Synthesis of Norbornenyl Telechelic Polyphosphazenes and Ring-Opening Metathesis Polymerization Reactions

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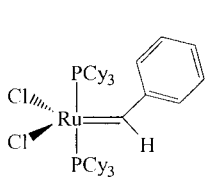
ABSTRACT: Mono- and ditelechelic linear polyphosphazenes, functionalized with a norbornene end group, were synthesized through the termination of living poly(dichlorophosphazene) with norbornenyl phosphoranimines. These materials were employed as macromonomers for the synthesis of graft copolymers via the ring-opening metathesis polymerization (ROMP) of the terminal norbornenyl component. Norbornenyl monotelechelic polyphosphazenes with various molecular weights yielded un-cross-linked graft copolymers when subjected to ROMP. The ditelechelic polyphosphazenes yielded branched or cross-linked materials due to the multiple reactive sites. In addition, the 5-norbornene-2-methoxy phosphoranimine was polymerized via ROMP to yield materials that consisted of a polynorbornene backbone with phosphoranimine pendent side groups.

Introduction

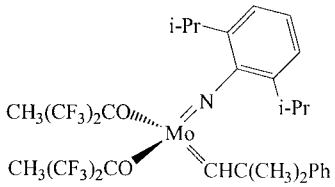
The synthesis of hybrid copolymers of polyphosphazenes with organic polymers is an important objective in both fundamental and applied research. In many cases the physical, mechanical, and electronic properties of a material can be altered through adjustments to the ratio of the copolymer's individual components. Thus, many of the valuable properties of polyphosphazenes can be incorporated into an organic polymer without sacrificing the overall mechanical properties of the material.[1,2] The range of physical and chemical properties associated with polyphosphazenes includes characteristics that are as diverse as elasticity, fire resistance, and solid polymer electrolyte behavior.[1−4]

One approach to the preparation of hybrid systems is through the synthesis of graft copolymers. Considerable interest exists in the development of graft copolymers that combine useful bulk characteristics with unique surface properties.[5] Totally organic graft copolymers with these attributes have been used as biomedical materials,[6−11] conductive polymers,[12,13] and elastomers.[14] Several examples exist in the literature in which "living" organic graft copolymers have been produced by a variety of polymerization methods which include cationic, anionic, atom transfer radical polymerization (ATRP), and ROMP.[15−20]

Recently we reported two synthetic methods which, when utilized together, provide a way to produce graft copolymers between polyphosphazenes and polynorbornene. These are (1) the synthesis of polynorbornenes with phosphazene-based side groups[21,22] and (2) the preparation of telechelic polyphosphazenes through a living, cationic polymerization mechanism.[23,24] The materials in (1) were produced via the ring-opening metathesis polymerization of norbornenyl-functionalized cyclotriphosphazenes. These polynorbornene polymerizations were induced by the Grubbs initiator $RuCl_2(CHC_6H_5)[P(C_6H_{11})_3]_2$ (**1a**) and resulted in polynorbornenes with pendent cyclophosphazene side units.[21,22] In general, these polymers have monomodal molecular weight distributions with polydispersities in the range 1.3−2.0. The use of relatively high monomer-to-initiator ratios typically resulted in greater deviations from linearity in the observed vs calculated molecular weights. Thus, these polymerizations are not viewed as "living". This was a consequence of the different reactivities of the two monomeric isomers.[25] For example, different transition state energies ($\Delta\Delta G^{\ddagger}$) for the *exo* and *endo* isomers presumably result in different rates of propagation. As a result, variations exist between the initiation rates and propagation rates (K_i/K_p) for each isomer. Hence, the resultant polymers can be described as *random* AB-*block*-copolymers, giving rise to higher polydispersities. These results suggested that linear norbornenyl telechelic polyphosphazenes could be polymerized by ROMP methods.



1a



1b

The work reported here involves the synthesis of two norbornenyl phosphoranimines and their use in the preparation of norbornenyl end-functionalized mono- and ditelechelic polyphosphazenes. We also describe the ring-opening metathesis polymerization of 5-norbornene-2-methoxy phosphoranimine and norbornenyl telechelic polyphosphazenes for the production of novel organic polymers with either phosphoranimine pendent groups or linear polyphosphazene grafts. This work provides a general approach to graft copolymers that can be easily modified by varying the number or length of the phosphazene pendent groups or by utilizing different side groups within the polyphosphazene component.

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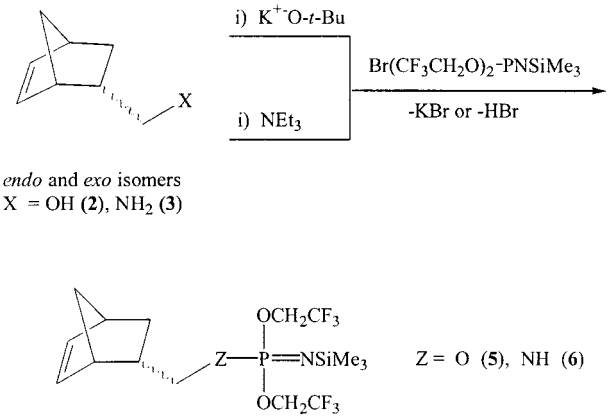
Scheme 1



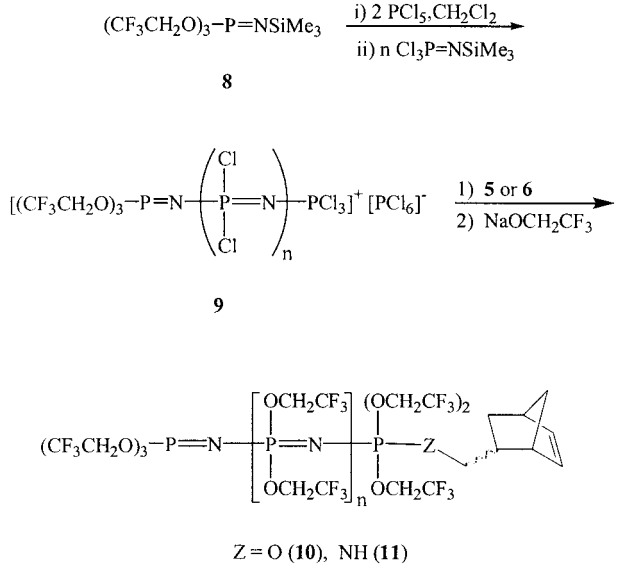
Results and Discussion

Synthesis of Norbornenyl Phosphoranimines (5, 6). Phosphoranimines such as $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**4**) readily undergo bromine replacement reactions in the presence of potassium salts of alcohols or phenols and with aliphatic amines to produce $X{-}(CF_3CH_2O)_2P{=}NSiMe_3$ species, where X = OR or NHR.[4,23] These nonhalogenated phosphoranimines can then be used to initiate or terminate living poly(dichlorophosphazene) chains to produce telechelic polymers. With this in mind, a stoichiometric amount of an alkoxynorbornene (**2**) or aminonorbornene (**3**) was allowed to react with **4** to yield phosphoranimine **5** or **6**. As shown in Scheme 1, the alcohol reacted as its potassium salt, while the amine reacted in the presence of triethylamine as a hydrohalide acceptor. For both the alkoxy and amino derivatized materials the ^{31}P NMR spectrum showed two singlets, in varying ratios, due to the presence of the *endo* and *exo* norbornene isomers. These results are consistent with those of other functionalized phosphoranimines.[23,26] The products, obtained as colorless oils after purification by vacuum distillation, were ring-open metathesis polymerized to give polynorbornenes with pendent phosphoranimine groups. The norbornenyl phosphoranimines were also used to terminate poly(dichlorophosphazene) produced by the living polymerization of trichlorophosphoranimine. This process yielded telechelic polyphosphazenes with norbornyl end units. The norbornenyl end-functionalized polymers were then employed as macromonomers in ROMP reactions to give materials comprised of a polynorbornene backbone with linear polyphosphazene grafts.

