Macromolecules **1992,** *25,* 2666–2670

Synthesis and Thermal Reaction of Acetylenic Group Substituted Poly(organophosphazene)s and Cyclotriphosphazene

Ji Young Chang and Suh Bong Rhee*

Polymer Research Laboratory 1, Korea Research Institute of Chemical Technology, P.O. Box 9, Daedeog-Danji, Taejon, Korea 305-606

Seonkyeong Cheong and Minjoong Yoon

Department of Chemistry, Chungnam National University, Taejon, Korea 305-764

Received November 13, 1991

ABSTRACT: Poly[bis[4-[(trimethylsilyl)ethynyl]anilino]phosphazene] was prepared by reaction of poly(dichlorophosphazene) with 4-[(trimethylsilyl)ethynyl]aniline. Cosubstituent poly(organophosphazene)s were synthesized by sequential reaction of poly(dichlorophosphazene) with 4-[(trimethylsilyl)ethynyl]aniline and sodium trifluoroethoxide. Trimethylsilyl groups were removed by treating the polymers with aqueous KOH in methanol to give acetylene-substituted polyphosphazenes. These polymers were soluble in common organic solvents including acetone, methanol, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. Thermal reactions of the polymers were studied by means of differential scanning calorimeter (DSC) and IR. Cross-linked polymer films were obtained by molding the polymers at 180 °C under pressure. Hexakis(4-ethynylanilino)cyclotriphosphazene was also prepared from hexachlorocyclotriphosphazene, and its thermal reaction was studied by DSC and IR. DSC measurement for the compound demonstrated a cure onset temperature at 180 °C and a cure maximum temperature of 236 °C.

Introduction

Cyclotriphosphazenes with skeletal nitrogen and phosphorus atoms exhibit unusual thermal properties such as flame retardancy and self-extinguishibility.[1] Their polymeric species, poly(organophosphazene)s, are generally prepared by ring opening polymerization of hexachlorocyclotriphosphazene and subsequent substitution reaction with various nucleophiles.[2] In addition to the thermal properties imparted by phosphorus and nitrogen elements on backbones, they can have the wide range of physical properties generated by variation in side groups.[3–7]

Cyclotriphosphazenes and polyphosphazenes have been used to improve thermal and physical properties of organic polymers. Cyclotriphosphazenes have incorporated into organic polymeric systems as pendants,[8–11] cross-linking agents,[12] and additives.[1] Several grafted copolymers between polyphosphazenes and organic polymers were also reported.[13,14]

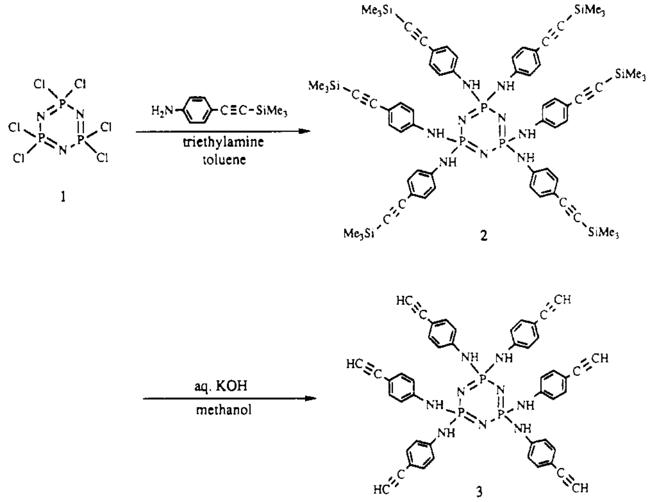
Thermal polymerization of thermally curable organic compound substituted cyclotriphosphazenes is an alternative route to obtain polymers containing the phosphazene moiety. For example, maleimido-substituted aromatic cyclotriphosphazenes were thermally polymerized to produce polymers with excellent flame retardancy and high char yields at 800 °C.[15–17] However, no polyphosphazene substituted by maleimido groups was reported, probably due to synthetic problems with substitution reaction. Rigid and polar nucleophiles often cause precipitation during substitution reaction with poly(dichlorophosphazene), which leads to incomplete replacement of chloro groups. The remaining chloro groups may react with moisture to initiate degradation of the polymer.

