–8.4 ppm. Elem. Anal. Calcd C, 42.40% H, 7.83%; N, 4.94%. Found: C, 41.28%; H, 7.85%; N, 4.96%. $M_w = 2 \times 10^6$.

Preparation of $[NP(HNCH_3)_2]_n$ (2). Polymer 2 was prepared by previously described methods.[25] The characterization data were consistent with previous preparations of this polymer: ^{31}P NMR +6.1 ppm(s); $M_w = 1 \times 10^6$.

Coating and Irradiation of Samples. Clean polymer film samples were dipped into 10% aqueous or methanolic solutions of 1 for 1 min and were then removed and allowed to dry. Each film was dipped a minium of five times. The multicoated films were dried for 24 h and were then sealed in an evacuated container. Samples were degassed and sealed under vacuum in freeze-dryer bottles. The samples were then irradiated with ^{60}Co γ-radiation at a dose rate of 0.222 Mrad/h for 0, 1, 5, or 10 Mrad. After irradiation, the films were soaked in and regularly shaken in deionized water for 5 days and were then soaked and shaken in ethanol for 1 day.

Three sets of controls were prepared. The first set was the pure polymer films that were simply soaked and shaken in water, as above. The second set were not coated with 1 but were exposed to 10 Mrad of γ-rays and then treated with water. The last control set was coated with 1 before exposure to water.

Stability of Hydrogel Grafts. Grafts of 1 were treated with 80% acetic acid, 0.1 N NaOH, THF, methanol, ethanol, hexane, and deionized water. During each treatment the samples were sonicated and agitated. The solutions were inspected visually to check for suspended hydrogel. In addition, the solutions were monitored by ^{31}P NMR spectroscopy to monitor for the presence of any dissolved polymer 1.

Acknowledgment. This work was supported by the National Institutes of Health, through the National Heart, Lung, and Blood Institute (Grant No. HL 11418) and by the Johnson and Johnson COSAT program.

Registry No. PTFE, 9002-84-0; Water, 7732-18-5.

Polyphosphazenes Bearing Polymerizable Pyrrole, Thiophene, and Furan Side Groups: Synthesis and Chemical Oxidation

Harry R. Allcock* and Jeffrey A. Dodge

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

Leon S. Van Dyke and Charles R. Martin*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521

Received April 2, 1992

The synthesis and chemical oxidation of linear poly(organophosphazenes) that bear polymerizable, heterocyclic side groups are described. The polymers were prepared for use as precursors to electronically conductive materials. The polymers have the general structure $[NP(OR)_2]_n$, where R is $-CH_2\overline{CCHSCHC}H$, $-CH_2CH_2\overline{CCHSCHC}H$, $-CH_2CH_2\overline{CSCHCHC}H$, $-CH_2CH_2CH_2\overline{NCHCHCHC}H$, $-CH_2\overline{CCHOCHC}H$, $-(CH_2)_{11}\overline{NCHCHCHC}H$, or $-(CH_2CH_2O)_2CH_2CH_2\overline{NCHCHCHC}H$, and $[NP(NHR)_2]_n$, where R is $-CH_2CH_2CH_2\overline{NCHCHCHC}H$ or $-CH_2CH_2\overline{CCHSCHC}H$. The cyclic trimer $[NP(OCH_2\overline{CCHSCHC}H)_2]_3$ was synthesized as a model compound and as a possible precursor to cyclomatrix conductive materials. Molecular structural characterization for the linear high polymers was achieved by the use of ^1H, ^{13}C, and ^{31}P NMR spectroscopy, gel permeation chromatography, and elemental microanalysis. The glass transition temperatures of the polymers were determined using differential scanning calorimetric analysis and were found to be in the range –48 to +1 °C. Chemical oxidation of the materials was carried out in solution using $Fe(ClO_4)_3$ or $FeCl_3$. The resultant dark, insoluble powders were compressed into pellets, and their electronic conductivities were measured. All the materials were found to be semiconductive with conductivities in the range 4×10^{-10}–5×10^{-5} S cm^{-1}. The results of attempted electrochemical oxidation and chemical oxidation using iodine are also described.

Introduction

In recent years, a growing interest has been evident in the development of electronically conductive organic polymers.[1,2] Such materials are technologically important because they offer the prospect of combining electronic conductivity with other useful properties such as toughness, flexibility, or ease of fabrication into devices. Among the most intensively studied conductive polymers are poly(pyrrole), poly(thiophene), and their derivatives. Research efforts in numerous laboratories are concentrated on improving the tractability of these materials.[3]

Poly(organophosphazenes) comprise a broad class of inorganic–organic polymers of general structure $[NPR_2]_n$.[4] The possibility that electronic conductivity might be induced in polyphosphazenes has been considered in earlier

---

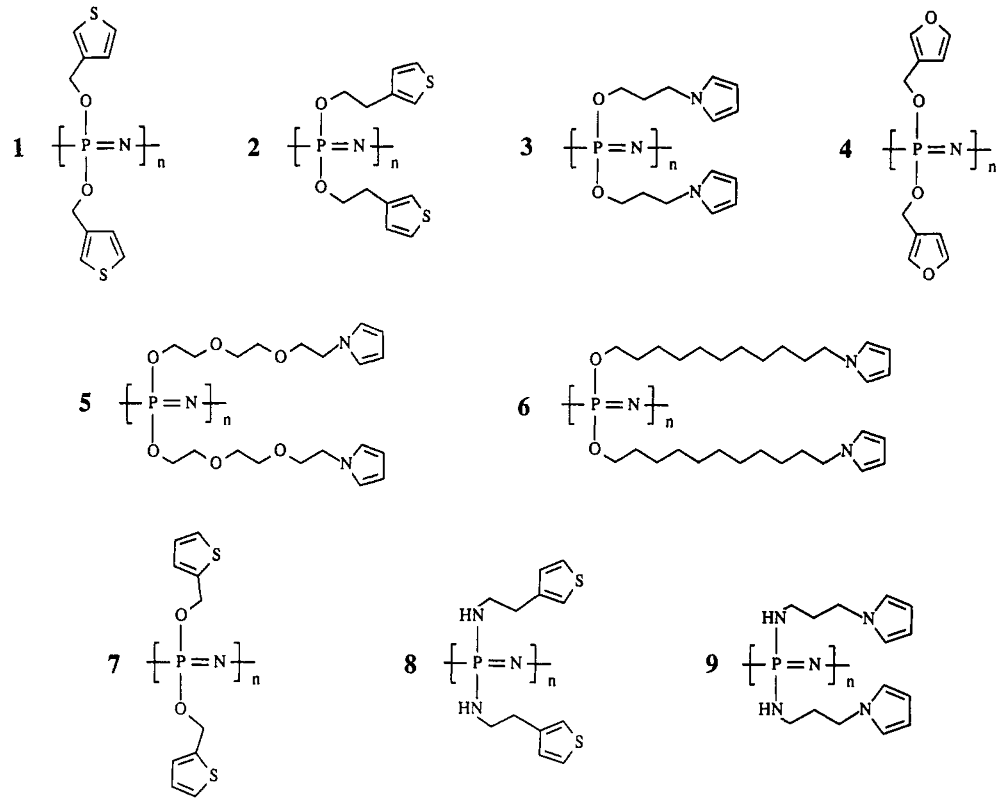
(1) *Handbook of Conductive Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.

(2) (a) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285. (b) Kanatzidis, M. G. *Chem. Eng. News* **1990**, *68* (49), 36.

