

Influence of Different Organic Side Groups on the Thermal Behavior of Polyphosphazenes: Random Chain Cleavage, Depolymerization, and Pyrolytic Cross-Linking

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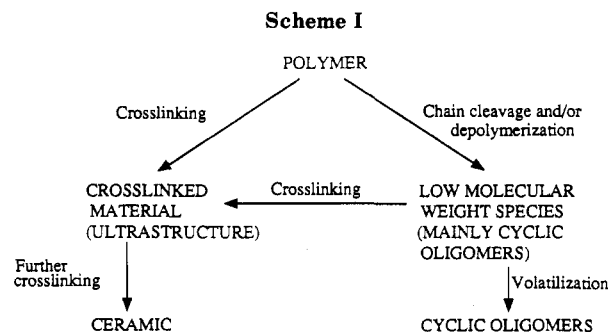
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The thermal behavior of several polyphosphazenes was examined. The polymers were studied by thermogravimetric analysis between 50 and 1000 °C, by bulk pyrolysis in a tube furnace over the same temperature range, and by thermolysis in a closed system. The volatile products were analyzed by a combination of ^{31}P NMR spectroscopy, vapor-phase chromatography, and mass spectrometry. Three distinct processes were identified: (1) random chain cleavage of the phosphazene backbone, (2) depolymerization to form small molecule cyclic phosphazenes, and (3) cross-linking reactions to form a network structure. During pyrolysis $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ underwent random chain cleavage and depolymerization followed by volatilization of the small-molecule cyclic products. Species $[\text{NP}(\text{CH}_3)_2]_n$ and $[\text{NP}(\text{CH}_3)(\text{C}_6\text{H}_5)]_n$ depolymerized to cyclic oligomers, which then volatilized. The aryloxy-substituted phosphazenes $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ and $[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_n$ underwent random chain cleavage, depolymerization to cyclic oligomers, and cross-linking of these cyclic species. High-temperature pyrolysis of $[\text{NP}(\text{NHC}_3\text{H}_7\text{-}n)_2]_n$ and other poly(aminophosphazenes) and the transannular metallocene polymers $[\text{NP}(\text{OCH}_2\text{CF}_3)_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]_n$ and $[\text{NP}(\text{OCH}_2\text{CF}_3)_4(\eta\text{-C}_5\text{H}_4)_2\text{Ru}]_n$ resulted exclusively in cross-linking reactions. Possible reaction mechanisms are considered.

Polymers with inorganic elements in the main chain should behave differently at high temperatures from their counterparts with carbon-containing backbones. This difference is the reason many inorganic backbone polymers are being investigated as high-temperature materials or preceramic polymers.¹

Polyphosphazenes contain a backbone of alternating phosphorus and nitrogen atoms, with two side groups linked to each phosphorus.^{2,3} It has been found that the nature of the side groups has a marked influence on the behavior of different polyphosphazenes at high temperatures. For example, some polymers undergo random skeletal cleavage reactions that bring about a marked decrease in molecular weight. Other polyphosphazenes depolymerize to give a broad range of cyclic oligomers. Alternatively, the side groups may participate in intermolecular coupling processes that bring about cross-linking of the chains. More than one of these pathways may be found in the thermolysis of any single polymer. Chain cleavage and depolymerization are important with regard to the general thermal stability of polyphosphazenes. The cross-linking pathway provides a potential route to ultrastructure materials.

The formation of ultrastructure materials requires the cross-linking route to be favored or, at least, to be the faster pathway. If the polymer undergoes chain cleavage and/or depolymerization and the resultant products either volatilize or degrade without cross-linking, network structures will not be formed (Scheme I). However, if the polymer depolymerizes, but the lower molecular weight species cross-link, ultrastructure materials may still be generated. A polymer that undergoes cross-linking reactions in preference to skeletal cleavage will form a stabilized, ultrastructure network system. On further pyrolytic cross-



linking, this material may form a ceramic.

Previous studies of the stability of phosphazene polymers have focused on experiments at moderate temperatures (below 400 or 600 °C), on a qualitative analysis of the products, or on the results of thermogravimetric analysis.⁴⁻¹³ In particular, the depolymerization of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ at temperatures up to 500 °C has been examined.^{10,12-15} Similar studies have been carried out with $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$.^{12,13,16} The cross-linking of various aminophosphazenes when heated to 400 °C has also been noted.^{4,5}

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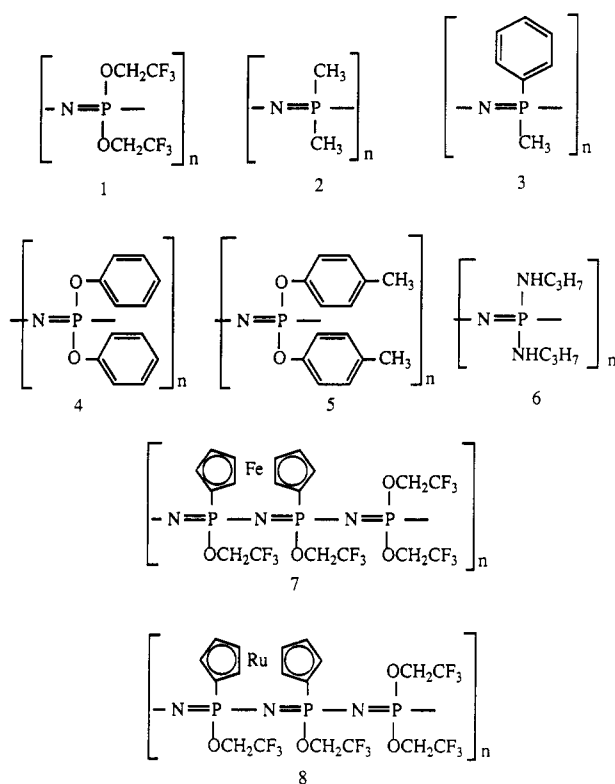
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Chart I



In this work we have studied the behavior of polyphosphazenes 1–8 (Chart I) at temperatures between 50 and 1000 °C and have correlated the different thermolysis reactions of the polymers with different side-group structures. The objectives of this investigation were (1) to compare the general thermal stabilities of a variety of phosphazene polymers, (2) to examine the chemistry that occurs during pyrolysis, and (3) to identify any potential ultrastructure systems.

Results and Discussion

Overall Approach and Summary. Three experimental techniques were employed to examine the thermal behavior of compounds 1–8. First, the compounds were heated at various temperatures in a tube furnace in a flow of dry nitrogen. Volatile small-molecule reaction products were collected by condensation from the effluent nitrogen stream and were analyzed by a combination of vapor-phase chromatography, mass spectrometry, and nuclear magnetic resonance. The nonvolatile residue that remained at the end of each experiment was examined by a range of analytical methods, including elemental microanalysis, infrared spectroscopy, and solid-state NMR.