In the present work, we synthesized soluble and thermally curable poly(organophosphazene)s as well as cyclotriphosphazene. We chose acetylenic compounds as reactive side groups, which are thermally curable under moderate conditions without the evolution of volatiles.[18–26]

Results and Discussion

Cyclotriphosphazene Containing Acetylenic Groups. Hexakis(4-ethynylanilino)cyclotriphosphazene (3) was prepared as described in Scheme I. Hexachlorocyclotriphosphazene was allowed to react with 4-[(trimethylsilyl)ethynyl]aniline in the presence of triethylamine to give compound 2. Deprotection reaction was carried out in a solution of aqueous KOH and methanol. Compound 3 was isolated as white solids by recrystallization from diethyl ether/*n*-hexane. No distinct melting point was observed by either a melting point apparatus or DSC up to 350 °C. In the ^{31}P NMR spectra, both compounds 2 and 3 showed singlet peaks at 3.0 ppm. In the ^{1}H NMR spectra, compound 2 showed a singlet peak at 0.2 ppm for trimethyl protons and two doublet peaks with an AB spin system centered at 7.0 and 7.4 ppm for benzene ring protons, while compound 3 exhibited two singlet peaks at 3.4 and 7.2 ppm corresponding to acetylenic protons and benzene ring protons, respectively (Figure 1a).

Scheme I



An attempt was made to synthesize compound 3 by substitution reaction of hexachlorocyclotriphosphazene with 4-ethynylaniline in the presence of triethylamine, but unidentified compounds for which ^{31}P NMR spectra

0024-9297/92/2225-2666$03.00/0

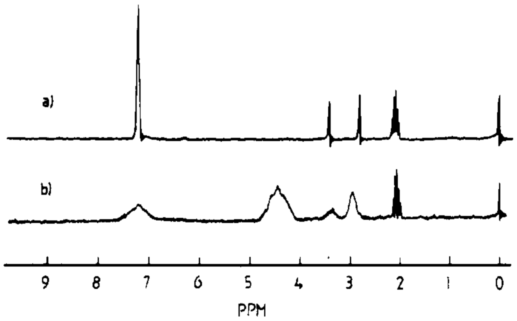


Figure 1. 60-MHz ^{1}H NMR spectra of cyclotriphosphazene **3** and polymer **9b**, both in acetone-d_6.

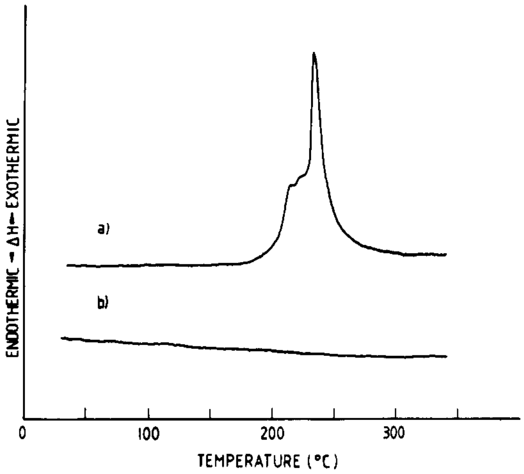


Figure 2. DSC thermograms of cyclotriphosphazene **3**: (a) first scan and (b) second scan, both with a heating rate of 10 °C/min under nitrogen atmosphere.