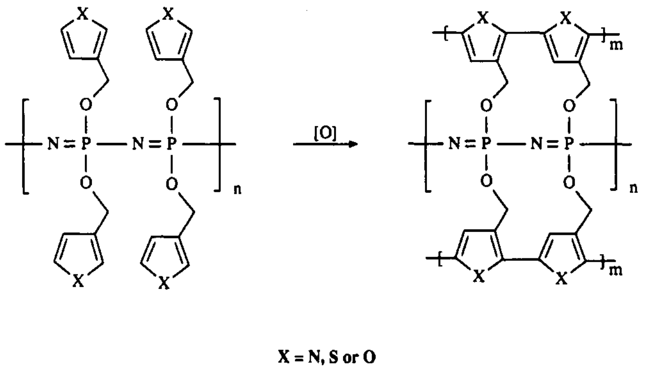
(3) *Processable Electronically Conductive Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1991.

(4) Allcock, H. R. *Phosphorus–Nitrogen Compounds: Cyclic, Linear, and High Polymeric Systems*; Academic Press: New York, 1972.

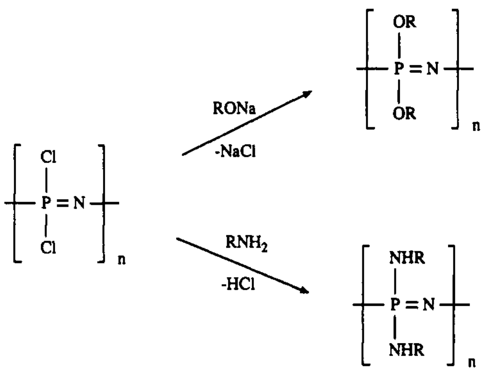
Chart I



Scheme I



Scheme II



work. However, attempts to generate conduction within the phosphorus–nitrogen backbone have not yet been successful.[5] Therefore, we and others have adopted an alternative "outrigger" approach in which the polymer backbone serves as a platform for the attachment of electroactive side groups.[6] For example, tetracyanoquinodimethane units have been attached as side groups to quaternized phosphazene polymers to provide materials that are inherent semiconductors.[7] Polyphosphazenes that contain phthalocyanine[8] and pyrrole[9] side groups have also been synthesized, and these polymers yield semiconductive materials following doping.

In this paper, we describe the synthesis and chemical oxidation of poly(organophosphazenes) that bear pyrrole, thiophene, or furan side groups. The objective was to prepare tractable, well characterized, high polymers that could be used as precursors to electronically conductive materials (Scheme I). Variations in the molecular structure of the side groups were explored, and these included changes in the type of heterocycle and the length and type of spacer group linking the heterocyclic unit to the polymer backbone. Conductivity measurements of the oxidized materials were taken from compressed pellets using both two- and four-point probe methods.

In the following discussion, the synthesis and characterization of compounds 1–10 is described first. The various oxidation experiments using these materials are then described together with a discussion of the conductivity measurements and materials characterization. The relationship between the conductivity of the oxidized materials and the structure of the side groups is also addressed.

Results and Discussion

Synthesis of Polymers 1–7. The overall synthetic pathway to single-substituent polymers 1–7 is summarized in Scheme II, and the corresponding molecular structures

---

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

(6) *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; American Chemical Society: Washington DC, 1988.

(7) Allcock, H. R.; Levin, M. L.; Austin, P. E. *Inorg. Chem.* **1986**, *25*, 2281.

(8) Allcock, H. R.; Neenan, T. X. *Macromolecules* **1986**, *19*, 1495.

(9) Haddon, R. C.; Stein, S. M.; Chichester-Hicks, S. V.; Marshall, J. H.; Kaplan, M. L.; Hellman, M. Y. *Mater. Res. Bull.* **1987**, *22*, 117.

Table I. Characterization Data for $[NP(OR)_2]_n$ and $[NP(NHR)_2]_n$

					EA	
compound	M_n	M_w	T_g, °C		calcd	found
$[NP(OCH_2\overline{CCHSCHCH})_2]_n$ (1)	1.2×10^5	2.0×10^6	−29	C	44.28	43.91
				H	3.69	3.64
				N	5.17	4.93
				Cl	0	0.05
$[NP(OCH_2CH_2\overline{CCHSCHCH})_2]_n$ (2)	9.8×10^4	8.5×10^5	−37	C	48.16	47.88
				H	4.68	4.81
				N	4.68	4.84
				Cl	0	0.24
$[NP(OCH_2CH_2CH_2\overline{NCHCHCHCH})_2]_n$ (3)	8.9×10^4	3.2×10^6	−35	C	57.34	57.64
				H	6.83	6.65
				N	14.33	14.64
				Cl	0	0.03
$[NP(OCH_2\overline{CCHOCHCH})_2]_n$ (4)	7.6×10^4	1.9×10^6	−44	C	50.21	52.33
				H	4.18	4.14
				N	5.86	5.82
				Cl	0	0.05
$[NP\{(OCH_2CH_2)_3\overline{NCHCHCHCH}\}_2]_n$ (5)	4.4×10^4	1.9×10^6	−48	C	54.42	54.48
				H	7.26	7.28
				N	9.52	9.42
				Cl	0	0.04
$[NP(O(CH_2)_{11}\overline{NCHCHCHCH})_2]_n$ (6)	4.5×10^4	1.7×10^6	−36	C	69.63	68.98
				H	10.06	10.11
				N	8.12	7.49
				Cl	0.	<0.4
$[NP(OCH_2CH_2\overline{CSCHCHCH})_2]_n$ (7)	6.7×10^5	1.4×10^6	−41	C	48.16	45.97
				H	4.68	5.00
				N	4.68	4.83
				Cl	0	0.44
$[NP(NHCH_2CH_2\overline{CCHSCHCH})_2]_n$ (8)	2.9×10^5	3.2×10^6	1	C	48.48	47.67
				H	5.39	5.49
				N	14.14	14.02
				Cl	0	0.61
$[NP(NHCH_2CH_2CH_2\overline{NCHCHCHCH})_2]_n$ (9)	1.3×10^5	4.1×10^6	−8	C	57.75	56.32
				H	7.56	7.53
				N	24.05	23.67
				Cl	0	0.61

Table II. NMR Data for $[NP(OR)_2]_n$ and $[NP(NHR)_2]_n$

compound	^{31}P, ppm	^{13}C, ppm	^{1}H, ppm
1	−7.4 (s)	138.5 (s), 127.3 (d), 125.5 (d), 123.0 (d), 63.2 (t)	7.0 (1 H), 6.9 (1 H), 6.8 (1 H), 4.9 (2 H)
2	−8.3 (s)	138.5 (s), 128.5 (d), 125.1 (d), 121.4 (d), 65.5 (t), 31.1 (t)	7.1 (1 H), 6.82 (1 H), 6.80 (1 H), 4.0 (2 H), 2.7 (2 H)
3	−7.7 (s)	120.3 (d), 108.3 (d), 62.8 (t), 45.4 (t), 32.0 (t)	6.5 (2 H), 6.1 (2 H), 3.7 (4 H), 1.8 (2 H)
4	−7.5 (s)	142.8 (d), 140.7 (d), 121.9 (s), 110.2 (d), 59.5 (t)	7.2 (m, 2 H), 6.2 (1 H), 4.7 (2 H)
5	−8.5 (s)	120.9, 108.1, 71.2, 70.4, 70.3, 49.3, 31.6, 14.1	6.6, 6.1, 4.0, 3.9 (all 2 H), 3.6 (m, 4 H), 3.4, 3.5 (both 2 H)
6	−8.5 (s)	120.3, 107.8, 65.4, 49.5, 31.6, 30.8, 30.0, 29.8, 29.4, 26.9, 26.2	6.6, 6.1 (both 2 H), 3.8 (4 H), 1.7 (2 H), 1.5 (2 H), 1.2 (16 H)
7	−8.4 (s)	140.4 (s), 126.8 (d), 125.2 (d), 123.3 (d), 66.2 (t), 31.1 (t)	7.0, 6.8, 6.7 (all 1 H), 4.0, 2.9 (both 2 H)
8	2.3 (s)	140.1 (s), 128.2 (d), 125.3 (d), 120.8 (d), 42.1 (t), 32.6 (t)	7.1 (1 H), 6.7 (2 H), 3.3 (1 H), 3.0 (2 H), 2.6 (2 H)
9	3.0 (s)	120.1 (d), 108.3 (d), 46.4 (t), 38.8 (t), 33.5 (t)	6.5, 6.1, 3.7 (all 2 H), 3.0 (1 H), 2.6, 1.7 (2 H)

are shown in Chart I. Characterization data for these products are listed in Tables I and II. Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of the cyclic trimer, $[NPCl_2]_3$.[10] All the products were prepared by a similar procedure, and the synthesis, purification and structural characterization of 1 will be discussed as a representative example.