The second method made use of thermogravimetric analysis. Here, the emphasis was on the pattern of loss of volatile thermolysis products and on the percentage of nonvolatile ultrastructure material remaining at different temperatures.

The first two methods are nonequilibrium reactions in the sense that the small-molecule volatile products formed during thermolysis are removed from the pyrolysis mixture and are thereby prevented from contributing further to the condensed-state reactions. Thus, the third experimental approach was designed to examine the thermolyses under conditions where loss of the more volatile products was prevented. These experiments involved heating of the polymers in evacuated glass tubes at different temperatures and for different times, followed by analysis of the products by vapor phase chromatography, mass spec-

Table I. Thermolysis of Poly(organophosphazenes) in a Closed System

| init poly | temp, °C | time, h | product distr | | |
|--|----------|---------|------------------|---------------|-----------------|
| | | | polymer | cyclic trimer | cyclic tetramer |
| [NP(OCH ₂ CF ₃) ₂] _n | 250 | 1 | 100 ^a | 0 | 0 |
| | | 4 | 100 ^a | 0 | 0 |
| | 300 | 1 | 100 ^a | 0 | 0 |
| | | 4 | 68 | 17 | 15 |
| | 350 | 1 | 78 | 13 | 19 |
| | | 4 | 9 | 32 | 59 |
| [NP(CH ₃) ₃] _n | 200 | 1 | 100 | 0 | 0 |
| | | 4 | 100 | 0 | 0 |
| | 250 | 1 | 93 | 5 | 2 |
| | | 4 | 79 | 17 | 12 |
| | 300 | 1 | 0 | 47 | 53 |
| | | 4 | 0 | 50 | 50 |
| [NP(CH ₃)(C ₆ H ₅)] _n | 350 | 1 | 0 | 53 | 47 |
| | | 4 | 0 | 56 | 44 |
| | 200 | 1 | 100 | 0 | 0 |
| | | 4 | 100 | 0 | 0 |
| | 250 | 1 | 100 | 0 | 0 |
| | | 4 | 91 | 3 | 6 |
| [NP(OC ₆ H ₅) ₂] _n | 300 | 1 | 56 | 21 | 23 |
| | | 4 | 0 | 32 | 68 |
| | 350 | 1 | 0 | 41 | 59 |
| | | 4 | 0 | 32 | 68 |
| | 250 | 1 | 100 ^a | 0 | 0 |
| | | 4 | 100 ^a | 0 | 0 |
| [NP(OC ₆ H ₄ - <i>p</i> -CH ₃) ₂] _n | 300 | 1 | 55 | 29 | 15 |
| | | 4 | 72 | 17 | 11 |
| | 350 | 1 | 21 | 47 | 32 |
| | | 4 | 17 | 49 | 34 |
| | 250 | 1 | 100 ^a | 0 | 0 |
| | | 4 | 100 ^a | 0 | 0 |
| | 300 | 1 | 100 ^a | 0 | 0 |
| | | 4 | 100 ^a | 0 | 0 |
| | 350 | 1 | 88 | 9 | 3 |
| | | 4 | 69 | 24 | 7 |

^a Although no cyclic oligomers were detected in these experiments, skeletal cleavage to medium molecular weight polymers was already in progress.

trometry, and NMR and infrared spectroscopy. The experimental results are summarized in Tables I and II and in Figures 1–7.

Polyphosphazenes [NP(OCH₂CF₃)₂]_n (1), [NP(CH₃)₂]_n (2), and [NP(CH₃)(C₆H₅)]_n (3) depolymerized when heated at moderate temperatures to yield small-molecule cyclic species. Polymers [NP(OC₆H₅)₂]_n (4) and [NP(OC₆H₄-*p*-CH₃)₂]_n (5) also depolymerized when heated, but the resultant small-molecule cyclic compounds then underwent cross-linking reactions to form an ultrastructure. The poly(aminophosphazene) [NP(NHC₂H₅)₂]_n (6) and transannular metallocene phosphazene polymers [NP(OCH₂CF₃)₄(η-C₅H₄)₂Fe]_n (7) and [NP(OCH₂CF₃)₄(η-C₅H₄)₂Ru]_n (8) underwent cross-linking reactions exclusively when heated. The details are as follows.

Trifluoroethoxy Side Groups. At temperatures below 250 °C, heating of poly[bis(trifluoroethoxy)phosphazene], [NP(OCH₂CF₃)₂]_n (1), in a sealed system resulted in skeletal cleavage without the detectable formation of small-molecule cyclic species (Table I and Figure 1). This initial chain cleavage is believed to be connected with the presence of low concentrations of P–Cl or P–OH “imperfections” along the chain, defects that result from a failure by the macromolecular substitution reaction to replace every single chlorine atom in the molecule.

At higher temperatures (above 250 °C) the molecular weight decline was accompanied by the formation of cyclic oligomers. Specifically, [NP(OCH₂CF₃)₂]_n (1) heated in a closed system at 250–350 °C for 4 h yielded appreciable amounts of the cyclic trimer [NP(OCH₂CF₃)₂]₃ and tet-

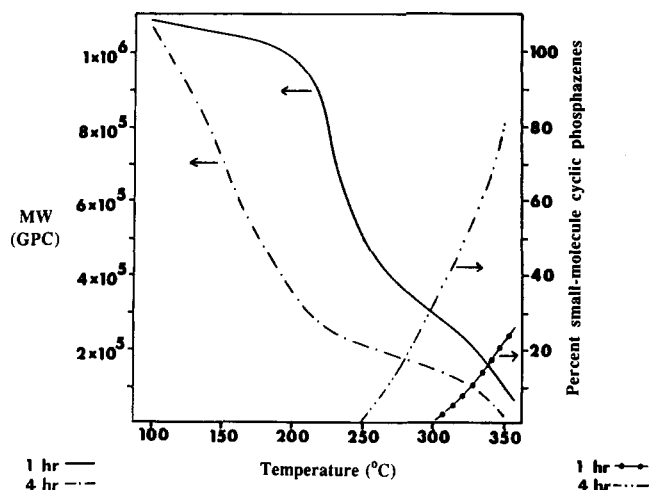


Figure 1. Variation in average molecular weight and percentage of small-molecule cyclic products as a function of temperature for $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ within a sealed system.

