(9-31), -20.4 (44-59), -48.9 (3-12), and -79.6 (0-5%) ppm. The areas were in the range -19.5 (20-26), -47.5 (33-44), and 79.3 (36-41%) ppm for the copolymer derived from $(NPCl_2)_3$ and $(NPBr_2)_3$.

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(23) As discussed previously, the conversion of $N_3P_3Cl_4BrMe$ to its high polymer is also accompanied by halogen migration from one repeating unit to another. New cyclic, trimeric phosphazenes were also formed by halogen scrambling processes and were identified by ^{31}P NMR spectroscopy, gas chromatography, and mass-spectrometric techniques (chemical ionization). In a typical experiment, $N_3P_3Cl_5Me$ (32%, P + 1 at *m/e* 326), *gem*-Me-Br-$N_3P_3Cl_4$ (34%, P + 1 at *m/e* 370), *non-gem*-Me-Br-$N_3P_3Cl_4$ (4%, P + 1 at *m/e* 370), *non-gem*-$N_3P_3Cl_3Br_2Me$ (22%, P + 1 at *m/e* 414), and $N_3P_3Cl_2Br_3Me$ (7%, P + 1 at *m/e* 458) were identified as cyclic products. The latter two products are methyl-substituted analogues of **18** and **19**, **20**. The formation of *non-gem*-Me-Br-$N_3P_3Cl_4$ was unexpected, and was not observed for the phenyl analogue.

(24) Because the conversion to polymer was so high (see Experimental Section), typically only 100-200 mg of cyclic phosphazenes were recovered. While ^{31}P NMR spectroscopy was useful to identify qualitatively the presence of P(Ph)Cl, PCl_2, and PClBr resonances, gas chromatography was a more accurate method to determine the relative proportions of **5a**, **5b**, **18**, and **19** in the product mixtures. Unless noted otherwise, the product ratios were from gas-chromatographic analyses.

(25) At this stage in the reaction, the ratio of cyclic species was very similar to that obtained by heating **5b** at 178 °C for 72 h.

(26) The small amount of scrambling and low yield of polymer after 2 h was not surprising, as studies with melting point standards indicated that 1.5 h was required, on the average, for the contents of the polymer tubes to reach 250 °C.

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(31) Failure to dry the bromine adequately results in a polymerization rate *increase*, but this effect can be attributed to the catalytic influence of water.[21]

(32) Polymerization of $(NPCl_2)_3$ in the presence of Br_2 brought about a curious change in the physical properties of the $(NPCl_2)_n$ high polymer, changes that could be attributed to a decrease in crystallinity. However, after treatment of the $(NPCl_2)_n$ with sodium trifluoroethoxide, the resultant $[NP(OCH_2CF_3)_2]_n$ was identical in molecular weight and appearance with that derived from pure $(NPCl_2)_3$. The lower yield of the resultant $[NP(OCH_2CF_3)_2]_n$, relative to the control, could indicate that a significant amount of lower molecular weight species was also formed.

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Ring-Opening Polymerization of Metallocene Cyclophosphazene Derivatives

Harry R. Allcock,* Karen D. Lavin, and Geoffrey H. Riding

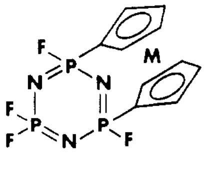
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received June 14, 1984

ABSTRACT: New and unusual metallocenylphosphazene high polymers have been prepared by the thermal ring-opening polymerization of metallocene-substituted cyclotriphosphazene derivatives. The transannular-linked cyclic trimers $[N_3P_3F_4(\eta\text{-}C_5H_4)_2M]$ (**1a**, M = Fe; **1b**, M = Ru) and the monosubstituted compounds $[N_3P_3F_5(\eta\text{-}C_5H_4)M(\eta\text{-}C_5H_5)]$ (**2a**, **2b**) serve both as reaction model compounds and as "monomers" for the analogous high polymeric derivatives **3a**, **3b**, and **8a**, **8b**. The hydrolytically unstable P-F bonds in the trimers and high polymers were replaced by treatment with sodium trifluoroethoxide to yield the corresponding air-stable trimeric and polymeric metallocenyl(trifluoroethoxy)phosphazenes (**4a**, **4b**, **9a**, **9b**). Compounds **1a** and **1b** were also copolymerized to yield a 1:1 copolymer which, after reaction with sodium trifluoroethoxide, yielded $[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe\text{-}N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Ru]_n$ (**7**). The properties, structure, and characterization of these new organometallic polyphosphazenes are discussed, together with the mechanism of thermal polymerization of cyclic phosphazenes.

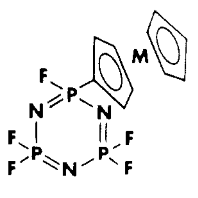
Introduction

The study of the iron group metallocenes has been one of the most active areas of chemistry since the discovery of ferrocene in 1951.[1] At the present time, considerable interest exists in the synthesis of metallocenes that are linked to macromolecules. Such polymers are important as prospective catalyst systems, electrode mediators, or electroactive solid-state materials.

In recent months, we have reported a number of different methods for the linkage of organometallic units to small molecule phosphazene rings.[2-9] These reactions have been developed as prototypes for the corresponding reactions of linear phosphazene high polymers. As part of that program, we reported recently the synthesis of the first cyclophosphazenes that bear metallocene side groups.[10,11] Two of these species are shown in structures **1** and **2**.