Polymer 1 was prepared by the reaction of poly(dichlorophosphazene) with sodium 3-thienylmethoxide ($NaOCH_2\overline{CCHSCHCH}$) in tetrahydrofuran (THF). After the reaction had proceeded at room temperature for 3 days, the ^{31}P NMR spectrum of the mixture showed a single sharp resonance at −7.4 ppm, suggesting that full chlorine atom replacement had been achieved. The product was isolated by several reprecipitations from THF into water and from THF into hexanes. The polymer was obtained as a colorless elastomeric material after drying in vacuum. Structural characterization was achieved by using high-field ^1H, ^{13}C, and ^{31}P NMR analysis. The polymeric nature of the product was confirmed by means of gel permeation chromatography (GPC). The weight-average molecular weight (M_w) was estimated to be 2.0×10^6, and the number-average molecular weight (M_n) was 1.2×10^5. Further molecular characterization was obtained by elemental microanalysis, which also indicated the absence of unreacted phosphorus–chlorine bonds. Differential scanning calorimetric (DSC) analysis showed that the glass transition temperature (T_g) of 1 was −29 °C.

Polymers 2–7 were synthesized, isolated, and characterized in a manner similar to that described above for 1. All the polymers are colorless elastomeric materials with glass transition temperatures in the range −48 to −35 °C.

Synthesis of Polymers 8 and 9. Aminophosphazene polymers 8 and 9 were prepared by the reaction of

---

[10] (a) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4612. (b) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.

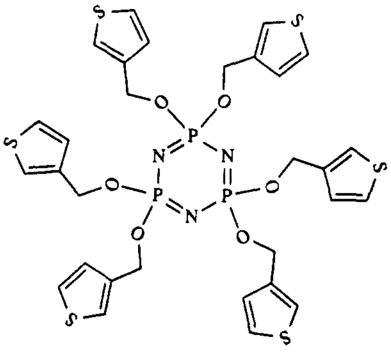
Table III. Characterization Data for $[\mathrm{NP(OCH_2\overline{CCHSCHC}H)_2}]_3$ (10)

^{31}P NMR, ppm	^{13}C NMR, ppm	^{1}H NMR, ppm	mass spectrom
+17.8 (s)	137.7 (s), 127.0 (d), 125.9 (d), 123.4 (d), 62.9 (t)	7.3–7.2 (m, 2 H), 7.1 (s, 1 H), 5.0 (s, 2 H)	calcd 813; found (EI) 768 $(M - HCS)^+$; found (FAB) 814 $(MH)^+$

$[NPCl_2]_n$ with excess $\mathrm{H_2NCH_2CH_2\overline{CCHSCHC}H}$ or $\mathrm{H_2NCH_2CH_2CH_2\overline{NCHCHCHC}H}$, respectively. Both reactions were carried out in the presence of triethylamine which functions as a hydrogen chloride acceptor. The products were isolated as white leathery materials following multiple reprecipitations from THF into water and from THF into hexanes. The molecular structures were confirmed by using high-field ^1H, ^{13}C, and ^{31}P NMR, GPC, and elemental microanalysis (Tables I and II). DSC analysis of 8 and 9 showed the glass transition temperatures to be +1 and −8 °C, respectively.

Properties of the Polymers. Polymers 1–9 were fully soluble in polar solvents such as THF, CH_2Cl_2, and $CHCl_3$ but were insoluble in water and ethanol. After standing in air for extended periods in the solid state, the materials darkened and became insoluble. This was attributed to oxidation and cross-linking of the side groups. The polymers may be stored without change in solution at low temperature (<0 °C) in the absence of light and oxygen.

Synthesis of Cyclic Trimer 10. Compound **10** was prepared by the treatment of $[NPCl_2]_3$ with excess sodium 3-thienylmethoxide. The product was purified by using liquid–liquid extraction. It is a colorless oil which is stable in solution but which decomposes rapidly when isolated.[11] The characterization data are listed in Table III. Elemental microanalyses were not obtained due to the tendency of this compound to decompose when isolated.



10

Attempted Electrochemical Oxidation of 1–10. Most polyphosphazenes are insulating materials.[4] The parent polymers in this work should also be insulating, since neither the phosphazene backbone nor the free side groups are electronically conductive. Conductivity measurements on the polymers revealed that they were insulating materials with conductivities of less than 10^{-10} S cm^{-1} (the lower limit of the instrumentation).

Electrochemical oxidations of the polyphosphazenes were attempted first, since the most common method for polymerizing heterocyclic monomers is via electrochemical oxidation.[12] Initial experiments were conducted with the use of acetonitrile-based electrolyte solutions, a common system for electrochemical polymerization of heterocyclic monomers. However, no current was detected at the phosphazene-coated electrodes when this solvent system was used, even when the potential was scanned to +3.0 V. Indeed, double-layer charging currents were absent with these film-coated electrodes because the polymers completely passivated the substrate electrode surface. This suggests that the polymer films were not solvated by acetonitrile since solvation of a film (to allow ion transport) is necessary if the electropolymerization reaction is to occur.

Table IV. Conductivities of Oxidized 1–10

polym	conductivity, S cm^{-1}	polym	conductivity, S cm^{-1}
1[a,b]	5×10^{-7}, 4×10^{-7}	6[c]	4×10^{-9}
2[c]	7×10^{-7}	7[d]	$<10^{-10}$
3[c]	5×10^{-5}	8[d]	2×10^{-7}
4[a]	2×10^{-7}	9[b,d]	1×10^{-6}, 2×10^{-6}
5[c]	1×10^{-7}	10[e]	4×10^{-10}

[a] Polymer was swollen with methylene chloride, oxidized with $Fe(ClO_4)_3$. [b] First value is two-point measurement; second value is four-point measurement. [c] Polymer was swollen with benzonitrile, oxidized with $Fe(ClO_4)_3$. [d] Polymer was dissolved in benzonitrile, oxidized with $Fe(ClO_4)_3$. [e] Cyclic trimer was dissolved in methylene chloride, oxidized with $FeCl_3$.

In an attempt to improve film solvation, analogous potential sweep experiments were conducted with the use of benzonitrile, nitrobenzene, and methylene chloride electrolyte solutions containing 0.2 M $n\text{-}Bu_4NBF_4$. With these systems, double-layer charging currents were detected at the substrate platinum electrode, and this indicated that the polymer films had been solvated and that ingress and egress of ions had occurred. However, even under these conditions, no oxidation currents were detected and only those currents associated with solvent breakdown at potentials greater than +2 V were apparent.

In addition to the potential sweep method described above, the application of a constant current to the working electrode has been used for electroctrochemical oxidative polymerization of heterocyclic monomers.[12] Therefore, a constant current of 1 mA/cm^2 was applied to the various polymer-coated electrodes. This resulted in potentials greater than 3 V. No visible change, such as darkening of the polymer films was observed, and no heterocyclic polymer electrochemistry was detected, even after several hours of applied current. The conclusion from these experiments was that electrochemical oxidation failed to bring about the polymerization of the polymer heterocyclic side groups (Scheme I).