Table II. Volatile Products Formed during the Pyrolysis of Polyphosphazenes^a

| init poly | pyrolysis temp, °C | cyclic phosphazenes (NPR_2) _x detected, % | | | other products |
|---|--------------------|---|-------|-------|---|
| | | x = 3 | x = 4 | x > 4 | |
| $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ | 420 | 70 | 20 | 10 | |
| $[\text{NP}(\text{CH}_3)_2]_n$ | 380 | 60 | 20 | 20 | |
| $[\text{NP}(\text{CH}_3)(\text{C}_6\text{H}_5)]_n$ | 500 | 72 | 28 | 0 | |
| $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ | 400 | 55 | 15 | 30 | $\text{C}_6\text{H}_5\text{OH}$ |
| $[\text{NP}(\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3)_2]_n$ | 400 | 71 | 13 | 16 | $\text{C}_6\text{H}_4(\text{CH}_3)\text{-OH}$ |

^a The products were formed when the polymers were heated in a flow of nitrogen within a tube furnace assembly, with the volatile species collected and analyzed by VPC/mass spectrometric and NMR techniques.

ramer $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_4$. After 4 h at 350 °C, less than 10% of the starting polymer, $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$, remained.

These chain cleavage and depolymerization processes are illustrated in the plots of molecular weight versus temperature and small-molecule cyclic products formed versus temperature (Figure 1). As the temperature was increased above 300 °C, depolymerization of the polymer to cyclic species became more obvious. These features are characteristic of polymers that depolymerize rather than undergo cross-linking reactions as they are heated. This is an important point since *thermogravimetric analysis of this system did not reveal any significant weight loss at temperatures up to 300 °C, although cleavage of the polymer backbone and formation of small-molecule cyclic oligomers clearly occurs below this temperature.* Above 300 °C, the cyclic species formed at lower temperatures begin to volatilize.

When the same polymer was heated in a nitrogen flow at 400 °C, it depolymerized completely to small-molecule cyclic species that volatilized from the reaction zone before any further reactions could occur. The thermolysis products were analyzed by ^1H NMR and ^{31}P NMR spectroscopy. The relative amounts of each cyclic compound were estimated by integration of the ^{31}P NMR spectrum (Table II).

Thermogravimetric analysis of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ indicated a complete volatilization of all material by 450 °C (Figure 2). No evidence was found that the polymer chains or small-molecule products underwent cross-linking reactions during thermolysis.

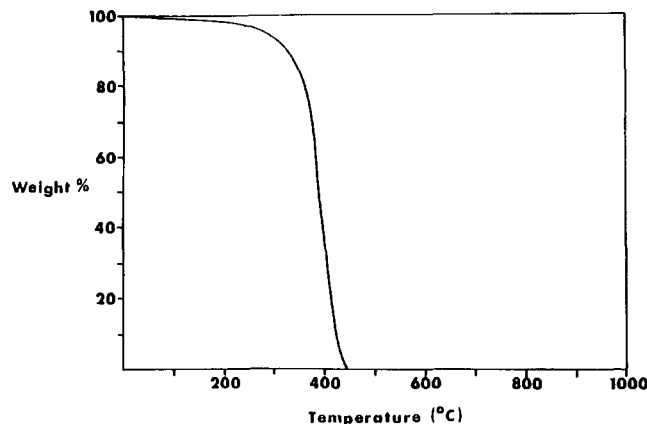


Figure 2. Thermogravimetric analysis curves for $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ (10 °C/min).

Methyl and Phenyl Side Groups. Phosphazene polymers of this type have been reported by Neilson, Wisian-Neilson, and their co-workers.¹⁷⁻²⁰ The alkyl- and alkylarylphosphazene polymers $[\text{NP}(\text{CH}_3)_2]_n$ (2) and $[\text{NP}(\text{CH}_3)(\text{C}_6\text{H}_5)]_n$ (3) depolymerized to cyclic oligomers when heated in a closed system at 250 °C or higher for 1–4 h (Table I). No residual polymer was detected by ^{31}P NMR spectroscopy after samples of $[\text{NP}(\text{CH}_3)_2]_n$ (2) had been heated at 300 °C. The alkylarylphosphazene polymer $[\text{NP}(\text{CH}_3)(\text{C}_6\text{H}_5)]_n$ appeared to be slightly more stable since more prolonged heating was required to convert all the polymer to cyclic trimer and tetramer at 300 °C than in the case of $[\text{NP}(\text{CH}_3)_2]_n$ (Table I). No cyclic products higher than the cyclic trimer or tetramer were detected in these experiments.

Similar conclusions were obtained when the same two polymers were heated in a continuous flow of nitrogen at temperatures between 300 and 500 °C. As shown in Table II, complete depolymerization occurred to yield cyclic oligomers. The cyclic trimer was the principal product in each case. Thermogravimetric analysis indicated that total volatilization of the system as cyclic oligomers occurred by the time the temperature had been raised to 475 °C in the case of the dimethyl derivative and to 500 °C in the case of the methyl phenyl species. No evidence was found for cross-linking of the rings or chains.

Phenoxy and *p*-Methylphenoxy Side Groups. The aryloxy polymers $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ (4) and $[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_n$ (5) underwent chain cleavage, depolymerization, and cross-linking reactions when heated. Each of these processes was detected by a different set of experiments. First, when the polymers were heated in a closed system and the products were analyzed by gel permeation chromatography, ^{31}P NMR, and vapor-phase chromatography/mass spectrometry, it was clear that at temperatures between 120 and 250 °C cleavage of the polymer chains to give shorter polymeric fragments was the main reaction (Figures 3 and 4). No cyclic oligomers were detected within this temperature range.

Second, at temperatures above 250 °C for $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ (4) or above 300 °C for $[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_n$ (5), small-molecule cyclic oligomers were detected, with the amounts increasing as the temperature was raised to

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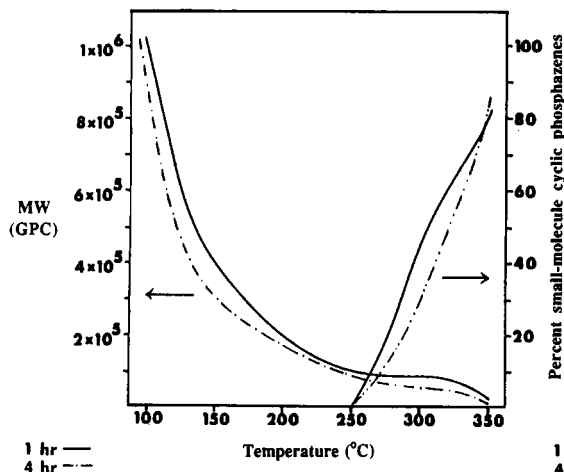


Figure 3. Variation in average molecular weight and percentage of small-molecule cyclic products as a function of temperature for $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$.