Table I
Cyclotriphosphazene Characterization Data

compd	^{1}H NMR,[a] ppm	^{31}P NMR,[a] ppm	elemental analysis, %
2	7.0, 7.4 (dd, 24 H, C_6H_4) 2.7 (s, H_2O, NH) 0.2 (s, 54 H, $SiCH_3$)	3.0	found: C, 62.39; H, 6.54; N, 9.63 calcd: C, 62.66; H, 6.71; N, 9.97
3	7.2 (s, 24 H, C_6H_4) 2.8 (s, H_2O, NH) 3.4 (s, 6 H, CH)	3.0	found: C, 68.96; H, 4.01; N, 14.95 calcd: C, 69.30; H, 4.37; N, 15.16

[a] The ^{1}H and ^{31}P NMR spectra were obtained in acetone-d_6.

showed a complicated pattern of peaks were obtained. This result may be ascribed to part of the substitution reaction occurring with acetylenic groups instead of amino groups. Characterization data for compounds **2** and **3** are summarized in Table I.

Cross-linking reaction of acetylenic groups was examined by DSC. Thermograms were obtained by scanning the sample twice from 30 to 350 °C with a heating rate of 10 °C/min under nitrogen atmosphere (Figure 2). In the first scan, a strong exotherm was observed between 180 and 280 °C due to inter- and intramolecular reaction of acetylenic groups. No significant exotherm appeared in the second scan, which indicated that most acetylenic groups had been reacted during the first scan. A shiny dark brown film (0.1 cm thick) was obtained by molding compound **3** at 220 °C under a pressure of 10 000 lb/in^2 for 1 h. The film was brittle and insoluble in organic solvents such as alcohols, *N,N*-dimethylformamide, and dimethyl sulfoxide. Figure 3 shows IR spectra of compound **3** and the cured material. The characteristic bands for C–H stretching and C–C triple bond stretching modes of the acetylenic groups appeared at 3200 and 2100 cm^{-1}, respectively.

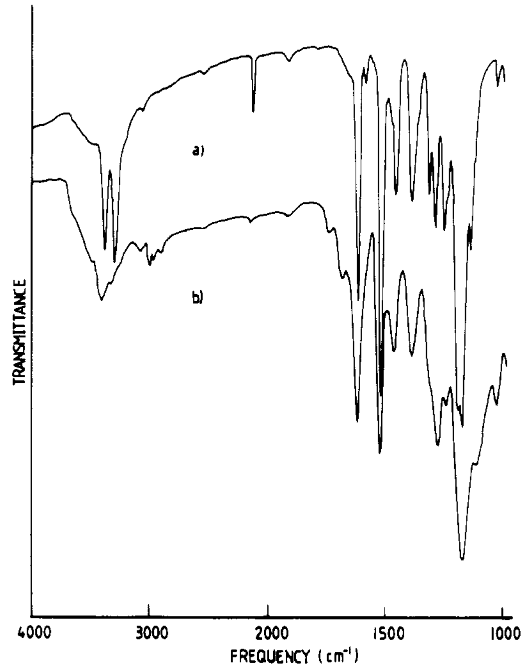


Figure 3. IR spectra of cyclotriphosphazene **3** (KBr pellet): (a) uncured and (b) cured at 220 °C under 10 000 lb/in^2 for 1 h.

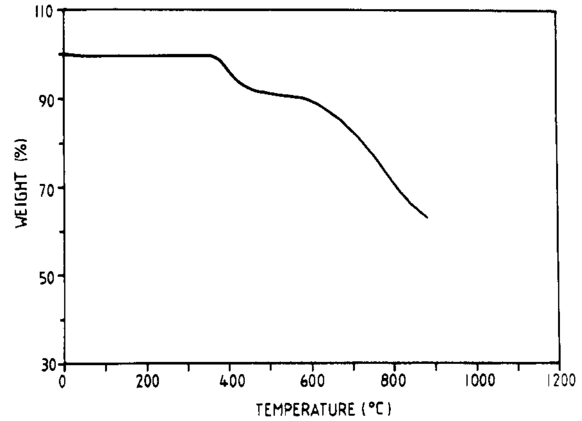
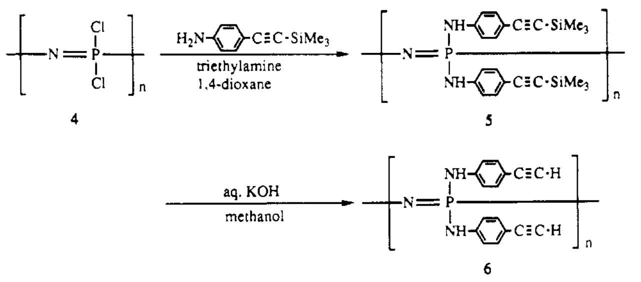