Chemical Oxidation of 1–10. Chemical oxidation is an alternative to electrochemical polymerization of heterocyclic monomers.[13-15] This is typically accomplished by using Fe(III) salts as the oxidant. This methodology was used here to oxidize compounds 1–10. Treatment of these species in solution with $Fe(ClO_4)_3$ or $FeCl_3$ yielded dark insoluble powders. These materials were ion exchanged using BF_4^- (to replace the explosive perchlorate anion), dried under vacuum, and then compressed into pellets. Table IV lists the measured conductivities of the resultant materials. In most cases, the conductivities did increase for the oxidized polymers. Indeed, the conduc-

---

(11) When isolated, compound **10** undergoes a spontaneous rearrangement to the corresponding phosphazane[4] (as determined using ^{31}P and ^{13}C NMR and mass spectral analysis).

(12) Diaz, A. F.; Bargon, J. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, p 81.

(13) Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, p 293.

(14) Myers, R. E. *J. Electron. Mater.* **1986**, *15*, 61.

(15) Machida, S.; Miyata, S.; Techagumpuch, A. *Synth. Met.* **1989**, *31*, 311.

tivities of polymers 3 and 9 increased by at least 4–5 orders of magnitude. These data suggest that a form of heterocyclic-based polymer is produced within the polyphosphazene matrix. The dark color of the oxidized materials provides additional evidence for this. Furthermore, the conductivities of oxidized 3 and 9 are not significantly lower than those of homopolymers prepared from the corresponding *N*-alkyl-substituted pyrroles.[12,16] For example, the conductivity of poly(*N*-*n*-butylpyrrole) is 1×10^{-4} S cm,[16] while the conductivity of oxidized 3 is 5×10^{-5} S cm^{-1}. In addition, the conductivities of oxidized 3 and 9 are comparable to that of oxidized poly[bis(pyrrolyl)-phosphazene] (10^{-6} S cm^{-1}).[9]

Polymers 5 and 6 also bear pyrrole side groups, but the spacer groups are much longer than those in 3 and 9. The longer spacer groups were incorporated into the structures to provide improved freedom of motion for the heterocyclic side groups. In principle, this should aid in the polymerization of the pyrrole units by providing more flexibility. However, the conductivities of oxidized polymers 5 and 6 (long spacer) are much lower than those of 3 and 9 (short spacer).

The lower conductivities of the polymers with the longer spacers may be explained as follows: Conductivity in electronically conductive polymers depends on both intrachain and interchain hopping rates.[17,18] An increase in the interchain hopping distance in substituted pyrroles leads to a decrease in the interchain hopping rate and thus to a decrease in the resultant conductivity. The length of the spacer groups in 5 and 6 probably increases the distance between the poly(pyrrole) chains within the polymer matrix and this may explain the reduced electronic conductivity.

With the exception of polymer 7 (vide infra), the thiophene (1, 2, and 8) and furan (4) polymers showed conductivities somewhat lower than those of the short chain pyrrole polymers, 3 and 9. The conductivity of poly(thiophenes) synthesized via chemical oxidation is often poor[13,19] probably because of the higher oxidation potentials for these monomers, relative to pyrrole.[20,21] This higher oxidation potential may lead to incomplete oxidation of the thiophene groups. Furthermore, because of the higher oxidation potential, the radical cations produced are more reactive. This may lead to side reactions such as the incorporation of oxygen, mislinking of the heterocyclic units, or other reactions that generate nonconductive materials.[20–22]

Iodine Oxidation. The conductivity of polymer 8 after oxidation using iodine vapor increased dramatically from $<10^{-10}$ to 10^{-2} S cm^{-1} over several hours. The conductivity was stable in the presence of iodine, but when the material was exposed to a dynamic vacuum, the conductivity decreased rapidly to a stable value of 10^{-6} S cm^{-1}. Similar behavior was found for control polymer 7 (see below). Iodine doping caused the conductivity of 7 to approach 10^{-5} S cm^{-1}, but following exposure to a dynamic vacuum, the conductivity quickly fell to below 10^{-8} S cm^{-1}.

High conductivity in the presence of iodine vapor, but low conductivity after evacuation has been reported for iodine-doped poly(phenylenevinylene)[23,24] and poly(phenylacetylene).[25,26] This behavior has been attributed to the formation of a charge-transfer complex between the iodine and the polymer. The mechanism for the resultant conductivity is still a subject for debate.[23,25–27] The highest reported conductivity for a polyphosphazene is 10^{-4} S cm^{-1} for iodine-doped poly[bis(4-(dimethylamino)phenoxy)-phosphazene].[28] It was reported that the conductivity level was stable in the presence of iodine, but the effect of dynamic vacuum on the conductivity of the material was not mentioned.

Control Polymers. Poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$,[10b] was used as a control for the oxidation experiments. The formation of a conductive material from this polymer would imply that the conduction is the result of oxidation of the phosphorus–nitrogen backbone. The trifluoroethoxy side groups should be inert to the oxidation conditions used in this work. If the compound could not be oxidized, then any electronic conductivity in oxidized materials 1–10 must be due to the side groups and not the polymer backbone.

Several attempts were made to oxidize $[NP(OCH_2CF_3)_2]_n$. Potential sweep experiments conducted in a variety of solvents (such as MeCN, PhCN, and $PhNO_2$) with 0.2 M n-Bu_4NBF_4 supporting electrolyte revealed no oxidation currents up to a potential of +3.0 V. Only currents associated with solvent breakdown were detected.

This polymer proved to be impervious to chemical oxidation as well. Attempted oxidation using $Fe(ClO_4)_3$, $FeCl_3$, and I_2 resulted in no detectable interaction and the polymer could be reisolated unchanged. Therefore, the phosphorus–nitrogen backbone in $[NP(OCH_2CF_3)_2]_n$ appears to be resistant to oxidation under the conditions used in this work and any conductivity in 1–10 is most likely a contribution from the heterocyclic side groups.

Compound 7 was also prepared for use as a control polymer; it has a structure more closely related to the heterocyclic polymers used in this work. Polymer 7 was designed so that although oxidation and cross-linking could take place through the open 5-position on the thiophene ring, polymerization could not occur to yield a conjugated heterocyclic polymer. Only nonconductive thiophene dimers should result from oxidation. It is known that reaction at the open 3 and 4 positions does not occur readily, and even if it did, this would yield nonconjugated, and therefore nonconductive, materials. Thus, any conductivity detected in 7 following oxidation would probably be a contribution from the polymer backbone.

Polymer 7 was oxidized chemically in benzonitrile using $Fe(ClO_4)_3$ as described below. Following anion exchange and drying, the conductivity was found to be $<10^{-10}$ S cm^{-1}. Electrochemical oxidation was not attempted. From this result, it is evident that conjugation within the heterocyclic polymer chains is required for electronic conduction in these materials and, as discussed, conduction resulting from oxidation of the phosphorus–nitrogen backbone can be ruled out.

---

(16) Diaz, A. F.; Castillo, J.; Kanazawas, K. K.; Logan, J. A.; Salmon, M.; Fajardo, O. *J. Electroanal. Chem.* **1982**, *133*, 233.

(17) Street, G. B. In *Handbook of Conductive Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, p 265.

(18) Ruhe, J.; Ezquerra, T. A.; Mohammadi, M.; Enkelmann, V.; Kremer, F.; Wegner, G. *Synth. Met.* **1989**, *28*, C217.

(19) Mermilliod-Thevenin Dein-Lera, N.; Bidan, G. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 227.

(20) Waltman, R. J.; Bargon, J. *Can. J. Chem.* **1986**, *64*, 76.

(21) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173.

(22) Lei, J.-T.; Cai, Z.; Martin, C. R. *Synth. Met.* **1992**, *46*, 53.

