Synthesis and Characterization of Photo-Cross-Linkable Small-Molecule and High-Polymeric Phosphazenes Bearing Cinnamate Groups

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ABSTRACT: Cyclic trimeric and high-polymeric phosphazenes bearing cinnamate groups were synthesized and characterized. Cyclic trimers with the general formula $N_3P_3R_yR'_x$ where R = $OC_6H_4OC(O)CH{=}CHPh$, R′ = OCH_2CF_3 (y = 1, x = 5 and y = 6, x = 0), and R = $(OCH_2CH_2)_2OC(O)CH{=}CHPh$ (y = 1, x = 5 and y = 6, x = 0) were synthesized. Also prepared were high-polymeric phosphazenes $[NPR_xR'_y]_n$, where R = $OC_6H_4OC(O)CH{=}CHPh$, R′ = OCH_2CF_3 ($y = x$ = 1 and y = 0, x = 2) and R = $(OCH_2CH_2)_2OC(O)CH{=}CHPh$ ($y = x$ = 1 and y = 0, x = 2). The photo-cross-linking of a representative polymer was studied by UV spectroscopy.

Introduction

Photo-cross-linkable polymers (photopolymers) are widely used in the fields of macro- and microlithography,[1] chemically-resistant coatings, and nonlinear optical (NLO) materials.[2,3] The field of photopolymers is evolving continuously, and a variety of photoactive groups (cinnamate and cinnamylidene esters, chalcone) are currently being used or investigated for cross-linking applications.

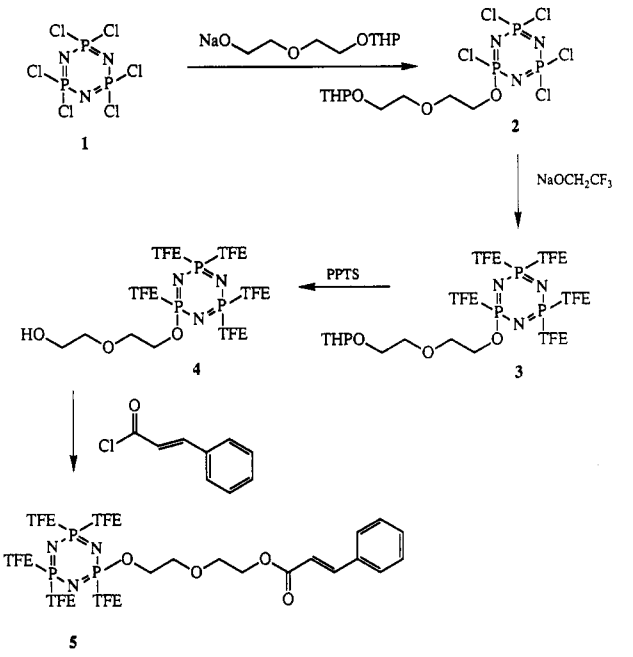
The best-known photosensitive moiety is the cinnamate group, which cross-links in a controlled 2 + 2 photoinduced cycloaddition. It is the cross-linking unit used in polymers for offset printing plates and microcomponents. Indeed, polymeric materials that incorporate the cinnamate group have existed since 1948.[4,5] The synthetic route to poly(vinyl cinnamate), in which poly(vinyl alcohol) is esterified with cinnamoyl chloride, serves as a model for the synthesis of a wide variety of photopolymers. Photopolymers that utilize acrylate,[6] siloxane,[7-9] and vinyl[4,5] backbones have also been synthesized. While the phosphazene backbone has been used in the field of UV-cross-linkable materials,[10-14] the use of a polyphosphazene backbone as a platform for photo-cross-linkable cinnamate side groups has not yet been reported.

The use of the phosphazene skeletal system has the following advantages for photopolymer applications: (1) The potential cross-link density and sensitivity to UV irradiation are greater than in classical organic-backbone polymers due to the presence of two photo-cross-linkable groups per repeat unit. (2) The ability to incorporate a wide variety of cosubstituents via macromolecular substitution in polyphosphazenes allows such properties as the glass transition and the solubility to be tailored at will. (3) The absence of an absorption by the polyphosphazene backbone in the mid-UV to the near-infrared region minimizes photoinduced reactions of the skeletal system during UV irradiation required for the photo-cross-linking procedure.

Results and Discussion

Synthesis and Characterization of Cyclic Phosphazene Model Compounds. The synthetic routes to the cyclic trimeric phosphazenes used as reaction models for the high polymers are shown in Schemes 1 and 2. The primary model system was simplified by use of monofunctional cyclotriphosphazenes. Hexasubstituted cyclic trimers **12** and **15** were used to model high polymers **23** and **26** in which each phosphorus atom bears two photoactive groups.

Scheme 1



Trimers **5** and **9** were synthesized similarly (see Schemes 1 and 2). Hexachlorocyclotriphosphazene was first treated with either $NaOC_6H_4$-*p*-OBz or $NaO(CH_2CH_2O)_2THP$[15] (THP = tetrahydropyranyl) to yield the pentachloro derivative **2** or **6**. The remaining five chlorine atoms per molecule were then replaced by treatment with $NaOCH_2CF_3$ to yield the fully substituted trimers **3** and **7**. Trimer **3** was deprotected to the free alcohol $N_3P_3(OCH_2CF_3)_5O(CH_2CH_2O)_2H$ (**4**) with the use of PPTS[16] (pyridinium-*p*-toluenesulfonate) in 95% ethanol. Trimer **7** required the use of iodotrimethylsilane[17] followed by hydrolysis of the resulting trimethylsilyl aryl ether with methanol to yield the free alcohol $N_3P_3(OCH_2CF_3)_5OC_6H_4OH$. Both trimers were esterified in pyridine solution with a slight excess of cinnamoyl chloride overnight at room temperature to yield cinnamate-substituted trimers **5** and **9**.

