Macromolecules **1996,** *29,* 5511−5512

Synthesis and Characterization of a Poly(phospholenazene), a New Phosphazene Polymer

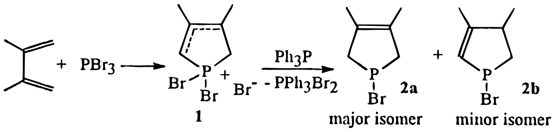
Jeffrey A. Gruneich and Patty Wisian-Neilson*

Department of Chemistry, Southern Methodist University, Dallas, Texas 75275-0314

Received April 12, 1996
Revised Manuscript Received May 17, 1996

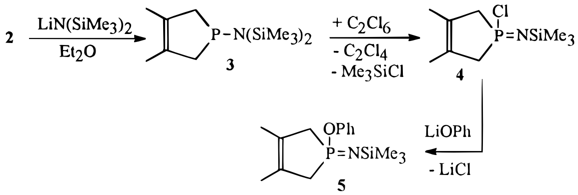
Introduction. Although several hundred poly(phosphazenes), $[RR'PN]_n$, with a variety of substituents R and R′ have been prepared,[1−3] non-cross-linked poly(phosphazenes) in which the backbone phosphorus atom and its two substituents are part of a ring system have not been reported to date. This may be explained by the fact that the well-studied substitution reactions of poly(dichlorophosphazene) ($(Cl_2PN)_n$) and difunctional reagents generally produce insoluble cross-linked materials. Ring-opening polymerization of spirocyclic phosphazenes is also not a feasible route to such polymers because non-halogen-substituted cyclic phosphazenes do not readily polymerize.[4] This paper describes how condensation polymerization is used to synthesize a novel poly(phospholenazene), a phosphazene polymer in which the backbone phosphorus is part of an unsaturated, heterocyclic hydrocarbon ring.

Results and Discussion. The preparation of poly(phosphazenes) by condensation polymerization of *N*-silylphosphoranimines provides direct access to polymers with P−C-bonded substituents,[2,5,6] thus avoiding the complications associated with reactions on preformed polymers such as poly(dichlorophosphazene).[7] Simple alkyl and aryl groups are readily incorporated into the P−N system in the first step of the preparation of the polymer precursors. This is a straightforward process involving the preparation of acyclic (silylamino)phosphines, $(Me_3Si)_2NPRR'$, by the sequential addition of $LiN(SiMe_3)_2$ and Grignard reagents to either PCl_3 or $PhPCl_2$.[8] However, because the analogous reaction with a di-Grignard reagent, $BrMg(CH_2)_4MgBr$, failed to give good yields of a cyclic phosphine, we chose to use the McCormack reaction to prepare an unsaturated cyclic *P*-bromophosphine (phospholene) (**2**) (eq 1).[9] Cycloaddition of a diene and PBr_3, followed by dehalogenation with Ph_3P yielded the isomers **2a** and **2b** in ca. 9:1 ratio. Although the reactions of both PCl_3 and PBr_3 were investigated, the reaction with PBr_3 was ca. 5 times faster[10] and gave higher yields of the symmetric isomer **2a**.[9b]



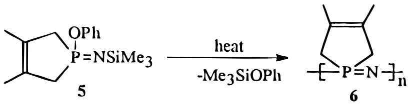
(1)

The bromophospholene **2a** (with only trace quantities of **2b** after distillation) was then sequentially treated with $LiN(SiMe_3)_2$, C_2Cl_6, and LiOPh in diethyl ether to produce the new cyclic (silylamino)phospholene **3** and *N*-silylphosphoranimines **4** and **5**, respectively (eq 2). This sequence is analogous to that used to prepare phosphoranimine precursors to poly(alkyl/arylphosphazenes).[5,6,11] The overall yield of **5** starting from phospholene **2a** was ca. 40%. Both **3** and **5** were isolated and characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy (see Experimental Section). Multiple distillations were used to separate the 2,3 and the 3,4 ring isomers of **5** (analogs to **2a** and **2b**) and afforded a pure sample of the 3,4 isomer as determined by ^{31}P and ^1H NMR spectroscopy.



(2)

Heating compound **5** in a sealed glass ampule at 190 °C for 10−14 days resulted in elimination of Me_3SiOPh and formation of the new polymer **6** (eq 3). Upon removal of Me_3SiOPh, the new polymer **6** was isolated as an off-white solid that was soluble in chlorinated hydrocarbons, but insoluble in hexane, ether, or THF. Brittle, translucent films are formed by solvent casting from CH_2Cl_2. By DSC, a glass transition and a melting transition were observed at 28 and 176 °C, respectively. The thermal and solubility properties of the new polymer are similar to those of symmetrically substituted, acyclic, semicrystalline poly(dialkylphosphazenes) such as $[Me_2PN]_n$.[5] The onset of decomposition in air was observed to be at ca. 180 °C by TGA.



