol), freshly distilled THF (200 mL). Column chromatography was performed in an 80%/20% mixture of hexanes and CH_2Cl_2 (4.21 g, 70.6% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.0−1.6 (24H), 1.9 (4H), 3.5 and 3.7 (4H), 4.9 (m, 4H), 5.7 (m, 2H), 6.8 (4H), 7.0−7.2 (m, 16H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.3, 25.4, 25.8, 28.9, 29.4, 29.9, 33.8, 62.3, 114.1, 121.2, 124.6, 129.2, 138.9, 150.9. ^{31}P NMR ($CDCl_3$): δ (ppm) 13.2 (d, 2P), 10.0 (t, 1P). ESI, $MH^+ = 818.3$.

Synthesis of $N_3P_3(OC_6H_5)_4(O(CH_2)_9CH{=}CH_2)_2$ (8). The synthesis of this compound has been described previously.[7]

Synthesis of $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_4Cl_2$ (9). Hexachlorocyclotriphosphazene, **1** (20 g, 57.47 mmol), was dissolved in 200 mL of THF. Methoxyethoxyethanol (32.41 g, 270.1 mmol) was distilled from CaH_2 and then added via syringe to a suspension of sodium hydride (10.92 g, 273.0 mmol) in 200 mL of THF. The resultant sodium alkoxide solution was added dropwise to the stirred solution of **1** at −78 °C. The reaction mixture was allowed to warm to room temperature overnight and was analyzed by ^{31}P NMR spectroscopy to show 61% tetra-substitution, 38% penta-substitution, and 1% tris-substitution. The solvent was removed by rotary evaporation, and the resultant oil was dissolved in 250 mL of diethyl ether. This solution was cooled to −55 °C and filtered cold to remove most of the NaCl generated during the reaction. The solvent was then removed by rotary evaporation. Column chromatography was performed using a 90% ethyl acetate/10% methanol elution mixture to separate the tetra- and penta-substituted products. Similar fractions were combined to yield a pale yellow oil. (6.4 g, 16.3%) ^{31}P NMR ($CDCl_3$), δ (ppm) 13.1 (tr, 2P), 16.0 (d, 1P), 25.3 (d, 2P), 28.0 (tr, 1P).

Synthesis of $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_4(OCH_2CH{=}CH_2)_2$ (10). Allyl alcohol (0.25 g, 4.46 mmol) was added to 95% sodium hydride (0.11 g, 4.46 mmol) in 100 mL of THF and refluxed for 24 h. The resultant sodium salt solution was cooled to room temperature and added dropwise to a solution of **9** (1.0 g, 1.46 mmol) in 200 mL of THF. This reaction mixture was monitored over 2 days by ^{31}P NMR and then heated to reflux for 24 h to complete the reaction. The product was purified first by the removal of THF by rotary evaporation and then by dissolution in diethyl ether. The ethereal solution was then cooled to −55 °C for 24 h and filtered cold to remove NaCl. This was repeated to ensure removal of all NaCl. The product was then recovered as a pale yellow oil (0.83 g, 78.3% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 3.2 (s, 12H), 3.4 (t, 8H), 3.5 (t, 8H) 3.6 (t, 8H), 4.0 (s, 8H), 4.3 (s, 4H), 5.0 and 5.2 (dblts, 4H), 5.8 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 57.9, 64.2, 64.5, 69.1, 69.6, 71.0, 116.0, 132.6. ^{31}P NMR ($CDCl_3$): δ (ppm) 17.9 (s, 3P). ESI, $MH^+ = 726.3$.

Synthesis of $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_4(O(CH_2)_2CH{=}CH_2)_2$ (11). This compound was synthesized as described for **10**. The following reagents and quantities were used: butenol (0.27 g, 3.69 mmol), 95% NaH (0.09 g, 3.69 mmol), **9** (1.5 g, 2.20 mmol), freshly distilled THF (200 mL) (1.23 g, 78.8% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.3 (quad, 4H), 3.3 (s, 12H), 3.4 (quad, 8H), 3.5 (quad, 8H), 3.6 (quad, 8H), 3.9 (m, 4H), 4.0 (s, 8H), 5.0 (m, 4H), 5.7 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 34.2, 58.6, 64.0, 64.6, 69.7, 70.1, 71.6, 116.8, 133.7. ^{31}P NMR (CD_2Cl_2): δ (ppm) 17.9 (m, 3P). ESI, $MH^+ = 754.3$.