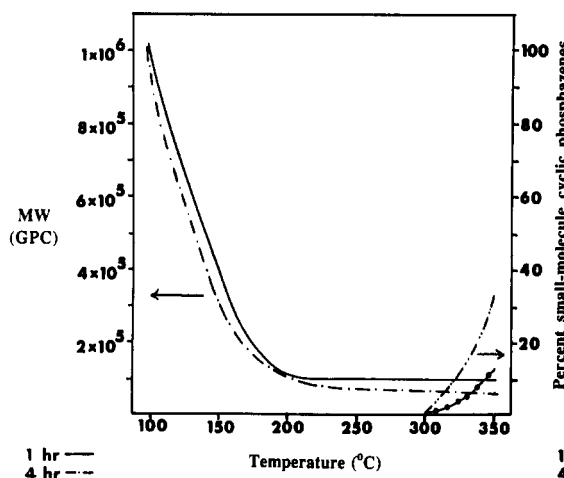


Figure 4. Variation in average molecular weight and percentage of small molecule cyclic products as a function of temperature for $[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_n$.

350 °C (Figures 3 and 4). The relative amounts of polymer, cyclic trimer, and cyclic tetramer in each system are shown in Table I. It was clear from the data that the *p*-methylphenoxy system derived from 5 was less prone to depolymerize to cyclic oligomers than was the phenoxy system derived from 4. In a nitrogen flow system at 400 °C, the polymers yielded cyclic trimer and tetramer plus mixtures of higher cyclic species (Table II). The same cyclization/depolymerization process is evident from the thermogravimetric analysis plots shown in Figure 5, where the sharp weight loss at 400 °C reflects the volatilization of cyclic phosphazenes formed by depolymerization. In this behavior the aryloxyphosphazene polymers resemble the trifluoroethoxy- and methyl- or methylphenylphosphazene polymers discussed earlier.

However, these similarities cease when the aryloxyphosphazene polymers are heated to between 400 and 1000 °C. Within this temperature range an unusual series of intermolecular coupling reactions takes place that involves the loss of phenol or *p*-methylphenol and the formation of a nonvolatile, black, pyrolytic solid. The existence of this product is evident from the TGA plots in Figure 5.

At temperatures between 400 and 1000 °C virtually all of the linear high polymers would have been converted to cyclic oligomers. Indeed, ^{31}P NMR spectroscopy of the liquid formed when $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ and $[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_n$ were heated to 400 °C indicated that the

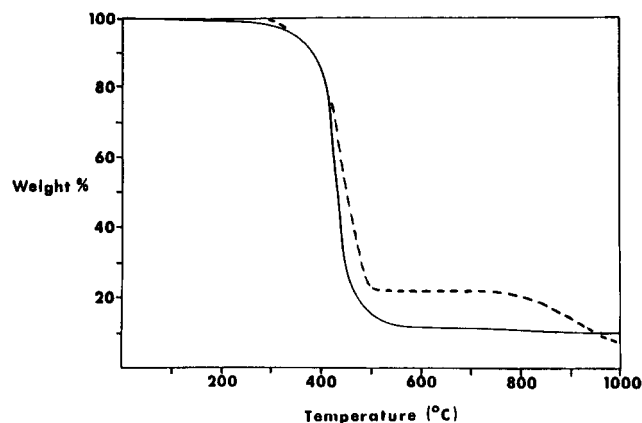
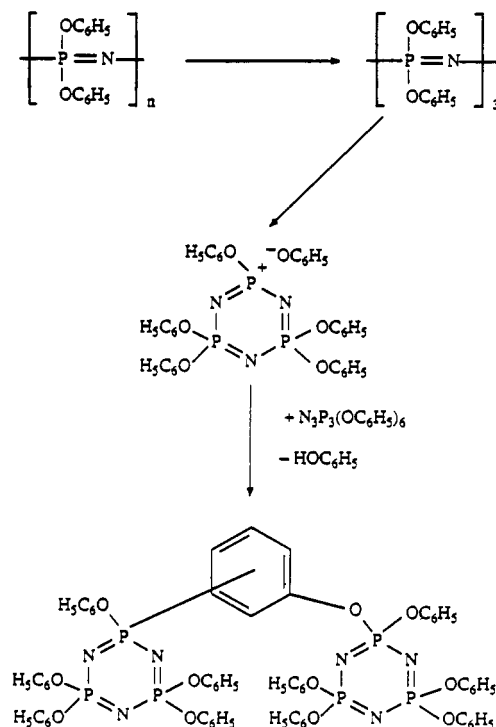


Figure 5. Thermogravimetric analysis curves for $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ (—) and $[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_n$ (---).

Scheme II



principal component was the cyclic trimer together with smaller quantities of the tetramer and higher cyclic species (Tables I and II). When heated to higher temperatures, this liquid became more viscous, solidified at 500 °C, and then rapidly formed an expanded solid. This product was colorless to light yellow initially but darkened rapidly on further heating. Analysis of the volatile products from the pyrolysis of 4 and 5 by gas chromatography/mass spectrometry confirmed that phenol and methylphenol, respectively, were the major products from the pyrolysis of the cyclic oligomers. The nonvolatile residue from both the independent thermogravimetric analysis and tube furnace pyrolysis of the cyclic trimer $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ were similar to that obtained by the pyrolysis of the polymer $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$, and it seems clear that the final pyrolyzate from both processes is formed from the cyclic depolymerization products rather than directly from the linear high polymer.

The evolution of a phenol during pyrolysis is evidence that the cross-linking in the aryloxy system appears to occur through reactions that involve the aryloxy side groups. A plausible pathway for the cross-linking of $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ is shown in Scheme II. Depolymerization

of the polymer in the 400 °C region gives a mixture of oligomers rich in the cyclic trimer. Heating of the mixture of cyclic phosphazenes results in heterolytic cleavage of P-O linkages to form a phosphazanium cation and a phenoxide anion. Electrophilic substitution by the phosphazanium ion on the phenyl ring of a second phosphazene could link the two molecules together. Further reactions of this type would generate cyclomatrix structures.

Evidence for the essential features of this mechanism was obtained through the following experiments. Exchange of phenoxy groups occurred in samples of $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ heated at 400 °C or higher. Thus, 50:50 mixtures of $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ and $[\text{NP}(\text{OC}_6\text{D}_5)_2]_3$ were heated at 300, 350, 400, 450, and 500 °C for 10 min. The samples were then analyzed by mass spectrometry. No $\text{OC}_6\text{H}_5/\text{OC}_6\text{D}_5$ exchange was detected in the samples heated to 300 or 350 °C. At 400 °C, trace amounts of $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5(\text{OC}_6\text{D}_5)$ and $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)(\text{OC}_6\text{D}_5)_5$ were detected. The sample heated to 450 °C showed all possible combinations of $-\text{OC}_6\text{H}_5$ and $-\text{OC}_6\text{D}_5$ groups, although peaks for the two single-substituted trimers were still the most intense.