(3)

The new polymer was also characterized by NMR spectroscopy and elemental analysis (see Experimental Section). The ^{31}P NMR spectra contained a major signal at δ 24, which is upfield from its monomer **5** (δ 42) by roughly the same amount as other poly(alkylphosphazene)/monomer systems.[5,12] A second, smaller signal (ca. 10%) was observed at δ 30, which is assigned to the 1,2 isomer. This difference in the ^{31}P NMR signals is consistent with those of the two isomers of precursors **2** and **5**. Moreover, the intensities of the ^1H NMR signals for the second isomer are consistent with the ^{31}P NMR data. Thus it appears that small amounts of the 3,4 isomer were converted to the 2,3 isomer during the thermolysis of **5**.

GPC of polymer **6** was first done in $CHCl_3$, giving a rough estimate of M_w to be ca. 50 000 by comparison to samples of $[Me(Ph)PN]_n$ with known molecular weights. Molecular weights determined in THF using polystyrene standards[5] were similar ($M_w = 44\,000$; $M_w/M_n = 3.25$). After extensive handling in air, the solubility of **6** decreased, presumably due to reactions at the unsaturated sites in the ring.

In summary, this method affords a new type of poly(phosphazene) in which the phosphorus atom is part of a five-membered ring. Related polymers should be accessible by using other dienes and via reactions of the C=C bond.

Experimental Section. Materials and General Comments. All reactions were performed under at atmosphere of dry nitrogen and all reagents were obtained from commercial sources and used without further purification. Diethyl ether, hexanes, and pentane were distilled from calcium hydride.

NMR spectra were obtained on either a IBM/Bruker WP 200 SY FT NMR or a 400 MHz Bruker AVANCE DRX multinuclear NMR spectrometer. Elemental analyses, thermal analyses, and gel permeation chromatography (GPC) measurements were performed as described elsewhere[13] with only the following modification of sample preparation for GPC. Due to the insolubility in THF, 0.1 g of polymer **6** was dissolved in 1 mL of $CHCl_3$. Then 0.1 mL of this solution was added to 1.0 mL of THF and 0.1 mL was used for GPC injection.

Preparation of 2. A 5 L, three-necked flask equipped with a nitrogen inlet, a magnetic stirrer, and a rubber septum was charged with Et_2O (500 mL), PBr_3 (0.778 mol, 73.1 mL), and 2,3-dimethyl-1,3-butadiene (0.778 mol, 88.0 mL). The mixture was stirred for 5 days, and solvent and excess reagents were removed under vacuum to yield phosphonium salt **1** as a white powder. Yield: ca. 97%.

To the same flask, pentane (300 mL) and CH_2Cl_2 (500 mL) were added and the resulting suspension of **1** was cooled to −78 °C. Then Ph_3P (0.625 mol) dissolved in 500 mL of CH_2Cl_2 was added via an addition funnel. This mixture was stirred until it reached room temperature, and pentane (500 mL) was added to precipitate PPh_3Br_2. After stirring for 2 h, the mixture was allowed to stand overnight. The clear solution was separated from the PPh_3Br_2 salts by cannulation through a filter and the salts were washed with hexanes (3 × 100 mL). Solvent was removed from the combined washings and filtrate under reduced pressure. Distillation afforded **2** as a clear, light yellow liquid that fumed in air: bp 100−103 °C/27 mmHg; yield 0.421 mol, 67.3% (ca. 10% **2b**); ^{31}P NMR δ 103 (**2a**), 114 (**2b**); ^1H NMR: **2a**, δ 1.69 (CH_3), 2.95 (PCH_2, J_{PH} = 19.5 Hz); **2b**, δ 1.19, 1.93 (CH_3), 3.01 (PCH_2, J_{PH} = 19.8 Hz), 6.08 (PCH, J_{PH} = 46.4 Hz).

Preparation of 3. Using a variation of the literature methods,[9] a 5 L, three-necked flask equipped with an addition funnel, a mechanical stirrer, and a nitrogen inlet was charged with Et_2O (500 mL) and $(Me_3Si)_2NH$ (109.5 mL, 0.519 mol). The solution was cooled to 0 °C and 207.6 mL of *n*-BuLi (2.5 M in hexane, 0.519 mol) was added dropwise (ca. 30 min). The mixture was warmed to room temperature, stirred for 1 h, and then cooled to −78 °C. Compound **2a** (100.1 g, 0.519 mol) was added dropwise via syringe over ca. 1 h. As the mixture warmed to room temperature, the color changed from off-white to red to dark brown. Compound **3** was isolated by removal of salts by filtration, solvent removal under reduced pressure, and vacuum distillation: bp 65−67 °C/0.15 mmHg; yield 45%; ^{31}P NMR δ 36 (**3a**), 55 (**3b**); ^1H NMR: **3a**, δ 0.15 ($SiMe_3$), 1.59 (CH_3), 2.47 (PCH_2); **3b**, δ 0.15 (Me_3Si), 1.12, 1.73 (CH_3), 2.47 (PCH_2, m), 5.77 (PCH, J_{PH} = 35.7 Hz).

