Title: POLYNORBORNENES WITH PENDANT CYCLOTRIPHOSPHAZENES

Abstract: A polymer composition comprising a polynorbornene backbone and pendant cyclotriphosphazene groups has been developed. The pendant cyclotriphosphazene group can have various substituents such as C1-C10 alkyl, C1-C10 haloalkyl, C3-C6 cycloalkyl, phenyl, substituted phenyl, aryl, -(CH2)nOCH2CH2)nOCH2, in which n is a positive integer, aminoalkyl, alkoxyalkyl, phenoxyalkyl, aryloxyalkyl and amidoalkyl. The polynorbornene backbone can have substituents such as H, CH3, X which is a halo group, and C2-C6 alkyl, C3-C6 cycloalkyl, C2-C6 alkoxy, phenoxy, and aryloxy. In a preferred embodiment, the pendant triphosphazene group can have either CH2CF3, phenyl, 4-ethylcarboxylatophenyl, CH2CH3, or CH2CH2OCH2CH2OCH3 while the polynorbornene backbone can have H and low alkyl groups. The polyphosphazene compositions can be prepared readily via ring-opening-metathesis-polymerization of an olefin having norbornene structure with pendant cyclotriphosphazene groups. The polyphosphazene compositions disclosed are useful as elastomers, optical materials, electrically conductive materials, biomedical materials, compatibilizing agents, surfactants, additives for coatings, and as flame retardants.
POLYNORBORNENES WITH PENDANT CYCLOTRIPHOSPHAZENES

Background of The Invention

The present invention relates generally to polynorbornene and cyclotriphosphazene compositions.

A large number of polymers containing a variety of phosphazene groups have been prepared in the past several decades. The focus of these efforts has been directed to the incorporation of phosphazene or polyphosphazene into organic or inorganic polymer backbones. Numerous polymer compositions containing phosphazene groups or polyphosphazene backbones are known which contain linear phosphazene or polyphosphazene structures. See, for example, Hybrid inorganic-organic polymers derived from organofunctional phosphazenes. Allen, C. W. NTIS Report (TR-7; Order No. AD-A183612) Gov. Rep. Announce. Index (U. S.) 1987, 87(23), Abstr. No. 753,600.

Phosphazene-containing compositions are useful in a variety of applications including elastomers, optical materials, electrically conductive materials, biomedical materials, compatibilizing agents, surfactants, additives for coatings, and flame retardants. The electronic structure of a phosphazene-containing material is critical as to the chemical, as well as physical, properties of a material made of such phosphazene-containing material. For example, the electric conductivity of a phosphazene-containing material, which largely reflects the ease of the electrons to flow along the molecular backbone of such material, correlates positively to the content of π-stacking structure in the molecular backbone of such material. See, for example, “Electrically conductive phosphazene polymer compositions” Jpn. Kokai Tokkyo Koho by Sato (1993); “Polyphosphazenes bearing polymerizable pyrrole, thiophene and furan side groups: synthesis and chemical oxidation” by Allcock, et al., NTIS. Report (TR-68; Order No. AD-A249747) Gov. Rep. Announce. Index (U. S.) 1992, 92(16), Abstr. No. 243,408; “Electrically conductive polyorganophosphazenes”. Jpn. Kokai Tokkyo Koho by Kajiwara, et al., (1989). Hence, the creation of a π-
stacking structure or modulation of the existing \(\pi\)-stacking structure in a composition will affect the electrical conductivity of the composition. Similarly, the creation of a \(\pi\)-stacking structure or modulation of the existing \(\pi\)-stacking structure in a composition will affect the heat-conductivity of the composition. Moreover, linear or non-linear optical properties of an optical material can be affected by the modulation of the electronic properties of the material.

It would therefore be advantageous to develop new polymer compositions having phosphazene or polyphosphazene groups or moieties, utilizing one or more of these properties.

Cyclotriphosphazene compositions are known. For example, U.S. Patent No. 4,668,589 to Kumar et al. discloses an adduct of epoxy resin and cyclotriphosphazene, wherein the three phosphorous atoms of the cyclotriphosphazene ring are modified with six phenoxy or aryloxy groups. The cyclotriphosphazene component serves as a curing agent of the epoxy resin. Similarly, U.S. Patent No. 4,614,788 to Dettloff, et al. discloses an epoxy resin cured by a cyclotriphosphazene compound such as hexakis(\(n\)-propylamino) cyclotriphosphazene. The resin reportedly has an enhanced glass transition temperature (Tg) value compared to a similar composition without the phosphazene compound.

U.S. Patent No. 4,405,738 to McNeely, et al. discloses polyester polymers and copolyester polymer compositions incorporating cyclotri- or cyclotetra-phosphazenes. The modifying groups on the cyclotriphosphazene or cyclotetraphosphazene ring are six or eight dialkylphosphinylmethylenoxy groups. Halogen-substituted tricyclicophosphazene compounds also have been added to polymers such as polyamides and polyolefins, as disclosed in U.S. Patent No. 4,029,634 to Meredith, et al. U.S. Patent No. 5,344,501 to Hashimoto et al. discloses a solar cell which includes a protective layer formed by polymerizing cyclotriphosphazene. These patents describe cyclophosphazenes as adducts, epoxy resin curing agents or solar cell protective materials. As adducts of polymer compositions, the cyclophosphazenes probably retain their respective free chemical compositions and structures. However, as curing agents or solar cell
protective materials, cyclophosphazenes probably polymerize during the
application process, destroying the cyclic structure of cyclophosphazene
molecules. The reactions of cyclophosphazenes in these references probably
produce linear polyphosphazenes. It would be advantageous to produce
polymer composition with cyclophosphazenes while retaining the cyclic
structure of cyclophosphazene molecules.