1a,b



2a,b

a, M = Fe; b, M = Ru

The availability of species **1** and **2** provides two potential routes for the synthesis of the corresponding linear high polymers. First, the high polymeric analogues of **1** and **2** might be prepared by the reactions of poly(difluorophosphazene), $(NPF_2)_n$, with mono- or dilithiometallocenes. This possibility is under investigation in our laboratory. Alternatively, **1** and **2** might be used as "monomers" for direct phosphazene ring-opening polymerization to the corresponding linear high polymers. Such a reaction would be analogous to the known polymerization

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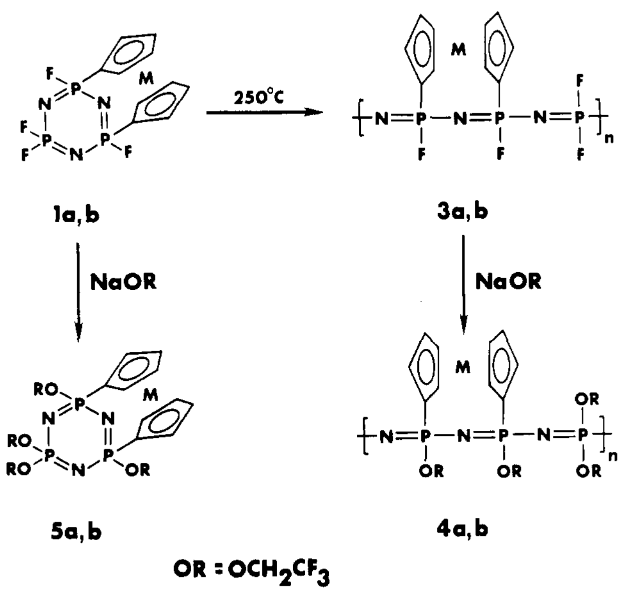
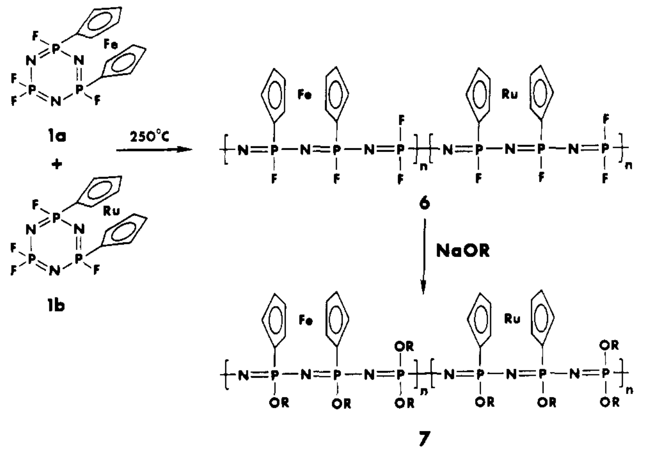
Scheme I



Scheme II



of $(NPF_2)_3$ to $(NPF_2)_n$. In this paper we describe our exploration of this possibility.

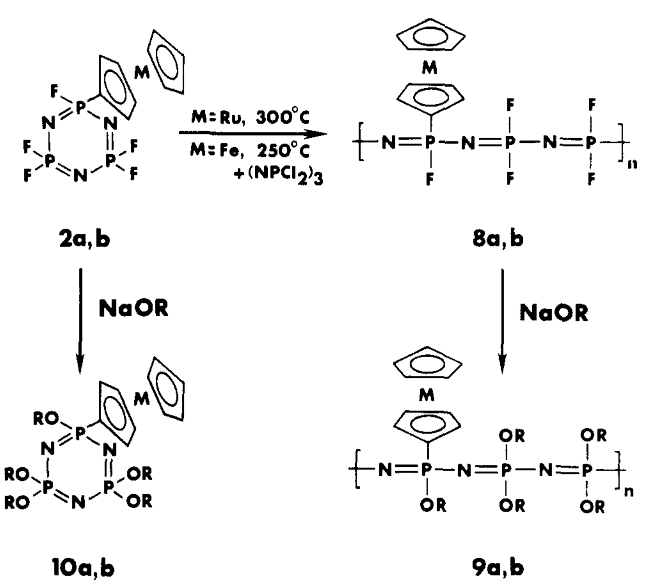
The objectives of this present work were to determine (1) whether compounds of type 1 or 2 would undergo a thermally induced ring-opening polymerization, (2) what influence, if any, the ring strain inherent in 1 might have on the polymerization process, and (3) the effect of the metallocene unit on the physical properties of the resultant polyphosphazenes.

Results and Discussion

The transannular metallocenylphosphazenes **1a** and **1b** polymerize to high molecular weight, open-chain macromolecules of type **3a** and **3b** when heated in the molten state at 250 °C. Because phosphorus–fluorine bonds are sensitive to hydrolysis, they were replaced by treatment of **3a** or **3b** with sodium trifluoroethoxide. The resultant hydrolytically stable polymers, **4a** and **4b**, are soluble in organic solvents such as tetrahydrofuran or acetone, a property that is consistent with an open-chain, un-cross-linked structure. These transformations, together with the small molecule model substitution process, are illustrated in Scheme I.

It was also found that **1a** and **1b** copolymerized when heated together in the molten state at 250 °C. The high polymer formed by this process (**6**) reacted with sodium trifluoroethoxide to yield the hydrolytically stable derivative **7** (Scheme II). This polymer was soluble in organic media. It was shown by ultraviolet–visible spectroscopy that equimolar amounts of **1a** and **1b** had been incorporated into the copolymer. This conclusion was confirmed by elemental microanalyses (see Experimental Section). Of special interest is the fact that **1a** and **1b** can be polymerized at 250 °C. The unsubstituted trimer, $(NPF_2)_3$, requires temperatures in the 350 °C region before polymerization will take place.

Scheme III



The monosubstituted ruthenocenylphosphazene, **2b**, polymerized to high polymer **8b** in the molten state at 300 °C (Scheme III). Replacement of the fluorine atoms by trifluoroethoxy groups was accomplished to give **9b**. This polymer was soluble in organic media.

However, all attempts to polymerize species **2a** by itself failed. At 300 °C, the trimer decomposed to give an insoluble solid and hydrogen fluoride. At 250 °C, the compound remained unchanged even after 17 days at this temperature. However, polymerization of **2a** was induced at 250 °C by the addition of 0.1 mol % of $(NPCl_2)_3$ to yield the open-chain macromolecule, **8a**. Treatment with sodium trifluoroethoxide yielded **9a**, a stable, soluble macromolecule. As shown in Scheme II, the fluorine replacement reactions were monitored first at the small molecule level to give **10a** and **10b**.