(23) Bradley, D. D. C.; Hartmann, T.; Friend, R. H.; Marseglia, E. A.; Lindenberger, H.; Roth, S. In *Electronic Properties of Conjugated Polymers*; Kuzmany, H., Mehring, M., Eds.; Springer-Verlag: Berlin, 1987; p 308.

(24) Liang, W. B.; Masse, M. E.; Karasz, F. E. *Polymer*, in press.

(25) Diets, W.; Cukor, P.; Rubner, M.; Jopson, H. *IE&C Prod. Res. Dev.* **1981**, *20*, 696.

(26) Cukor, P.; Krugler, J. I.; Rubner, M. F. *Makromol. Chem.* **1981**, *182*, 165.

(27) Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209.

(28) Haddon, R. C.; Chichester-Hicks, S. V. *Macromolecules* **1989**, *22*, 1027.

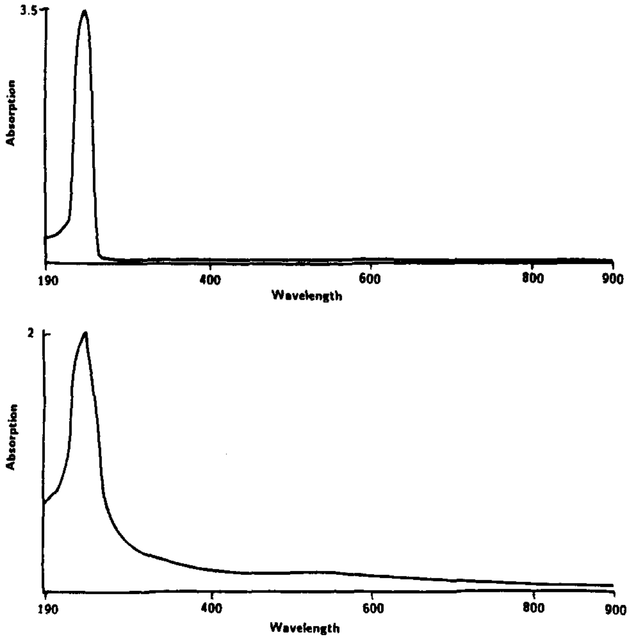


Figure 1. UV-visible absorption spectra of polymer 1 in methylene chloride: (a, top) as-synthesized polymer; (b, bottom) polymer oxidized with $Fe(ClO_4)_3$.

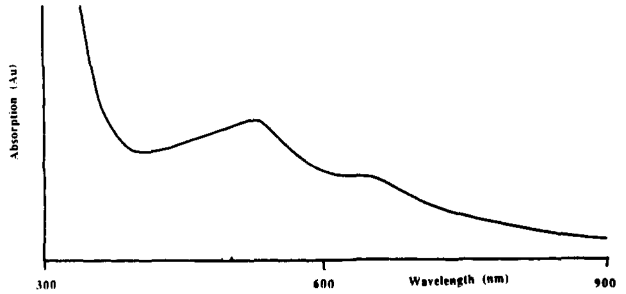


Figure 2. Visible portion of absorption spectrum for polymer 1 in methylene chloride.

Optical Properties. High conductivity in heterocyclic polymers is associated with the presence of conjugated sequences in the polymer chain. This requires that the polymer be α,α bonded and that the constituent heterocyclic rings be oriented coplanar to each other.[29] The relatively low conductivity of oxidized materials 1–10 suggests that the degree of conjugation in the polymerized heterocyclic groups in these polymers is low. UV-visible spectroscopic analysis can be used to estimate the degree of conjugation.[13,30,31] For example, the λ_{max} of thiophene is 240 nm, while the λ_{max} for completely α,α-bonded alkyl-derivatized thiophene chains is 345, 412, and 462 nm for the trimer, pentamer, and undecimer, respectively.[31] In contrast to these conjugated systems, a polymer comprised of thiophene units linked at the 2 and 4 positions is nonconjugated and has the same λ_{max} as the monomer.[13]

In general, the polyphosphazene backbone absorbs only at wavelengths below 210 nm.[4] Thus, any absorption at wavelengths longer than 210 nm can probably be attributed to the side groups. Figure 1a shows the UV-visible absorption spectrum of pure polymer 1 in methylene chloride. The only absorption peak is at 235 nm, and this corresponds closely to the absorption for thiophene. The oxidized polymer retains a very strong absorption peak at 235 nm (Figure 1b), but this peak now tails much further into the visible region of the spectrum.

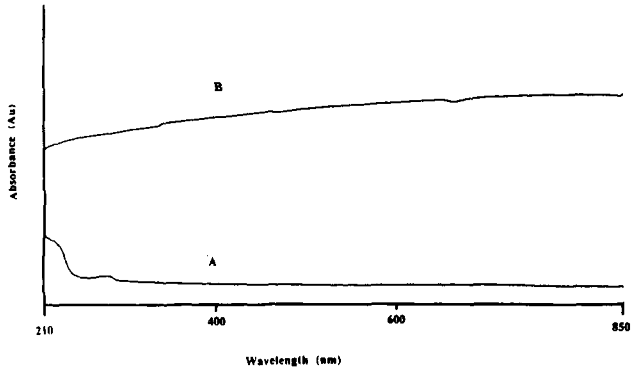


Figure 3. UV-visible absorption spectra of polymer 3: (A) as-synthesized polymer; (B) polymer after oxidation with $Fe(ClO_4)_3$.

Table V. Elemental Analysis of Oxidized Polymer 3[a]

atom	elem anal, %	atomic ratio[b]	theor atomic ratio
C	42.90	14.1	14
H	5.14	20.1	16
N	10.66	3.0	3
P	7.84	1.0	1
F	11.53	2.4	
Fe	0.07		

[a] Polymer was swollen with benzonitrile, oxidized with $Fe(ClO_4)_3$, and then ion exchanged with BF_4^- (see text for details). [b] Calculated from elemental analysis assuming a ratio of one for phosphorus.

This tailing into the visible region is characteristic of doped polythiophenes.[32] Thus, it seems clear that some thiophene polymerization occurred upon oxidation of polymer 1. However, the peak at 235 nm is still intense after the oxidation, and this suggests that a large percentage of the side groups were either not oxidized or reacted to give nonconjugated sequences. Figure 2 shows the visible portion of the spectrum of oxidized polymer 1 at a higher concentration in methylene chloride. The absorption at 525 nm is often found in lightly doped poly(3-alkylthiophenes).[32] This suggests that at least some of the thiophene groups were polymerized.

Figure 3 shows the UV-visible spectra for both the pristine and oxidized forms of polymer 3. Like polymer 1 above, the compound shows transitions typical of the side groups. By contrast, the oxidized polymer absorbs strongly throughout the visible region of the spectrum. However, unlike the oxidized form of polymer 1, no strong monomer peak remained in oxidized material 3. This suggests that most of the pyrrole groups in polymer 3 have been polymerized and this may explain the higher conductivity of the oxidized material.

Elemental Analyses of Polymer 3. Another assessment of the effectiveness of chemical oxidation is by the use of elemental analysis to estimate the doping level of the polymer. Because polymer 3 had the highest conductivity, elemental analyses were obtained for this material. Table V lists the analysis data for 3 after oxidation in benzonitrile using $Fe(ClO_4)_3$ and ion exchange using BF_4^-. The atomic ratios of carbon, nitrogen, and phosphorus are very close to the theoretical values. This suggests that the polymer structure has remained intact during oxidation. The hydrogen content is higher than predicted, as is often found for heterocyclic polymers.[33]

---

(29) Daoust, G.; Lerclerc, M. *Macromolecules* **1991**, *24*, 455.

(30) Roncali, J.; Tassar, A.; Garnier, F. *J. Chem. Soc., Chem. Commun.* **1988**, 581.