It is therefore an object of the present invention to provide new
polymer compositions having various organic or inorganic functionalities
and, thus, having different chemical and physical properties.

It is another object of the present invention to provide synthetic
methods for the preparation of polymer compositions incorporating
cyclotriphosphazene groups.

**Summary of The Invention**

Polymer compositions and methods for their synthesis are provided
wherein the compositions include a polynorbornene backbone and pendant
cyclotriphosphazene groups, having the formula

![Cyclotriphosphazene Structure](image)

wherein R^1 is C1-C10 alkyl, C1-C10 haloalkyl, C3-C6 cycloalkyl,
phenyl, substituted phenyl, aryl, -(CH_2CH_2OCH_2CH_2)_nOCH_3 in which n is a
positive integer, aminoalkyl, alkoxyalkyl, phenoxyalkyl, aryloxalkyl and
amidoalkyl; and

wherein R^2, R^3, R^4, R^5, R^6, R^7, R^8 and R^9 are groups selected from the
group consisting of H, CH_3, X which is a halo group, and C2-C6 alkyl, C3-
C6 cycloalkyl, C2-C6 alkoxy, phenoxy, and aryloxy.

In a preferred embodiment, R^1 is either -CH_2CF_3, phenyl,
4-ethylcarboxylatophenyl, -CH₂CH₃, or -CH₂CH₂OCH₂CH₂OCH₃. In another preferred embodiment of the polymer composition, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ are H.

The polyphosphazene compositions can be prepared via ring-opening-metathesis-polymerization of an olefin having norbornene structure with pendant cyclotriphosphazene groups. The polyphosphazene compositions described herein are useful as elastomers, optical materials, electrically conductive materials, biomedical materials, compatibilizing agents, surfactants, additives for coatings, and flame retardants.

**Brief Description of The Drawings**

Figure 1 illustrates one embodiment for the synthesis of polynorbornene compositions having pendant cyclotriphosphazene groups. In Figure 1 is shown the synthesis of cyclotriphosphazene derived norbornenes and their subsequent polymerization with a late transition metal carbene complex known as Grubbs Catalyst. In this context, initiator will be used instead of catalyst. Five of the chlorine atoms of hexachlorocyclotriphosphazene (1) are carefully substituted with the shown side groups to form a penta-substituted monochloro cyclotriphosphazene trimer (2). The side groups differ with regard to their hydrophobicity, hydrophilicity, steric bulk, aromaticity, conformational flexibility, and electron donating/withdrawing properties at the site of attachment with the phosphorus atoms. The remaining chlorine atom of 2 is treated with the metal-alkoxide derivative of the norbornene derivative 3 (mixture of *endo* and *exo* isomers). This results in complete replacement of the chlorine atoms to form a penta-substituted mono-norbornenyl cyclotriphosphazene (4).

Polymerization of 4 to yield structure 6 occurs upon contact of the monomer with the Grubbs initiator (5) in solvents such as methylene chloride, chloroform, chlorobenzene, toluene, and benzene. The polymerizations are highly efficient and the yields are moderate to above average. The appearance of the resultant polymers range from viscous liquids to adhesive gums to elastomers to fibrous solids to hard glasses. The resultant properties are influenced, in part, by the molecular weight, choice of side groups, polymerization conditions (solvent, temperature, reaction time), and initiator
used. Polymerizations also occur with the use of commercially available molybdenum-based Schrock type catalysts.

**Detailed Description of The Invention**

Methods have been developed to synthesize polynorbornene compositions having pendant cyclotriporphazene groups.

1. **Cyclotriporphazene**

Cyclotriporphazene has an electronic structure closely resembling benzene. The three nitrogen (N) atoms and three phosphorous (P) atoms in cyclotriporphazene constitute a six member ring. Each of the three N atoms adopts SP² hybridization. So does each of the three phosphorous atoms (Corbridge, D.E.C. Top. Phosphorus Chem. (1966), 3: 57-394). The six P and N atoms are in a same plane. The six-member ring system has three alternating P-N single bonds and three alternating P=N double bonds. The average P-N distance in cyclotriporphazene may be shorter than a normal P-N bond. On the other hand, the average P=N distance in cyclotriporphazene may be longer than a normal P=N bond. Therefore, the P-N single bond and the P=N double bond are averaged, which is similar to the C-C and C=C bonds in benzene. In addition, the number of electrons in the close π-stacking system, which is six, satisfies the formula 4N + 2 wherein N is a positive integer. The cyclotriporphazenes, therefore, have a resonance or π-stacking structure very close that in benzene. Such an electronic structure differs dramatically from the one in a linear phosphazene- or polyphosphazene material. Thus, the incorporation of cyclotriporphazene groups into a polymeric molecule would have a marked effect upon properties of such polymeric molecule. In addition, the properties of such polymeric molecule would be different from those in a polymer molecule incorporating linear phosphazene groups.

In addition, the six-member ring of cyclotriporphazene leaves significant room for further modification of the polymer composition. For example, various electrically withdrawing or electrically donating groups can be attached to the phosphorous atom to influence the d-π bonding between the d orbital and the π-stacking of the cyclophosphazene ring. See.

As described above in the background, currently known methods do not provide for the incorporation of intact cyclophosphazene groups into a polymeric composition through covalent-bonding.

Therefore, a polynorbornene composition having pendant cyclophosphazene groups would be highly desirable. Further, the repeating unit of the polynorbornene composition has a carbon-carbon double bond and a aromatic cyclophosphazene ring. The polynorbornene composition can be modified to attach different electronically withdrawing or electronically donating or hydrophobic or hydrophilic groups to the composition. Therefore, various materials can be made of such polynorbornene compositions.