Synthesis of Monotelechelic Polyphosphazenes (10, 11). Monotelechelic polymers are attractive precursors for the preparation of graft copolymers.[24] Their functional end groups can be utilized in coupling reactions with other polymers or they can be copolymerized with various monomers to produce well-defined polymeric systems.[4,24,27,28] Specifically, monotelechelic linear polyphosphazenes with a terminal norbornenyl unit can, under ideal conditions, be polymerized via ROMP methods to produce polynorbornene-*graft*-polyphosphazenes.

Two different approaches were attempted for the preparation of a norbornenyl terminated polyphosphazene (**5**) via the living, cationic polymerization of phosphoranimines. In the first approach $(C_8H_{11}O)(CF_3CH_2O)_2P{=}NSiMe_3$ (**5**) was treated with 2 mol equiv of PCl_5 in CH_2Cl_2 at −78 °C in an attempt to form the ionic species $(C_8H_{11}O)[(CF_3CH_2O)_2P{=}NPCl_3]^+[PCl_6]^-$ (**7**). However, substitution of the chlorine atoms on **7** with trifluoroethoxy indicated that **7** was not produced. Instead, we believe the addition of PCl_5 to **7** yielded $Cl[(CF_3CH_2O)_2P{=}NPCl_3]^+[PCl_6]^-$ and $C_8H_{11}O{-}SiMe_3$. The cleavage of the norbornenyl end group has been detected with other alkoxy and aryloxy phosphazene derivatives synthesized in our program.[29] In addition, Matyjaszewski et al. reported similar findings with *N*-silylphosphoranimines that bear three alkoxide units at the chain terminus.[30]

Scheme 2



To circumvent this problem, a second strategy was employed to produce norbornenyl monotelechelic polyphosphazenes. The reaction sequence is outlined in Scheme 2. Two molar equivalents of PCl_5 was allowed to react with the nonhalogenated phosphoranimine $(CF_3CH_2O)_3P{=}NSiMe_3$ (**8**) at −78 °C in CH_2Cl_2 to generate the ionic species $[(CF_3CH_2O)_3P{=}N{-}PCl_3]^+$-$[PCl_6]^-$ (**9**).[31] The formation of this species was confirmed in situ by the presence of two doublets in the ^{31}P NMR spectrum for the $N{-}PCl_3^+$ (8.12 ppm) and $(CF_3CH_2O)_3P{=}N$ (−12.46 ppm) units. The addition of $Cl_3P{=}NSiMe_3$ to this reaction mixture produced living poly(dichlorophosphazene) (**9**) with chain lengths that could be controlled by varying the monomer-to-initiator ratio. The progress of the polymerization, which was complete within 24 h at room temperature, was monitored by ^{31}P NMR spectroscopy which showed the conversion of $Cl_3P{=}NSiMe_3$ to polymer. Monotelechelic polyphosphazenes were then obtained when the active terminus of the polyphosphazene (**9**) was quenched with an excess of the norbornenyl phosphoranimine, **5** or **6**. Macromolecular replacement of the chlorine atoms along the $[Cl_2P{=}N]_n$ component by $NaOCH_2CF_3$ or $NaOC_6H_5$ yielded hydrolytically stable, chlorine-free macromonomers (**10** or **11**) without the loss of the norbornyl unit.

The conversion of living poly(dichlorophosphazene), $[(CF_3CH_2O)_3P{=}N{-}(Cl_2P{=}N)_n{-}PCl_3]^+[PCl_6]^-$ (**9**), to the macromonomer **10** was followed by ^{31}P NMR spectroscopy. A typical ^{31}P NMR spectrum for a living poly(dichlorophosphazene) is shown in Figure 1a with peak assignments of +8 ppm (d, terminal PCl_3), −12 ppm (d, $(CF_3CH_2O)_3P$), −14 ppm (t, $PCl_2{=}N{-}PCl_3$), −15 ppm (t, $Cl_2P{=}N{-}Cl_2P{=}N{-}PCl_3$), and −17 ppm (br s, $[Cl_2P{=}N]_n$). The living polyphosphazene chains were termi-

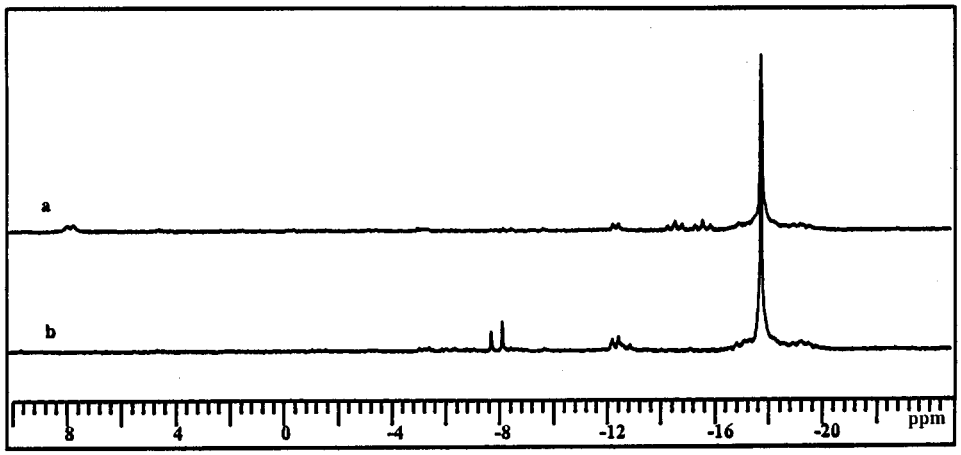


Figure 1. ^{31}P NMR spectrum for (a) a living poly(dichlorophosphazene) chain (**9**). (b) Slight excess of a norbornenyl phosphoranimine added to quench the polymerization process (**10**).

Table 1. Molecular Weight Data for Mono- and Ditelechelic Macromonomers

		$M_n \times 10^{-4}$			
macromonomer	M:I	calcd[a]	found[b]	PDI	T_g[c]
10a[d]	10:1	0.32	1.25	1.19	−50
10b[d]	20:1	0.57	1.37	1.16	−49
10c[d]	25:1	0.69	1.46	1.17	−55
10d[d]	40:1	1.05	1.87	1.14	−56
11a[d]	20:1	0.57	2.36	1.11	−56
11b[d]	40:1	1.05	2.66	1.19	−58
12a[e]	10:1	0.59	1.03	1.18	−49
12b[e]	20:1	1.08	1.27	1.24	−54
12c[e]	40:1	2.05	4.73	1.07	−53
12d[e]	60:1	3.02	5.47	1.47	−59

[a] Calculated from the initial ratio of monomer to PCl_5 initiator at 100% conversion. [b] Obtained by GPC vs polystyrene standards. [c] Measured by DSC and recorded in °C. [d] Toluene as solvent. [e] CH_2Cl_2 as solvent.

nated by the addition of phosphoranimine **5**, to produce the chloro derivative of **10**. This was indicated by the disappearance of the resonance for the PCl_3^+ and the formation of the new resonance for the 5-norbornene-2-methoxy-P end group which appears at −8 ppm (Figure 1b). The ^1H NMR spectra of the macromonomers showed *endo* and *exo* olefinic resonances between 5.9 and 6.2 ppm, which are resolved from the OCH_2CF_3 protons due to the polyphosphazene (4.3−4.5 ppm). Molecular weights obtained from GPC vs polystyrene standards spanned the range of 1.25×10^4 to 2.66×10^4 with polydispersities of 1.11 to 1.19 (Table 1). The polyphosphazene to norbornene molar ratios calculated from the integration of the olefinic and trifluoroethoxy proton resonances agreed, within reason, with those calculated from GPC analysis.