(31) ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887.

(32) Roncali, J.; Marque, P.; Garreau, R.; Garnier, F.; Lemaire, M. *Macromolecules* **1990**, *23*, 1347.

The excess may result from hydrogen which failed to eliminate during polymerization of the pyrrole groups (such as at chain ends) or from absorbed water. The oxidized forms of heterocyclic polymers are often hygroscopic and can absorb large amounts of water.[33]

The mass balance for the polymer was poor; the percent composition did not total to 100%. Addition of the theoretical quantities of boron (1.6%) and oxygen (8.1%) brings the total to only 88%. The discrepancy is most likely due to excess oxygen in the material. This oxygen may be covalently bound to the heterocyclic polymer chains, or it may be present as absorbed water.[33]

The most important information obtained from the elemental analysis data is the doping level. The ratio of fluorine to phosphorus (2.4:1) corresponds to an approximately 30% doping level (one BF_4^- anion for every three pyrrole units). Typical doping levels for heterocyclic polymers are 25–33%.[12] This suggests that the oxidized form of polymer **3** is highly doped. The relatively low conductivity of this material may therefore result from a low degree of conjugation in the heterocyclic side-group chains.

Factors Affecting Oxidation. Both the spectroscopic and the conductivity data indicate that a relatively low degree of conjugation was obtained in these systems. In fact, it may be sterically difficult to achieve a high degree of conjugation in the outrigger side groups along a single unoriented polymer chain.

First, consider the effect of size of the heterocyclic units compared to the bond lengths and bond angles in the polyphosphazene backbone. Crystallographic studies on 2,2,4,4,6,6-hexa(1-pyrrolyl)cyclotriphosphazene have been reported.[34] These studies indicated that the distance between directly P-bonded pyrrole groups is probably too great to allow formation of a continuous chain if the phosphazene backbone occupies the preferred cis–trans conformation.[4] However, the work suggested that if the phosphorus–nitrogen backbone is in an all trans conformation, polymerization of the pyrrole units may be possible. Since the polyphosphazene backbone is inherently flexible, it is theoretically possible for the backbone to adopt the conformation necessary for polymerization of the heterocyclic side groups in the polymers used here.

In addition to polymerization of side groups along the same chain, cross-linking of heterocyclic units between different polymer chains undoubtedly occurs. However, it may be difficult to obtain the planarity necessary for long-range conjugation and high conductivity. Even assuming the formation of long-chain heterocyclic polymers, the lack of a planar conformation would lower conductivity.

Another way in which cross-linking may influence the degree of oxidation is by its effect on polymer solubility. Even a low degree of cross-linking can render a polymer insoluble. Such lightly cross-linked materials generally swell but do not dissolve in polar solvents. Moderate to heavy cross-linking can cause a polymer to be unswellable, even in good solvents such as DMSO. In the chemical oxidation experiments described in this work, a significant amount of cross-linking occurred to give insoluble and unswellable, solids. Chemical oxidation may be restricted in these materials because the oxidant cannot penetrate into the polymer matrix. Therefore, once insolubilization occurs, further oxidation may be inhibited and heterocyclic chain growth stops. This would serve to keep heterocyclic chain length short and the resultant conductivities low.

Extensive cross-linking would also "immobilize" the heterocyclic side groups. Once this occurs, the side groups would be anchored within the polymer matrix and would be unable to diffuse within the material to continue polymerization.

Conclusions

A range of poly(organophosphazenes) that bear polymerizable, heterocyclic side groups has been synthesized. These polymers can be oxidized chemically to give semiconductive materials. A number of possible explanations exist for the relatively low conductivity values. These include the relatively large interchain hopping distance, the insolubility of the cross-linked polymers, and the immobilization of the heterocyclic side groups. The last two factors might serve to minimize heterocyclic polymer chain growth, thereby keeping the resultant conductivities low.

Experimental Section

Equipment. NMR spectra were recorded for $CDCl_3$ solutions using a Bruker WM-360 NMR spectrometer. Chemical shifts are relative to external 85% H_3PO_4 (^{31}P) or internal chloroform (^1H and ^{13}C). Glass transition temperatures were measured with the use of a Perkin-Elmer DSC 7 instrument. Sample weights were between 8 and 11 mg. The samples were initially heated to 115 °C to remove residual solvent and were then cooled rapidly to −100 °C. Measurements were made at a heating rate of 20 °C/min. Polymer molecular weights were estimated by using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector. A calibration curve was established using polystyrene standards. Fractionated samples of poly[bis(trifluoroethoxy)phosphazene] of known molecular weight averages (as determined by light scattering and membrane osmometry) were provided by Drs. R. Singler, M. Sennett, and G. Hagnauer (Army Materials Technology Laboratory, Watertown, MA) and were used as controls for our GPC work. Satisfactory agreement was obtained between the polystyrene calibration curve and the polyphosphazene controls. Polymer samples were prepared at a concentration of 1% w/w and were eluted with a 0.1% w/w solution of n-Bu_4NBr in THF through Polymer Laboratories PLgel columns (10^6-, 10^6-, 10^4-Å pore sizes, 10 μm particle size). Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN. Mass spectral data were obtained by using a Kratos MS-9/50 (electron impact) or a Kratos MS-50 (fast atom bombardment) instrument. Four-point conductivity measurements were made with the use of a probe built in-house.[35] Two-point conductivity measurements were obtained with the use of a Keithly 617 electrometer. UV–vis absorption spectra were obtained for CH_2Cl_2 solutions using a Perkin-Elmer Lambda 4B spectrophotometer or a Hitachi 3501 UV–vis–NIR spectrometer. Quartz cuvettes were used for the analyses. Solid-state spectra were obtained on films cast from solution onto quartz slides. Electrochemical measurements were made with the use of an EG&G PAR273 potentiostat. Platinum disk working electrodes were constructed for these studies.[36] The counter electrode was a Pt flag (separated from the main cell compartment by a frit), and the reference electrode was a silver wire quasi-reference.

Materials and Procedures. All reactions were carried out under an atmosphere of dry argon by using standard Schlenk and drybox techniques. Tetrahydrofuran and diethyl ether (both Omnisolv) were dried before use by distillation from sodium benzophenone ketyl under an atmosphere of dry nitrogen. Anhydrous benzonitrile (Aldrich), spectral grade acetonitrile (Burdick and Jackson), CH_2Cl_2, electrometric grade n-Bu_4NBF_4 (Southwestern Analytical), Et_4NBF_4 (Aldrich), $Fe(ClO_4)_3$, and anhydrous $FeCl_3$ were used as received. Nitrobenzene was distilled under

---

(33) Salmon, M.; Diaz, A. F.; Logan, A. J.; Krounbi, M.; Bargon, J. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 265.

(34) Craig, S. L.; Cordes, A. W.; Stein, S. M.; Chichester-Hicks, S. V.; Haddon, R. C. *Acta Crystallogr.* **1987**, *C43*, 1978.

(35) Reynolds, J. R., Ph.D. Dissertation, University of Massachusetts, 1984.