Figure 4. TGA thermogram of cured cyclotriphosphazene **3** obtained with a heating rate of 10 °C/min under nitrogen atmosphere.

After curing, the bands from the acetylenic groups almost disappeared and new bands near 2840–2960 cm^{-1} appeared. The thermal stability of the cured material was investigated by a thermogravimetric analysis. The result showed that the onset temperature of decomposition was 360 °C and the total weight loss at 600 °C was about 10% (Figure 4). The compound had char yields of 70% at 800 °C.

Poly(organophosphazene)s Containing Acetylenic Groups. The reaction of poly(dichlorophosphazene) with 4-[(trimethylsilyl)ethynyl]aniline was carried out in 1,4-dioxane (Schemes II and III). The resulting polymer **5** showed a broad peak centered at −3.0 ppm in the ^{31}P NMR spectrum. The cosubstituent polymers (**8a–c**) were prepared by sequential treatment of poly(dichlorophosphazene) with 4-[(trimethylsilyl)ethynyl]aniline and sodium trifluoroethoxide in tetrahydrofuran. In the ^{1}H NMR spectra, three peaks appeared at 0.2, 4.5, and 7.2 ppm, corresponding to trimethyl, methylene, and benzene ring protons, respectively. Contents of trifluoroethoxy groups were determined from the peak areas of benzene ring protons and methylene protons. ^{31}P NMR spectroscopy showed three peaks around −2.5 and −6.5 ppm for geminally substituted phosphorus nuclei and −4.6 ppm for mixed substituted phosphorus nuclei.

Scheme II



Scheme III

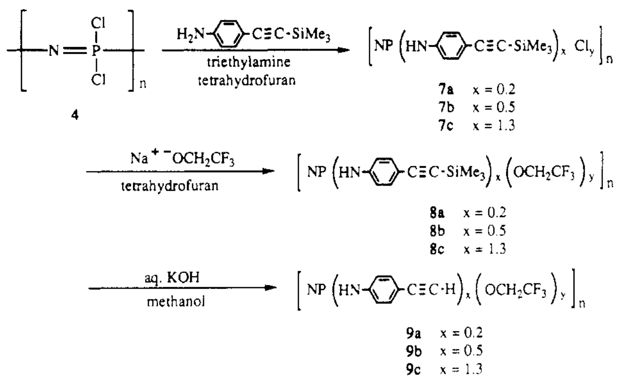


Table II
Poly(organophosphazene) Characterization Data

polymer	^{31}P NMR,[a] ppm	elemental analysis, %	M_w × 10^{-5}	M_n × 10^{-4}
5	-3.0	found: C, 61.96; H, 6.73; N, 9.31 calcd: C, 62.60; H, 6.71; N, 9.97	8.2	9.0
6	-3.0	found: C, 68.42; H, 4.52; N, 14.55 calcd: C, 69.30; H, 4.37; N, 15.16		
8a	-6.5, -3.0	found: C, 25.45; H, 2.54; N, 5.87 calcd: C, 26.70; H, 2.48; N, 6.44	13	11
8b	-6.5, -4.6, -2.0	found: C, 33.84; H, 3.71; N, 6.52 calcd: C, 35.40; H, 3.51; N, 7.30	12	16
8c	-7.0, -2.5	found: C, 51.10; H, 5.61; N, 8.05 calcd: C, 52.50; H, 5.51; N, 8.97	9.5	15
9a	-6.5, -3.0	found: C, 24.71; H, 2.03; N, 7.06 calcd: C, 25.34; H, 1.97; N, 6.82		
9b	-6.5, -4.6, -2.0	found: C, 31.95; H, 2.51; N, 7.83 calcd: C, 33.41; H, 2.41; N, 8.35		
9c	-7.0, -2.5	found: C, 51.87; H, 3.56; N, 11.92 calcd: C, 53.42; H, 3.50; N, 12.15		

[a] The ^{31}P NMR spectra were obtained in acetone-d_6.