Synthesis of Ditelechelic Macromonomers (12). Recent advances in the termination of living poly(dichlorophosphazene) with functional phosphoranimines have allowed the synthesis of telechelic materials with the controlled introduction of two terminal units onto the polymer chain.[22] Following this approach, ditelechelic macromonomers (**12**) were synthesized as outlined in Scheme 3. Living poly(dichlorophosphazene) was first synthesized via the initiation of $Cl_3P{=}NSiMe_3$ by PCl_5 in toluene at room temperature. The living poly(dichlorophosphazene) was then quenched with *an excess* of the norbornenyl phosphoranimine **5**. Finally, replacement of the chlorine atoms by trifluoroethoxy groups resulted in the production of a hydrolytically

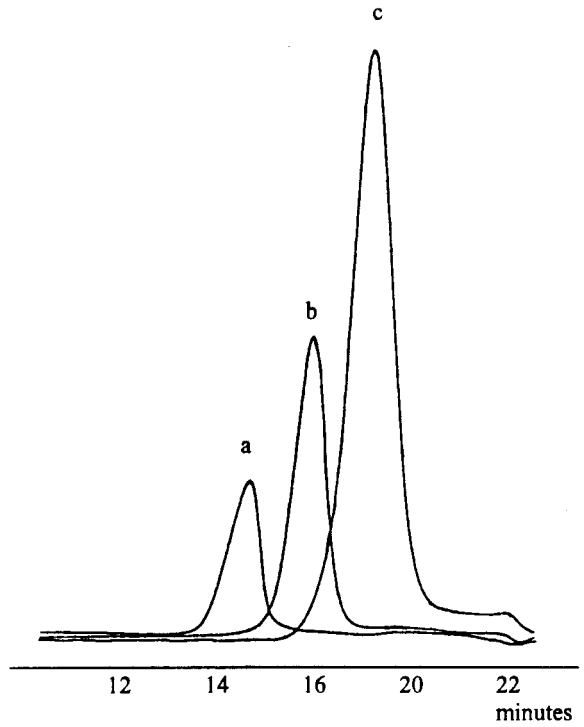
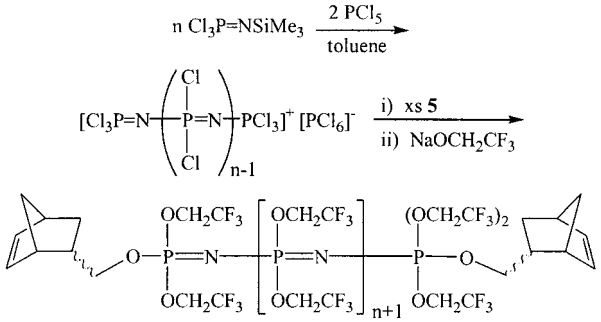


Figure 2. Comparative GPC plots for polymers (a) **12d**, (b) **12c**, and (c) **12b**.

Scheme 3



12

stable polyphosphazene (**12**) that contained a norbornene unit on both ends of the polymer chain.

The chain lengths of the ditelechelic polyphosphazene (**12**) were controlled by the ratio of $Cl_3P{=}NSiMe_3$ to PCl_5

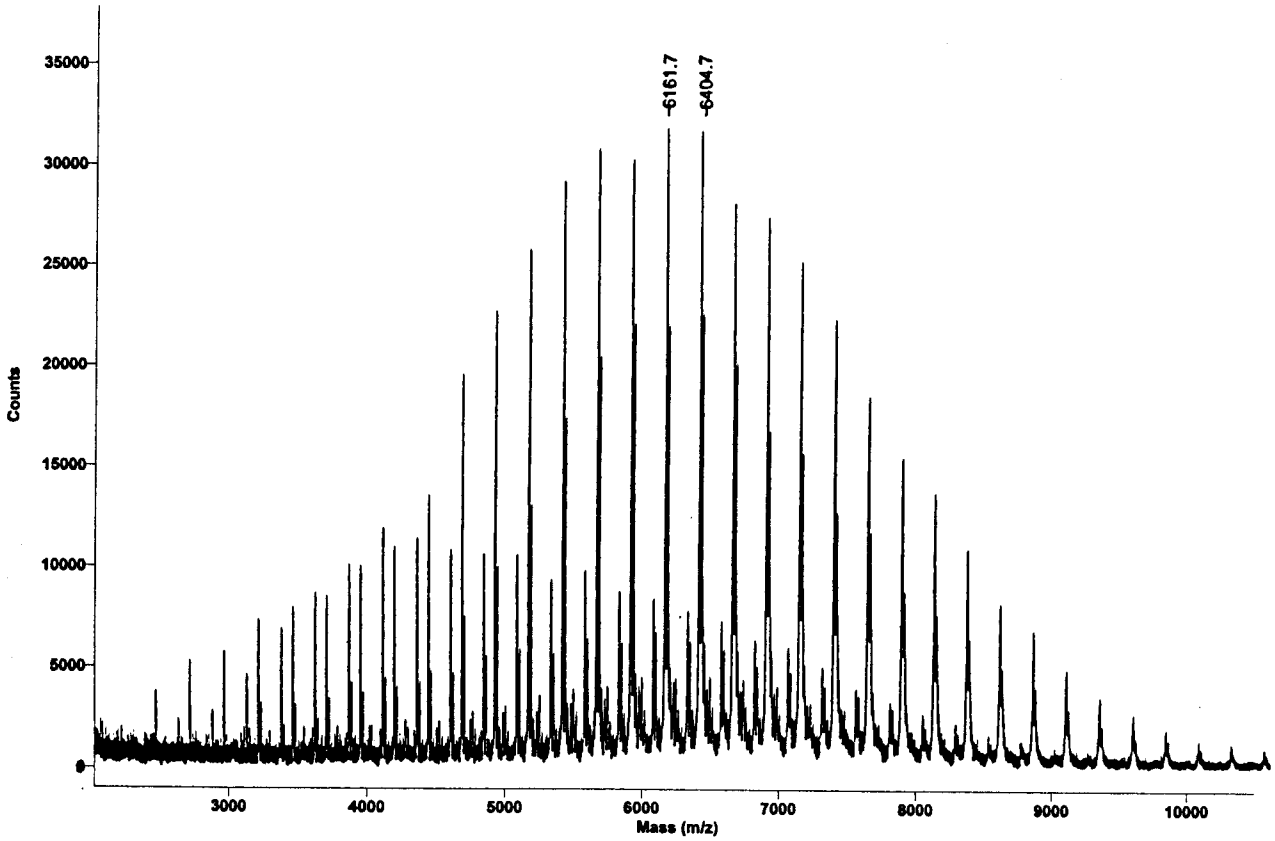


Figure 3. MALDI mass spectra for a monotelechelic polyphosphazene **10**.

in the initial step of the reaction. Three gel permeation chromatography spectra of ditelechelic polyphosphazenes **12** synthesized with varying monomer-to-initiator ratios are shown in Figure 2. These spectra illustrate the degree to which the molecular weights of these materials can be controlled. As determined by gel permeation chromatography, the number-average molecular weights of these ditelechelic polymers ranged from 1.03×10^4 to 5.47×10^4 (Table 1). All these materials were isolated as white, adhesive solids for the low molecular weight species or as semicrystalline, fiber-forming materials for the higher molecular weight polymers. The discrepancies between the theoretical molecular weights and measured molecular weights are due to an overestimation of molecular weight by GPC.[22,31,32]

The identity of the functional end groups was confirmed via multinuclear NMR spectroscopy. MALDI mass spectroscopy was also used to verify the formation of the norbornenyl telechelic polyphosphazenes by providing molecular weight data on the polymers. The MALDI spectrum of a monotelechelic polymer **10** is shown in Figure 3. The signals depict a monotelechelic polyphosphazene (**10**) with an average repeat unit $[(CF_3CH_2O)_2P{=}N]_{22}$ plus a sodium atom (mass 6162). The weight of the polymer, mass 6139, can be described as the weight of the two end groups, its repeating unit, and a sodium atom; $-P-(OCH_2CF_3)_3-OC_8H_{11}$ (mass 451), $(CF_3CH_2O)_3P{=}N$ (mass 342), $[(CF_3CH_2O)_2P{=}N]_{22}$ (mass 5346), and Na (mass 23). Thus, the series of signals is representative of polymer chains with an average repeat unit length of 23, where the distance between the peaks is that of the repeat unit, $[(CF_3CH_2O)_2P{=}N]_n$ with a mass of 243.