II. Polynorbornene Compositions

Polynorbornenes with pendant cyclophosphazenes can be synthesized via ring-opening-metathesis-polymerization (ROMP) of olefins having a norbornene structure with a pendant cyclophosphazene group. The olefin can have various lower alkyl substituents while the cyclophosphazene group can have various electronically withdrawing or electronically donating groups.

Polymer compositions of Formula I having a polynorbornene backbone and pendant cyclophosphazene groups are provided:
wherein R¹ is C1-C10 alkyl, C1-C10 haloalkyl, C3-C6 cycloalkyl, phenyl, substituted phenyl, aryl, -(CH₂CH₂OCH₂CH₂)ₙOCH₃ in which n is a positive integer, aminoalkyl, alkoxyalkyl, phenoxyalkyl, aryloxyalkyl and amidoalkyl;
and wherein R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ are H, CH₃, X which is a halo group, and C2-C6 alkyl, C3-C6 cycloalkyl, C2-C6 alkoxy, phenoxy, and aryloxy.

In one preferred embodiment, R¹ is either -CH₂CF₃, phenyl, 4-
ethylcarboxylatophenyl, -CH₂CH₃ or -CH₂CH₂OCH₂CH₂OCH₃. In one of the most preferred embodiments, R¹ is -CH₂CF₃.

The preferred polymer compositions are wherein R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ are H, CH₃, or CH₂CH₃. The most preferred polymer compositions are wherein R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ are H groups.

Exemplary polymer compositions of the present invention are:
poly{[(5-norbornene-2-methoxy)pentaphenoxy]cyclotriphosphazene};
poly{[(5-norbornene-2-methoxy)penta(trifluoroethoxy)]cyclotriphosphazene};
poly{[(5-norbornene-2-methoxy)penta(4-ethylcarboxylatophenoxy)]cyclotriphosphazene}; and
poly{[(5-norbornene-2-methoxy)pentaethoxy]cyclotriphosphazene}.

III. Synthesis
In a preferred embodiment, synthesis of the polynorbornenes with pendant cyclotriphosphazene groups is performed via ring opening metathesis polymerization (ROMP) reaction of olefins having a norbornene
structure with a cyclotriphosphazene group in the presence of a catalyst such as 5, as outlined in Figure 1.

The term "ring opening metathesis polymerization" (ROMP) as used herein means

ROMP is a specific type of ring opening polymerization which is
driven predominantly by the release of ring strain. It is a process that
involves simultaneous bond breaking and bond formation. Metathesis comes
from the Greek words meta (change) and tithemi (place) and involves the
switching of ligands on two olefins. In the context of this work, the

norbornenyl portion of the phosphazene functionalized monomer reacts with
Grubbs initiator to undergo ring opening at the olefinic functional group.
The ligands of the olefin monomer and olefin catalyst also switch places. As
a result, the initiating species is chemically different that the propagating
species. Upon initiation, propagation occurs with the successive addition of

monomer. Typically the molecular weight increases continuously as the
reaction proceeds, until all the monomer is consumed. Olefin catalysts are
typically based on transition metals. Catalysts that incorporate tungsten or
molybdenum have been widely used. However, titanium, osmium,
ruthenium, vanadium and iridium catalysts can also been used. A distinctive
feature of ROMP is that double bonds are present in both monomer and
resultant polymer. Because of this, the double bonds of the polymer can also
be reactive to transition metal complexes. Therefore, the reactions must be
carefully monitored to prevent backbiting and other side reactions. Large
polydispersities and low molecular weights are usually attributed to these
side reactions. The advent of Schrock and Grubbs type initiators has allowed
for the development of polymers with controlled molecular weights and
narrow polydispersities. ROMP with Schrock initiators occur in an
analogous manner to living chain anionic polymerizations of vinyl
monomers such as styrene. The initiator polymerizes the total monomer
present, but does not terminate. This is ideal for the synthesis of block
copolymers since new monomers can be added to the reaction pot at any time
throughout the course of a polymerization.
R¹ can be attached to the cyclophosphazene ring via replacement of the five halo groups in a hexahalocyclotriphosphazene molecule. In one embodiment, sodium phenoxide can be allowed to react with a hexahalocyclotriphosphazene such as hexachlorocyclotriphosphazene (1) to generate (pentaphenoxycyclotriphosphazene (2a). In another embodiment, trifluoroethoxide can be allowed to react with 1 to generate penta(trifluoroethoxy)cyclotriphosphazene (2b). In still another embodiment, sodium 4-ethylcarboxylatophenoxy or ethoxide can be allowed to react in a solvent such as to replace the five chloro groups to make penta(4-ethylcarboxylatophenoxy) cyclotriphosphazene (2c) and 2d, respectively.

The attachment of a cyclotriphosphazene group to a norbornene group can be carried out via reaction of a norbornenyl alcohol such 5-norbornene-2-methanol (3) with 2 in the presence of a base such as NaH. In one embodiment, monomer [(5-norbornene-2-methoxy)pentaphenoxycyclotriphosphazene (4a) can be synthesized using 2a and 3. In another embodiment, monomer [(5-norbornene-2-methoxy)penta(trifluoroethoxy) cyclotriphosphazene (4b) can be synthesized using 2b and 3. In still another embodiment, monomer [(5-norbornene-2-methoxy)penta(4-ethylcarboxylatophenyl) cyclotriphosphazene (4c) can be synthesized using 2c and 3. In still another embodiment, [(5-norbornene-2-methoxy)pentaethoxy cyclotriphosphazene (4d) can be synthesized using 2d and 3.