Trimethylsilyl groups were removed by treating the polymers with a aqueous KOH solution in methanol. No decomposition was detected by ^{31}P NMR spectroscopy, which showed spectra similar to those of the protected polymers. In the ^{1}H NMR spectra, the peak for ethynyl protons appeared at 3.4 ppm (Figure 1b).

Cosubstituent polymers (**9a–c**) were soluble in various organic solvents including tetrahydrofuran, methanol, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. Polymer **6** dissolved in methanol, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. Characterization data for the polymers are summarized in Table II.

DSC thermograms of the polymers were obtained by scanning the sample twice from -50 to 350 °C with a heating rate of 10 °C/min under nitrogen atmosphere. Figure 5 shows the DSC thermogram of polymer **9b**. In the first scan, a small inflection and a strong exotherm appeared at 10 °C and around 230 °C due to glass transition and cross-linking reaction, respectively. No exotherm or distinct transition was observed in the second scan. The polymers exhibited no discernible glass transition as contents of 4-ethynylanilino groups increased. Cure onset temperatures in all of the polymers were near 180 °C. In cases of the polymers with high contents of acetylenic groups (**6** and **9c**), exotherms were still observed in the second scan.

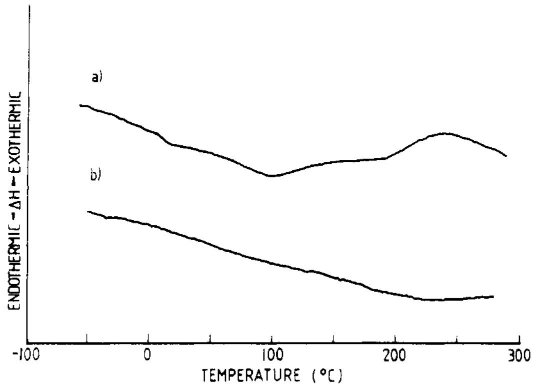


Figure 5. DSC thermograms of polymer **9b**: (a) first scan and (b) second scan, both with a heating rate of 10 °C/min under nitrogen atmosphere.

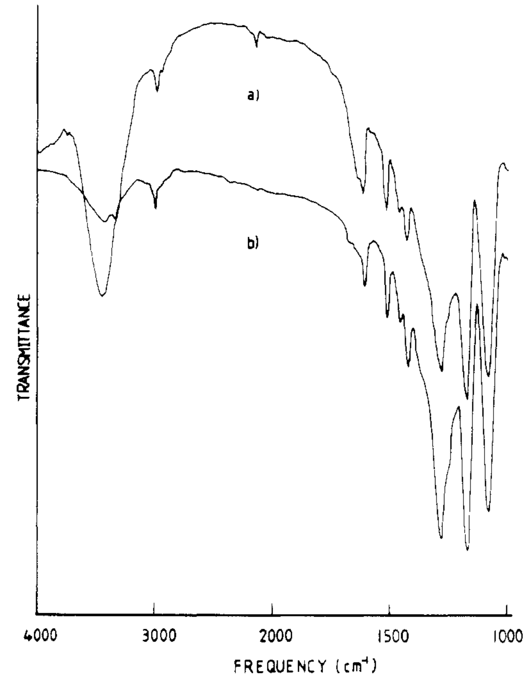


Figure 6. IR spectra of polymer **9b** (KBr pellet): (a) uncured and (b) cured at 180 °C under 10 000 lb/in^2 for 20 min.