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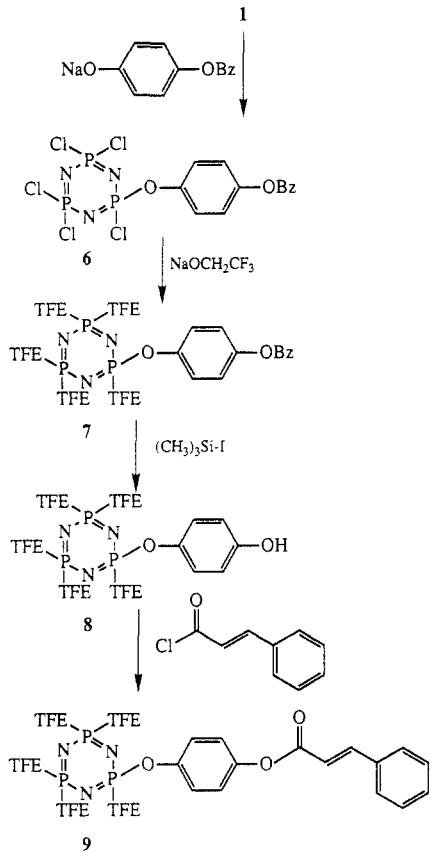
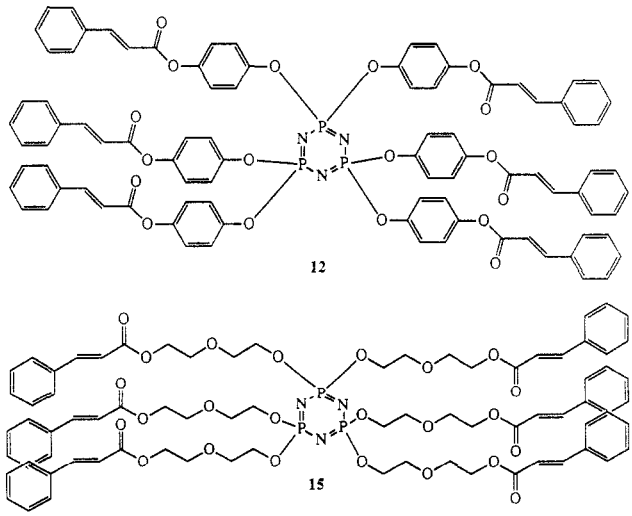
Scheme 2



However, the fully substituted trimers **12** and **15** required slightly different synthetic routes due to the nature and steric bulk of the side groups. Trimer **10** was synthesized from hexachlorocyclotriphosphazene (**1**) and 8 equiv of $NaOC_6H_4$-*p*-OBz. This species was deprotected with BBr_3[18,19] to yield the hexahydroxy compound $[NP(OC_6H_4$-*p*-$OH)_2]_3$ (**11**), which was esterified with cinnamoyl chloride as described above.

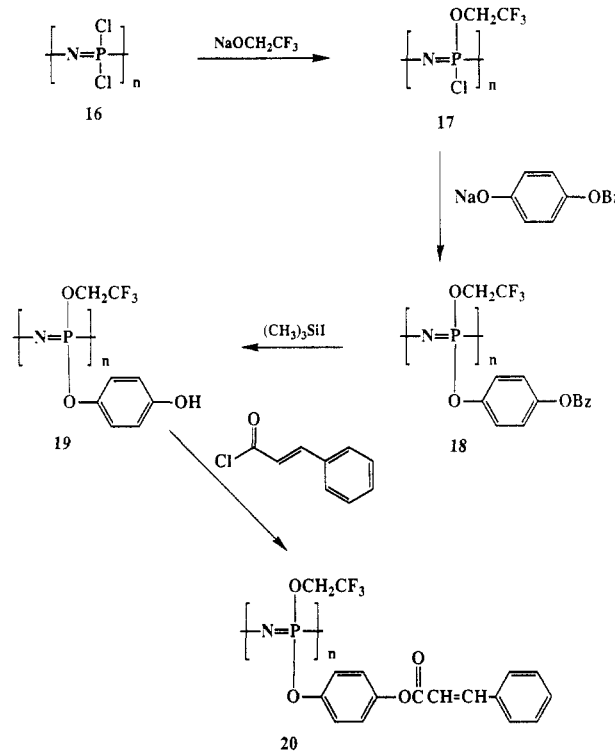


Trimer **13** was synthesized analogously to trimer **10**. Deprotection to yield the hexahydroxy compound **14** was accomplished with the use of HCl in ethanol to cleave the tetrahydopyranyl ether and give the trimer $[NP(O(CH_2CH_2O)_2H)_2]_3$. This trimer was esterified as described above to give $[NP(O(CH_2CH_2O)_2C(O)CH{=}CHC_6H_5)_2]_3$ (**15**).

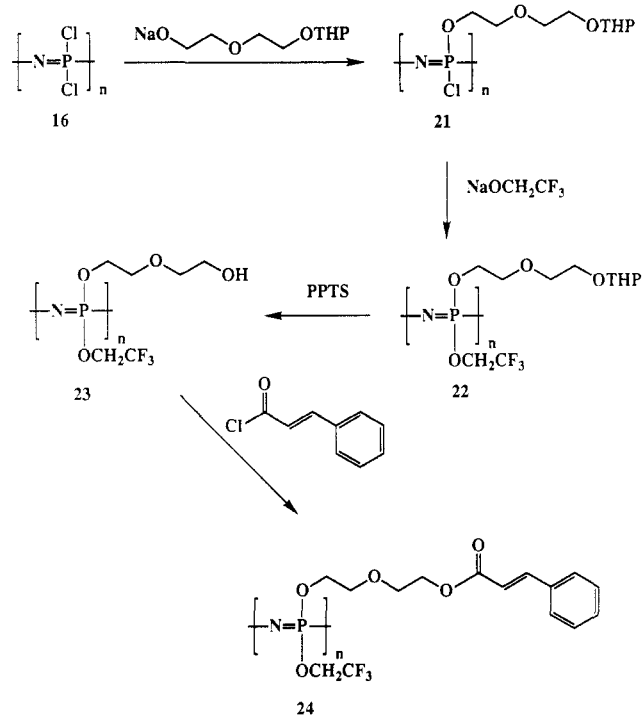
Synthesis and Characterization of High-Polymeric Phosphazenes. The synthetic pathways to polymers **20** and **24** are depicted in Schemes 3 and 4. Poly(dichlorophosphazene) (**16**) was prepared by the thermal ring-opening polymerization of **1**. Trifluoroethoxy cosubstituent polymer **17** was prepared by allowing a stoichiometric deficiency of $NaOCH_2CF_3$ to react with polymer **16**. The remaining P–Cl reactive sites were replaced by the use of $NaOC_6H_4$-*p*-OBz to give fully substituted polymer **18** (see Scheme 3). Polymer **22** was prepared in a slightly different manner by the addition of sodium trifluoroethoxide nucleophile last (see Scheme 4).