A control experiment was carried out to determine if any exchange occurred under the conditions of the mass spectrometric analysis. A 50:50 mixture of $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ and $[\text{NP}(\text{OC}_6\text{D}_5)_2]_3$ was analyzed in the mass spectrometer. The resultant spectrum suggested that no exchange occurred. Also, no exchange of hydrogen for deuterium within the phenyl rings was detected in any of the experiments.

Further evidence in favor of coupling reactions at the side groups was obtained from infrared analysis of the pyrolysis products. Infrared spectra of the phenoxy-substituted cyclic trimer $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$, tetramer $[\text{NP}(\text{OC}_6\text{H}_5)_2]_4$, and high polymer $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ contain bands at 1592 and 1489 cm^{-1} assigned to the C=C stretching mode of the phenyl rings. The insoluble colorless solid obtained by heating $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ at 500 °C under nitrogen for 20 min showed broad absorbances between 1650 and 1400 cm^{-1} with distinct peaks at 1610 (sh), 1601 (s), 1570 (m), 1485 (s), 1470 (s), and 1450 (s) cm^{-1} , again assigned to the skeletal stretching modes of the phenyl rings. This increased complexity in the aromatic ring stretching bands was attributed to the presence of additional substituent groups connected to the aromatic rings.

Amino Side Groups. Poly(aminophosphazenes) of formula $[\text{NP}(\text{NHR})_2]_n$ are characterized by a tendency to undergo side-group condensation and cross-linking reactions rather than skeletal cleavage or depolymerization to cyclic oligomers. For this reason, the experimental methods used to study the polymers discussed earlier (^{31}P NMR, GPC, VPC/mass spectrometry) are of only limited value in the study of aminophosphazene systems. The main factors that can be studied are the volatile products generated by condensation, their sequence of elimination, and the composition and character of the ultrastructure material left after pyrolysis.

An early indication of the behavior of aminophosphazenes at elevated temperatures was contained in a brief report published in 1977.⁵ In that work it was shown that cyclotriphosphazenes with $\text{CH}_3\text{NH}-$, $\text{H}_2\text{N}-$, or $(\text{CH}_3)_2\text{N}-$ side groups eliminated amines when heated and generated a cross-linked matrix of cyclophosphazene rings. The high polymer, $[\text{NP}(\text{NHCH}_3)_2]_n$, underwent a similar condensation reaction.

In this present work, the thermally induced condensation reactions of $[\text{NP}(\text{NHCH}_3)_2]_n$, $[\text{NP}(\text{NHC}_3\text{H}_7)_2]_n$, $[\text{NP}(\text{NHC}_4\text{H}_9)_2]_n$, $[\text{NP}(\text{N}(\text{CH}_3)_2)_2]_n$, and $[\text{NP}(\text{NHC}_6\text{H}_5)_2]_n$

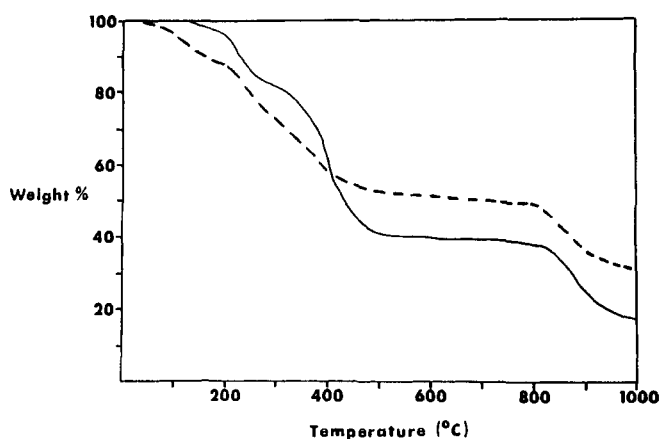


Figure 6. Thermogravimetric analysis curves for $[\text{NP}(\text{NHC}_3\text{H}_7)_2]_n$ (—) and $[\text{NP}(\text{NHC}_6\text{H}_5)_2]_n$ (---).

$[\text{NHC}_6\text{H}_5)_2]_n$ were examined. The experimental techniques employed included pyrolysis in a nitrogen flow tube furnace and thermogravimetric analysis. A few pyrolyses were also conducted under argon or ammonia atmospheres. All five polymers underwent elimination of amines at temperatures above 100–150 °C. At higher temperatures, yellow-brown and orange products deposited from the vapor state onto the walls of the silica flow tube. The ultimate nonvolatile residues were black, ceramic-type solids. Each of these processes and products will be described in turn. The behavior of $[\text{NP}(\text{NHC}_3\text{H}_7)_2]_n$ (6) was typical, and this system will be described in the greatest detail.

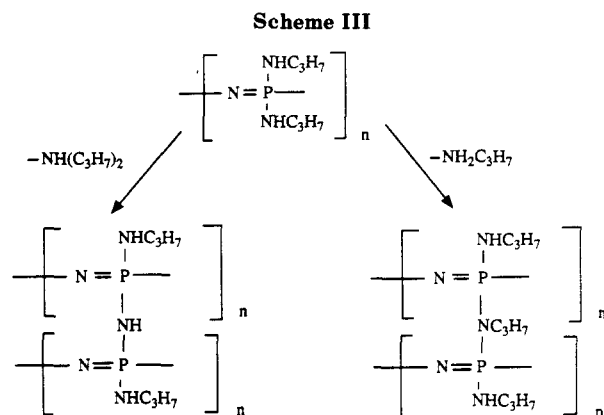
Pyrolysis of $[\text{NP}(\text{NHC}_3\text{H}_7)_2]_n$ in a nitrogen flow system generated *n*-propylamine, 2-propenylpropylamine, and di-*n*-propylamine. The proportion of these products varied with the pyrolysis temperature as follows: 25–270 °C, $\text{C}_3\text{H}_7\text{NH}_2$ (91–99%) and $\text{CH}_3\text{CH}=\text{CHNHC}_3\text{H}_7$ (1–9%); 280–500 °C, $\text{C}_3\text{H}_7\text{NH}_2$ (90%), $\text{CH}_3\text{CH}=\text{CHNHC}_3\text{H}_7$ (6%), and $(\text{C}_3\text{H}_7)_2\text{NH}$ (4%); 510–740 °C, $\text{C}_3\text{H}_7\text{NH}_2$ (80%) $\text{CH}_3\text{CH}=\text{CHNHC}_3\text{H}_7$ (11%), and $(\text{CH}_3\text{H}_7)_2\text{NH}$ (4%). These ratios were determined by VPC/MS techniques and were confirmed by ^{31}P and ^1H NMR analysis of the material condensed from the nitrogen flow. The dipropylamine was formed via the well-known amine equilibration reactions, and the alkeneamine was presumably generated by hydrogen elimination. The loss of these amines is reflected in the thermogravimetric analysis curve shown in Figure 6. Similar processes underlie the weight losses detected for the other polymers at temperatures below 800 °C.