Structure Determination

The basic structures of polymers **3**, **4**, and **7–9** were determined by a combination of NMR and infrared spectroscopy and by elemental analyses. The molecular weights were estimated by gel permeation chromatography. Because polyphosphazenes **3** and **8** are sensitive to moisture, most of the macromolecular characterization was carried out with hydrolytically stable trifluoroethoxy derivatives **4** and **9**. The elemental analysis data for **4** and **9** (see Experimental Section) were compatible with one metallocene unit for every three P=N units. Hence, the ratio of repeating units in the trimer was retained in the polymer.

The ^1H decoupled ^{31}P NMR spectrum of **3a** consisted of a doublet of doublets at 11.2 (J_{PF_1} = 920 Hz) ppm which was assigned to the phosphorus atoms that bear the cyclopentadienyl units, and a triplet of triplets at −25.8 (J_{PF_2} = 890 Hz) ppm which was attributed to the PF_2 units. A ^{19}F NMR spectrum of **3a** consisted of two doublets at 76.4 (J_{PF_1} = 910 Hz) and 59.7 (J_{PF_2} = 870 Hz) ppm which were

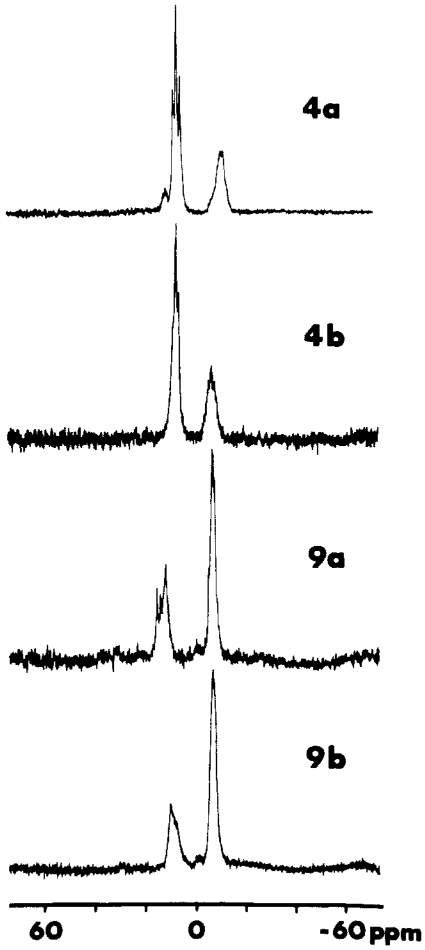


Figure 1. ^{31}P NMR spectra (^1H decoupled) of 4 and 9.

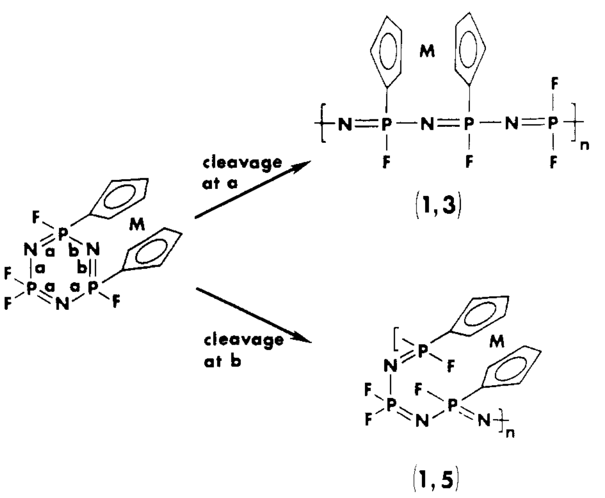
assigned to the fluorine atoms attached to the phosphorus-bound cyclopentadienyl units and to the PF_2 units, respectively. ^{31}P and ^{19}F NMR spectra of **3a** are provided as supplementary material (see paragraph at end of text regarding supplementary material).

The ^1H decoupled ^{31}P NMR spectra of **4a** and **4b** (Figure 1) consisted of two complex resonances at 8.3 and −11.8 ppm for **4a** and at 7.4 and −10.0 ppm for **4b**. Those peaks at −11.8 and −10.0 ppm were assigned to $P(OCH_2CF_3)_2$ units by comparison with the similar value (−7.0 ppm) found in the homopolymer, $[NP(OCH_2CF_3)_2]_n$. Thus, peaks at 8.3 and 7.4 ppm were assigned to the metallocenyl-P-OCH_2CF_3 units. The peak areas were in a ratio of 1:2 for the $P(OR)_2$:P(Cp)OR groups. The ^1H NMR spectra of **4a** and **4b** consisted of two overlapping resonances at 4.5 ppm and two broad multiplets centered at 4.9 and 4.5 ppm, which were assigned to overlapping resonances for the cyclopentadienyl and trifluoroethoxy protons, respectively.

The ^1H decoupled ^{31}P NMR spectra of **9a** and **9b** (Figure 1) consisted of two complex resonances at 13.2 and −8.9 ppm for **9a** and at 10.5 and −8.8 ppm for **9b**. Those peaks at −8.9 and −8.8 ppm were assigned, as described above, to the $P(OCH_2CF_3)_2$ units, and the peaks at 13.2 and 10.5 ppm were attributed to the metallocenyl–P–OCH_2CF_3 units. The peak areas were in a ratio of 2:1 for $P(OR)_2$:P(Cp)OR groups. The ^1H NMR spectrum of **9b** contained two broad peaks centered at 4.6 and 4.5 ppm of equal intensity, which corresponded to the cyclopentadienyl and trifluoroethoxy protons, respectively.