(36) Penner, R. M.; Van Dyke, L. S.; Martin, C. R. *J. Phys. Chem.* **1988**, *92*, 5274.

nitrogen before use. Gold paste (Pellco SEM, Ted Pella) was used for making electrical contacts. Potassium, sodium, and $Li[AlH_4]$ (all Adrich) were used as received and were handled in an inert atmosphere. 2-(2-Thienyl)ethanol, 2-(3-thienyl)ethanol, 3-thiopheneacetonitrile, 3-thiophenemethanol, pyrrole, 3-furanmethanol, *N*-pyrrolepropionitrile, Et_3N, and 2-[2-(2-chloroethoxy)ethoxy]ethanol (all Adrich) were distilled from CaH_2 before use. 11-Bromo-1-undecanol (Aldrich) and hexachlorocyclotriphosphazene (Ethyl Corp.) were both purified by sublimation. Poly(dichlorophosphazene) and poly[bis(trifluoroethoxy)phosphazene] were synthesized as previously described.[10]

Synthesis of Polymers 1–7. The polymer structures are shown in Chart I, and characterization data are listed in Tables I and II. Polymers 1–7 were all prepared in the same manner. Yields of 40–60% were obtained. The following procedure for the synthesis and isolation of 1 is typical. A solution of sodium 3-thienylmethoxide was prepared from 3-thiophenemethanol (8.3 g, 64.5 mmol) and Na (1.4 g, 58.6 mmol) in THF (200 mL). This solution was added to a solution of $[NP(Cl)_2]_n$ (2.0 g, 17.2 mmol) in THF (200 mL) at room temperature. After the mixture had been stirred for 3 days, the solution was concentrated by using rotary evaporation. The solution was then slowly poured into stirred distilled/deionized water. White polymeric 1 precipitated from solution. The product was further purified by additional reprecipitations from THF into water (2×) and from THF into hexanes (3×), yield = 2.1 g (45%).

Synthesis of 8 and 9. The procedure described here for the preparation of 8 was also used for 9. To a mixture of $[NP(Cl)_2]_n$ (6.0 g, 51.7 mmol) and Et_3N (20.2 g, 0.2 mol) in THF (450 mL) at room temperature was added a solution of 3-thienylethylamine (**8a** below, 19.7 g, 155.0 mmol) in THF (50 mL). After the mixture had been stirred for 2 days, it was concentrated and was slowly poured into stirred distilled/deionized water. Pure 8 was obtained by additional reprecipitations from THF into water (2×) and from THF into hexanes (3×), yield = 8.2 g (53%).

Synthesis of 10. A solution of $NaOCH_2\overline{CCHSCHCH}$ (34.5 mmol, prepared as above) in THF was added to a solution of $[NP(Cl)_2]_3$ (1.0 g, 2.9 mmol) in THF (50 mL) at room temperature. After the mixture had been stirred for 1 day, the solvent was removed using a rotary evaporator and the resultant oil was quickly dissolved in CH_2Cl_2 (50 mL). This solution was then washed several times with distilled/deionized water.[37] The organic layer contained 10 in high enough purity for high-field NMR analysis. A sample for NMR analysis was obtained by removing the CH_2Cl_2 and quickly dissolving the resultant colorless oil in $CDCl_3$. Characterization data for 10 are listed in Table III. See note above regarding the stability of 10.

Synthesis of $HOCH_2CH_2CH_2\overline{NCHCHCHCH}$ (3a). 1-Pyrrolepropionitrile (100 g, 0.8 mol) was added to a mixture of water (1000 mL) and NaOH (160 g). This solution was heated to reflux until the mixture assumed a transparent amber color and a litmus test showed that no more NH_3 had evolved (ca. 2 h). The solution was cooled to room temperature and was then acidified to pH 5 using aqueous HCl. The product, 1-(2-carboxyllic acid ethyl)pyrrole, was extracted with Et_2O while maintaining the pH of the aqueous solution at pH 5. The Et_2O was removed and the resultant oil was extracted several times with boiling heptane. After removal of the solvent, an off-white crystalline solid was obtained which was dried thoroughly in vacuum (crude yield = 46 g, 41%).

This carboxylic acid derivative was then reduced to **3a** by a standard procedure using $Li[AlH_4]$.[38] The product was purified by using column chromatography (silica gel, VWR, 60–200 mesh). Elution with 1:2 THF/Et_2O gave a colorless band which afforded **3a** as a colorless oil. The product was dried thoroughly in vacuum and was stored over molecular sieves, yield = 11.0 g (69%).

For **3a**: MS calcd 125; found 125.

Synthesis of 5a and 6a. Compounds **5a** and **6a** were used for the preparation of polymers 5 and 6, respectively, and both were obtained by the same procedure. The synthesis of **5a** is described here. To a solution of potassium pyrrole (from K (7.82 g, 0.2 mol) and pyrrole (14.1 g, 0.21 mol) in THF) was added slowly a solution of $HOCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$ (16.9 g, 0.1 mol) in THF (50 mL). The mixture was stirred at room temperature for 2 h and was then poured into distilled water (1000 mL). The solution was extracted several times with Et_2O. The organic extracts were combined and dried over $MgSO_4$. The oil obtained by removal of the solvent was introduced onto a silica gel column. Elution with Et_2O first yielded the elimination product, $HOCH_2CH_2OCH_2CH_2OCH{=}CH_2$, identified by ^{13}C NMR analysis. Continued elution with Et_2O gave **5a**, yield = 11.5 g (58%).

For **5a**: ^1H NMR 6.8, 6.2, 4.1, 3.82 (all t), 3.79, 3.71, 3.64 (all m) ppm; ^{13}C NMR 120.8, 107.9, 72.3, 71.1, 70.4, 61.5, 49.2 ppm; MS calcd 199, found (EI) 199.

For **6a**: ^1H NMR 6.8, 6.4, 4.8, 4.6 (all t), 3.8 (br, s), 3.3, 3.1 (both m), 2.9 (br, s) ppm; ^{13}C NMR 120.2, 107.5, 62.5, 49.4, 32.5, 31.4, 29.4, 29.29, 29.27, 29.23, 28.99, 26.5, 25.6 ppm; MS calcd 237; found (EI) 237.

Synthesis of 8a and 9a. Compounds **8a** and **9a** were both prepared by standard chemical reduction of the corresponding nitriles (3-thiopheneacetonitrile and *N*-pyrrolepropionitrile, respectively) using $Li[AlH_4]$.[38] Both products were purified by vacuum distillation from CaH_2.

For **8a**: ^1H NMR 7.1 (m, 1 H), 6.9 (m, 2 H), 4.0 (t, 2 H), 3.8 (t, 2 H), 2.7 (s, 2 H) ppm; ^{13}C NMR 140.5 (s), 128.3 (d), 125.6 (d), 121.1 (d), 43.4 (t), 35.1 (t) ppm; MS calcd 127; found (EI) 111 $(M - NH_2)^+$.

For **9a**: ^1H NMR 6.6 (m, 2 H), 6.1 (m, 2 H), 3.9 (t, 2 H), 2.6 (t, 2 H), 1.8 (m, 2 H), 1.1 (s, 2 H) ppm; ^{13}C NMR 120.0, 107.4 (both d), 46.6, 38.8, 34.6 (all t) ppm; MS calcd 124; found (EI) 124.

Electrochemical Experiments. Films of polymers 1, 2, 3, and 9 were cast from tetrahydrofuran solution onto Pt disk working electrodes. These film-coated electrodes were then immersed, along with the reference and counter electrodes, in electrolyte solutions prepared from various polar organic solvents. The solvents used were acetonitrile, nitrobenzene, methylene chloride, and benzonitrile. In all cases, the supporting electrolyte was n-Bu_4NBF_4 at a concentration of 0.2 M. The solutions were degassed using nitrogen and the potential of the working electrode was scanned from 0 to 3.0 V versus the Ag wire quasi-reference.

Solution Oxidations. Chemical polymerization of heterocycles is typically accomplished using Fe(III) salts as the oxidant.[13–15] To induce the chemical oxidations in this work, a solvent was chosen which dissolves the Fe(III) salt and which dissolves, or at least highly swells, the parent polymer. Benzonitrile proved to be the best solvent for the polymers used here. Some oxidations were conducted using CH_2Cl_2 solutions. Table IV lists which solvent was used for each material. The swollen polymers formed translucent gels with volumes many times larger than the original (dry) polymer.