The additional volatile products were formed when the systems were heated (in a nitrogen flow) at temperatures between 800 and 1000 °C. These products collected by vapor deposition on the inside walls of the quartz flow tube at points beyond the heated zone. The product deposited closest to the heated zone, at 400–500 °C, was a yellow-brown material with a metallic appearance. The second product, an orange material, was deposited further from the heated zone in regions of the tube that had a temperature of 300–400 °C. Both products had infrared spectra in the P–N region (820–940 cm^{-1}) that were similar to those of various phosphorus nitrides, including P_3N_5 ,^{21–23} but neither spectrum exactly matched those reported for known phosphorus nitrides. The loss of these products can be detected also from the thermogram (Figure 6).

(21) Corbridge, D. E. C. *Phosphorus: An Outline of its Chemistry, Biochemistry, and Technology*; Elsevier Scientific: New York, 1980.

(22) Veprek, S.; Roos, J. J. *Phys. Chem. Solids* 1976, 37, 554.

(23) Hirota, Y.; Kobayashi, T. *J. Appl. Phys.* 1982, 53, 5037.



The yellow-brown product was identified as a phosphorus nitride by transmission electron microscopy and energy-dispersive spectroscopy. This material formed an extremely hard coating on the inside of the quartz tube. An attempt to obtain a SIMS analysis of this material was frustrated by the tendency of the compound to react with the substrate platinum foil on which it was deposited during vapor deposition. The orange product was completely amorphous (by X-ray analysis). It was insoluble in common organic solvents but was partly soluble in concentrated hydrochloric acid. When exposed to the atmosphere within a short time of its deposition, it proved to be pyrophoric but lost this property after storage in nitrogen for several hours.

The residue left after heating of the polymer to 1000 °C was a black, porous material that consisted of a graphitic matrix containing regions of crystalline phosphorus nitride. Energy-dispersive spectroscopy and solid-state ^{13}C NMR spectroscopy provided the evidence for the presence of graphitic carbon. Transmission electron microscopy generated d spacings that corresponded closely to those of $\gamma\text{-P}_3\text{N}_5$. Elemental microanalysis indicated the presence of carbon, hydrogen, phosphorus, and nitrogen, although the material was so inert that complete analysis could not be obtained.

Polymer $[\text{NP}(\text{NHC}_3\text{H}_7)_2]_n$ was also pyrolyzed in argon, ammonia, and under vacuum (0.5 Torr) to give a completely amorphous residue. The pyrolysis in argon yielded a different product from the reaction in nitrogen, and this suggested that the nitrogen gas is a participant in the reactions at the highest temperatures. Pyrolysis in vacuum yielded similar products to the reaction in argon. Heating in ammonia generated a hard, white, chemical vapor deposition product at the higher temperatures, and it was clear that the overall chemistry of the thermolysis was modified by the participation of this reagent.

The behavior of the other aminophosphazene polymers during pyrolysis in a flow of nitrogen generally followed a profile similar to that described above for the n -propylamino derivative. The main differences were connected with the amount of volatile material lost by the time the temperature had reached 1000 °C. For $[\text{NP}(\text{NHC}_6\text{H}_5)_2]_n$ approximately 30% remained at 1000 °C. For $[\text{NP}(\text{NHCH}_3)_2]_n$, the corresponding value was also 30%, while for $[\text{NP}(\text{NHC}_4\text{H}_9)_2]_n$ the value was 17%.

Although the exact structures of the products formed from these polymers at high temperatures are not known, the initial side-group condensation/elimination reactions appear to follow the reactions shown in Scheme III. Continued loss of amines eventually leaves a highly cross-linked material that approaches the composition of phosphorus nitride. Those polymers with the highest initial concentration of carbon atoms in the side groups also

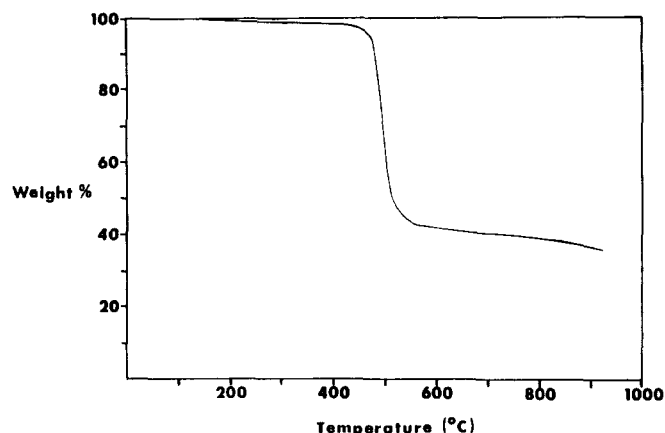


Figure 7. Thermogravimetric analysis curve for $[\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_4(\text{C}_5\text{H}_4)_2\text{Fe}]_n$.

give rise to the carbonaceous phase that forms one component of the heterogeneous graphitic/phosphorus nitride residue. At temperatures above 800 °C, part of the phosphorus nitride component volatilizes to give the species that generate the yellow-brown and orange phosphorus-nitrogen vapor deposition products.

Metallocene Side Groups. The transannular metallocene polymers $[\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]_n$ (7) and $[\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_4(\eta\text{-C}_5\text{H}_4)_2\text{Ru}]_n$ (8), underwent cross-linking reactions exclusively in the temperature range 200–450 °C. Samples heated at 200 and 250 °C swelled in solvents in which they were previously soluble, but they did not dissolve. A sample heated at 300 °C did not swell. No weight loss occurred at these temperatures. It seems probable that cross-linking of these polymers occurs either through intermolecular exchange of cyclopentadiene units (Scheme IV, pathway A) or by cleavage of the P–N backbone and subsequent exchange of skeletal bonds with another macromolecule (Scheme IV, pathway B). On the basis of the study of poly[bis(trifluoroethoxy)phosphazene], cross-linking through the trifluoroethoxy side groups is not likely.