The ^1H decoupled ^{31}P NMR spectrum of **7** comprised two complex resonances at 8.4 and −8.5 ppm. The peak at −8.5 ppm was assigned, as described above, to the $P(OCH_2CF_3)_2$ units, and the peak at 8.4 ppm to the metallocenyl–P–OCH_2CF_3 units. The peak areas were in a ratio of 1:2 for $P(OR)_2$:P(Cp)OR groups. The ^1H NMR spectrum of **7** contained two broad resonances centered at 4.8 and 4.5 ppm, which corresponds to the cyclopentadienyl and trifluoroethoxy protons, respectively.

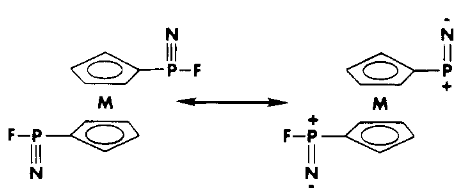
Scheme IV



The GPC molecular weights of **4a** and **4b** were higher than 2 × 10^6 (**4a** yielded a partly bimodal distribution with a second maximum above molecular weight 1 × 10^6). The intrinsic viscosity of **4a** in acetone at 25 °C was found to be 1.2 dL/g. This viscosity is similar to values reported earlier [12] for other high molecular weight fluoroalkoxyphosphazene copolymers. The GPC molecular weight of **9a** was distinctly bimodal in distribution, with maxima at values higher than 1 × 10^5 and above 2 × 10^6. The molecular weights of **9b** and **7** were higher than 2 × 10^6.

Mechanism of Polymerization

First, the isolation of high molecular weight un-cross-linked linear polyphosphazenes from the transannular-linked trimers **1a** and **1b** is strong evidence that the mechanism of polymerization involves a "ring-opening" reaction of the trimeric ring by a single cleavage of the cyclotriphosphazene ring. An alternative mechanism involving deoligomerization of the trimeric ring and the formation of highly reactive "phosphazene monomers" would, for compounds **1a** and **1b**, lead to the formation of intermediates **11** or **12**. The experimental evidence is



11 12

not compatible with a mechanism of this type. Intermediates, such as **11** or **12**, would generate cross-links. Moreover, the ratios of the side groups in the trimer persist in the high polymers. This is incompatible with a mechanism that involves monomer formation.

Second, the site of cleavage within the trimeric ring has an important influence on the structure of the metallocene polymers **3** and **4**. This is illustrated in Scheme IV. Cleavage of bonds a would generate a polymer containing a 1,3 bridged structure. Cleavage of bonds b would give rise to a polymer containing a 1,5 structure. The spectroscopic evidence is consistent with a 1,3 structure. A ^{19}F

NMR spectrum of the polymer contained two doublets. This is consistent with a linear macromolecular structure. For the 1,5 structure, three sets of resonances would be expected as a consequence of the inequivalence of the two fluorine atoms of the PF_2 unit. In addition, the $P(OCH_2CF_3)_2$ groups in **4a** and **4b** have ^{31}P NMR chemical shifts similar to those found in $[NP(OCH_2CF_3)_2]_n$.[12] If the polymer possessed a 1,5 structure, the ^{31}P NMR chemical shifts for the $P(OCH_2CF_3)_2$ units should be closer to that found in $[N_3P_3(OCH_2CF_3)_6]$.

Third, it was found that the transannular-linked metallocenylphosphazenes polymerized readily at 250 °C. This temperature is considerably lower than that required to induce the polymerization of other fluorophosphazenes (e.g., 350 °C for $N_3P_3F_6$ and 300 °C for $N_3P_3F_5Ph$). An explanation for this lowering of polymerization temperature is that ring opening reduces the steric strain imposed by the bridging substituent on the phosphazene ring. The presence of ring strain in these transannular-linked phosphazenes was indicated by an X-ray diffraction study of **1b**.[10]

The *difference* in the "span" of the ruthenium and iron metallocenes should generate different degrees of ring strain in the two phosphazene trimers **1a** and **1b**. This differing ring strain might be expected to give rise to different monomer reactivities. However, as discussed, a low-yield copolymerization of equimolar quantities of **1a** and **1b** generated **7**, a 1:1 copolymer.

The difference in the polymerization behavior of the monosubstituted **2a** and **2b** is probably a result of the lower thermal stability of the ferrocenyl derivative **2a** compared to the ruthenium analogue **2b**. This view is supported by the influence of ferrocene and ruthenocene on the polymerization of $N_3P_3F_5(C_6H_5)$. As reported previously, $N_3P_3F_5(C_6H_5)$ polymerizes thermally at 300 °C during a 24–48-h period to give the high polymer $[N_3P_3F_5(C_6H_5)]_n$. This polymerization reaction was unaffected by the addition of ruthenocene (18 mol %). The ruthenocene was recovered unchanged after the polymerization was complete. However, the presence of ferrocene (18 mol %) generated an insoluble, brown, brittle solid on prolonged heating in a manner reminiscent of the behavior of **2a** at 300 °C. Compound **2a** polymerized thermally at lower temperatures only when the polymerization was initiated by a small quantity of $(NPCl_2)_3$. This previously unobserved catalysis of the thermal polymerization of a *fluoro*phosphazene by hexa*chloro*cyclotriphosphazene was also demonstrated in the polymerization of $N_3P_3F_5(C_6H_5)$. The addition of 1 mol % $(NPCl_2)_3$ to $N_3P_3F_5(C_6H_5)$ reduced the polymerization time at 290 °C from 24–48 to 6 h, while the addition of 10 mol % $(NPCl_2)_3$ reduced the polymerization time to less than 20 min. In all cases, the $(NPCl_2)_3$ appeared to become incorporated into the polymeric chain. These results are consistent with a polymerization mechanism that involves a thermal ionization of halogen from phosphorus during the initiation process.[12]

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (Ethyl Corp.), was purified by recrystallization and by sublimation. $(NPF_2)_3$ and $N_3P_3F_5(C_6H_5)$ were prepared by literature procedures.[14,15] Chloromercuriferrocene and ruthenocene were also prepared by literature procedures.[16,17] Ferrocene (Strem), $RuCl_3^{III}\cdot 3H_2O$ (Strem), zinc dust (Aldrich), *n*-butyllithium (Aldrich) (1.6 M solution in hexane), and sodium spheres (Aldrich) were used as received. Trifluoroethanol (Halocarbon Products Corp.) was dried over 4-Å molecular sieves before use. Tetrahydrofuran (THF) (MCB reagent), diethyl ether (Fisher), and hexane (Fisher) were dried and distilled from sodium benzophenone ketyl. All reactions were performed under an atmosphere of dry nitrogen by using standard airlessware, or an inert atmosphere glovebox (Vacuum Atmospheres). All the metallocene monomers were purified by two recrystallizations (dichloromethane/hexane solution), followed by four high-vacuum sublimations at 50 °C and 1×10^{-4} torr before polymerization.