Cross-linked polymer films were prepared by curing the polymers at 180 °C under a pressure of 10 000 lb/in^2 for 20 min. Figure 6 shows IR spectra of polymer **9b**. The bands at 3450, 3300, and 2060 cm^{-1} were interpreted as the stretching modes of N–H, C–H, and C–C triple bonds, respectively. The IR spectrum of the cured polymer did not show much difference from that of polymer **9b** except that the absorbances of the C–H band and of the C–C triple bond band decreased, which indicated intra- and intermolecular cross-linking reactions occurred only between acetylenic groups. The cured polymer films prepared from the polymers with low contents of acetylenic groups (**9a,b**) were pale brown and transparent, while the films from polymers **6** and **9c** were dark brown and brittle. All cured polymers were insoluble in organic solvents such as acetone, alcohols, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. Thermogravimetric analysis results showed that the onset of decomposition occurred in the cured polymers around 290 °C.

Experimental Section

Materials and Instrumentation. Hexachlorocyclotriphosphazene (Aldrich) was purified by fractional vacuum sublimation at 60 °C at 0.5 Torr. Reagent grade solvents were dried and purified as follows: Triethylamine was distilled over BaO. Tetrahydrofuran and 1,4-dioxane were distilled over sodium–potassium alloy. Toluene was distilled over CaH_2. All of the other reagents were purchased from Aldrich and were used without further purification. Poly(dichlorophosphazene) was prepared by the thermal polymerization of hexachlorocyclotriphosphazene at 250 °C. An average of 40–50% conversion to the linear polymer was obtained. Proton-decoupled ^{31}P NMR spectra were obtained with the use of a Bruker AM-300 spectrometer. Chemical shifts were reported in parts per million relative to 85% H_3PO_4 at 0 ppm. ^1H NMR spectra were recorded on a Bruker AM-300 or a JEOL PMX60 spectrometer. IR spectra were obtained with the use of a Bio-Rad Digilab Division FTS-80 spectrometer. Gel permeation chromatography was carried out with a Spectra-Physics SP8810 liquid chromatograph fitted with a SP8430 refractive index detector and a Doyosoda TSK gel column. Tetrahydrofuran was used as the eluent. Approximate calibration of the column was accomplished by means of a narrow molecular weight polystyrene standard obtained from Doyosoda. Thermal analyses were performed by a Du Pont 910 differential scanning calorimeter and a Du Pont 951 thermogravimetric analyzer fitted with a 9900 computer thermal analyzer. Elemental analyses were performed by a Carlo Erba 1108 or a Perkin-Elmer 240C elemental analyzer at Korea Research Institute of Chemical Technology and Korea Basic Research Center.

4-[(Trimethylsilyl)ethynyl]aniline.[27] To a solution of 4-iodoaniline (10 g, 45.7 mmol) in triethylamine (100 mL) and (trimethylsilyl)acetylene (7.7 mL, 54.5 mmol) under nitrogen were added dichlorobis(triphenylphosphine)palladium (1.3 g, 1.85 mmol) and copper iodide (0.2 g, 1.05 mmol). The reaction mixture was stirred at 0 °C for 2 h. After an additional 10 h of stirring at room temperature, the reaction mixture was concentrated to dryness by evaporation under reduced pressure. The crude product was isolated by sublimation (35–45 °C, 0.1 mmHg) and further purified by column chromatography on silica gel (ethyl acetate–hexane) to yield 4.95 g (57.3%), mp 99–101 °C (lit.[27] 95–96 °C).