Ring-Opening Metathesis Polymerization of Norbornenyl Phosphoranimines (5). Much of the work in other laboratories on ROMP-derived graft copolymers has been based on anionically derived styrene macroinitiators terminated with norbornene units.[18,19,33] In addition, the synthesis of organic block and graft copolymers via coupled atom-transfer radical polymerization (ATRP) and ROMP methods has been reported.[16,34] Polymers produced via ROMP methods typically have narrow or monodisperse molecular weight distributions. In addition, because the polymerization process has been shown to occur in a "living" manner,[33−40] ROMP is a superior method for the synthesis of di- and triblock copolymers.[41] The advent of Grubbs (**1a**) and Schrock-type initiators (**1b**) has also made it feasible to incorporate a wide range of polar functional groups into olefin-based polymer systems.[42−46]

The ring-opening metathesis polymerization of norbornenyl functionalized phosphazenes was first carried out on the small-molecule phosphoranimine $(C_8H_{11}O)(CF_3CH_2O)_2P{=}NSiMe_3$ (**5**) (Scheme 4). The polymerizations of this model system, with monomer-to-initiator ratios up to 250:1, were promising. The reactions were carried out with high concentrations of the reactants. Thus, increases in viscosity or gelation of the reaction mixture as the polymerization proceeded were more pronounced at higher monomer-to-initiator ratios. Isolation and purification of the polymers resulted in well-defined materials that contained pendent phosphoranimine side groups attached to a polynorbornene backbone (**13**). Table 2 shows the molecular weight data obtained via ROMP of **5** with varying percentages of norbornene.

Scheme 4

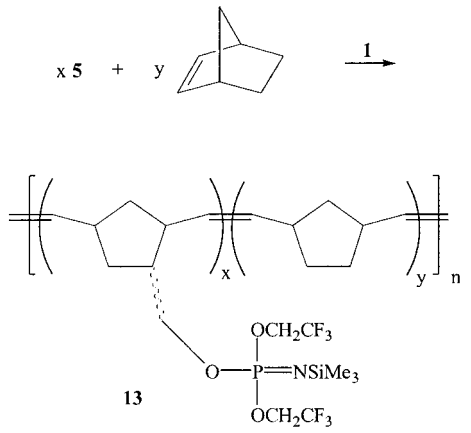


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Table 2. Molecular Weight Data for Phosphoranimine-Functionalized Polynorbornenes

polymer	[M]/**1**	mol % norbornene	$M_n \times 10^{-4}$ calcd[a]	$M_n \times 10^{-4}$ found[b]	PDI	T_g[c]
13a	50	0	2.20	4.60	1.22	40
13b	100	0	4.39	4.95	1.54	39
13c	250[d]	0	11.0	7.13	1.45	41
13d	200	0	8.78	8.24	1.57	37
13e	200	20	7.40	8.13	1.85	36
13f	200	40	6.02	7.87	1.76	31
13g	200	60	4.64	7.21	1.63	41
13h	200	80	3.26	7.06	1.87	43
13i	200	90	2.57	6.63	1.87	38
13j	200	95	2.23	4.81	1.82	35
13k	200	98	2.02	2.58	1.81	36
13l	200	99	1.95	4.58	1.58	36

[a] Calculated from the initial [M]/**1** ratios at 100% conversion. [b] Obtained by GPC vs polystyrene standards. [c] Measured by DSC and recorded in °C. [d] Polymer was only partially soluble in THF.

Polymer **13**, with its pendent phosphoranimine groups, was examined as a potential precursor for the production of polynorbornene-*graft*-polyphosphazenes. However, attempts to cationically polymerize $Cl_3P{=}NSiMe_3$ from the pendent phosphoranimine side groups were unsuccessful. The addition of PCl_5 and $Cl_3P{=}NSiMe_3$ to **13** resulted in the cleavage of the phosphoranimine side units from the polynorbornene backbone, as confirmed by ^1H and ^{13}C NMR and FTIR. Despite the inability to produce graft copolymers by this method, the synthesis of **13** did offer information on norbornene−phosphorus containing material. This work demonstrates the feasibility of producing polynorbornenes that contain noncyclic phosphazene components as pendent groups the ring-opening metathesis polymerization of phosphorus−norbornene species. Furthermore, the successful ROMP reactions of **5** confirm that a carbene initiator can be used to polymerize phosphorus species that contain a norbornene functionality.

Ring-Opening Metathesis Polymerization of Monotelechelic Polyphosphazenes (10). Earlier work in our program has shown that the functional end groups on monotelechelic polyphosphazenes can be utilized to produce both block and graft copolymers.[4,24,27] For example, a styrenyl monotelechelic polyphosphazene was copolymerized with styrene to produce polystyrene-*graft*-polyphosphazenes.[24] These results, coupled with the successful ROMP reactions of **5**, led us to explore the production of polynorbornene-*graft*-polyphosphazenes via the ring-opening metathesis polymerization of monotelechelic polyphosphazenes.

Scheme 5

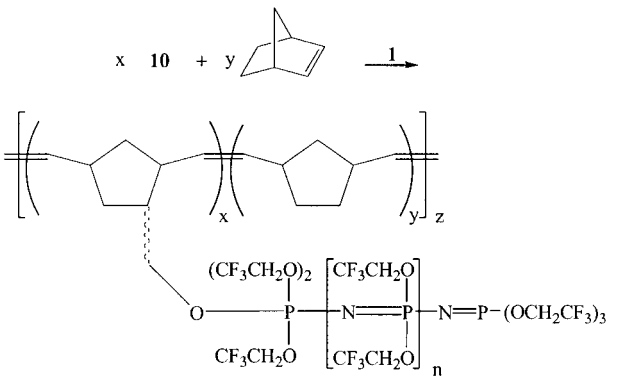

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Table 3. Molecular Weight Data for Polynorborne-*graft*-polyphosphazene

graft copolymer[a]	starting macro-monomer	mol % **10**	$^bM_n \times 10^{-4}$ calcd[b]	$^bM_n \times 10^{-4}$ found[b]	PDI	T_g[c]
14a	**10a**	1	2.50	0.95	1.51	43
14b	**10a**	2	3.12	1.59	1.65	48
14c	**10b**	1	3.00	4.07	1.70	43
14d	**10b**	2	4.12	5.41	1.57	44
14e	**10c**	1	3.24	5.12	1.42	44
14f	**10c**	2	4.60	7.04	1.29	46
14g	**10c**	5	8.69	7.88	1.84	47
14h	**10c**	25	35.9	11.4	1.42	47
14i	**10c**	50	69.9	21.7	1.36	43
14j	**10c**	75	104	43.5	1.40	32
14k	**10c**	100	138	32.2	1.74	31
14l	**10d**	1	3.96	3.38	1.60	53
14m	**10d**	25	53.9	21.2	1.72	54
14n	**10d**	50	106	27.4	1.87	44
14o	**10d**	75	158	50.4	1.77	43
14p	**10d**	100	210	103	2.07	44

[a] Polymerizations run at 200:1. [b] Obtained by GPC vs polystyrene standards. [c] Measured by DSC and recorded in °C.

Scheme 5 outlines the synthetic approach used to synthesize the polynorbornene-*graft*-polyphosphazene materials. Homo- and co-ring-opening metathesis polymerizations were carried out on the monotelechelic macromonomer **10** and norbornene using **1a** as the initiating species. In a typical polymerization reaction the macromonomer was dissolved in a minimal amount of THF. To this was added a solution of the initiator **1a** in THF. The homo- and copolymerization reaction mixtures became viscous or solidified within 40 min after the addition of the initiator. In all cases, polymerizations were carried out with a monomer-to-initiator ratio of 200:1. As seen in Table 3, the molecular weight and the mole percent of the monotelechelic polyphosphazene were varied in order to examine the range of materials that could be obtained by this method. In addition, Figure 5 shows GPC traces of polymers **14m**, **14n**, and **14o** and illustrates the well-defined increases in the molecular weight of the graft copolymer as the mole percent of the starting macromonomer is increased.