Synthesis of $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_4(O(CH_2)_3CH{=}CH_2)_2$ (12). This compound was synthesized as described for **10**. The following reagents and quantities were used: pentenol (0.38 g, 4.47 mmol), 95% NaH (0.11 g, 4.47 mmol), **9** (1.0 g, 1.11 mmol), freshly distilled THF (200 mL). After 48 h at reflux two more equivalents of pentenol sodium salt was prepared and added, and the mixture was heated to reflux for an additional 24 h in order to complete the reaction (0.88 g, 76.5% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.7 (quint, 4H), 2.1 (quad, 4H), 3.3 (s 12H), 3.5 (t, 8H), 3.6 (t, 8H), 3.7 (s, 8H), 3.9

(s, 4H), 4.1 (s, 8H), 4.9 (m, 4H), 5.8 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 29.2, 29.6, 58.8, 64.8, 65.3, 69.9, 70.4, 71.8, 115.0, 137.5. ^{31}P NMR ($CDCl_3$): δ (ppm) 18.1 (m, 3P). ESI, $MH^+ = 782.4$.

Synthesis of $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_4(O(CH_2)_9CH{=}CH_2)_2$ (13). The synthesis of this compound has been described previously.[7]

General Polymerization Procedure for Monomers 3−8 and 10−13. Each of the monomers was polymerized by placing 0.5 g of the monomer into a 25 mL Schlenk flask and drying under vacuum for 24 h. The dry monomer was then taken into an inert atmosphere drybox where the Grubbs catalyst was added (typically 100:1 monomer:catalyst ratio). This mixture was stirred in the drybox until the catalyst was completely dissolved in the monomer, and a pale purple solution resulted. The Schlenk flask was then removed from the drybox, and the contents were stirred under vacuum until the evolution of ethylene was no longer visible (typically 24−48 h). At this time the reaction mixture was reintroduced into the drybox, and an additional aliquot of catalyst was added (typically half the amount added initially). This reaction mixture was again stirred to dissolve the catalyst before removal from the drybox. The mixture was then stirred until the evolution of ethylene was no longer visible (typically less than 24 h) and was then heated to 60 °C. Some polymerizations reached very high viscosities, and when this was the case, 1 mL of *o*-dichlorobenzene was added to solubilize the reaction mixture and facilitate stirring and reaction. The reaction was terminated by exposure to air and precipitation into hexanes. The resultant polymer was dissolved in THF and precipitated into hexanes a second time before drying under reduced pressure to yield off-white polymer. Yields were typically very high ranging from 85 to 95% with most of the lost yield attributed to polymer lost in the precipitation. This was verified by the lack of monomer present in NMR traces of the reaction mixture prior to workup.

Polymer 4. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.9−2.3 (m), 3.5 (m), 3.8 (m), 4.9 (m), 5.1−5.4 (m), 5.5−5.9 (m), 6.9 (tr), and 7.0−7.3 (m). ^{31}P NMR ($CDCl_3$): δ (ppm) 13.2 (d, 2P), 9.9 (t, 1P).

Polymer 5. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.1−2.2 (m), 3.4 (m), 3.7 (m), 4.9 (m), 5.0−5.5 (m), 5.6−5.9 (m), 6.8 (tr), and 6.9−7.3 (m). ^{13}C NMR ($CDCl_3$): δ (ppm) 28.8, 28.9, 65.8, 121.0, 125.2, 128.6, 129.0, 151.1. ^{31}P NMR ($CDCl_3$): δ (ppm) 13.0 (d, 2P), 9.9 (t, 1P).

Polymer 6. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.0−1.6 (m, 8H), 1.7−2.0 (quad, 4H), 3.4 and 3.7 (4H), 5.2 (m, 2H), 6.8 (tr, 4H), and 7.0−7.3 (m 16H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.6, 29.7, 32.2, 66.6, 121.3, 124.9, 129.5, 130.3, 151.0. ^{31}P NMR ($CDCl_3$): δ (ppm) 13.2 (d, 2P), 9.9 (t, 1P).