Hexakis[4-[(trimethylsilyl)ethynyl]anilino]cyclotriphosphazene (2). To a solution of 4-[(trimethylsilyl)ethynyl]aniline (8.05 g, 42.6 mmol) and triethylamine (5 mL) in toluene (50 mL) was added dropwise a solution of hexachlorocyclotriphosphazene (1.23 g, 3.53 mmol) in toluene (20 mL). The solution was stirred at refluxing temperature for 3 days. The solvent was removed by evaporation under reduced pressure. The product was isolated by column chromatography on silica gel (30% ethyl acetate in hexane) and further purified by recrystallization from diethyl ether/*n*-hexane to yield 2.31 g (51.7%).

Elemental analysis, ^1H NMR, and ^{31}P NMR data are given in Table I.

Hexakis(4-ethynylanilino)cyclotriphosphazene (3). To a solution of compound **2** (0.68 g, 0.54 mmol) in 5% tetrahydrofuran in methanol (100 mL) was added 1 N aqueous KOH (3.2 mL). The solution was stirred at room temperature for 10 h. The solvent was removed by evaporation under reduced pressure. The product was isolated and purified by recrystallization twice from diethyl ether/*n*-hexane to yield 0.38 g (84.6%).

Elemental analysis, ^1H NMR, and ^{31}P NMR data are given in Table I.

$[NP(NHC_6H_4\text{-}p\text{-}C_2SiMe_3)_2]_n$ (5). To a solution of 4-[(trimethylsilyl)ethynyl]aniline (4.64 g, 24.6 mmol) and triethylamine (5 mL) in 1,4-dioxane (90 mL) was added a solution of poly(dichlorophosphazene) (0.71 g) in 1,4-dioxane (30 mL). The reaction mixture was stirred at refluxing temperature for 3 days. After concentration of the reaction mixture to 30 mL by evaporation under reduced pressure, the polymer was precipitated in hexane and further purified by precipitation from tetrahydrofuran into water and tetrahydrofuran into hexane to yield 1.52 g (58.9%).

^1H NMR (DMSO-d_6) δ 6.9–7.4 (8 H, C_6H_4), 3.5–4.1 (H_2O, N*H*), 0.2 (18 H, $SiCH_3$).

Elemental analysis, ^{31}P NMR, and molecular weight data are given in Table II.

Typical Procedure for Synthesis of Polymers 8a–c: Preparation of 8b. Poly(dichlorophosphazene) (1.5 g) dissolved in tetrahydrofuran (20 mL) was added slowly to a stirred solution of 4-[(trimethylsilyl)ethynyl]aniline (1.46 g, 7.71 mmol) and triethylamine (1.1 mL) in tetrahydrofuran (30 mL). The reaction mixture was stirred at refluxing temperature for 5 h and was then cooled to room temperature. To the mixture was added dropwise a solution of sodium trifluoroethoxide prepared from trifluoroethanol (36.1 mmol) and sodium hydride (36.0 mmol) in tetrahydrofuran (60 mL). The reaction mixture was stirred at refluxing temperature for 40 h. After concentration of the reaction mixture to 30 mL, the polymer was precipitated into hexane and further purified by precipitation from tetrahydrofuran into water to yield 2.25 g (60.0%).

^1H NMR (acetone-d_6) δ 7.0–7.6 (2 H, C_6H_4), 4.3–4.7 (3 H, CH_2CF_3), 3.0 (H_2O, N*H*), 0.2 (4.5 H, $SiCH_3$).

Elemental analysis, ^{31}P NMR, and molecular weight data are given in Table II.

Typical Procedure for Synthesis of Polymers 6 and 9a–c: Preparation of 9b. To a solution of polymer **8b** (0.2 g) in methanol (20 mL) was added 1 N aqueous KOH (0.9 mL). The solution was stirred at room temperature for 3 h. After removal of the solvent by evaporation under reduced pressure, the polymer residue was washed with water. The polymer was further purified by precipitation from methanol into water to yield 0.08 g (45.7%).

^1H NMR (acetone-d_6) δ 7.0–7.6 (2 H, C_6H_4), 4.2–4.8 (3 H, CH_2CF_3), 3.4 (0.5 H, C*H*), 3.0 (H_2O, N*H*).