Monomers 4 then are subject to ROMP reaction in the presence of a catalyst such as 5 to generate polymers 6. In one embodiment, monomer 4a can be subjected to ROMP reaction in the presence of 5 to generate poly{[(5-norbornene-2-methoxy)pentaphenoxycyclotriphosphazene} (6a). In another embodiment, monomer 4b can be subject to ROMP reaction in the presence of 5 to generate poly{[(5-norbornene-2-methoxy)penta(trifluoroethoxy)] cyclotriphosphazene} (6b). In still another embodiment, monomer 4c can be subject to ROMP reaction in the presence of 5 to generate poly{[(5-norbornene-2-methoxy)penta(4-ethylcarboxylatophenoxy)] cyclotriphosphazene} (6c). In another
embodiment, monomer 4d can be subject to ROMP reaction in the presence of 5 to generate poly{[(5-norbornene-2-methoxy)pentaethoxy] cyclotriphosphazene} (6d).

In general, five major components are needed for the successful polymerization of monomers described herein: 1) a cyclotriphosphazene ring, 2) a nucleophile that can be attached to the phosphazene ring, 3) a norbornene derivative that can be attached to the phosphazene ring, 4) an initiator as described herein, and 5) a solvent as described herein.

Hexachlorocyclotriphosphazene is treated with a variety of nucleophiles to yield a pentasubstituted cyclotriphosphazene. This leaves a single chlorine atom available for attachment of the norbornenyl group. If more than one chlorine atom is left available to react with the norbornenyl group, then branching and crosslinking will occur. Thus, the correct stoichiometry is important. Polymerization of the pentasubstituted mononorbornenyl cyclotriphosphazene results in polymers with controlled molecular weights and moderate to high yields.

IV. Applications for the Polymer Compositions

The polymer compositions disclosed herein have many applications. Exemplary applications include use as elastomers, optical materials, electrically conductive materials, biomedical materials, compatibilizing agents, surfactants, additives for coatings, and flame retardants. In one embodiment, a polynorbornene composition can be used as an electric conductor or as linear or nonlinear optical materials. Also, because of the hydrophobic and elastomeric nature of some of the disclosed polynorbornene compositions, the polyborbornene compositions can be used as vascular graft materials. The ester group in 6c can be cleaved by strong base to form free carboxylate groups which can be further cross-linked by divalent cations such as Ca\(^{++}\) via the carboxylate groups to yield hydrogels which have a number of potential applications in the medical and industrial areas. Some of other compositions with oxyethylene groups on the phosphazene ring can act as binding sites for metal salts. Therefore, the polymers can have ionic conductivity behavior and thus be useful for battery applications.
The polymers and methods described herein can be further understood by the following non-limiting examples.

**Examples**

**Overview**

All manipulations were carried out under an inert and dry atmosphere such as one provided by dry argon using standard Schlenk line techniques. The compounds were identified following standard organic and inorganic analytical procedures using standard analytical equipment: i.e., Bruker WM360 spectrometer operated at 146, 90.27, and 360 MHz, respectively, for $^{31}$P, $^{13}$C, or $^1$H NMR spectroscopy; Perkin-Elmer 1600 series FT-IR spectrometer for IR spectra; Hewlett-Packard HP 1090 gel permeation chromatograph equipped with two Phenomenex Phenogel linear 10 columns and a Hewlett-Packard 1047A refractive index detector for gel permeation chromatograms; Hewlett-Packard Chemstation equipped with Hewlett-Packard and Polymer Laboratories software for data collection and calculations; Perkin-Elmer DSC-7 differential scanning calorimeter controlled by a PE7500 computer for Differential scanning calorimetry. Heating rates of 10-40 °C/min and sample sizes of 20-30 mg were used. Elemental analysis was performed by Quantitative Technologies, Inc.

**Materials**

Hexachlorocyclotriphosphazene was isolated from a cyclic trimer-tetramer mixture by sublimation. All other materials were either purchased from distributors such as Aldrich or prepared following standard procedures in organic or inorganic synthesis. The organic solvents were purified and dried following standard procedure. Examples of organic solvents are oxygen containing solvents and halogenated solvents such as tetrahydrofuran ("THF") and methylene chloride.

**Example 1: Preparation of pentaphenoxy(monochloro)cyclotriphosphazene (2a)**

A solution of 30.9 g of phenol (328 mmol) in 200 mL of dry THF was added dropwise to a stirred suspension of 7.9 g of NaH (328 mmol, 60% dispersion in mineral oil) in 100 mL of dry THF, all at room temperature. The mixture was stirred at room temperature overnight and was then added
dropwise to a stirred solution of 20 g of hexachlorocyclotriphosphazene (1) (57.5 mmol) in 150 mL of dry THF. The mixture was refluxed overnight, cooled to room temperature, and washed with 5% HCl (3 x 50 mL). The organic layer was concentrated and purified by column chromatography (silica, 55/45 CH₂Cl₂/hexanes) to yield 15 g (47%) of a white solid 2a.

Identification and characterization data are listed as follows: ¹H NMR (CDCl₃): 6.96 (aromatic); ¹³C NMR (CDCl₃): 147.1, 140.0, 127.8, 119.6; ³¹P NMR (CDCl₃): 22.88 (t, 1P), 7.6 (d, 2P); Mass spectroscopy (m/e): 636 M⁺.

**Example 2: Preparation of [(5-norbornene-2-methoxy)pentaphenoxy)cyclotriphosphazene (4a)**

A solution of 4.0 g of 5-norbornene-2-metanol (3) (32 mmol) in 50 mL of dry THF was added dropwise to a stirred suspension of 1.3 g of NaH (32 mmol, 60% dispersion in mineral oil) in 100 mL of dry THF at room temperature. The mixture was stirred at room temperature overnight and was then added dropwise to a stirred solution of 17.9 g of 2a (32.4 mmol) in 300 mL of dry THF at room temperature. The reaction was allowed to warm to room temperature and was then refluxed gently overnight, cooled to room temperature, and quenched with water. The organic layer was concentrated and then dried under high vacuum for 48 hours to yield 3.0 g (89%) of a viscous noncrystallizable oil 4a containing both endo and exo isomers.