Polymer 7. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.9−1.6 (24H), 1.9 (4H), 3.4 and 3.7 (4H), 5.3 (m, 2H), 6.8 (4H), 6.9−7.3 (m, 16H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.6, 25.7, 25.9, 29.7, 30.0, 34.3, 65.1, 119.6, 123.9, 127.9, 129.6, 150.8. ^{31}P NMR ($CDCl_3$): δ (ppm) 13.2 (d, 2P), 9.9 (t, 1P).

Polymer 8. ^{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).

Polymer 11. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.3−2.4 (m), 3.3 (s), 3.4−3.7 (m), 3.9 (m), 4.0 (m), 4.9−5.1 (m), 5.2−5.4 (m), 5.7−5.9 (m). ^{13}C NMR ($CDCl_3$): δ (ppm) 34.5, 58.9, 64.3, 65.0, 70.1, 70.3, 71.7, 126.7. ^{31}P NMR (CD_2Cl_2): δ (ppm) 18.0 (m, 3P).

Polymer 12. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.6 (m, 4H), 2.0 (m, 4H), 3.3 (s, 12H), 3.5 (m, 8H), 3.6−3.7 (m, 16H), 3.9 (s, 4H), 4.0 (s, 8H), 5.4 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 27.7, 29.1, 58.0, 63.9, 64.5, 69.0, 69.5, 70.9, 128.8. ^{31}P NMR ($CDCl_3$): δ (ppm) 18.1 (m, 3P).

Polymer 13. ^{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).

Synthesis of Copolymers. Appropriate amounts of catalyst **A** (500:1 total molar ratio), monomer **8**, and 1,9-decadiene (distilled from CaH_2) were weighed out separately in an inert atmosphere drybox and then added to a 25 mL Schlenk flask. The reaction mixture was stirred in the drybox until all the catalyst was dissolved, and the flask was then removed from the drybox and attached to a Schlenk line that was modified to apply variable pressures through the use of a screw valve that allowed an argon leak into the system. This mixture was then stirred at room temperature and ~10 mmHg pressure until evolution of ethylene had ceased or until the viscosity had risen to the point that stirring was no longer possible. At this point the reaction mixture was reintroduced into the drybox where another equivalent of catalyst was added together with 1−3 mL of *o*-dichlorobenzene to solubilize the polymer and facilitate stirring. The reaction proceeded for another 24 h and was gradually heated to 60 °C. The polymer was then isolated by precipitation first into methanol and then into cold CH_2Cl_2 to remove any residual monomer. The reaction was terminated by exposure to air and precipitation into hexanes. Yields were typically very high, ranging from 85 to 95% with the lost yield attributed to polymer not recovered from the precipitation. This was verified by the lack of monomer peaks present in NMR spectrum of the reaction mixture prior to workup. Because of the similar structure of each of the copolymers, and therefore identical shifts in ^{1}H, ^{31}P, and ^{13}C NMR spectra, only a representative ^{1}H NMR spectrum is shown in Figure 2. The relative concentrations of phosphazene monomer as calculated from the integration of peaks in the ^{1}H NMR spectra are reported in Table 2 for each copolymer.

General Procedure for Hydrogenation. The general procedure of Hahn[35] was followed as reported in several publications by Wagener. A sample of polymer (typically 0.2 g) was placed in a 25 mL flask equipped with a condenser. To this flask was added tripropylamine, TPA (2 equiv per mole of olefin present), *p*-toluenesulfonhydrazide, TSH (2 equiv per mole of olefin present), and 15 mL of *o*-xylene. This mixture was refluxed for 3 h and then allowed to cool to room temperature. An additional equivalent of TPA and TSH was then added to the mixture, and the temperature was increased to reflux for an additional 3 h. After cooling, the entire reaction mixture was added to methanol, and the product was recovered by filtration. Yields for the hydrogenation reactions were all above 80% with some loss in yield attributed to polymer lost in the workup.

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