Ring-Opening Metathesis Polymerization of Ditelechelic Polyphosphazenes (12). Norbornenyl ditelechelic polyphosphazene **12** was treated with various amounts of initiator **1a** in CH_2Cl_2 to induce the ring-opening metathesis polymerization of the norbornene end group. Immediate gelation occurred following the

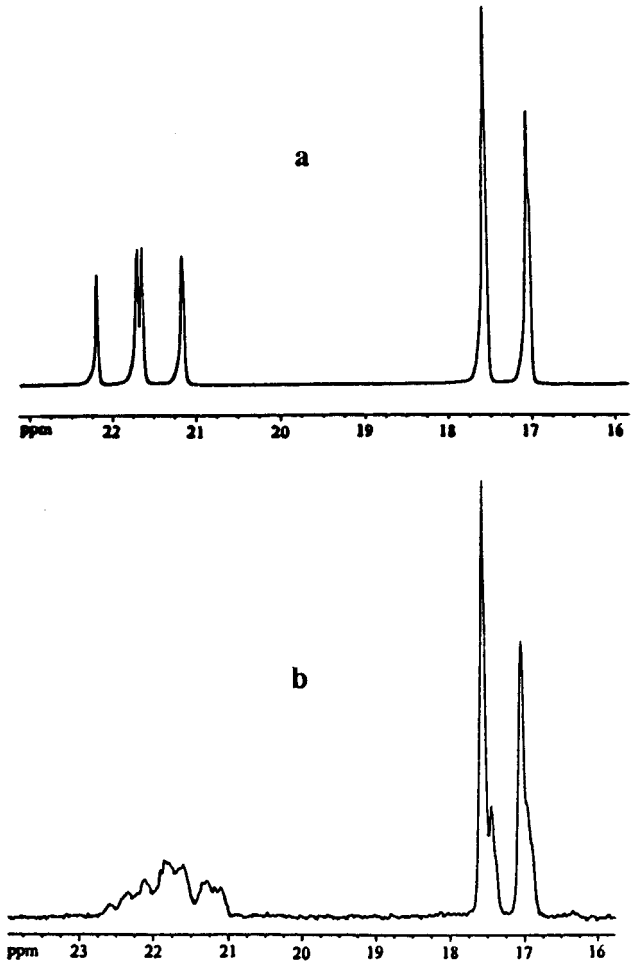

Figure 4. (a) Amine-substituted cyclotriphosphazene (**15a**) and (b) complexation with initiator **1**.

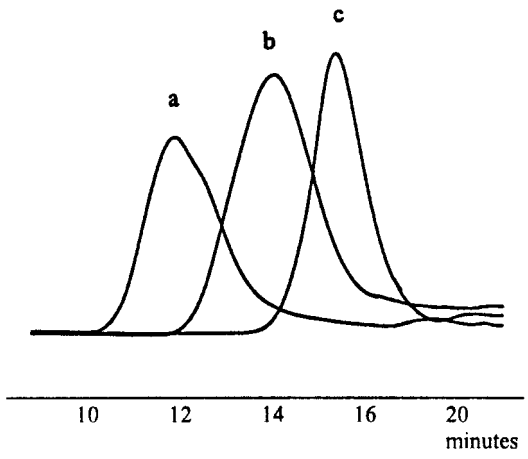

Figure 5. Comparative GPC plots for polymers (a) **14o**, (b) **14n**, and (c) **14m**.

addition of **1a** to **12**. The products were highly cross-linked, as evidenced by the insolubility in organic solvents and could not be characterized. Difunctional macromonomers often yield cross-linked materials. However, these results confirm that the norbornyl end groups on **12** are highly reactive to **1a**. Therefore, these difunctional polymers may be suitable cross-linking agents for organic systems.

Ring-Opening Metathesis Polymerization of Polyphosphazenes Derived from 6. Neither the mono- nor ditelechelic macromonomers derived from **6** underwent ROMP reactions when treated with initiator **1a**. This was attributed to coordination of the amino groups to the metal center of the initiator. Coordination was evident from the ^{31}P NMR spectrum, which showed a marked change in splitting pattern of the phosphorus atoms adjacent to the amino groups. Despite the high tolerance to polar functional groups that has been demonstrated by this well-known initiator, functional groups with active protons may be detrimental and probably hinder the activity of the initiator.[36,45]

The complexation between initiator **1a** and the phosphazene−amine unit was examined further by the synthesis of a *cyclo*triphosphazene bearing an amine-based norbornene unit (**15a** and **15b**). Trifluoroethoxy side groups on the cyclic trimer were used to parallel the analogous trifluoroethoxy substituted telechelic macromonomers. Phenoxy groups were also examined for comparative purposes. The addition of initiator **1a** resulted in immediate discoloration of the reaction mixture, from purple to yellow-green, for both the trifluoroethoxy and phenoxy systems. This color change suggested a change in the oxidation state of the metal center and possible coordination with the metal center. The ^{31}P NMR spectra of $N_3P_3(OCH_2CF_3)_5(C_8H_{12}N)$ (**15a**), before and after the addition of **1a**, are shown in Figure 4. The A_2B splitting pattern is clearly altered at the P_b phosphorus atom as a result of coordination by **1a**. A similar experiment was carried out with the use of the Schrock-carbene initiator (**1b**) with similar coordination results that were confirmed by ^{31}P NMR spectroscopy. Although recent progress has been made with ROMP reactions of amine-functionalized norbornenes with the use of tungsten-based initiators, the work described here confirms the limitation of metathesis initiators, such as **1a** and **1b**, with amino species.

NMR Characterization of Polymers Produced via ROMP. Polymers **13** and **14** were examined by multinuclear NMR spectroscopy. ^{31}P NMR signals were broadened due to the immobilized $[(CF_3CH_2)_2P{=}N]_n$ repeat units close to the polynorbornene backbone. The ^{1}H NMR spectrum of the graft copolymers showed characteristic upfield shifts of the olefinic groups at 5.2−5.6 ppm relative to the monomer (5.9−6.2 ppm). The exo and *endo* 5-norbornene-2-methoxy isomers further complicated the NMR spectra since the macromonomer **10** and the polyphosphazene graft possessed both *exo* and *endo* configurations. In addition to *cis* and *trans* vinylene units and *meso* or *racemic* dyads, a complex microstructure is presumed to develop during the polymerization, leading to random head−tail, head−head, and tail−tail additions.[15] Thus, the complexity of the polymer microstructure helps to explain the many unresolved and broad multiplet peaks in the ^{1}H and ^{13}C NMR spectra.

Molecular Weights and Polydispersities of Polymers Produced via ROMP. The molecular weights of polynorbornene-*graft*-phosphoranimine (**13**) and polynorbornene-*graft*-polyphosphazene (**14**) were estimated by GPC and are shown in Tables 2 and 3, respectively. Molecular weights for **13** ranged from 2.58×10^4 to 8.24×10^4 with polydispersities between 1.22 and 1.87. Polymer **14** gave molecular weight values that ranged from 0.95×10^4 and 103×10^4 with polydispersities between 1.29 and 2.07. The significantly higher polydispersities for the polymers synthesized in this work are probably a result of the bulkiness of monomer **5** and macromonomer **10**. The literature indicates that

the polymerization of norbornenes with bulky side groups do not always occur in a living manner.[21] The discrepancy between theoretical and experimentally obtained molecular weights is assumed to be a result of the calibration of the GPC with linear polystyrene. To determine the effects of the grafts on GPC molecular weights, a polynorbornene with 200 repeating units was synthesized as a control by the reaction of norbornene with **1a**. The different M_n values for the graft copolymer **13d** (8.24×10^4) and **14f** (32.2×10^4) compared to the polynorbornene control (2.72×10^5) are presumed to be a result of the difference in hydrodynamic volumes of these graft copolymers compared to linear polystyrene standards and not a result of incomplete ROMP reactions. Conformation that the ROMP reactions went to completion came from the examination of the reaction mixtures which by ^{1}H and ^{31}P NMR showed no traces of the starting norbornene or phosphazene monomer.