Identification and characterization data for 4a are listed as follows: ¹H NMR (CDCl₃) (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); ¹³C NMR (CDCl₃) 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; ³¹P NMR (CDCl₃): 13.4-11.9 (m 1P), 9.9-9.3 (m 2P); Mass spectroscopy (m/e) 724 M⁺.

**Example 3: Preparation of penta[(trifluoroethoxy) (monochloro)cyclotriphosphazene (2b)]**

A solution of 37.4 g (364 mmol) of trifluoroethanol in 200 mL of dry THF was added dropwise to a stirred suspension of 14.9 g of NaH (364
mmol, 60% dispersion in mineral oil) in 100 mL of dry THF at room temperature. The mixture was stirred at room temperature overnight and was then added dropwise to a stirred solution of 22.8 g of 1 (65.6 mmol) in 150 mL of dry THF at −30 °C. The mixture was allowed to warm to room temperature and was then refluxed overnight, cooled to room temperature, and used for the subsequent synthesis of 4b. Identification and characterization data for 2b are listed as: \(^{31}\text{P NMR (D}_2\text{O)}\) 27.3 (t, 1P), 17.8 (s, 3P) (hexa), 15.3 (d, 2P).

**Example 4: Preparation of (5-norbornene-2-methoxy)penta(trifluoroethoxy)cyclotriphosphazene (4b)**

A solution of 8.1 g of 3 (66 mmol) in 20 mL of dry THF was added dropwise to a stirred suspension of 2.6 g of NaH (66 mmol, 60% dispersion in mineral oil) in 80 mL of dry THF at room temperature. The mixture was stirred at room temperature overnight and was then added dropwise to a stirred solution of 43.7 g (66 mmol) of 2b in 300 mL of dry THF at room temperature. The reaction was allowed to warm to room temperature and was then refluxed gently overnight, cooled to room temperature, and quenched with water. The organic layer was concentrated and the crude product purified by column chromatography (silica, 50/50 hexanes/ethyl acetate). The resulting oil was fractionally distilled twice under reduced pressure to yield 29 g (58%) of a clear and colorless oil (4b) containing both endo and exo isomers. Identification and characterization data for 4b are listed as: \(^{1}\text{H NMR (CDCl}_3\text{)}\) (exo and endo isomers) 6.08 (dd, 1H), 6.06 (dd, 1H), 6.00 (dd, 1H), 5.90 (dd, 1H), 4.19 (m, 10H), 3.97 (m, 1H), 3.79 (m, 1H), 3.64 (m, 1H), 3.51 (m, 1H), 2.82-2.66 (m, 2H), 2.36 (m, 1H), 2.00 (m, 1H), 1.73 (m, 1H), 1.41 (m, 1H), 1.29 (m, 1H), 1.19 (m, 1H), 1.06 (m, 1H), 0.79 (m, 1H), 0.42 (m, 1H); \(^{13}\text{C NMR (CDCl}_3\text{)}\) 137.9, 136.0, 131.8, 71.0, 70.9, 63.7-62.3, 49.2, 44.6, 43.7, 39.2, 29.1; \(^{31}\text{P NMR (CDCl}_3\text{)}\) 18.3-17.6 (m, 2P), 16.8-15.5 (m, 1P), Mass spectroscopy (m/e) 753 M\(^+\).
Example 5: Preparation of penta[(4-ethylcarboxylatophenoxy) (monochloro)cyclotriphosphazene (2c)]

A solution of 4-ethylhydroxybenzoate (68.1 g, 410 mmol) in 300 mL of dry THF was added dropwise to a stirring suspension of NaH (16.4 g, 410 mmol, 60% dispersion in mineral oil) in 200 mL of dry THF at room temperature. The mixture was stirred at room temperature overnight and was then added dropwise to a stirred solution of 25 g of 1 (71.9 mmol) in 150 mL of dry THF. The mixture was refluxed overnight, cooled to room temperature, and washed with 5% HCl (3 x 50 mL). The organic layer was concentrated and purified by column chromatography (silica, 70/30 hexanes/ethylacetate) to yield 40 g (49%) of a noncrystallizable oil 2c.

Identification and characterization data for 2c are listed as: \(^1\)H NMR (CDCl\(_3\)) 7.91 (m, 10H), 7.05 (m, 10H), 4.32 (q, 10H), 1.33 (t, 15H); \(^31\)P NMR (CDCl\(_3\)) 21.39 (t, 1P), 5.86 (d, 2P).

Example 6: Preparation of [(5-norbornene-2-methoxy)penta (4-ethylcarboxylatophenoxy)cyclotriphosphazene (4c)]

A solution of 1.56 g of 3 (124 mmol) in 20 mL of dry THF was added dropwise to a stirred suspension of 0.48 g of NaH (12 mmol, 60% dispersion in mineral oil) in 50 mL of dry THF at room temperature. The mixture was stirred at room temperature overnight and was then added dropwise to a stirred solution of 10 g of 2c (10 mmol) in 150 mL of dry THF at room temperature. The mixture was allowed to warm to room temperature and was then refluxed gently overnight, cooled to room temperature, and quenched with water. The organic layer was concentrated and the product dried under high vacuum with gentle heating for 72 hours to yield 8 g (71%) of a viscous noncrystallizable oil 4c containing both endo and exo isomers.