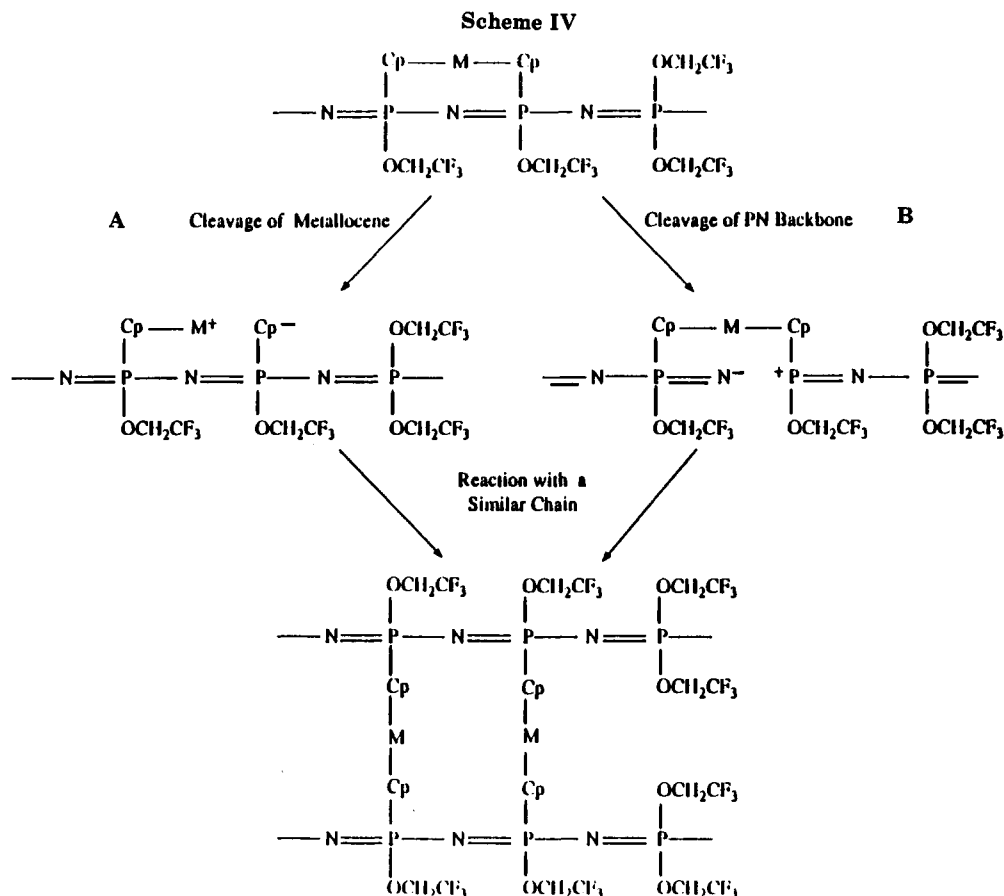
To examine the plausibility of mechanism A, it was necessary to obtain experimental evidence for the cleavage and reformation of the bond between iron and cyclopentadienyl groups at elevated temperatures.²⁴ Thus, an equimolar mixture of $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ and $\text{Fe}(\eta\text{-C}_5\text{H}_4\text{Me})_2$ was heated in an evacuated sealed glass tube at 250 °C. After 14 days the reaction products were analyzed by ^{13}C NMR and were shown to consist of the ligand-exchanged species $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{H}_4\text{Me})$ (yield ca. 60%), together with unreacted starting materials. One possible mechanism for this exchange involves an initial iron-cyclopentadienyl bond cleavage followed by formation of a triple-decker “turntable” intermediate (or transition state) that then undergoes cleavage to afford the ligand-exchanged species.²⁵ A triple-decker species of this type has been detected by mass spectrometry as a product of the ion-molecule reaction between $\text{Fe}(\eta\text{-C}_5\text{H}_5)^+$ and ferrocene.^{26,27} This experiment demonstrates that a cross-linking mechanism that involves ligand exchange between iron-cyclopentadienyl groups is a clear possibility. However, the

(24) Cyclopentadienyl ligand exchange has been detected between cobalt atoms of different transition metals in various organometallic complexes. See: Garrou, P. E. *Adv. Organomet. Chem.* 1984, 23, 95.

(25) An analogous mechanism involving neutral, radical intermediates instead of cationic species is also possible.

(26) Schildcrout, S. M. *J. Am. Chem. Soc.* 1973, 95, 3846.

(27) The isolatable triple-decker species $[(\eta\text{-C}_5\text{H}_5)_2\text{Ni}(\eta\text{-C}_5\text{H}_5)]^+$ is also known; see: Werner, H.; Ulrich, B.; Salzer, A. *J. Organomet. Chem.* 1977, 141, 339.



alternative mechanism (Scheme IV, mechanism B) is more difficult to test experimentally and cannot be ruled out.

At 500 °C the system eliminated small molecules that when analyzed by VPC/MS methods were found to contain the transannular phosphazene cyclic trimer $N_3P_3(OCH_2CF_3)_4(C_5H_4)_2Fe$. This process is illustrated by the thermogravimetric analysis plot shown in Figure 7. After the systems had been heated to 1000 °C, the ultrastructure residue amounted to 28% of the original weight in the case of the ferrocenyl derivative and 25% for the ruthenocenyl system.

It seems clear that the metallocenyl side groups stabilize the polyphosphazenes against depolymerization in the 150–250 °C temperature range, but at the expense of cross-linking to form insoluble ultrastructure materials.

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, was supplied by Ethyl Corp. Poly(dichlorophosphazene) was prepared by a method described previously.²⁸ Tetrahydrofuran and dioxane were distilled into the reaction flask under an atmosphere of dry argon from a sodium benzophenone ketyl drying agent. Hexane and tetramethylenediamine were distilled from calcium hydride before use. Methylamine was used as received from Matheson. *n*-Propylamine and *n*-butylamine were obtained from Alfa and were distilled under nitrogen before use. Phenol and *p*-methylphenol were obtained from Aldrich and were purified by sublimation. Ferrocene (Aldrich) was purified by vacuum sublimation (50 °C/0.002 mmHg). Butyllithium (1.6 M in hexane) was obtained from Aldrich. Methyl iodide (Aldrich) was distilled before use.

Analytical Equipment and Techniques. 1H , ^{13}C , and ^{31}P NMR spectra were recorded with the use of a JEOL FX-90Q spectrometer operated at 36 MHz or a Bruker WP-360 spec-

trometer. Positive chemical shifts are downfield from external phosphoric acid. Thermogravimetric analyses were recorded with the use of a Perkin-Elmer TGA-7 unit equipped with a PE 7500 computer. Electron impact mass spectra were obtained on a AEI MS 950 instrument. Volatile byproducts were analyzed by using a Varian 3700 gas chromatograph and a Finnigan gas chromatograph/mass spectrometer. The molecular weights of the polymers were estimated by gel permeation chromatography with the use of a Hewlett-Packard HP 1090 liquid chromatograph equipped with a refractive index detector. Polymer Laboratories PLgel (10^6 , 10^5 , 10^3 Å) columns were calibrated with narrow molecular weight polystyrene standards. A 0.1% *n*-Bu₄Br solution in THF was used as the eluent.