Elemental analysis, ^{31}P NMR, and molecular weight data are given in Table II.

Curing of Compound 3 and the Polymers 6 and 9a–c. A Carver Laboratory press (Model 2518) was used. An appropriate amount of a polymer or compound **3** was placed between 1 cm × 1 cm pieces of polyimide film (Kapton H-type, 25 μm thick). Curing of compound **3** and a polymer was carried out at 220 °C under 10 000 lb/in^2 for 1 h and at 180 °C under 10 000 lb/in^2 for 20 min, respectively. The resulting film was removed from the polyimide film, washed with methanol and water, and dried under 1–2 mmHg at 100 °C for 12 h.

Acknowledgment. This work was supported by the Ministry of Science and Technology, Republic of Korea.

References and Notes

(1) Krishnamurthy, S. S.; Sau, A. C.; Woods, M. In *Advances in Inorganic Chemistry and Radiochemistry*; Academic Press: New York, 1978; Vol. 1, p 41.

(2) Allcock, H. R. *Polymer* **1980**, *21*, 673.

(3) Allcock, H. R. *Chem. Eng. News* **1985**, *63* (11), 22.

(4) Allcock, H. R. *CHEMTECH* **1975**, *5*, 552.

(5) Allcock, H. R.; Patterson, D. B.; Evans, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6095.

(6) Allcock, H. R.; Scopelianos, A. G. *Macromolecules* **1983**, *16*, 715.

(7) Allcock, H. R.; Chang, J. Y. *Macromolecules* **1991**, *24*, 993.

(8) Inoue, K.; Nitta, H.; Tanigaki, T. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 467.

(9) Inoue, K.; Nakamura, H.; Ariyoshi, S.; Takagi, M.; Tanigaki, T. *Macromolecules* **1989**, *22*, 4466.

(10) Inoue, K.; Nakano, M.; Takagi, M.; Tanigaki, T. *Macromolecules* **1989**, *22*, 1530.

(11) Inoue, K.; Takagi, M.; Nakano, M.; Nakamura, H.; Tanigaki, T. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 345.

(12) Yamamoto, T.; Takahashi, K.; Kon, Y.; Kobayashi, K. *Kobunshi Ronbunshu* **1989**, *46*, 177.

(13) Gleria, M.; Bolognesi, A.; Porzio, W.; Catellani, M.; Destri, S.; Audisio, G. *Macromolecules* **1987**, *20*, 469.

(14) Wisian-Neilson, P.; Schaefer, M. A. *Macromolecules* **1989**, *22*, 2003.

(15) Kumar, D.; Fohlen, G. M.; Parker, J. A. *Macromolecules* **1983**, *16*, 1250.

(16) Kumar, D.; Fohlen, G. M.; Parker, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 3155.

(17) Kumar, D.; Fohlen, G. M.; Parker, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1141.

(18) Muller, W. T.; Ringsdorf, H. *Macromolecules* **1990**, *23*, 2825.

(19) Nye, S. A. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 2633.

(20) Wei, Y.; Hariharan, R.; Ray, J. K. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 749.

(21) Abraham, T.; Soloski, E. J.; Benner, C. L. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 4305.

(22) Callstrom, M. R.; Neenan, T. X.; Whitesides, G. M. *Macromolecules* **1988**, *21*, 3528.

(23) Rutherford, D. R.; Stille, J. K. *Macromolecules* **1988**, *21*, 3530.

(24) Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M. *Macromolecules* **1988**, *21*, 3525.

(25) Takeichi, T.; Stille, J. K. *Macromolecules* **1986**, *19*, 2093.

(26) Hergenrother, P. M. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1985; Vol. 1, p 61.

(27) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

Registry No. **1**, 940-71-6; **2**, 139583-41-8; **3**, 139606-44-3; IC_6H_4-*p*-NH_2, 540-37-4; TMSC≡CH, 1066-54-2; TMSC≡CC_6H_4-*p*-NH_2, 75867-39-9.