Single-substituent polymers $[NP(OC_6H_4OBz)_2]_n$ (**28**) and $[NP(O(CH_2CH_2O)_2THP)_2]_n$ (**25**) were synthesized by the reaction of macromolecular intermediate **16** with $NaOC_6H_4$-*p*-OBz and $NaO(CH_2CH_2O)_2$ THP.

Scheme 3



Scheme 4



Polymers **22** and **25** (see the Experimental Section), bearing the THP ether protecting group, were deprotected to the free hydroxyl polymers **23** and **26**, respectively, with the use of PPTS in 95% ethanol solution.

The initial reagent explored to bring about the cleavage of the benzylic ether to obtain hydroxy-substituted polymers[19,20] was BBr_3. In both homopolymer **28** and trifluoroethoxy cosubstituent polymer **18**, BBr_3 afforded nearly complete deprotection to the free hydroxy group to give polymers **29** and **19**. However, the conditions (30 min with a slight excess of BBr_3 at room temperature) resulted in a noticeable molecular weight decline, especially with trifluoroethoxy cosubstituent polymer **18**, as estimated by the viscosity of THF solutions. Similar results were obtained when the trifluoroethoxy cosubstituent polymer was deprotected for 5 min at room temperature. It is speculated that the molecular weight decline results from the lone pair electrons on the backbone nitrogen atoms coordinating to the boron atom and leading to backbone scission.

Therefore, the use of *B*-Br-9-BBN[21] (9-bromo-9-borabicyclo[3.3.1]nonane), a milder and much more sterically hindered reagent for the cleavage of benzyl ethers than BBr_3, was attempted for the deprotection reaction. This reagent was used in the anticipation that a more sterically crowded environment would allow the deprotection reaction to occur, while retarding the lone pair coordination which may lead to backbone degradation. The level of deprotection of both the trifluoroethoxy cosubstituent polymer **18** and homopolymer **28** was so low as to be undetectable by ^1H NMR even in the presence of more than 10 equiv of *B*-Br-9-BBN.

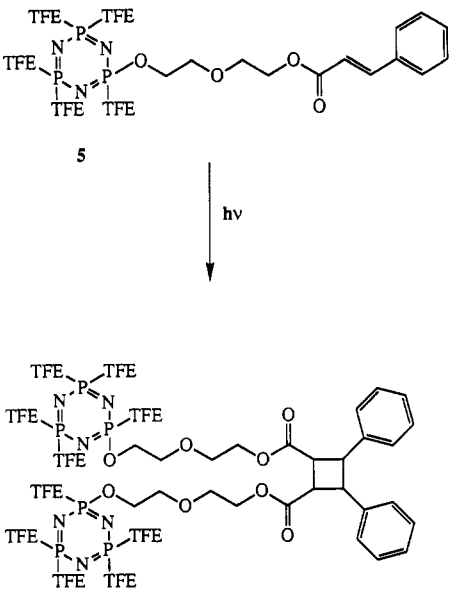
The last deprotection reagent investigated was iodotrimethylsilane. This reagent provided almost full deprotection of the trifluoroethoxy cosubstituent polymer **18** without the catastrophic molecular weight degradation that occurred with the use of BBr_3. However, in contrast to the trifluoroethoxy cosubstituent polymer, homopolymer **28** was completely unaffected by iodotrimethylsilane. The difference in reactivity may reflect the sterically crowded environment around the benzyl ether linkage in polymer **28** relative to copolymer **18**.

The only reagent to fully deprotect homopolymer **28** is the relatively harsh reagent BBr_3. Backbone degradation was minimized by short (5 min) reaction times rather than the initially long times (30 min).

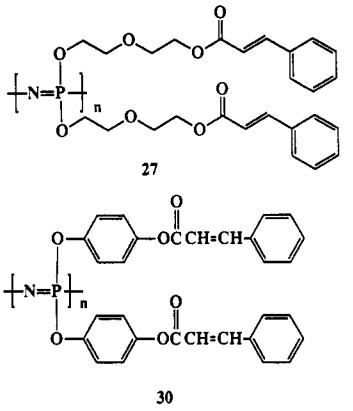
Ultraviolet Absorption Studies of Cyclic Trimers. The UV-induced 2 + 2 cycloaddition reaction of cyclic trimers that bear cinnamate side groups was investigated by the irradiation of trimer **5** with a medium-pressure Hg lamp (see Scheme 5). Trimer **5** had an absorption at 280 nm (CH_2Cl_2 solvent). Species **5** was irradiated in the solid state for 2 h 10 cm from the UV lamp to induce the formation of dimer **31**. Dimer **31** was characterized in its impure form by ^{31}P and ^1H NMR spectroscopy and mass spectrometry. Positive FAB mass spectrometry detected the protonated molecular ion MH^+ at 1731 mass units, which matches the mass of the expected cyclobutane-type dimer. The mass spectrum showed no evidence of open-chain (non-cyclobutane) saturated species (M^+ = 1732). The ^1H NMR spectrum of **31** consisted of two doublets (J = 14 Hz) centered at 7.0 and 6.0 ppm, which, due to symmetry considerations, indicate the formation of dimer **31** with the phenyl groups in the *Z* configuration about the cyclobutane ring.

Ultraviolet Absorption of Polymers 27 and 30. The ultraviolet absorption behavior of polymers **27** and **30** was investigated by UV spectroscopy. Thin films of polymers

Scheme 5



27 and **30** were cast onto quartz plates from inhibitor-free THF, and the solvent was removed under vacuum. The λ_{max} due to the cinnamate chromophore of both polymer **27** and polymer **30** was found to be at 276 nm, which compares favorably to other similar aliphatic cinnamate esters.



Photolytic Cross-Linking Behavior of Polymers 27 and 30. The high loading of cinnamate groups in **27** and **30** made these species the most useful candidates for photo-cross-linking studies. The photolytic cross-linking of polymer **27** was followed by UV spectroscopy (see Figure 1). The polymer film was irradiated with an unfiltered sunlamp UV source. The decrease in the 274-nm absorption was used to monitor the progress of cross-linking. The photo-cross-linking presumably occurs mainly via the formation of cyclobutane-type dimers, perhaps accompanied by various free-radical cross-linking reactions. Cross-linking was confirmed by the insolubility of polymer **27** in common organic solvents after irradiation.

The photolytic cross-linking of polymer **30** was also followed by UV spectroscopy (see Figure 2). As can be seen in Figure 2, the photo-cross-linking behavior and the λ_{max} of polymer **30** are essentially identical to those of polymer **27**. These results indicate a minimal influence on the cross-linking process by the type of spacer group.