Identification and characterization data of 4c are listed as: \(^1\)H NMR (CDCl\(_3\)) (exo and endo isomers) 7.85 (d, 10H), 7.01 (d, 10H), 6.10 (dd, 1H), 5.92 (dd, 1H), 4.29 (m, 10H), 4.16-4.02 (m, 1H), 3.82-3.71 (m, 1H), 2.85 (m, 1H), 2.74 (m, 1H), 2.68 (m, 1H), 2.62 (m, 1H), 2.44 (m, 1H), 2.04 (m, 1H), 1.81 (m, 1H), 1.37 (m, 1H), 1.26 (m, 15H), 1.17 (m, 1H), 1.09 (m, 1H), 0.78 (m, 1H), 0.56 (m, 1H); \(^13\)C NMR (CDCl\(_3\)) 165.4, 153.8, 137.6, 132.1, 131.0, 126.6, 120.4, 68.4, 63.3, 61.0, 49.3, 43.9, 42.1, 37.8, 28.9, 15.6, 14.2; \(^31\)P
NMR (CDCl₃): 11.0-12.3 (m, 1P), 8.0-8.6 (m, 2P); Mass spectroscopy (m/e) 1084 M⁺.

Example 7: Preparation of [pentaethoxy(monochloro)]cyclotriposphazene (2d)

A solution of 12.3 g of ethanol (268 mmol) in 50 mL of dry THF was added dropwise to a stirred suspension of 10.7 g of NaH (364 mmol, 60% dispersion in mineral oil) in 100 mL of dry THF at room temperature. The mixture was stirred while refluxing overnight, cooled to room temperature, and added dropwise to a stirred solution of 17.6 g of 1 (50.5 mmol) in 200 mL of dry THF at room temperature. The mixture was allowed to reflux overnight, cooled to room temperature, and used for the subsequent synthesis of 4d. Identification and characterization data for 2d are listed as: ³¹P NMR (D₂O) δ 27.80 (t, 1P), 18.8 (s, 3P) (hexa), 15.8 (d, 2P).

Example 8: Preparation of [(5-norbornene-2-methoxy)pentaethoxy]cyclotriposphazene (4d)

A solution of 9.5 g of 3 (77 mmol) in 50 mL of dry THF was added dropwise to a stirred suspension of 3.1 g of NaH (77 mmol, 60% dispersion in mineral oil) in 50 mL of dry THF at room temperature. The mixture was stirred overnight at room temperature, then added dropwise to a stirred solution of 19.9 g of 2d (50.5 mmol) in 500 mL of dry THF at room temperature. The mixture was allowed to reflux overnight, cooled to room temperature, and quenched with water. The organic layer was concentrated and the resultant oil purified by column chromatography (70/30 hexanes/ethylacetate) to yield 13 g (53%) of clear colorless oil 4d. Identification and characterization data for 4d are listed as: ¹H NMR (CDCl₃) (exo and endo isomers) 6.07 (dd, 1H), 6.06 (dd, 1H), 6.02 (d, 1H), 5.93 (d, 1H), 3.93 (m, 10H), 3.73 (m, 1H), 3.62 (m, 1H), 3.42 (m, 1H), 2.90 (m, 1H), 2.72 (m, 1H), 2.39 (m, 1H), 1.99 (m, 1H), 1.72 (m, 1H), 1.33 (m, 1H), 1.23 (m, 1H), 1.22 (m, 15H), 1.21 (m, 1H), 1.18 (m, 1H), 1.09 (m, 1H), 0.46 (m, 1H); ³¹P NMR (D₂O) 27.8 (t, 1P), 18.8 (s, 3P), 15.8 (d, 2P); Mass spectroscopy (m/e) 484 M⁺.
Example 9: Poly{[(5-norbornene-2-methoxy)pentaphenoxy]cyclotriphosphazene} (6a)

A polymerization reaction was conducted as follows. Under an inert atmosphere, a 20 mL vial was charged with 4.75 g of degassed 4a (3.64 mmol) and a magnetic stirrer. A solution of 15 mg of 5 (0.018 mmol) ([4a]/[5]=200) in 1 mL of methylene chloride was added to the vial via pipet. The vial was capped and stirred at room temperature. Within 2 minutes, the dark red solution became progressively more viscous, and after 10 minutes the contents of the vial were solid. After 24 h the polymer gel was transferred to a separate container and 0.5 mL ethyl vinyl ether, and 50 mL of chloroform were added. Most of the solid dissolved. The soluble portion was poured into 500 mL of methanol and stirred. The off-white solid that precipitated was collected, and dried overnight under vacuum to yield 2.4 g 6a (50 %) (Table 1). 6a was characterized by $^1$H, $^{13}$C, $^{31}$P NMR spectroscopy and C, H, N analysis. The data for 6a are presented below: $^1$H NMR (CDCl$_3$) 7.18-6.85 (m, 25H), 5.47-4.98 (bd 2H), 3.62-3.01 (bm, 4H), 2.98 (bm, 1H), 2.71 (bm, 1H), 2.68 (bm, 1H), 2.12 (bs, 1H), 1.95 (bs, 1H), 1.55 (bm, 1H), 1.29 (bm, 1H), 1.17 (m, 1H), 1.03 (m, 1H), 0.98 (m, 1H), 0.80 (m, 1H); $^{13}$C NMR (CDCl$_3$) 151.1, 137.4-132.6 (backbone C-olefin), 130.0, 124.9, 121.7, 69.2, 49.8, 45.4-39.1 (backbone C-alkyl), 29.1; $^{31}$P NMR (CDCl$_3$) 13.2-12.1 (t, 1P), 9.7-9.1 (d, 2P); Anal. Calculated for C$_{38}$H$_{36}$O$_6$N$_3$P$_3$: C, 63.07; H, 5.01; N, 5.81; Found: C, 63.18; H, 5.10; N, 5.65.