Preparation of 5. Although pure **3** could be isolated and used in the following sequence, the simplest method involved using the reaction mixture obtained as described above prior to removal of the salts. This mixture was cooled to 0 °C and hexachloroethane (117 g) in Et_2O (600 mL) was added over ca. 1 h to afford the *P*-chlorophosphoranimine **4**. Meanwhile LiOPh was prepared in a separate flask by treating 46.65 g of PhOH in 600 mL of ether with BuLi (198.2 mL, 2.5 M) at 0 °C, followed by stirring at room temperature for 1 h. Then the LiOPh was added slowly (ca. 1 h) to the mixture of **4** that had been cooled to 0 °C. After stirring overnight, ca. 2 L of solvent was removed, and the mixture was filtered. The salts were washed with hexanes (3 × 150 mL), solvent was removed under reduced pressure, and the residue was distilled under vacuum to give **5**. The first distillation yielded a significant amount of Me_3SiOPh at 26−33 °C/1.0 mmHg and **5** at 103−120 °C/1.0 mmHg. Subsequent distillation gave 62.0 g of **5a** (0.212 mol, 41% based on **2**): bp 116−120 °C/1.00 mmHg; ^{31}P NMR δ 42; ^1H NMR δ −0.06 ($SiMe_3$), 1.68 (CH_3), 2.55 (PCH_2), 7.0−7.3 (OPh); ^{13}C NMR δ 3.1 (Me_3Si), 16.5 (CCH_3, J_{PC} = 15.0 Hz), 40.0 (PCH_2, J_{PC} = 90.2 Hz), 129.4 (C═C), 151.8, 120.1−127.8 (Ph).

Preparation of 6. The *P*-phenoxyphosphoranimine **5** (0.141 mol) was distilled into a glass ampule and degassed. The ampule was sealed and then heated for 14 days at 190 °C to yield polymer **6**. Workup consisted of removal of Me_3SiOPh by decantation, dissolution of **6** in CH_2Cl_2, and precipitation into Et_2O. The polymer was collected by filtration, washed with 500 mL of ether, and dried under vacuum at room temperature. Yield 90%; ^{31}P NMR δ 24, 30 (ca. 10%); ^1H NMR: major isomer, δ 1.60 (CH_3), 2.40 (PCH_2, J_{PH} = 9.5 Hz); minor isomer, δ 1.06 ($CHCH_3$, J_{PH} = 7.0 Hz), 1.2−1.4 (CH, m), 1.75 (═CCH_3), 2.62 (PCH_2, m), 5.64 (═CH, J_{PH} = 22.3 Hz); ^{13}C NMR δ 16.5 (CH_3, J_{PC} = 13.7 Hz), 42.3 (PCH_2, J_{PC} = 88.7 Hz), 127.4 (C═C, J_{PC} = 8.0 Hz). Anal. Calcd for $C_6H_{10}PN$: C, 56.69; H, 7.93; N, 11.02. Found: C, 56.77; H, 8.02; N, 11.07. T_g = 28 °C, T_m = 176 °C, T_{onset} = 180 °C, M_w = 44 000, M_n = 14 000, M_w/M_n = 3.25.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support of this project and the Polymers Division of the American Chemical Society for a POLYED Undergraduate Summer Scholarship for J.A.G.

References and Notes

(1) (a) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice-Hall: Englewood Cliffs, NJ, 1992; Chapter 3.

(2) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.

(3) Wisian-Neilson, P. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: Chichester, England, 1994; Vol. 7, p 3371.

(4) When cyclotriphosphazenes, 1,1-[$(RX_2)(CF_3CH_2O)_4P_3N_3$] (where RX_2 = 2,2′-dioxybiphenyl, 1,8-dioxynaphthyl, and 1,8-diaminonaphthyl), were heated to 200 °C in the presence of 1% $(NPCl_2)_n$, small amounts of low molecular weight poly(phosphazenes) were detected. Allcock, H. R.; Turner, M. L. *Macromolecules* **1993**, *26*, 3.

(5) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K. *Macromolecules* **1987**, *20*, 910.

(6) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Synth.* **1989**, *25*, 69.

(7) Allcock, H. R.; Evans, T. L.; Patterson, D. B. *Macromolecules* **1980**, *13*, 201.

(8) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1982**, *21*, 3568.

(9) (a) McCormack, W. B. U.S. Patent 2 663 736, 1953. (b) Myers, D. K.; Quin, L. D. *J. Org. Chem.* **1971**, *30*, 1285.

(10) Hasserodt, U.; Hunger, K.; Korte, F. *Tetrahedron* **1963**, *19*, 1563.

(11) Neilson, R. H. *ACS Symp. Ser.* **1994**, *572*, 232.

(12) Jinkerson, D. L. Ph.D. Thesis, Texas Christian University, August 1989.

(13) Wisian-Neilson, P.; Bailey, L.; Bahadur, M. *Macromolecules* **1994**, *27*, 7713.

MA960546Z