Conclusions

The synthesis and characterization of cyclic and high-polymeric cinnamate phosphazenes has been investigated.

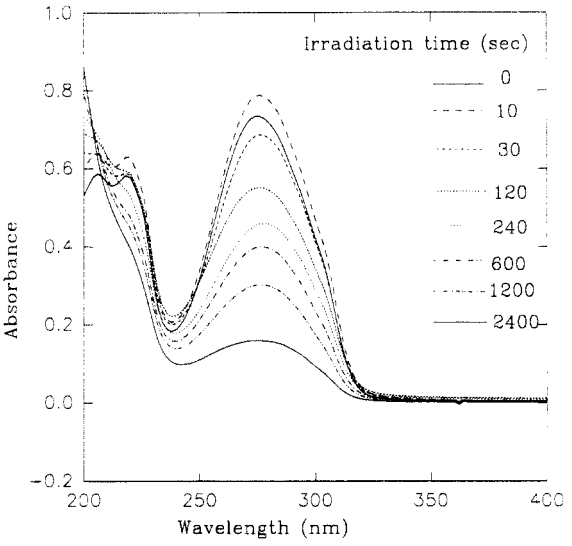


Figure 1. Effect of UV irradiation time on the UV spectrum of polymer **27**.

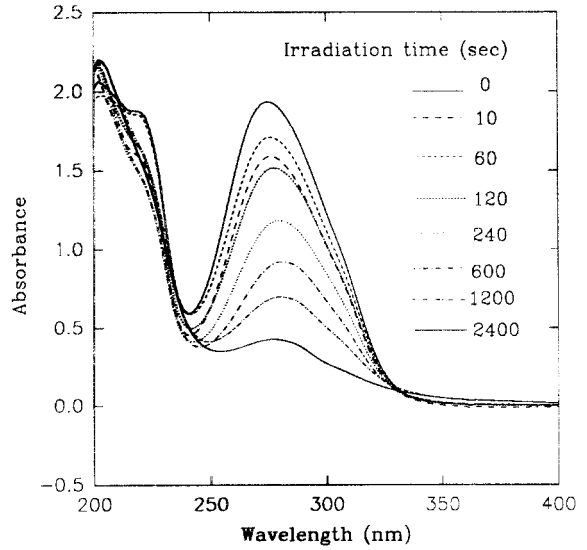


Figure 2. Effect of UV irradiation time on the UV spectrum of polymer **30**.

The results indicate that polymers **27** and **30** undergo a photochemically induced 2 + 2 cycloaddition reaction to form a cross-linked matrix.

The synthetic routes to phosphazene-based cinnamate photopolymers described here have some limitations. The most obvious problem is a lowering of molecular weight during the deprotection and the esterification steps. This can be avoided by the derivatization of macromolecular intermediate **16** with the photoactive *chalcone* group (see the following paper). Lastly, an ideal photoresist has a glass transition temperature significantly above room temperature and an even higher T_g after cross-linking. Although polymer **30** has a T_g of 59 °C, polymers **24** and **27** have T_g's of −25 and −16 °C, respectively. The photolytic cross-linking behavior of polymers **27** and **30** is very similar. This is consistent with a minimal influence by the T_g on photo-cross-linking behavior. However, the effectiveness of the cross-linking step raises the possibility that this system may be useful for the cross-linking of macromolecular surface coatings.

For these reasons, further research was directed toward the incorporation of the chalcone group into the phosphazene system rather than the cinnamate unit. The synthesis of chalcone-bearing polyphosphazenes is a one-step reaction and the resultant polymers have higher glass transition temperatures than do cinnamate-bearing polyphosphazenes.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was provided by Ethyl Corp. It was recrystallized from hexane and sublimed (40 °C, 0.05 mmHg) before use. Tetrahydrofuran and dioxane were distilled from sodium benzophenone under dry argon before use. 2,2,2-Trifluoroethanol (Halocarbon) was distilled from anhydrous barium oxide and was stored over 4-Å molecular sieves. All other reagents and solvents were used as received. The reactions were performed with the reactants under an atmosphere of dry argon using standard Schlenk line techniques. Column chromatography was carried out with the use of silica as a stationary phase with the eluents as indicated in the text. Polymer **16**, $[NPCl_2]_n$, was prepared by the standard literature procedure.[22-24]

Equipment. High-field ^{31}P (146 MHz), ^{13}C (90 MHz), and ^{1}H (360 MHz) NMR spectra were obtained with a Bruker WM360 spectrometer. ^{13}C (50 MHz) and ^{1}H (200 MHz) NMR spectra were also obtained with a Bruker WP200 spectrometer or a Bruker ACE200 spectrometer. Both ^{13}C and ^{31}P NMR spectra were proton decoupled unless specified otherwise. ^{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 NMR spectra were referenced to external tetramethylsilane. Elemental analyses were by Galbraith Laboratories (Knoxville, TN). Irradiations were accomplished with a "Blak-Ray" ultraviolet lamp (Ultra-Violet Products, Inc., San Gabriel, CA) or a Canrad-Hanovia medium-pressure quartz mercury vapor lamp equipped with a water-cooled quartz immersion well. Electron-impact mass spectra (EI/MS) were obtained with a Kratos MS 9/50 spectrometer. Chemical ionization (CI) mass spectra were obtained with a Kratos MS-25 spectrometer. Fast atom bombardment (FAB) mass spectra were obtained with a Kratos MS-50 spectrometer. Molecular weights were determined with a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a HP-1037A refractive index detector and a Polymer Laboratories PL gel 10-μm column. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF. The GPC column was calibrated with polystyrene standards (Waters) and with fractionated samples of poly[bis(trifluoroethoxy)phosphazene] provided by Drs. R. Singler and G. Hagnauer of the U.S. Army Materials Research Laboratories, Watertown, MA. UV–visible spectra of all compounds as solutions in spectroscopic grade methylene chloride were obtained with a Hewlett-Packard Model HP8450A UV–visible spectrometer. The samples were in quartz cells (1-cm path length) or on quartz plates for solid polymeric samples. Glass transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer 7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. Heating rates of 10–40 °C/min under a nitrogen atmosphere were used. Sample sizes were between 10 and 30 mg.