Thermal Properties. The thermal properties of the polymers were analyzed by differential scanning calorimetry (DSC). The glass transition temperatures of the telechelic polyphosphazenes are listed in Table 1. Similar to those of short-chained poly(bistrifluoroethoxyphosphazene), these telechelic polyphosphazenes had T_g's well below room temperature. Polymers **13** and **14** had T_g's above room temperature that ranged from 31 to 54 °C as outlined in Tables 2 and 3. It may be noted that the T_g of prepolymer **10** increased roughly 80 °C following copolymerization with norbornene via ROMP reactions. It was also observed that the T_g decreased for the graft copolymer **14** as the percentage of polyphosphazene was increased.

Conclusions

Mono- and dinorbornenyl telechelic polyphosphazenes were synthesized via an ambient temperature living cationic polymerization process. The length of the polyphosphazene chain was easily controlled to produce telechelic polymers with well-defined molecular weights and narrow polydispersities. ROMP of the monotelechelic polyphosphazenes gave soluble graft copolymers. The 5-norbornene-2-methoxy phosphoranimine was also polymerized via ROMP to yield polynorbornenes with phosphoranimine pendent groups that could be isolated in nonprotic media. The ditelechelic polyphosphazenes produced cross-linked materials when subjected to ROMP reactions. The preparation of these polynorbornenes with pendent phosphazene side units demonstrates the versatility of the living, cationic polymerization of phosphoranimines that allows both the percentage and length of the phosphazene graft to be controlled.

Experimental Section

Materials. Lithium bis(trimethylsilyl)amide (97%), phenol (99%), 5-norbornene-2-methanol (98%, equimolar mixture of *exo* and *endo* isomers), 1,1,1-trifluoroethanol (99%), acrylonitrile, dicyclopentadiene, lithium aluminum hydride, CaH_2 (90−95%), benzophenone (99%), and sodium hydride (66%) were obtained from Aldrich and were used without further purification. Phosphorus pentachloride (Aldrich, 95%) was purified by sublimation under vacuum prior to use. $Cl_3P{=}NSiMe_3$, $Br(CF_3CH_2O)_2P{=}NSiMe_3$, $(CF_3CH_2O)_3P{=}NSiMe_3$, $N_3P_3(OCH_2CF_3)_5Cl$, and $N_3P_3(OC_6H_5)_5Cl$ were synthesized and purified by literature procedures.[22,31,36] Tetrahydrofuran, toluene, and hexanes (EM Science) were distilled into the reaction flask from sodium benzophenone ketyl under an atmosphere of dry argon. Dichloromethane (EM Science) was dried and distilled from CaH_2.

All glassware was dried overnight in an oven or flame-dried under vacuum before use. The reactions were performed using standard Schlenk techniques or in an inert atmosphere glovebox (Vacuum Atmospheres) under an atmosphere of dry argon or nitrogen.

Equipment. ^{1}H, ^{13}C, and ^{31}P spectra were recorded on a Bruker WM-360 NMR spectrometer operated at 360, 146, and 90.27 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to solvent signals while ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. All chemical shifts are reported in ppm, while coupling constants are reported in hertz. Differential scanning calorimertry was carried out using Perkin-Elmer DSC 7 equipment and an empty aluminum pan as a reference. Samples (10−15 mg) were examined in aluminum pans under an atmosphere of dry nitrogen. The samples were heated to 200 °C to remove traces of solvents and were then cooled rapidly to −150 °C. The measurements were performed at an advancing heating rate of 20 °C/min. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector and American Polymer Standards AM gel 10 mm and AM gel 10 mm 10^4 Å columns and calibrated vs polystyrene standards (Polysciences). The samples were eluted at 40 °C with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv). MALDI mass spectra were collected using a Voyager DESTR MALDI-TOF spectrometer.

Preparation of Norbornyl Intermediate 5-Aminomethyl Bicylco[2.2.1]hept-2-ene (3). The amine-based norbornene (**5**) was made via Diels Alder coupling of cyclopentadiene and acrylonitrile. With the use of a simple distillation apparatus, dicyclopentadiene was cracked in silicone oil at 180 °C, and the freshly distilled material (32.7 g, 0.247 mol) was added dropwise to 2 mol equiv of acrylonitrile (32.5 mL, 0.495 mol). The mixture was warmed to room temperature and then stirred overnight. Excess acrylonitrile was removed by distillation at ambient pressure, and the resultant liquid was purified by vacuum distillation (43 °C/0.1 mmHg). The product (22.8 g, 80% yield) was a clear colorless liquid containing both *exo* and *endo* isomers (approximately equimolar amounts).

The resultant nitrile (9.1 g, 76 mmol) was dissolved in 30 mL of diethyl ether and added dropwise to a mixture of lithium aluminum hydride (4.34 g, 114 mmol) in 50 mL of diethyl ether. The reaction mixture was stirred under argon at room temperature for 24 h. The excess $LiAlH_4$ was destroyed by the dropwise addition of deionized water. The lithium and aluminum hydroxide salts were filtered off. The organic layer was dried over $MgSO_4$. The solvent was removed in vacuo to yield a pale yellow oil and was distilled under reduced pressure to separate the *exo* and *endo* isomers. ^{1}H NMR ($CDCl_3$) *endo* isomer: 6.07 (m, 1H), 5.86 (m, 1H), 2.81 (m, 1H), 2.72 (m, 1H), 2.37 (m, 1H), 2.29 (m, 1H), 2.03 (m, 1H), 1.76 (m, 1H), 1.37 (d, 1H), 1.18 (d, 1H), 0.42 (m, 1H); *exo* isomer: 6.03 (m, 1H), 5.96 (m, 1H), 2.73 (m, 1H), 2.65 (m, 2H), 2.59 (m, 1H), 1.35 (m, 1H), 1.24 (m, 1H), 1.22 (d, 1H), 1.14 (d, 1H), 1.04 (m, 1H). ^{13}C NMR ($CDCl_3$) *endo* isomer: 136.70, 131.37, 48.91, 45.68, 43.26, 42.02, 41.71, 29.61; *exo* isomer: 135.71, 135.63, 47.13, 44.45, 43.44, 42.30, 41.03, 30.50. IR (neat): 3400, 3300, 3080, 1580.

Synthesis of $(C_8H_{11}O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ (5). A mixture of $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**4**) (5.0 g, 12.6 mmol) in THF (200 mL) was cooled to −78 °C. To this solution was added 1.8 g (12.6 mmol) of the potassium salt of **2** in THF (50 mL) over a period of 20 min. The reaction mixture was warmed to room temperature and stirred for 20 h. ^{31}P NMR was used to verify consumption of **4**. All volatiles were removed in vacuo, and the salts were washed with hexanes. The salts were subsequently filtered and the volatiles removed under reduced pressure to yield the alkoxy-linked norbornenyl phosphoranimine (**5**) as a slightly yellow oil. Pure alkoxy-derived phosphoranimine (77% yield) was isolated via distillation under reduced pressure. ^{1}H NMR ($CDCl_3$): 6.16−6.19 (m, 1H, alkene), 6.10 (br s, 1H, norb), 5.93−5.96 (m, 1H, norb), 4.34 (m, 4H, OCH_2CF_3), 3.74 (m, 2H, OCH_2), 3.56 (m, 2H, OCH_2), 2.92, 2.83, 2.76 (3 br s, 4H, norb), 2.41 (m, 1H, norb), 1.80 (m, 2H,

norb), 1.46 (m, 1H, norb), 1.26 (m, 1H, norb), 1.09 (m 1H, norb), 0.53 (m, 1H, norb), 0.06 (br s, 9H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$) (*exo* and *endo* isomers): −8.18 (d). ^{13}C NMR ($CDCl_3$): 138.33, 137.73, 136.92, 133.04 (4C, norb), 124.24 (q of d, J = 276.94, 10.43, 2C OCH_2CF_3), 72.37 (d, J = 6.75, 1C, OCH_2), 71.72 (d, J = 6.54, 1C, OCH_2), 63.31−64.53 (m, 2C, OCH_2CF_3), 49.89, 45.42, (1C, norb) 44.40, (d, J = 4.14, norb), 44.05 (d, J = 5.40, norb), 42.98 (d, J = 5.40, norb), 42.35 (norb), 40.27 (d, J = 7.14, norb), 40.00 (d, J = 7.01, norb), 29.69, 29.08 (2C, norb) 3.16 (s, 3C, $Si(CH_3)_3$). MS (FAB+): m/z = 439 (MH^+, 21%), 316 ($M-C_8H_{11}O$, 35%), in good agreement with isotopic abundance calculations.