A typical chemical oxidation procedure is as follows. The polymer (ca. 0.1 g) was dissolved (or very highly swollen) in ca. 20 mL of solvent. The resultant polymer solution or gel was added to about 50 mL of a saturated solution of either $Fe(ClO_4)_3$ or $FeCl_3$ in the same solvent. After addition of the polymer, the solution darkened, and in the case of the pyrrole polymers, a black powdery precipitate formed within a few minutes. Black precipitates were formed more slowly (hours or days) with the thiophene and furan polymers.

Each precipitate was collected by vacuum filtration using Anopore microporous alumina filters with 0.2-μm diameter pores. The precipitate was washed with several portions of acetonitrile to remove the excess solvent and oxidizing agent. **WARNING**: Like other organic perchlorate salts, these perchlorate-doped polymers are potentially explosive when dry. In the experiments where $Fe(ClO_4)_3$ was used as the oxidizing agent, the precipitate was rinsed with acetonitrile, then Et_4NBF_4 in acetonitrile, and finally more acetonitrile. This induced a replacement of the perchlorate anion for the tetrafluoroborate anion.[39] The materials were then dried under vacuum at 40 °C.

Cyclic trimer 10 was chemically oxidized in a manner similar to high polymers 1–9. Ferric chloride was added to a methylene chloride solution of the trimer. This caused the colorless solution

---

(37) Attempted isolation of 10 by using column chromatography (silica gel) was not successful due to decomposition of the product.

(38) Vogel, A. *Textbook of Practical Organic Chemistry*, 4th ed.; Longman: New York, 1978; pp 302.

(39) Curtin, L. S.; Komplin, G. C.; Pietro, W. J. *J. Phys. Chem.* **1988**, *92*, 12.

to turn green. Over a period of several days, a dark precipitate formed slowly. The material was collected and treated as above.

Another method by which polymeric materials may be chemically oxidized involves exposure to iodine vapor.[40,41] Films of polymers 7 and 8 were cast from THF solution onto a poly(tetrafluoroethylene) sheet. The resultant polymer films were removed and attached to a four-point probe using gold paste. The apparatus and procedure for doping conductive polymers with iodine vapor has been described previously.[42] Exposure to iodine vapor caused the polymers to become dark purple. The conductivity was monitored continuously during this process.

Conductivity Measurements. Conductivity measurements of the pristine polymers were measured on films cast from THF solution. Conductivities of the solution-oxidized polymers were measured for powder samples which were pressed into pellets.[22] The powder samples were placed in a die with a 0.67 cm^2 area bore. A pressure of 5 tons was applied to the die by means of a laboratory press to form the pellets. The resultant pellets usually had poor mechanical properties. As a result, it was difficult to obtain four-point conductivity measurements for many of the samples. Therefore, a two-point method was used when necessary. The two-point conductivity measurements were taken across the pellet while still under pressure. In cases where four-point measurements could be obtained, the conductivities measured by both the two-point and four-point methods were similar (Table IV).

Acknowledgment. The synthetic work described here was conducted at The Pennsylvania State University. The oxidation experiments and conductivity measurements were carried out at Texas A&M University and Colorado State University. We thank the U.S. Army Research Office (H.R.A. and J.A.D.) and the Office of Naval Research and the Air Force Office of Scientific Research (C.R.M. and L.S.V.) for financial support.

Registry No. **3a**, 50966-69-3; **5a**, 141485-35-0; **6a**, 96625-75-1; **8a**, 59311-67-0; **9a**, 60794-90-3; **10**, 141485-33-8; NaOCH$_2$CCHSCHCH, 141485-27-0; [NP(Cl)$_2$]$_3$, 940-71-6; H(OCH$_2$CH$_2$)$_3$Cl, 141485-34-9; Fe(ClO$_4$)$_3$, 13537-24-1; FeCl$_3$, 7705-08-0; I$_2$, 7553-56-2; 1-pyrrolepropionitrile, 43036-06-2; 1-(2-carboxyethyl)pyrrole, 89059-06-3; 3-thiopheneacetonitrile, 13781-53-8; potassium pyrrole, 16199-06-7.

---

[40] Kang, E. T.; Neoh, K. G.; Tan, T. C.; Ong, Y. K. *J. Macromol. Sci. Chem., A* **1987**, *24*, 631.

[41] Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578.

[42] Gibson, H. W.; Pochan, J. M. In *Electrical and Electronic Properties of Polymers: A State-of-the Art Compendium*; Kroschwitz, J. I., Ed.; Wiley: New York, 1988; p 15.

Hot-Wall Chemical Vapor Deposition of Copper from Copper(I) Compounds. 2. Selective, Low-Temperature Deposition of Copper from Copper(I) β-Diketonate Compounds, (β-diketonate)CuL$_n$, via Thermally Induced Disproportionation Reactions

H. K. Shin,[†] K. M. Chi,[†] M. J. Hampden-Smith,*[,†] T. T. Kodas,*[,‡] J. D. Farr,[§] and M. Paffett[§]

Departments of Chemistry and Chemical Engineering, Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, New Mexico 87131, and CLS-1, Los Alamos National Laboratories, Los Alamos, New Mexico 87545

Received November 8, 1991. Revised Manuscript Received March 2, 1992

Chemical vapor deposition of copper using (β-diketonate)Cu(PR$_3$)$_n$ (n = 1 and 2), (β-diketonate)Cu(1,5-COD), and (β-diketonate)Cu(alkyne) (where β-diketonate = hexafluoroacetylacetonate (hfac), trifluoroacetylacetonate (tfac), and acetylacetonate (acac); R = Me and Et; 1,5-COD = 1,5-cyclooctadiene; alkyne = bis(trimethylsilyl)acetylene (BTMSA), trimethylsilylpropyne (TMSP), and 2-butyne) has been studied on Pt, W, Cu, and SiO$_2$ substrates over the temperature range 100–400 °C. Large variations in the selectivity were observed as a function of the nature of the copper ligands, substrate temperature, and nature of the substrate. In the series of compounds (hfac)Cu(PMe$_3$), (hfac)Cu(PMe$_3$)$_2$, (hfac)Cu(PEt$_3$), (hfac)Cu(PEt$_3$)$_2$, (hfac)Cu(1,5-COD), and (hfac)Cu(2-butyne), where the number and nature of the neutral Lewis base ligand was varied, only (hfac)Cu(PMe$_3$) and (hfac)Cu(PEt$_3$) exhibited selective deposition. The lowest temperature at which deposition occurred changed dramatically as a function of the number and nature of Lewis base ligands. Deposition rates as high as 1200 Å/min were observed under unoptimized conditions. The copper films were characterized by Auger electron spectroscopy (AES), which showed pure copper within the detection limits. Resistivities varied from 1.7 to 8 $\mu\Omega$ cm depending on deposition conditions. All of the compounds investigated deposited copper via the thermally induced disproportionation reaction 2(β-diketonate)CuL$_n$ $\rightarrow$ Cu + Cu(β-diketonate)$_2$ + 2nL. This reaction stoichiometry was quantified for (hfac)Cu(1,5-COD) and (hfac)Cu(2-butyne) and explains the high purity of the films which results from the absence of thermally induced ligand decomposition.

Introduction

Chemical vapor deposition (CVD) allows formation of thin films of a variety of materials via decomposition of molecular, metal–organic species. The primary advantages of CVD over other methods such as physical vapor deposition (PVD) are that conformal coverage of complex structures and selective deposition are possible.[1] These two aspects are particularly important in electronics applications in which surfaces with complex topographies must be coated. An example is the formation of metal

---

[†] Department of Chemistry.

[‡] Department of Chemical Engineering.

[§] Los Alamos National Laboratories.

* Authors to whom correspondence should be addressed.

[1] Hess, D. W.; Jensen, K. F. *Microelectronics Processing*; American Chemical Society: Washington, DC, 1989.

0897-4756/92/2804-0788$03.00/0