Synthesis of $N_3P_3Cl_5(OCH_2CH_2)_2OTHP$ (2). $H(OCH_2CH_2)_2OTHP$ (1.63 g, 8.58 mmol) was added to NaH (0.34 g, 14.2 mmol) in THF (50 mL), and the mixture was stirred overnight at room temperature. This solution was added dropwise over 15 min to 1 (3.0 g, 8.58 mmol) in THF (25 mL) with stirring, followed by stirring overnight at room temperature. Trimer **2** was used directly in the synthesis of **3**. ^{31}P NMR AX_2, ν_A = 15.9, ν_B = 23.2 ppm, J_{PNP} = 64 Hz.

Synthesis of $N_3P_3(OCH_2CF_3)_5\{(OCH_2CH_2)_2OTHP\}$ (3). The above reaction mixture was cooled to −78 °C, $NaOCH_2CF_3$ {from $HOCH_2CF_3$ (5.17 g, 51.7 mmol) and sodium (1.4 g, 61 mmol) in THF (30 mL)} was added dropwise, and the reaction was allowed to warm to room temperature slowly. The solvent was removed by rotary evaporation, CH_2Cl_2 (150 mL) was added, and the organic layer was washed with water (3 × 100 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica, 1:3 ether–hexane) to give trimer **3**. ^{31}P NMR ($CDCl_3$) AB_2, 17.7 ppm (m). ^{1}H NMR ($CDCl_3$) δ 4.6 (t, 1 H), 4.30 (m, 10 H), 4.1 (q, 2 H), 3.85 (m, 2 H), 3.75 (m, 2 H), 3.50–3.65 (m, 2 H), 1.45–1.90 (m, 6 H).

Synthesis of $N_3P_3(OCH_2CF_3)_5\{(OCH_2CH_2)_2OH\}$ (4). Trimer **3** (2.10 g, 2.56 mmol) was dissolved in 95% ethanol (50 mL),

PPTS (0.064 g, 0.25 mmol) was added, and the mixture was stirred at room temperature. The solvent was removed by rotary evaporation, and the volatiles were removed under high vacuum. Confirmation of deprotection was accomplished by establishing the absence of the protecting group signals in the ^{1}H NMR spectrum. ^{31}P NMR AB_2, 19.4–21.6 ppm.

Synthesis of $N_3P_3(OCH_2CF_3)_5\{(OCH_2CH_2)_2OC(O)CH{=}CHPh\}$ (5). Trimer 4 (1.80 g, 2.45 mmol) was dissolved in anhydrous pyridine (50 mL), PhCH=CHC(O)Cl (0.61 g, 3.68 mmol) was added, and the reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum, water (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure. Column chromatography (silica gel, 10% EtOAc/hexane) was used to isolate pure 5. ^{31}P NMR AB_2, 16.3–18.5 ppm. ^{1}H NMR ($CDCl_3$) δ 7.7 (d, 1 H, J = 16 Hz), 7.5 (m, 2 H), 7.4 (m, 3 H), 6.5 (d, 1 H, J = 16 Hz), 4.2–4.4 (m, 12 H), 4.1 (m, 2 H), 3.8 (m, 4 H). MS m/z calcd 865, m/z found 866 (MH^+) (+FAB).

Synthesis of $N_3P_3Cl_5\{OC_6H_4$-p-$OBz\}$ (6). Solid HOC_6H_4-p-OBz (1.55 g, 7.75 mmol) was added to NaH (0.182 g, 7.6 mmol) in THF (60 mL), and the mixture was stirred for 3 h. This solution was added to $[NPCl_2]_3$ in THF (25 mL), and the mixture was stirred warm overnight. The solvent was removed by rotary evaporation, ether (50 mL) was added, the solution was washed with water (3 × 30 mL) and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. Warming under vacuum removed residual $[NPCl_2]_3$. Yield: 3.08 g (78%). ^{31}P NMR AX_2, ν_A = 13.8 ppm, ν_B = 23.2 ppm, J_{AB} = 59 Hz. ^{1}H NMR ($CDCl_3$) δ 7.4 (m, 5 H), 7.2 (d, 2 H), 6.9 (d, 2 H), 5.05 (s, 2 H). MS m/z calcd 509, m/z found 512 $[(M + 2)H^+]$ (CI).

Synthesis of $N_3P_3(OCH_2CF_3)_5\{OC_6H_4$-$p$-$OBz\}$ (7). 2,2,2-Trifluoroethanol (4.80 g, 48 mmol) was added to sodium metal (1.10 g, 48 mmol) in THF (40 mL), and the mixture was stirred overnight at room temperature. This solution was added over 1 h to a solution of 6 in THF (25 mL) at −78 °C and was then allowed to warm slowly to room temperature before being stirred overnight at room temperature. The solvent was removed by rotary evaporation, and the solids were dissolved in ether (100 mL) and washed with water (3 × 50 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed by rotary evaporation. The beige solid was purified by removing $[NP(OCH_2CF_3)_2]_3$ by vacuum distillation. ^{31}P NMR ($CDCl_3$) AB_2, ν_A = 18.0, ν_B = 14.9 ppm, J_{PNP} = 90 Hz. ^{1}H NMR ($CDCl_3$) δ 7.4 (m, 5 H), 7.1 (d, 2 H), 6.9 (d, 2 H), 5.0 (s, 2 H), 4.4 (q, 2 H), 4.35 (m, 4 H), 3.8 (m, 4 H). MS m/z calcd 829, m/z found 830 (MH^+) (CI).

Synthesis of $N_3P_3(OCH_2CF_3)_5\{OC_6H_4$-$p$-$OH\}$ (8). A solution of 7 (0.50 g, 0.30 mmol) in CH_2Cl_2 (30 mL) and $(CH_3)_3SiI$ (0.36 g, 1.80 mmol, 3 equiv) was heated to reflux for 8 days. The reaction was allowed to cool to room temperature, and methanol (2 mL) was added slowly. The solvent was removed by rotary evaporation, and the solid was purified by column chromatography (silica gel, 2:3 EtOAc–hexane). ^{31}P NMR ($CDCl_3$) AB_2, ν_A = 14.4, ν_B = 17.5 ppm. ^{1}H NMR ($CDCl_3$) δ 7.1 (d, 2 H), 6.8 (d, 2 H), 4.4 (q, 2 H), 4.2 (m, 4 H), 3.85 (m, 4 H). MS m/z calcd 739, m/z found 740 (MH^+) (+FAB).