Equipment. ^1H, ^{31}P, ^{13}C, and ^{19}F NMR spectra were recorded on Varian EM 360 and CFT-20 NMR, JEOL PS-100 FT NMR, and Bruker WP-200 and WH-360-MHz FT NMR spectrometers. The ^{31}P shifts are relative to aqueous 85% H_3PO_4, with positive shifts downfield from this reference.[18] The ^1H NMR and ^{13}C NMR shifts were referenced to internal $CHCl_3$ or acetone. The ^{19}F NMR shifts were referenced to external C_6H_5F in a chloroform or acetone solution. Infrared (KBr or NaCl plate) spectra were recorded on a Perkin-Elmer 283B grating spectrometer. Electron impact mass-spectral results were obtained by using an AEI MS 950 spectrometer and were tabulated by a linked computer. UV spectra in THF solution were recorded on a Hewlett-Packard Model 8450 A spectrometer. Approximate molecular weights (M_{GPC}) were determined with the use of a Waters ALC 201 GPC instrument with acetone as a solvent, and with the use of Corning glass bead columns ($^3/_8$ in. × 2 ft) (2000, 700, 175, 75 Å) at an elution rate of 3.0 mL/min. Intrinsic viscosities were measured with an Ubbelohde viscosimeter (Cannon) in a thermoregulated water bath (25 °C).

Improved Synthesis of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (1a). The transannular-linked ferrocenylfluorophosphazene **1a** was prepared both as described previously[10] and by the higher yield synthesis described here. 1,1′-Dilithioferrocene-TMEDA was prepared by the use of a published procedure[19] by the addition of a solution of *n*-butyllithium (375 mL, 600.0 mmol) to a solution of TMEDA in hexane (10 mL) followed by stirring of the mixture for 30 min. This mixture was then added to a solution of ferrocene (50 g, 268.8 mmol) in hexane, and the mixture was stirred for 8 h at room temperature. The reaction was then cooled to −78 °C and a solution of $(NPF_2)_3$ (90 g, 361.4 mmol) in THF (200 mL) was added slowly. The reaction was then allowed to warm to room temperature and was stirred for 17 h. 2-Propanol (20 mL) was added to quench any unreacted anion. The solvent was removed and the mixture was chromatographed. Elution with hexane gave ferrocene, identified by ^1H NMR. Further elution with dichloromethane–hexane (1:4) gave $N_3P_3F_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (**2a**) (0.05 g, 0.04%), identified by ^1H NMR and ^{31}P NMR. Continued elution with dichloromethane–hexane (1:1) gave $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1a**) (50.0 g, 47.1%), identified by ^1H and ^{31}P NMR. Further elution with dichloromethane gave a final, yellow band which yielded 0.30 g (0.20%) of orange crystals of *gem*-$N_3P_3F_3[(\eta\text{-}C_5H_4)_2Fe][(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$ (**15**): mp 238 °C; IR 3080 (w, CH), 1210, 1180 (s, PN), cm^{-1}; ^1H NMR δ 5.0161 (m, 1 H), 4.9208 (m, 2 H), 4.7763 (m, 1 H), 4.6879 (m, 2 H), 4.5874 (m, 1 H), 4.5084 (m, 1 H), 4.4456 (m, 2 H), 4.3754 (m, 1 H), 4.2926 (m, 1 H), 4.2284 (s, 5 H); ^{31}P NMR 46.5 (dm, J_{PF_1} = 935 Hz), 35.3 (m), 10.9 (tm, J_{PF_2} = 908 Hz); ^{19}F NMR 63.5 (dm, J_{PF_1} = 895 Hz), 55.9 (dm, J_{PF_2} = 925 Hz), 50.4 (d, J_{PF_3} = 905 Hz) ppm; *m/e* calcd for $C_{20}H_{17}N_3F_3FeP_3$ 560.9285, found 560.9271 (deviation 2.5 ppm). Anal. Calcd: C, 42.82; H, 3.05; N, 7.49; F, 10.16. Found: C, 41.36; H, 2.83; N, 7.50; F, 10.25.

Improved Synthesis of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (1b) and $N_3P_3F_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (2b). The ruthenocene-substituted fluorophosphazenes **1b** and **2b** were prepared as described previously[10] except that the period of the lithiation step was increased from 17 to 48 h. This led to improved yields of $N_3P_3F_4(\eta\text{-}C_5H_5)_2Ru$ (**1b**) (1.33 g, 34.9%) and $N_3P_3F_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (**2b**) (0.57 g, 14.3%).

For **1b**: UV λ_{max} 270, 324 nm.