Synthesis of $(C_8H_{12}N)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ (6). To a mixture of **4** (1.6 g, 4.1 mmol) in CH_2Cl_2 (20 mL) was added Et_3N (0.8 mL, 4.1 mmol). The mixture was cooled to −78 °C. To this was added **3** (0.70 g, 5.7 mmol) in CH_2Cl_2 (10 mL) over a period of 20 min. The reaction was stirred for 20 h, and ^{31}P NMR was used to verify the consumption of **4**. The product was worked up and isolated in a manner similar to **5** to yield a clear colorless liquid (74% yield). ^1H NMR ($CDCl_3$): 6.16−6.19 (m, 1H, C*H*=C*H*), 6.09 (br s, 1H), 5.91−5.95 (m, 1H), 4.20 (m, 4H, OCH_2CF_3), 2.85, 2.81, 2.64 (3 br s, 4H), 2.56 (m, 1H), 2.48 (m, 1H), 2.17 (m, 1H), 1.84 (m, 1H), 1.48 (m, 1H), 1.28 (m, 1H), 1.10 (m, 1H), 0.54 (m, 1H), 0.05 (br s, 9H, $Si(CH_3)_3$). ^{13}C NMR (*exo* and *endo* isomers): 137.8, 136.9, 136.2, 131.7, 62.4, 49.5, 46.9, 45.6, 44.9, 43.9, 41.7, 40.8, 30.9, 30.0. ^{31}P NMR ($CDCl_3$) (*exo* and *endo* isomers): −0.9 (d, 1P). MS (FAB+): m/z = 406 MH^+.

Formation of $[(C_8H_{11}O)(CF_3CH_2O)_2P{=}NPCl_3]^+[PCl_6]^-$ (7). To a stirred solution of PCl_5 (1.9 g, 0.91 mmol) in CH_2Cl_2 (60 mL) at −78 °C was added **5** (2.0 g, 0.25 mmol) in THF (5 mL). The reaction mixture was stirred at −78 °C for 1 h and then warmed to room temperature. The solvents were removed in vacuo to yield 1.8 g (53%) of a yellow oil. ^{31}P NMR spectroscopy confirmed the presence of the desired product as evidenced by two doublets for the terminal PCl_3^+ and the $(C_8H_{11}O)(CF_3CH_2O)_2P$ phosphorus atoms. ^1H NMR ($CDCl_3$) (*exo* and *endo* isomers): 5.99−6.01 (m, 2H), 5.45−5.48 (m, 2H), 4.91 (m, 1H), 4.74 (m, 1H), 4.47 (m, 1H), 4.27 (m, 4H, OCH_2CF_3), 3.97 (m, 1H), 3.32 (m, 1H), 2.67 (m, 1H), 2.47 (m, 1H), 2.08 (m, 1H), 1.89 (m, 1H), 1.59 (m, 1H), 1.48 (m, 1H), 1.30 (m, 1H). ^{31}P NMR ($CDCl_3$): −3.51 (d, 1P, $(C_8H_{11}O)(CF_3CH_2O)_2P{=}N$), −8.22 (d, 1P, $Cl_3P{=}N$).

Formation of $[(CF_3CH_2O)_3P{=}NPCl_3]^+[PCl_6]^-$. To a stirred solution of PCl_5 (0.104 g, 0.5 mmol) in CH_2Cl_2 (50 mL) at −78 °C was added 0.25 mmol (0.104 g) of the $(CF_3CH_2O)_3P{=}NSiMe_3$ phosphoranimine quickly via syringe. The reaction mixture was stirred at −78 °C for 1 h and allowed to warm to room temperature. ^{31}P NMR spectroscopy of the reaction mixture indicated the presence of the desired product as evidenced by two doublets for the terminal PCl_3^+ and the $(CF_3CH_2O)_3P$ phosphorus atoms. ^{31}P NMR (D_2O): 22.78 (d, J = 57.44, $(CF_3CH_2O)_3P{=}N$), −9.91 (d, J = 57.15, $Cl_3P{=}N$).

General Procedure for $[(CF_3CH_2O)_3P{=}N(Cl_2P{=}N)_n PCl_3]^+[PCl_6]^-$ (9). To a stirred solution of the initiator $[(CF_3CH_2O)_3P{=}NPCl_3]^+[PCl_6]^-$ was added a solution of $Cl_3P{=}NSiMe_3$ in CH_2Cl_2. After a given amount of time (2−24 h, dependent on monomer-to-initiator ratios), all of the $Cl_3P{=}NSiMe_3$ had reacted, as confirmed by the disappearance of the ^{31}P NMR resonance for $Cl_3P{=}NSiMe_3$ at −54 ppm and the presence of a new resonance at −17.6 ppm for $[Cl_2P{=}N]_n$. ^{31}P NMR (D_2O): 8.12 (d, 1P, J = 29.02, $-PCl_3^+$), −12.46 (d, 1P, J = 30.76, $(CF_3CH_2O)_3P$), −14.5, −15.5 (t, 2P, J = 40.11, $-Cl_2P{=}N-Cl_2P{=}N-[Cl_2P{=}N]_n$), −17.6 ppm (br s, $[Cl_2P{=}N]_n$).

General Procedure for the Synthesis of Monotelechelic Macromonomer $(CF_3CH_2O)_3P{=}N[(CF_3CH_2O)_2P{=}N)]_n P(CF_3CH_2O)_3(OC_8H_{11})$ (10). To intermediate **9** was added a solution of **5** in CH_2Cl_2, and the mixture was stirred for 8 h. The volatiles were removed, and the residue was redissolved in THF and subsequently treated with a 2-fold excess per chlorine atom of 1.5 M sodium trifluoroethoxide in THF. The mixture was stirred at 25 °C for 24 h to produce the fully substituted product. The polymer was isolated via precipitation into deionized water (3×) and hexane (2×). ^1H NMR (acetone-d_6): 6.11−5.96 (m, 2H), 4.76−4.26 (m, OCH_2CF_3), 3.67−3.61 (m, 1H), 3.49−3.44 (m, 1H), 2.91 (br s, 1H), 2.82−2.79 (m, 2H), 2.40 (br s, 1H), 1.83−1.76 (m, 1H), 1.38−1.17 (m, 1H), 0.52−0.48 (br s, 1H). ^{31}P NMR (acetone-d_6): −6.39 (br s, $[(CF_3CH_2O)_2P{=}N]_n$), −1.61 (d, J = 68.05, $Norb-O-(CF_3CH_2O)_2P{=}N$), −0.98 (d, J = 51.96, $CF_3CH_2O)_3P{=}N$). ^{13}C NMR (acetone-d_6): 137.68, 137.31, 136.89, 132.99, 123.82 (q, J = 270.58, OCH_2CF_3), 49.54, 45.31, 44.25, 44.00, 42.87, 43.01, 42.21, 42.18, 40.21, 64.14 (q, J = 40.41, OCH_2CF_3), 63.01, 62.65.