Synthesis of $N_3P_3(OCH_2CF_3)_5\{OC_6H_4$-$p$-$OC(O)CH{=}CHPh\}$ (9). A solution of trimer 8 (0.18 g, 0.24 mmol) and PhCH=CHC(O)Cl (0.018 g, 0.48 mmol) in pyridine (20 mL) was stirred at room temperature for 4 days. The solvent was removed under vacuum and the product was purified by preparative TLC (1:4 EtOAc–hexane). Further purification to remove $N_3P_3(OCH_2CF_3)_4\{OC_6H_4$-$p$-$OC(O)CH{=}CHPh\}_2$ was not possible. MS m/z calcd 869, m/z found 870 (MH^+) (+FAB).

Synthesis of $[NP(OC_6H_4$-p-$OBz)_2]_3$ (10). To a solution of $NaOC_6H_4$-p-OBz (prepared from 6.89 g (34.4 mmol) of HOC_6H_4-p-OBz and NaH (0.82 g, 34.4 mmol)) in THF (100 mL) was added solid $[NPCl_2]_3$. The solution was heated to reflux overnight. The reaction mixture was allowed to cool, the solvent was removed by rotary evaporation, and the residue was extracted with boiling water (4 × 250 mL). The solid was recrystallized from 1:1 THF–hexane to yield beige needles. ^{31}P NMR δ +11 (s). ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 30 H), 6.8 (m, 24 H), 4.95 (s, 12 H). ^{13}C NMR ($CDCl_3$) δ 155.7, 144.4, 128.5, 128.0, 127.4, 121.9, 115.3, 70.4. MS m/z calcd 1330, m/z found 1331 (MH^+) (+FAB).

Synthesis of $[NP(OC_6H_4$-p-$OH)_2]_3$ (11). Trimer 10 (1.0 g, 0.75 mmol) was dissolved in CH_2Cl_2 (30 mL), and BBr_3 (6.0 mL of a 1 M solution in CH_2Cl_2 (6 mmol)) was added over 5 min with the formation of a heavy precipitate. The mixture was stirred for 30 min and then methanol (10 mL) was added slowly. The solvent was removed by rotary evaporation, and the residue was dried under vacuum for 24 h and used directly in the synthesis of 12. MS m/z calcd 789, m/z found 790 (MH^+) (+FAB).

Synthesis of $[NP(OC_6H_4$-p-$OC(O)CH{=}CHPh)_2]_3$ (12). Trimer 11 was dissolved in anhydrous pyridine (75 mL), PhCH=CHC(O)Cl (0.91 g, 5.5 mmol) was added, and the mixture was stirred at room temperature for 5 days. Most of the solvent was removed under vacuum, and water (200 mL) was added to precipitate trimer 12. Recrystallization from THF/hexane gave a beige powder. ^{31}P NMR ($CDCl_3$) δ 9.9 (s). ^{13}C NMR ($CDCl_3$) δ 165.1, 147.7, 146.5, 134.1, 131.2, 128.9, 128.2, 122.7, 121.8, 117.2. ^{1}H NMR ($CDCl_3$) δ 7.84 (d, 6 H, J = 16 Hz), 7.5 (m, 12 H), 7.35 (m, 18 H), 7.05 (m, 24 H), 6.60 (d, 6 H, J = 16 Hz). MS m/z calcd 1570, m/z found 1571 (MH^+) (+FAB). Anal. Calcd for $C_{90}H_{66}N_3O_{18}P_3$: C, 68.83; H, 4.23; N, 2.68. Found: C, 67.60; H, 4.18; N, 2.23.

Synthesis of $[NP\{(OCH_2CH_2)_2OTHP\}_2]_3$ (13). $H(OCH_2CH_2)_2OTHP$ (4.36 g, 23.1 mmol) was added to NaH (60%, 0.91 g) in THF (50 mL), and the mixture was stirred overnight at room temperature. Solid $[NPCl_2]_3$ (1.0 g, 2.8 mmol) was then added, and the reaction mixture was stirred at room temperature for 3 days. The solvent was removed by rotary evaporation, water (100 mL) was added, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed by rotary evaporation. Column chromatography (10% MeOH/$CHCl_3$) isolated pure 13. ^{31}P NMR ($CDCl_3$) δ 18.6 (s). ^{1}H NMR ($CDCl_3$) δ 4.6 (t, 6 H), 4.05 (m, 12 H), 3.9 (m, 12 H), 3.75–3.40 (m, 36 H), 1.9–1.45 (m, 36 H). ^{13}C NMR ($CDCl_3$) δ 98.9, 70.5, 70.0 (m), 66.6, 65.0, 62.2, 30.5, 25.4, 19.5.

Synthesis of $[NP\{(OCH_2CH_2)_2OH\}_2]_3$ (14). Trimer 13 (3.50 g, 2.75 mmol) was dissolved in methanol (100 mL), 0.5 mL of concentrated HCl was added, and the reaction mixture was stirred for 3 days at room temperature. The solvent was removed by rotary evaporation, and the oil was dried overnight under high vacuum. ^{31}P NMR δ 19.2 (s). ^{13}C NMR δ 72.3 (m), 69.3, 64.7, 60.2 (m). ^{1}H NMR (acetone-d_6) δ 3.9 (br, 2 H), 3.6 (m, 2 H), 3.3–3.5 (m, 4 H).

Synthesis of $[NP\{(OCH_2CH_2)_2OC(O)CH{=}CHPh\}_2]_3$ (15). Trimer 14 (2.10 g, 2.75 mmol) and PhCH=CHC(O)Cl (3.66 g, 22.0 mmol) were dissolved in anhydrous pyridine (75 mL) and were stirred for 3 days at room temperature. The solvent was removed under vacuum, water (100 mL) was added, and the aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The remaining oil was purified by column chromatography (5% MeOH/CH_2Cl_2, silica gel). ^{31}P NMR δ 18.6 (s). ^{1}H NMR δ 7.7 (d, 1 H, J = 16 Hz), 7.5 (m, 2 H), 7.4 (m, 3 H), 6.45 (d, 1 H, J = 16 Hz), 4.35 (m, 2 H), 4.1 (br, 2 H), 3.75 (m, 6 H). MS m/z calcd 1547, m/z found 1548 (MH^+) (+FAB).