Thermal Ring-Opening Polymerization of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (1a). A pure sample of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1a**) (22 g, 55.7 mmol) was sealed under vacuum 1×10^{-4} torr) in a Pyrex glass tube (18 cm × 2 cm). The tube was heated in a thermoregulated oven at 250 °C for 17 h. During this time, the contents of the tube were agitated by a mechanical rocking device. After 10 h, a gradual increase in viscosity was noted. The contents of the tube were cooled to room temperature and were found to contain a mixture of the cyclic trimer and the polymer, $[N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe]_{1\text{ and }n}$ (**1a** and **3a**). The mixture of these compounds was dissolved in THF (250 mL). A solution of sodium trifluoroethoxide, prepared from sodium (16.5 g, 717.9 mmol) and trifluoroethanol (77.3 g, 772.8 mmol) in THF (250 mL), was added, and the mixture was heated to reflux for 72 h. The polymer was isolated by addition of a stoichiometric amount of concentrated hydrochloric acid (36.5%, 52.3 g, 717.4 mmol) to the reaction mixture to quench any excess base. The solution was then immediately poured into distilled water (2 L). The resultant oily precipitate was then dissolved in THF and added slowly to hexane (2 L). A yellow polymeric material, $[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe]_n$ (**4a**) (6.0 g, 15.1%) precipitated. The polymer was purified further by reprecipitations from THF into water (once) and into hexane (twice). The hexane solutions were combined, filtered through a layer of silica gel, dried over $MgSO_4$, filtered, and finally concentrated to give orange crystals of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (**5a**) (18.5 g, 46.5%, mp. 87 °C).

For **3a** (after solvent separation from **1a** by precipitation into *n*-hexane): IR 3100 (w, CH), 1275 (s, br, PN), 850 (s, PF) cm^{-1}; ^{31}P NMR 11.2 (dd, $J_{PF_1} = 920$ Hz), −25.8 (tt, $J_{PF_2} = 890$ Hz) ppm; ^{19}F NMR 76.4 (d, $J_{PF_1} = 910$ Hz), 59.7 (d, $J_{PF_2} = 870$ Hz) ppm.

For **4a**: IR 2960 (w, CH), 1170 (s, br, PN) cm^{-1}; ^1H NMR δ 4.5 (br, m); ^{31}P NMR 8.3 (m), −11.8 (m) ppm; ^{19}F NMR 38.7 (s) ppm; molecular weight (M_{GPC}) $>2 \times 10^6$; intrinsic viscosity (in acetone solution at 25 °C) 1.2 dL/g. Anal. Calcd: C, 30.23; H, 2.26; N, 5.88. Found: C, 30.22; H, 2.17; N, 5.75. T_g (by DSC and thermomechanical analysis) 61 °C.[20]

For **5a**: IR 2980 (s, CH), 1200 (s, PN) cm^{-1}; ^1H NMR δ 4.859 (m, 2 H), 4.620 (m, 2 H), 4.481 (m, 2 H), 4.376 (m, 2 H), 4.353 (m, 4 H); ^{31}P NMR 21.2 (t), 41.9 (d, $J_{PNP} = 55$ Hz) ppm; ^{13}C NMR δ (Cp) 81.4 (dm, 2 C, $J_{PC} = 198$ Hz), 77.6 (m, 2 C), 74.3 (m, 2 C), 72.3 (m, 2 C), 70.1 (m, 2 C), (CF_3) 125.9 (m, 4C), (CH_2) 62.8 (m, 1 C), 62.5 (m, 1 C), 62.2 (m, 2 C) ppm; ^{19}F NMR 38.7 (s) ppm; mass spectrum, *m/e* calcd for $C_{18}H_{16}N_3F_{12}FeO_4P_3$ 714.9511, found 714.9516 (deviation 0.6 ppm). Anal. Calcd: C, 30.23; H, 2.26; N, 5.88; F, 31.88. Found: C, 30.07; H, 2.14; N, 5.68; F, 31.98. UV λ_{max} 335, 436 nm.

Thermal Ring-Opening Polymerization of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (1b). This polymerization reaction was performed in a manner identical with that described above for $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1a**) except that $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (**1b**) (1.11 g, 25.3 mmol) was used with a polymerization time of 12 h. The contents of the tube, which contained a mixture of the cyclic trimer and the polymer $[N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru]_{1\text{ and }n}$ (**1b** and **3b**), were dissolved in THF (250 mL) and were allowed to react as before with a solution of sodium trifluoroethoxide, prepared from sodium (7.25 g, 315.2 mmol) and trifluoroethanol (40 g, 400 mmol) in THF (250 mL). The trifluoroethoxy-substituted phosphazenes **4b** and **5b** were isolated after neutralization of the excess base with concentrated hydrochloric acid (36.5%, 11.5 g, 315.2 mmol). Reprecipitations as before from THF into water (twice) and into hexane (3 times) gave the polymeric material $[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Ru]_n$ (**4b**) (3.5 g, 18.2%), and pale yellow crystals of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Ru$ (**5b**) (8.7 g, 45.3%, mp 180 °C dec).

For **4b**: IR 2960 (w, CH), 1170 (s, br, PN) cm^{-1}; ^1H NMR δ 4.918 (m), 4.479 (m); ^{31}P NMR 7.35 (m), −9.95 (m) ppm; ^{19}F NMR 38.8 (s) ppm. Anal. Calcd: C, 28.44; H, 2.12; N, 5.53; Ru, 13.29. Found: C, 27.28; H, 2.07; N, 5.34; Ru, 13.23. Molecular weight (M_{GPC}) (in acetone solution) (bimodal) $>2 \times 10^6$, $>1 \times 10^6$; UV λ_{max} 327 nm; T_g 50.6 °C.[20]

For **5b**: IR 2950 (w, CH), 1200 (s, br, PN) cm^{-1}; ^1H NMR δ 5.227, 5.162, 4.979, 4.740 (all m, 2 H), 4.431 (m, 2 H), 4.311 (m, 2 H), 4.287 (m, 4 H); ^{13}C NMR δ (Cp) 87.7 (d, 2C, $J_{PC} = 195$ Hz), 80.4 (m, 2 C), 76.5 (m, 2 C), 74.0 (m, 2 C), 73.5 (m, 2 C), (CF_3) 123.7 (m. 4 C), (CH_2) 62.8 (m, 1 C), 62.6 (m, 2 C), 62.5 (m, 1 C); ^{31}P NMR 22.8 (t), 38.8 (d, $J_{PNP} = 54$ Hz) ppm; ^{19}F NMR 38.8 (s) ppm; mass spectrum, *m/e* calcd for $C_{14}H_{16}N_3O_4F_{12}RuP_3$ 760.9265, found 760.9233 (deviation 3.6 ppm). Anal. Calcd: C, 28.44; H, 2.12; N, 5.53; F, 19.98. Found: C, 28.61; H, 2.20; N, 5.73; F, 19.50. UV λ_{max} 267, 324 nm.