Example 10: Poly{[(5-norbornene-2-methoxy)penta(trifluoroethoxy)]cyclotriphosphazene} (6b)

A polymerization reaction was conducted as follows. Under an inert atmosphere, a 20 mL vial was charged with 4.75 g of degassed 4b (3.64 mmol) and a magnetic stirrer. A solution of 15 mg of 5 (0.018 mmol) ([4b]/[5]=200) in 1 mL of methylene chloride was added to the vial via pipet. The vial was capped and stirred at room temperature. Within 2 minutes the dark red solution became progressively more viscous, and after 10 minutes the contents of the vial were solid. After 24 h the polymer gel was transferred to a separate container and 0.5 mL ethyl vinyl ether, and 50 mL of chloroform were added. Most of the solid dissolved. The soluble portion
was poured into 500 mL of methanol and stirred. The off-white solid that precipitated was collected, and dried overnight under vacuum to yield 2.4 g of 6b (50 %) (Table 1). 6b was characterized by $^1$H, $^{13}$C, $^{31}$P NMR spectroscopy and C, H, N analysis. The characterization data for 6b are presented below: $^1$H NMR (CDCl$_3$) 5.54-5.03 (bd, 2H), 4.25 (bs, 10H), 4.00 (bm, 1H), 3.81 (bm, 1H), 3.70 (m, 1H), 2.92 (bm, 1H), 2.73 (bm, 1H), 2.33 (m, 1H), 1.95 (bs, 1H), 1.48 (bm, 1H), 1.17 (m, 1H), 0.75 (m, 1H); $^{13}$C NMR (CDCl$_3$) 137.8, 136.0, 137.3-133.6 (backbone C-olefin), 123.9, 70.7, 62.8, 48.8-43.4 (backbone C-alkyl), 43.3, 39.3, 29.1; $^{31}$P NMR (CDCl$_3$) 18.3-17.5 (m, 2P), 16.8-15.6 (m, 1P); Anal. Calculated for C$_{18}$H$_{21}$O$_6$N$_3$P$_3$F$_{15}$: C, 28.70; H, 2.81; N, 5.58 and Anal. Found: C, 28.02; H, 2.47; N, 5.31.

**Example 11: Poly[(5-norbornene-2-methoxy)penta-(4-ethylcarboxylatophenoxy)cyclotriphosphazene] (6c)**

A polymerization reaction was conducted as follows. Under an inert atmosphere, a 20 mL vial was charged with 4.75 g of degassed 4c (3.64 mmol) and a magnetic stirrer. A solution of 15 mg of 5 (0.018 mmol) ([4c]/[5]=200) in 1 mL of methylene chloride was added to the vial via pipet. The vial was capped and stirred at room temperature. Within 2 minutes the dark red solution became progressively more viscous, and after 10 minutes the contents of the vial were solid. After 24 h the polymer gel was transferred to a separate container and 0.5 mL ethyl vinyl ether, and 50 mL of chloroform were added. Most of the solid dissolved. The soluble portion was poured into 500 mL of methanol and stirred. The off-white solid that precipitated was collected, and dried overnight under vacuum to yield 2.4 g of 6c (50 %) (Table 1). 6c was characterized by $^1$H, $^{13}$C, $^{31}$P NMR spectroscopy and C, H, N analysis. The data for 6c are presented below: $^1$H NMR (CDCl$_3$) 7.82 (d, 10H), 7.00 (d, 10H), 5.52-5.01 (bd, 2H), 4.31 (m, 10H), 4.02-3.88 (bm, 2H), 3.70 (m, 1H), 3.01 (bm, 1H), 2.62 (bm, 1H), 2.40 (bs, 1H), 1.91 (bs, 1H), 1.50 (bm, 1H), 1.28 (m, 15H), 1.12 (m, 1H), 1.02 (m, 1H), 0.72 (m, 1H); $^{13}$C NMR (CDCl$_3$) 165.4, 153.5, 138.6-134.6 (backbone C-olefin), 131.2, 127.7 120.7, 67.6, 63.4 61.1.1, 47.1-36.0 (backbone C-alkyl), 29.7, 15.8, 14.3; $^{31}$P NMR (CDCl$_3$) 18.3-17.6 (m, 2P), 16.9-15.6 (m, 1P);

Example 12: Poly[(5-norbornene-2-methoxy) pentaethoxy]cyclotriphosphazene] (6d)

A polymerization reaction was conducted as follows. Under an inert atmosphere, a 20 mL vial was charged with 4.75 g of degassed 4d (3.64 mmol) and a magnetic stirrer. A solution of 15 mg of 5 (0.018 mmol) ([4d]/[5]=200) in 1 mL of methylene chloride was added to the vial via pipet. The vial was capped and stirred at room temperature. Within 2 minutes the dark red solution became progressively more viscous, and after 10 minutes the contents of the vial were solid. After 24 h the polymer gel was transferred to a separate container and 0.5 mL ethyl vinyl ether, and 50 mL of chloroform were added. Most of the solid dissolved. The soluble portion was poured into 500 mL of methanol and stirred. The off-white solid that precipitated was collected, and dried overnight under vacuum to yield 2.4 g 6d (50 %) (Table 1). 6d was characterized by 1H, 13C, 31P NMR spectroscopy and C, H, N analysis. The data for 6d are presented below: 1H NMR (CDCl₃) 5.51-5.02 (bd, 2H), 3.87 (bs, 10H), 2.90 (bm, 1H), 2.66 (bm, 1H), 2.31 (bs, 1H), 1.88 (bs, 1H), 1.78 (bm, 1H), 1.62-0.20 (bm, 15H); 13C NMR (CDCl₃) 135.9, 133.9, 135.2-131.2 (backbone C-olefin), 124.0, 67.6, 61.7, 47.6-37.8, 34.4, 30.4, 16.1; 31P NMR (D₂O) 20.4-17.5 (bm, penta + hexa-substituted); Anal. Calculated for C₁₈H₁₆O₆N₃P₅ C, 44.72; H, 7.51; N, 8.69; Anal. Found C, 46.10; H, 7.17; N, 7.67.
Table 1. Polymerization Results for Norbornenes 4a, 4b, 4c, 4d