Synthesis of $[NP(OCH_2CF_3)_1(OC_6H_4$-p-$OBz)_1]_n$ (18). Poly(dichlorophosphazene) (16) (5.0 g, 43 mmol) was dissolved in warm dioxane (700 mL) overnight with stirring. 2,2,2-Trifluoroethanol (4.31 g, 43.1 mmol) was added to sodium metal (1.05 g, 45.7 mmol) in dioxane (100 mL), and HOC_6H_4-p-OBz (2.6 g, 13.0 mmol) was added to NaH in dioxane and stirred overnight at room temperature. The solution of 2,2,2-trifluoroethoxide was added to the polymer solution and was stirred and warmed overnight. Finally, the solution of $NaOC_6H_4$-p-OBz was added to the partially substituted polymer, and the solution was heated to reflux for 5 days. The solvent was removed by rotary evaporation, and the solution was poured slowly into water (4 L). Further purification was accomplished by additional precipitations of THF solutions into water (4× total), iPrOH (2×), and hexane (1×). Yield: 9.8 g (66%). ^{31}P NMR δ −17.6. ^{1}H NMR ($CDCl_3$) δ 7.25 (5 H, br), 6.4–7.0 (4 H, br), 4.6 (br, 2 H), 3.75 (br, 2 H).

Synthesis of $[NP(OCH_2CF_3)_1(OC_6H_4$-p-$OH)_1]_n$ (19). Polymer 18 (0.50 g, 1.46 mmol) was dissolved in dry CH_2Cl_2 (100 mL), $(CH_3)_3SiI$ (1.46 g, 7.3 mmol) was added, and the mixture was heated to reflux for 3 days. Methanol (4 mL) was added at reflux

and the solvent was decanted from the precipitated polymer. Further solvent removal was achieved by vacuum drying overnight. ^{1}H NMR ($CDCl_3$) δ 6.9 (2 H, br), 6.6 (2 H, br), 4.1 (2 H, br).

Synthesis of [NP(OCH$_2$CF$_3$)$_1$(OC$_6$H$_4$-*p*-OC(O)CH=CHPh)$_1$]$_n$ (20). Polymer **19** (0.37 g, 1.46 mmol) was dissolved in anhydrous pyridine (100 mL), PhCH=CHC(O)Cl (0.24 g, 1.44 mmol) was added, and the solution was stirred overnight at room temperature. Most of the solvent was removed under vacuum, and water (100 mL) was added to precipitate the polymer. Further purification was accomplished by precipitation of THF solutions of **20** into water. ^{31}P NMR δ −17.65 (br). ^{1}H NMR ($CDCl_3$) δ 8.25 (br, 1 H), 7.7 (br, 2 H), 7.4 (br, 2 H), 7.0 (br, 4 H), 6.7 (br, 2 H), 4.25 (br, 2 H). Anal. Calcd: C, 50.15; H, 3.65; N, 3.90; Cl, 0. Found: C, 50.00; H, 3.50; N, 4.42; Cl, 0.022.

Synthesis of [NP(OCH$_2$CF$_3$)$_1${(OCH$_2$CH$_2$)$_2$OTHP}$_1$]$_n$ (22). Poly(dichlorophosphazene) (**16**) was dissolved in THF (400 mL) overnight with stirring. H(OCH$_2$CH$_2$)$_2$OTHP (3.93 g, 20.7 mmol) was added to NaH (60%, 0.83 g) in THF (50 mL). 2,2,2-Trifluoroethanol (1.72 g, 17.2 mmol) was added to Na (0.40 g, 17.4 mmol) in THF (50 mL), and the mixture was stirred overnight at room temperature. The THF solution of NaOCH$_2$CF$_3$ was added to **16** and stirred warm overnight. Na(OCH$_2$CH$_2$)$_2$OTHP was added to the polymer solution and stirred warm for 2 days. The solution was concentrated by rotary evaporation, and the polymer was precipitated by pouring into water. Two additional precipitations from THF into water yielded pure **22**. Yield: 5.6 g (98%). ^{31}P NMR δ −6.5 (br). ^{1}H NMR ($CDCl_3$) δ 4.6 (br, 1 H), 4.3 (br, 2 H), 4.1 (br, 2 H), 3.8 (br, 4 H), 3.7–3.4 (br, 4 H), 1.9–1.0 (br, 6 H).

Synthesis of [NP(OCH$_2$CF$_3$)$_1${(OCH$_2$CH$_2$)$_2$OH}$_1$]$_n$ (23). Polymer **22** (2.0 g, 6.0 mmol) was dissolved in ethanol (100 mL), PPTS (1.50 g, 6.0 mmol) was added, and the reaction mixture was stirred warm for 5 days. Dialysis against water (8 days) and then methanol (7 days), rotary evaporation of the solvent, and then vacuum drying yielded pure **23**. ^{31}P NMR δ −4.9, −6.3. ^{1}H NMR δ 4.5 (2 H, br), 4.2 (br, 2 H), 4.0–3.5 (br, 6 H), 2.85 (br, 1 H).

Synthesis of [NP(OCH$_2$CF$_3$)$_1${(OCH$_2$CH$_2$)$_2$OC(O)CH=CHPh}$_1$]$_n$ (24). Polymer **24** was prepared by the same method as described for **20**, with the reagents and quantities as follows. **23**, 1.2 g (4.8 mmol); pyridine, 75 mL; PhCH=CHC(O)Cl, 0.96 g (5.8 mmol). ^{31}P NMR δ −6.1, −7.3. ^{1}H NMR δ 7.65 (d, 1 H, J = 14 Hz), 7.5–7.3 (br, 5 H), 6.41 (d, 1 H, J = 17 Hz), 4.3 (br, 4 H), 4.1 (br, 2 H), 3.7 (br, 4 H). Anal. Calcd: C, 47.5; H, 4.52, N, 3.69. Found: C, 47.05; H, 4.93; N, 3.59. T_g = −25 °C. M_w = 1.8 × 10^5, M_n = 6.6 × 10^5.

Synthesis of [NP{O(CH$_2$CH$_2$O)$_2$THP}$_2$]$_n$ (25). Polymer **24** was prepared by the same method as described for **20**, with the reagents and quantities as follows. **16**, 3.0 g (26 mmol in THF (500 mL)); HO(CH$_2$CH$_2$O)$_2$THP, 14.7 g (77.6 mmol); NaH, 2.79 g (69.8 mmol (60% dispersion in mineral oil) in THF (100 mL)). ^{31}P NMR δ −7.87. ^{13}C NMR δ 98.8, 66.6, 65.0, 62.0, 30.6, 25.5, 19.5. ^{1}H NMR δ 4.6 (br, 1 H), 4.1–3.3 (br, 10 H), 1.7–1.0 (br, 6 H).