Thermal Ring-Opening Polymerization of $N_3P_3F_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (2b). This polymerization reaction was performed in a manner identical with that described above. $N_3P_3F_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (**2b**) (3.0 g, 6.52 mmol) polymerized during a 24-h period at 300 °C. The contents of the tube, which contained a mixture of the cyclic trimer and the polymer, $[N_3P_3F_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)]_{1\text{ and }n}$ (**2b** and **8b**), were dissolved in THF (250 mL) as before and allowed to react with a solution of sodium trifluoroethoxide, prepared from sodium (0.45 g, 19.6 mmol) and trifluoroethanol (3.0 g, 30.0 mmol) in THF (250 mL). The trifluoroethoxy-substituted phosphazenes, **9b** and **10b**, were isolated after neutralization of the excess base with concentrated hydrochloric acid (36.5%, 0.72 g, 19.6 mmol). Reprecipitations from THF into water (twice) and into hexane (3 times) gave the polymeric material $[N_3P_3(OCH_2CF_3)_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)]_n$ (**9b**) (1.2 g, 21.4%) and pale yellow oil of $N_3P_3(OCH_2CF_3)_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (**10b**) (1.8 g, 32.1%).

For **9b**: IR 2950 (w, CH), 1230 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.681 (m), 4.512 (m); ^{31}P NMR 10.5 (m), −8.8 (m) ppm; ^{19}F NMR 38.6 (s) ppm. Anal. Calcd: C, 27.92; H, 2.23; N, 4.48. Found: C, 26.68; H, 2.26; N, 5.34. T_g 32.1 °C.[20]

For **10b**: IR 2950 (w, CH), 1230 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.861 (m, 2 H), 4.777 (m, 2 H), 4.654 (s, 5 H), 4.281 (m, 10 H); ^{31}P NMR 35.6 (t), 15.4 (d, $J_{PNP} = 55$ Hz) ppm; ^{13}C NMR δ (Cp) 75.4 (dt, 1 C, $J_{PC} = 210$ Hz, $J_{PNPC} = 8$ Hz), 73.5 (d, 2 C, $J_{PC} = 14$ Hz), 72.6 (d, 2 C, $J_{PC} = 17$ Hz), 72.5 (s, 5 C), (CF_3) 123.1 (m, 5 C), (CH_2) 62.7 (m, 5 C); ^{19}F NMR 38.0 (s) ppm; mass spectrum, *m/e* calcd for $C_{20}H_{19}N_3F_5O_5P_3Ru$ 860.9341, found 860.9409 (deviation 7.9 ppm). Anal. Calcd: C, 27.92; H, 2.23; N, 4.88. Found: C, 28.07; H, 2.15; N, 5.02.

Thermal Ring-Opening Polymerization of $N_3P_3F_5(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_5)$ (2a). This polymerization reaction was performed in a manner identical with that described for the polymerization of **1a** and **1b**, except $N_3P_3F_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (**2a**) (2.5 g, 6.02 mmol) was used together with $(NPCl_2)_3$ (0.02 g, 0.06 mmol) as an "initiator". The polymerization reaction was carried out over a 40-h period at 250 °C. (An attempt to perform this reaction in the absence of $(NPCl_2)_3$ at 250–300 °C yielded no polymer.) The product mixture of the cyclic trimer and the polymer, $[N_3P_3F_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_{1\text{ and }n}$, was dissolved in THF (150 mL) and was allowed to react with a solution of sodium trifluoroethoxide prepared from sodium (2.72 g, 118.3 mmol) and trifluoroethanol (3.5 g, 354.8 mmol) in THF (150 mL). The trifluoroethoxy-substituted phosphazenes, **9a** and **10a**, were isolated by treatment with concentrated hydrochloric acid (36.5%, 4.5 g, 123.3 mmol). Reprecipitations from THF into water (twice) and into hexane (3 times) gave the polymeric material $[N_3P_3(OCH_2CF_3)_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_n$ (**9a**) (1.0 g, 20.4%) and pale yellow orange crystals of $N_3P_3(OCH_2CF_3)_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (**10a**) (2.5 g, 51.0%, mp 44.5 °C) identified by ^{31}P NMR spectroscopy.[10]

For **9a**: IR 2970 (w, CH), 1250 (s, br, PN) cm^{-1}; ^1H NMR δ 4.54 (m), 4.33 (m); ^{31}P NMR 13.2 (m), −8.9 (m) ppm; ^{19}F NMR 38.6 (s) ppm. Anal. Calcd: C, 29.47; H, 2.35; N, 5.16. Found: C, 29.27; H, 2.49; N, 5.04. Molecular weight (M_{GPC}) (bimodal) $>2 \times 10^6$, $>1 \times 10^5$ (in acetone solution); T_g 28.2 °C.[20]

Copolymerization of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (1a) and $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (1b). Equimolar mixtures of pure samples of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1a**) (2.2 g, 5.7 mmol) and $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (**1b**) (2.5 g, 5.7 mmol) were heated together in a sealed glass tube at 250 °C for 8 h. The contents of the tube, which consisted of the cyclic trimers and the polymer $[N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe\text{–}N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru]_n$ (**1a**, **1b**, and **6**) were dissolved in THF (250 mL) and were allowed to react with a solution of sodium trifluoroethoxide prepared from sodium (2.38 g, 103.5 mmol) and trifluoroethanol (30 g, 300.0 mmol) in THF (250 mL). The trifluoroethoxy-substituted phosphazenes, **5a**, **5b**, and **7**, were isolated by treatment with concentrated hydrochloric acid (36.5%, 9.2 g, 252.1 mmol). Reprecipitations from THF into water (twice) and into hexane (3 times) gave the pale yellow polymeric material $[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe\text{–}N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Ru]_n$ (**7**) (1.1 g, 23.4%) and an equimolar mixture of **5a** and **5b** (2.7 g, 57.4%). The substituent ratios were estimated by ^{31}P NMR spectroscopy. Polymer **7** was found to contain a 1:1 mixture of ferrocenyl and ruthenocenyl units by UV spectroscopy and elemental analysis.