General Procedure for the Synthesis of Ditelechelic Macromonomer $(C_8H_{11}O)(CF_3CH_2O)_2P{=}N[(CF_3CH_2O)_2P{=}N)]_n P(CF_3CH_2O)_3(OC_8H_{11})$ (12). A solution of PCl_5 (10 mg, 0.048 mmol) in 10 mL of CH_2Cl_2 or toluene was placed in a flask and was stirred for 1 h. A solution of $Cl_3P{=}NSiMe_3$ in 2 mL of CH_2Cl_2 was then added to the flask. The reaction mixture was monitored by ^{31}P spectroscopy until complete conversion of $Cl_3P{=}NSiMe_3$ to polymer had occurred. A slight excess of **5** (based on the ratio of PCl_5 to $Cl_3P{=}NSiMe_3$) was then added, and the solution was stirred for 6−24 h. All volatiles were removed under reduced pressure, and the end-capped poly(dichlorophosphazene) was dissolved in 10 mL of THF. To this was added a 2-fold excess, per chlorine atom, of 1.5 M sodium trifluoroethoxide in THF, and the reaction mixture was stirred for 24 h at 25 °C. Macromonomer **12** was then recovered via precipitation into deionized water (3×) and hexane (2×). ^1H NMR (acetone-d_6): 6.21−5.98 (m, 4H, C*H*=C*H*), 4.55−4.29 (m, 8H, OCH_2CF_3), 3.82−3.46 (m, 6H), 2.91 (m, 2H), 2.82 (m, 2H), 2.4 (br m, 2H), 1.91−1.82 (m, 2H), 1.45−1.19 (m, 6H), 0.52 (m, 2H). ^{31}P NMR (acetone-d_6): −6.27 (s, $[(CF_3CH_2O)_2P{=}N]_n$), −1.60 (d, J = 68.55, $R-O-(CF_3CH_2O)_2P{=}N$). ^{13}C NMR (acetone-d_6): 138.15, 137.53, 137.02, 133.09, 124.03 (q, J = 276.58, OCH_2CF_3), 64.22 (q, J = 37.39, OCH_2CF_3), 63.19, 62.80, 49.89, 45.47, 44.50, 44.17, 43.03, 42.99, 42.43, 42.30, 40.23.

General ROMP Polymerization Procedure for 13. An example of the polymerization procedure is described for the synthesis of polymer **13a**. Because of the insolubility of monomer **5** in CH_2Cl_2 and $CHCl_3$, THF was used as solvent, despite its unfavorable Lewis base properties. Under a N_2 atmosphere, a 50 mL round-bottom flask containing a magnetic stir bar was charged with **5** (440 mg, 1.0 mmol) and 0.6 mL of THF. A solution of Grubbs initiator (**1a**), $RuCl_2(CHC_6H_5)[P(C_6H_{11})_3]_2$ (16 mg, 0.020 mmol), in 0.2 mL of THF was added to the flask via pipet. The flask was capped, and the red/purple reaction mixture was stirred for 1.5 h at room temperature. Within 10 min the contents were noticeably thicker. To the flask was added 0.5 mL of ethyl vinyl ether and 20 mg of catechol. It should be noted that to prevent the loss of TMS groups on the phosphoranimine pendent groups the polymer was precipitated into aprotic solvents, as followed by ^1H NMR. Polymer **13a:** ^1H NMR ($CDCl_3$): 5.31 (bd, 2H), 4.30 (m, 4H, OCH_2CF_3), 4.12 (bm, 1H), 3.86 (bm, 1H), 3.68 (m, 1H), 3.16 (bm, 1H), 3.03 (bm, 1H), 2.88 (bm, 1H), 2.59 (bm, 1H), 2.41 (bm, 1H), 2.22 (bm, 1H), 1.80 (bm, 1H), 1.58 (bm, 1H), 1.29 (m, 1H), 1.20 (bm, 1H), 0.03 (d, 9H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): 10.2 (d, 1P).

General ROMP Polymerization Procedure for 14. An example of the polymerization procedure is described for the synthesis of polymer **14a**. Because of the insolubility of polymer **10** in CH_2Cl_2 and $CHCl_3$, THF was used as solvent. Under a N_2 atmosphere, a 50 mL round-bottom flask containing a magnetic stir bar was charged with **10c** (0.25 g) and 2.0 mL of THF. A solution of Grubbs initiator (**1a**), $(PCy_3)_2Cl_2Ru{=}CHPh$ (16 mg, 0.020 mmol), in 0.2 mL of THF was added to the flask via pipet. The flask was capped, and the red/purple reaction mixture was stirred for 2 h at room temperature. The contents of the polymerization became noticeably thicker and often solidified within 40 min. To the flask was added 0.5 mL of ethyl vinyl ether and 20 mg of catechol. The solid polymerization mixture was dissolved in refluxing THF, and the polymer was isolated by precipitation into hexane. Polymer **14a:** ^1H NMR ($CDCl_3$): 5.43 (bd, 2H), 4.34 (m, 4H, OCH_2CF_3), 4.17 (bm, 1H), 3.89 (bm, 1H), 3.66 (m, 1H), 3.14 (bm, 1H), 3.01 (bm, 1H), 2.92 (bm, 1H), 2.57 (bm, 1H), 2.40 (bm, 1H), 2.21 (bm, 1H), 1.80 (bm, 1H), 1.57 (bm, 1H), 1.27 (m, 1H), 1.20 (bm,

1H), 0.02 (d, 9H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): 6.98 (bs, $[(CF_3CH_2O)_2P{=}N]_n$).

[(5-Norbornene-2-methylamino)pentakis(α,α,α-trifluoroethoxy)]cyclotriphosphazene (15a). To a mixture of the HCl salt derivative of **3** (4.5 g, 28 mmol) was added Et_3N (59 mL, 42 mmol). The mixture was heated at 55 °C for 2 h and cooled to room temperature, and the salts were removed by filtration. The resultant liquid was added to $N_3P_3(OCH_2CF_3)_5Cl$ (12.5 g, 18.8 mmol) in THF (150 mL) and warmed to 50 °C. After 24 h the reaction mixture was cooled to room temperature, and the salts were removed by centrifugation. The liquid was dried with $MgSO_4$, filtered, and then concentrated by rotary evaporation. The resultant oil was purified by column chromatography (70/30 hexanes/ethyl acetate) to yield 10.6 g (75%) of a slightly yellow liquid. ^1H NMR ($CDCl_3$) (*exo* and *endo* isomers): 6.04 (m, 2H), 5.89 (dd, 1H), 4.22 (m, 10H, OCH_2CF_3), 4.19 (m, 2H), 2.96 (m, 1H), 2.87 (m, 1H), 2.80 (br s, 1H), 2.61 (m, 1H), 2.18 (m, 1H), 1.80 (m, 1H), 1.45 (m, 1H), 1.31 (m, 1H), 1.24 (m, 1H), 1.10 (m, 1H), 0.54 (m, 1H). ^{13}C NMR ($CDCl_3$) (*exo* and *endo* isomers): 137.7, 136.7, 135.9, 131.3, 127.2, 123.8, 120.8, 117.4, 63.4, 63.0, 62.6, 62.2, 49.2, 45.8, 44.6, 43.7, 42.1, 40.5, 40.4, 30.5, 29.7. ^{31}P NMR ($CDCl_3$) (*exo* and *endo* isomers): 21.7 (t, 1P), 17.1 (d, 2P). MS (FAB+): *m/e* 752 MH^+.

[(5-Norbornene-2-methylamino)pentakis(phenoxy)]cyclotriphosphazene (15b). The product was isolated similar to **15a**. The organic layer was concentrated and the product recrystallized in hexanes to yield a crystalline solid containing both *endo* and *exo* isomers (89%). ^1H NMR ($CDCl_3$) (*exo* and *endo* isomers): 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 ($CDCl_3$): 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 ($CDCl_3$): 13.4−11.9 (m, 1P), 9.9−9.3 (m, 2P); *m/e* 724 MH^+.

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