Synthesis of the Poly(organophosphazenes). The alkoxy-, aryloxy-, amino-, and metallocenylphosphazene polymers were prepared and characterized by using procedures described in the literature.^{28–32} The methyl- and methylphenylphosphazene polymers were prepared by the procedure developed by Neilson, Wisian-Neilson, and co-workers.¹⁷

Synthesis of $Fe(\eta-C_5H_4Me)_2$. To a stirred suspension of $Fe(\eta-C_5H_5)_2$ (10.1 g, 54.3 mmol) in hexane (200 mL) was added slowly and dropwise a mixture of *n*-butyllithium (75 mL of a 1.6 M solution, 120 mmol) and tetramethylenethylenediamine (21 mL, 139 mmol). After 24 h at 25 °C the reaction mixture was cooled to –50 °C and a solution of excess methyl iodide (22.0 g, 155.0 mmol) in THF (50 mL) was added dropwise. When the addition was complete, the reaction mixture was stirred for 24 h at 25 °C and was filtered to remove lithium iodide, and the solvent was removed under vacuum. Chromatography on silica gel, using hexane as the eluent, afforded an orange, oily solid. Three vacuum sublimations (40 °C/0.002 mmHg) onto a cooled (–78 °C) probe afforded pure $Fe(\eta-C_5H_4Me)_2$ as orange-yellow

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(30) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.

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(32) Allcock, H. R.; Lavin, K. D.; Riding, G. H. *Macromolecules* **1987**, *20*, 6.

(28) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.

crystals (yield 6.3 g, 54%). The purity of the product was confirmed by ^{13}C NMR.³³

Reactions in Sealed Glass Tubes. The polymers were heated in sealed Pyrex tubes, 220 mm long, 12-mm o.d., and 10-mm i.d., with a constriction 100 mm from the open end. The tubes were cleaned with ethanolic potassium hydroxide and were then washed in turn with tap water, 2% aqueous hydrochloric acid, and distilled deionized water. The tubes were then dried at 140 °C for 48 h. Each tube was charged with 10–15 g of polymer in a nitrogen-filled drybox and was then connected to a vacuum line for evacuation for 30 min at 0.005 Torr. The tubes were sealed at the constriction, wrapped in aluminum gauze, and placed on a rocking device in a Freas thermoregulated oven equilibrated at the required temperature. The tubes were removed from the oven, placed in a desiccator, and allowed to cool to room temperature. They were then opened under dry nitrogen within a drybox, and the contents were dissolved in THF (5–10 mL) before analysis by ^{31}P NMR spectroscopy.

Pyrolysis of the Polymers in a Tube Furnace. The polymer samples were placed in a ceramic boat, which was placed in a quartz flow tube and heated in a Linderberg 55035A tube furnace. The entire pyrolysis was carried out under a constant flow of nitrogen. The samples were heated from 25 to 1000 °C over 2 h, and fractions of the volatile byproducts were collected in a trap cooled to -196 °C. The volatile products were analyzed by gas chromatography/mass spectrometry and, when appropriate, by NMR spectroscopy.

The temperatures within the quartz tube downstream of the heated zone were measured in the following way. The tube furnace

was operated under the conditions normally employed for the pyrolysis reactions. A nitrogen flow was established at a flow rate of 50–75 mL/min, and the furnace was allowed to reach operating temperature. Temperatures within the flow tube were measured by means of a Cole Parmer Digi-Sense unit with type K thermocouple. Higher temperatures were detected near the inside wall of the tube than in the center of the gas flow, and the reaction temperatures quoted take this into account.

Thermogravimetric Analyses of the Polymer Systems. The polymer samples (1–3 mg) were analyzed under a constant flow of nitrogen in platinum pans at a heating rate of 2 °C/min with an initial temperature of 50 °C and a final temperature of 1000 °C. The instrument was calibrated by using the magnetic standards alumel (163 °C), nickel (354 °C), and peralloy (596 °C) samples.

Thermally Induced Cyclopentadienyl Ligand Exchange between $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ and $\text{Fe}(\eta\text{-C}_5\text{H}_4\text{Me})_2$. A solid mixture of $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ (0.64 g, 3.44 mmol) and $\text{Fe}(\eta\text{-C}_5\text{H}_4\text{Me})_2$ (0.74 g, 3.46 mmol) was placed in a thick-walled Pyrex glass tube that was then cooled to -196 °C, sealed under vacuum (0.002 mmHg), and heated to 250 °C. After 14 days the contents of the tube were dissolved in CDCl_3 (5 mL) and were analyzed by high-field ^{13}C NMR spectroscopy. The product mixture consisted of the ligand-exchanged product $\text{Fe}(\eta\text{-C}_5\text{H}_4\text{Me})(\eta\text{-C}_5\text{H}_5)^{33}$ (ca. 60%) and the starting materials (each ca. 20%).

^{31}P Chemical Shifts Used for Product Identification. The ^{31}P NMR shifts (in parentheses) were as follows: $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$, $n = 10\text{--}15\,000$ (-7.9 ppm), $n = 3$ (+17.0 ppm), $n = 4$ (-2.0 ppm).

Acknowledgment. We thank the U.S. Air Force Office of Scientific Research for support of this work. We also thank R. Minard for the GC/mass spectrometry analyses.

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Metallaboranes as Molecular Precursors to Thin Metal-Boride Films. Conversion of $\text{HFe}_3(\text{CO})_9\text{BH}_4$ to Amorphous $\text{Fe}_{75}\text{B}_{25}$

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The thermal decomposition of $\text{HFe}_3(\text{CO})_9\text{BH}_4$ on glass or aluminum substrates at 175–200 °C at pressures between 10^{-5} and 10^{-4} Torr results in the deposition of uniform, amorphous alloy films of approximate composition $\text{Fe}_{75}\text{B}_{25}$ with individual film thicknesses ranging from 1000 to 10 000 Å. The glassy metal films have been characterized by Auger, X-ray, and Mössbauer spectroscopies. The Mössbauer spectra show that the local structure of the film is similar to that observed for films prepared by rapid quenching techniques. In contrast, magnetically ordered films prepared from $\text{HFe}_3(\text{CO})_9\text{BH}_4$ exhibit magnetic moments having a preferential orientation normal to rather than parallel with the film plane. Although the films are stable in air, oxidation during deposition readily takes place under poor vacuum conditions and leads to films containing oxidized boron. The stoichiometry of the oxide phase has been shown to be B_2O_3 (oxygen content 3–11%). The film resistivity increases with increasing oxygen content.

Introduction

Chemical vapor deposition (CVD) is a well-established methodology for the production of materials from molecular precursors.¹ In the early and current use of this

method, appropriate mixtures of small molecules containing the elements of interest are used. Recently it has been recognized that there are advantages to using sophisticated molecular precursors for the generation of solid-state materials. These advantages include milder deposition conditions, higher purities, better stoichiometry control, and better kinetic control of product formation. Hence, organic and inorganic chemists have become in-

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