For **7**: IR 2940 (w, CH), 1280 (s, br, PN) cm^{-1}; ^1H NMR δ 4.8 (m), 4.5 (m); ^{31}P NMR (m), −8.5 (m) ppm; ^{19}F NMR 38.8 (s) ppm. Anal. Calcd.: C, 29.31; H, 2.19; N, 5.70; Fe, 3.79; Ru, 6.85. Found: C, 29.17; H, 2.09; N, 5.59; Fe, 3.74; Ru, 6.76. Molecular weight (M_{GPC}) (in acetone solution) $>2 \times 10^6$; UV λ_{max} 321, 434 nm.

Thermal Polymerization of $N_3P_3F_5(C_6H_5)$ (13). This reaction was performed in a manner similar to that reported previously.[13] A sample of $N_3P_3F_5(C_6H_5)$ (13) (6.0 g, 1.95 mmol) was vacuum-transferred into a small Pyrex tube and the tube was sealed. The tube was then heated in a thermoregulated oven at 290 °C. The contents of the tube gradually polymerized over a 48-h period to give the elastomeric polymer $[N_3P_3F_5(C_6H_5)]_n$ (14) in almost quantitative yield.

Thermal Polymerization of $N_3P_3F_5(C_6H_5)$ (13) with (a) 1% $(NPCl_2)_3$ and (b) 10% $(NPCl_2)_3$ as Initiator. The polymerization reactions with performed as above for $N_3P_3F_5(C_6H_5)$ (13), (13), that $(NPCl_2)_3$ [(a) 1%, 0.06 g, 0.01 mmol; (b) 10%, 0.60 g, 1.0 mmol)] was added as initiator. The tubes were heated to 290 °C in a thermoregulated oven. The contents of the tube a polymerized during a 6-h period, while the contents of tube b polymerized within 20 min to yield $[N_3P_3F_5(C_6H_5)]_{0.99}[N_3P_3Cl_6]_{0.01}$ (16) and $[N_3P_3F_5(C_6H_5)]_{0.9}[N_3P_3Cl_6]_{0.1}$ (17), respectively, in almost quantitative yield.

Attempted Polymerization of $N_3P_3F_5(C_6H_5)$ (13) with 18 mol % of $Fe(\eta\text{-}C_5H_5)_2$. This reaction was carried out as described above for $N_3P_3F_5(C_6H_5)$ (13), except that $Fe(\eta\text{-}C_5H_5)_2$ (0.065 g, 18 mol %) was added. The tube was heated to 290 °C in a thermoregulated oven. An orange, nonviscous, homogeneous solution was obtained. After 30 h, the contents of the tube appeared unchanged. However, after 36 h, the color darkened and after 40 h the contents of the tube became dark brown and immobile. After being cooled, the tube was found to contain an acidic gas. The dark brown, brittle, solid material in the tube was insoluble in all common solvents.

Thermal Polymerization of $N_3P_3F_5(C_6H_5)$ (13) with 18 mol % of $Ru(\eta\text{-}C_5H_5)_2$. The polymerization reaction was performed as above for $N_3P_3F_5(C_6H_5)$ (13) except that $Ru(\eta\text{-}C_5H_5)_2$ (0.82 g, 18 mol %) was added. The tube was heated at 290 °C in a thermoregulated oven. The $N_3P_3F_5(C_6H_5)$ (13) gradually polymerized over a 48-h period to give a mixture of $[N_3P_3F_5(C_6H_5)]_n$ (14) and $Ru(\eta\text{-}C_5H_5)_2$. These were separated by dissolving the mixture in THF (150 mL) and precipitation of the polymer into hexane (2 L). The ruthenocene was recovered quantitatively from the hexane.

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Supplementary Material Available: ^{31}P and ^{19}F NMR spectra of **3a** and ^{31}P NMR spectrum of **7** (1 page). Ordering information is given on any current masthead page.

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Notes

Similar Matrix Expressions Describe Configuration Partition Functions for Intrachain Formation of Antiparallel β Sheets and Interacting α Helices

WAYNE L. MATTICE

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804.

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Recently we described a tractable matrix formulation for the intramolecular transition from a statistical coil to a β sheet with tight bends (β bends). The formulation can be specialized so that all strands in a particular β sheet have the same number of residues, but in general there is no artificial restraint on the number of residues in a strand. Recently the method has been extended so that contigous strands in a particular β sheet may be connected by loops of arbitrary size.[3] Although statistical weight matrices may become extremely large under some circumstances,[4] computations required for extraction of the statistical mechanical averages of configuration-dependent physical properties require remarkably little memory or execution time. Two features of the matrix formulation are responsible for the ease of implementation: (1) The matrices are sparse, and (2) simple summarizing statements provide the location and identity of all nonzero elements. The computational algorithm is based on the simple summarizing statements. The huge statistical weight matrices need never be formulated and manipulated.

Figure 1 depicts an example of the type of chain that is included in the ensemble that was described in the original formulation.[1] This chain contains three intramolecular β sheets. One "sheet" consists of a single extended strand. Strands in the two multistranded sheets are connected by tight bends. The statistical weights assigned to each of these sheets are noted outside the parentheses in Figure 1. Residues in the disordered regions contribute a factor of 1 to the statistical weight. Each residue in a sheet contributes a β-sheet propagation factor denoted by t. Two additional parameters arise from edge effects. Each sheet residue that does not have a partner in a preceeding strand contributes an additional factor of τ, and each tight