Synthesis of [NP{O(CH$_2$CH$_2$O)$_2$H}$_2$]$_n$ (26). Polymer **26** was prepared by the same method as described for **23**, with the reagents and quantities as follows. **25**, 1.2 g (2.8 mmol); 95% EtOH, 100 mL; PPTS, 0.07 g (0.28 mmol). ^{31}P NMR δ −7.98. ^{13}C NMR δ 74.3, 73.0, 67.3, 63.0. ^{1}H NMR δ 4.16 (br, 1 H), 3.73–3.56 (m, 8 H).

Synthesis of [NP{O(CH$_2$CH$_2$O)$_2$C(O)CH=CHPh}$_2$]$_n$ (27). Polymer **27** was prepared by the same method as described for **20**, with the reagents and quantities as follows. Polymer **26**, 2.4 g (9.4 mmol); pyridine, 75 mL; PhCH=CHC(O)Cl, 3.14 g (18.9 mmol). ^{31}P NMR ($CDCl_3$) δ −7.4 (s). ^{13}C NMR ($CDCl_3$) δ 166.8, 145.0, 134.3, 130.2, 128.8, 128.2, 117.8, 70.3, 69.0, 65.1, 63.5. ^{1}H NMR δ 7.6 (d, 1 H, J = 16 Hz), 7.4 (br, 2 H), 7.25 (br, 3 H), 6.4 (d, 1 H, J = 16 Hz), 4.3 (br, 4 H), 4.1 (br, 2 H), 3.7 (br, 4 H). T_g = −16 °C. Anal. Calcd: C, 58.65; H, 6.15; N, 2.85; Cl, 0. Found: C, 59.35; H, 6.15; N, 2.46; Cl, <0.5. M_w = 5.6 × 10^4, M_n = 1.4 × 10^5.

Synthesis of [NP(OC$_6$H$_4$-*p*-OBz)$_2$]$_n$ (28). Polymer **28** was prepared by the same method as described for **18**, with the reagents and quantities as follows. **16**, 2.0 g (1.7 mmol); dioxane, 400 mL; HOC$_6$H$_4$-*p*-OBz, 12.7 g (6.4 mmol); NaH (60% dispersion in mineral oil), 1.52 g, all in dioxane (100 mL). Yield: 4.6 g (65%).

Synthesis of [NP(OC$_6$H$_4$-*p*-OH)$_2$]$_n$ (29). Polymer **28** (0.50 g, 1.13 mmol) was dissolved in dry CH_2Cl_2 (100 mL) overnight with stirring. BBr_3 (2.7 mL, 1 M in CH_2Cl_2) was added, and the reaction was stirred for 5 min at room temperature. Ethanol (3 mL) was added slowly, the solvent was decanted from the polymeric precipitate, and the polymer was dried under vacuum overnight. ^{31}P NMR δ −16.1. ^{13}C NMR (DMSO-d_6) δ 153.5, 121.6, 115.0, 95.4. ^{1}H NMR (DMSO-d_6) δ 6.64 (br, 2 H), 6.31 (br, 2 H).

Synthesis of [NP(OC$_6$H$_4$-*p*-OC(O)CH=CHPh)$_2$]$_n$ (30). Polymer **30** was prepared by the same method as described for **20**, with the reagents and quantities as follows. **29**, 0.29 g (1.10 mmol); pyridine, 75 mL; PhCH=CHC(O)Cl, 0.44 g (2.64 mmol). ^{31}P NMR δ −16.8 (br). ^{1}H NMR δ 6.4–7.6 (br). Anal. Calcd: C, 68.83; H, 4.24; N, 2.68; Cl, 0. Found: C, 64.31; H, 4.06; N, 3.29; Cl, 0.0299. T_g = 59 °C.

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References and Notes

(1) Reiser, A. *Photoreactive Polymers*; Wiley-Interscience: New York, 1988.
(2) Tripathy, S. K.; Mandal, B. K.; Jeng, R. J.; Kumar, J. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 607.
(3) Tripathy, S. K.; Mandal, B.; Jeng, R. J.; Lee, J. Y.; Kumar, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 94.
(4) Minsk, L. M.; Van Deusen, W. P. U.S. Patent 2 690 966, 1948.
(5) Minsk, L. M.; Smith, J. G.; Van Deusen, W. P.; Wright, J. F. *J. Appl. Polym. Sci.* **1959**, *11*, 302.
(6) Nishikubo, T.; Iizawa, T.; Tsuchiya, K. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 377.
(7) Mercier, R.; Coqueret, X.; Lablache-Combier, A.; Loucheux, C. *Eur. Polym. J.* **1988**, *24*, 639.
(8) Keller, P. *Chem. Mater.* **1990**, *2*, 3.
(9) Coqueret, X.; El Achari, A.; Hajaiej, A.; Lablache-Combier, A.; Loucheux, C.; Randrianarisoa, L. *Makromol. Chem.* **1991**, 1517.
(10) Gleria, M.; Minto, F.; Flamigni, L.; Bortolus, P. *J. Inorg. Organomet. Polym.* **1992**, *2*, 329.
(11) Gleria, M.; Minto, F.; Bortolus, P.; Porzio, W. *Eur. Polym. J.* **1989**, *25*, 1039.
(12) Gleria, M.; Minto, F.; Flamigni, L.; Bortolus, P. *Polym. Degrad. Stab.* **1988**, *22*, 125.
(13) Nelson, C. J.; Coggio, W. D.; Allcock, H. R. *Chem. Mater.* **1991**, *3*, 786.
(14) O'Brien, J. P.; Ferrar, W. T.; Allcock, H. R. *Macromolecules* **1979**, *12*, 108.
(15) Allcock, H. R.; Kim, C. *Macromolecules* **1991**, *24*, 2846.
(16) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3761.
(17) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3772.
(18) Benton, F. L.; Dillon, T. E. *J. Am. Chem. Soc.* **1942**, *64*, 1128.
(19) Medici, A.; Fantin, G.; Pedrini, P.; Gleria, M.; Minto, F. *Macromolecules* **1992**, *25*, 2569.
(20) Fantin, G.; Medica, A.; Fogagnolo, M.; Pedrini, P.; Gleria, M.; Bertrani, R.; Facchin, G. *Eur. Polym. J.* **1993**, *29*, 1571.
(21) Bhatt, M. V. *J. Organomet. Chem.* **1978**, *156*, 221.
(22) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(23) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(24) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.