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

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the present application described herein. Such equivalents are intended to be encompassed by the following claims.
We claim:

1. A polymer composition comprising a polynorbornene backbone and a cyclotriphosphazene pendant group, having the formula

   \[ \text{\includegraphics[width=0.5\textwidth]{polymer_formula.png}} \]

   wherein \( R^1 \) is C1-C10 alkyl, C1-C10 haloalkyl, C3-C6 cycloalkyl, phenyl, substituted phenyl, aryl, alkylcarboxylatophenyl, \(-(CH_2CH_2OCH_2CH_2)_nOCH_3\) in which \( n \) is a positive integer, aminoalkyl, alkoxyalkyl, phenoxyalkyl, aryloxyalkyl and amidoalkyl; and

   wherein \( R^2, R^3, R^4, R^5, R^6, R^7, R^8 \) and \( R^9 \) are groups selected from the group consisting of H, CH₃, X which is a halo group, and C2-C6 alkyl, C3-C6 cycloalkyl, C2-C6 alkoxy, phenoxy, and aryloxy.

2. The polymer composition of claim 1 wherein \( R^2, R^3, R^4, R^5, R^6, R^7, R^8 \) and \( R^9 \) are H groups.

3. The polymer composition of claim 2 wherein \( R^1 \) is a group selected from the group consisting of phenyl, \(-CH_2CF_3\), alkylcarboxylatophenyl, and \(-CH_2CH_2OCH_2CH_2OCH_3\).

4. The polymer composition of claim 2 wherein \( R^1 \) is phenyl.

5. The polymer composition of claim 2 wherein \( R^1 \) is 4-ethylcarboxylatophenyl.

6. The polymer composition of claim 2 wherein \( R^1 \) is \(-CH_2CH_2OCH_2CH_2OCH_3\).

7. A method of preparing polynorbornenes with pendant cyclotriphosphazene groups comprising:

   a) preparing a norbornene molecule with a cyclotriphosphazene group by reacting a norbornenyl alcohol with a halocyclotriphosphazene; and
b) polymerizing the norbornene molecule in the presence of a catalyst.

8. The method of claim 7 wherein the catalyst is a chemical compound comprising a metal selected from the group consisting of Ru, Rh, Pt, Os, Ni, Fe, Co, Pd, and Ir.

9. The method of claim 8 wherein the metal is Ru.

10. The method of claim 7 wherein the polynorbornene is catalyzed using a catalyst with the formula

\[
\begin{align*}
&\text{PCy}_3 \\
&\text{Cl} \\
&\text{Ru} \\
&\text{Cl} \\
&\text{HC=CH} \\
&\text{PCy}_3
\end{align*}
\]

11. An article of manufacture comprising a polymer composition comprising a polynorbornene backbone and a cyclotriphosphazene pendant group, having the formula

\[
\begin{align*}
&\text{R}^4 \\
&\text{R}^5 \\
&\text{R}^6 \\
&\text{R}^7 \\
&\text{R}^8 \\
&\text{R}^9 \\
&\text{R}^1 \text{O} \\
&\text{R}^1 \text{O} \\
&\text{OR}^1 \\
&\text{OR}^1
\end{align*}
\]

wherein \( \text{R}^1 \) is C1-C10 alkyl, C1-C10 haloalkyl, C3-C6 cycloalkyl, phenyl, substituted phenyl, aryl, alkylcarboxylatophenyl,
\[-(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)_n\text{OCH}_3\] in which \(n\) is a positive integer, aminoalkyl, alkoxyalkyl, phenoxyalkyl, aryloxyalkyl and amidoalkyl; and

wherein \(R^2, R^3, R^4, R^5, R^6, R^7, R^8\) and \(R^9\) are groups selected from the group consisting of \(\text{H}, \text{CH}_3, \text{X}\) which is a halo group, and \(\text{C}_2\text{-C}_6\) alkyl, \(\text{C}_3\text{-C}_6\) cycloalkyl, \(\text{C}_2\text{-C}_6\) alkoxy, phenoxy, and aryloxy.

12. The article of claim 11 wherein the polymer composition is an elastomer.

13. The article of claim 11 wherein the polymer composition is selected from the group consisting of a linear optical material, a nonlinear optical material, and an electrically conductive material.

14. The article of claim 11 wherein the polymer composition is biocompatible.

15. The composition of claim 13 wherein the article is a battery material.

16. The article of claim 11 wherein the polymer composition is a flame retardant.
Figure 1
# INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

<table>
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<th>IPC(7)</th>
<th>: C08F 26/06</th>
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According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

| U.S. | : 526/171, 258, 263, 276 |

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

- WEST 2.0
- norbornene, cyclotriphosphazene, ROMP (ring-opening metathesis polymerization)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>A</td>
<td>US 4,772,722 A (LUKACS, III) 20 September, 1988, col. 1, lines 6-11; col. 12, lines 1-46.</td>
<td>1-6 and 16</td>
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<td>A</td>
<td>US 5,344,501 A (HASHIMOTO et al) 06 September, 1994, col. 13, lines 10-34; col. 14, lines 1-2 and lines 11-32.</td>
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<td>A</td>
<td>US 4,029,634 A (MEREDITH) 14 June, 1977, col. 12, lines 43-67; col. 13, lines 1-2 and 38-68; col. 14, lines 1-40.</td>
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☐ Further documents are listed in the continuation of Box C.  ☐ See patent family annex.

* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier document published on or after the international filing date
  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "O" document referring to an oral disclosure, use, exhibition or other means
  - "P" document published prior to the international filing date but later than the priority date claimed
  - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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  - "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  - "&" document member of the same patent family

Date of the actual completion of the international search: 13 NOVEMBER 2000

Date of mailing of the international search report: 28 DECEMBER 2000

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