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

by

Harry R. Allcock, Jeffrey A. Dodge, Leon S. Van Dyke
and Charles R. Martin

Department of Chemistry
Colorado State University
Ft. Collins, CO 80523

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19. ABSTRACT (continued) The polymers have the general structure $[NP(OR)_2]_n$, where R is $-\text{CH}_2\overline{\text{CCHSCHCH}}$, $-\text{CH}_2\text{CH}_2\overline{\text{CCHSCHCH}}$, $-\text{CH}_2\text{CH}_2\overline{\text{CSCHCHCH}}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\overline{\text{NCHCHCHCH}}$, $-\text{CH}_2\overline{\text{CCHOCHCH}}$, $-(\text{CH}_2)_{1,1}\overline{\text{NCHCHCHCH}}$ or $-(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\overline{\text{NCHCHCHCH}}$, and $[NP(NHR)_2]_n$, where R is $-\text{CH}_2\text{CH}_2\text{CH}_2\overline{\text{NCHCHCHCH}}$ or $-\text{CH}_2\text{CH}_2\overline{\text{CCHSCHCH}}$. The cyclic trimer $[NP(\text{OCH}_2\overline{\text{CCHSCHCH}})_2]_3$ 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, 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 of -48°C to $+1^\circ\text{C}$. Chemical oxidation of the materials was carried out in solution using $\text{Fe}(\text{ClO}_4)_3$ 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 semi-conductive with conductivities in a range from $4 \times 10^{-10} \text{ S cm}^{-1}$ to $5 \times 10^{-5} \text{ S cm}^{-1}$. The results of attempted electrochemical oxidation and chemical oxidation using iodine are also described.

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, PA 16802

Leon S. Van Dyke and Charles R. Martin*

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

Abstract. The synthesis and chemical oxidation of linear poly(organophosphazenes) that bear polymerizable, heterocyclic side groups is 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 $-\text{CH}_2\overline{\text{CCHSCHCH}}$, $-\text{CH}_2\text{CH}_2\overline{\text{CCHSCHCH}}$, $-\text{CH}_2\text{CH}_2\overline{\text{CSCHCHCH}}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\overline{\text{NCHCHCHCH}}$, $-\text{CH}_2\overline{\text{CCHOCHCH}}$, $-(\text{CH}_2)_{1,1}\overline{\text{NCHCHCHCH}}$ or $-(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\overline{\text{NCHCHCHCH}}$, and $[NP(NHR)_2]_n$, where R is $-\text{CH}_2\text{CH}_2\text{CH}_2\overline{\text{NCHCHCHCH}}$ or $-\text{CH}_2\text{CH}_2\overline{\text{CCHSCHCH}}$. The cyclic trimer $[NP(\text{OCH}_2\overline{\text{CCHSCHCH}})_2]_3$ 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

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by the use of ^1H , ^{13}C and ^{31}P NMR, 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 of -48°C to $+1^\circ\text{C}$. Chemical oxidation of the materials was carried out in solution using $\text{Fe}(\text{ClO}_4)_3$ 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 semi-conductive with conductivities in a range from $4 \times 10^{-10} \text{ S cm}^{-1}$ to $5 \times 10^{-5} \text{ S cm}^{-1}$. 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 $[\text{NPR}_2]_n$.⁴

The possibility that electronic conductivity might be induced in polyphosphazenes has been considered in earlier 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 phthalocyanine⁸ and pyrrole⁹ 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.

Scheme I



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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 are shown in Chart 1. 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, $[\text{NPCl}_2]_3$.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.

Scheme II

Chart 1

Tables I and II

Polymer 1 was prepared by the reaction of poly(dichlorophosphazene) with sodium 3-thienylmethoxide

($\text{NaOCH}_2\overline{\text{CCHSCHCH}}$) 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 of the polymers are colorless elastomeric materials with glass transition temperatures in a range from -48°C to -35°C .

Synthesis of Polymers 8 and 9. Amino-phosphazene polymers 8 and 9 were prepared by the reaction of $[\text{NPCl}_2]_n$ with excess $\text{H}_2\text{NCH}_2\text{CH}_2\overline{\text{CCHSCHCH}}$ or $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\overline{\text{NCHCHCHCH}}$,

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 $+1^\circ\text{C}$ 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 crosslinking of the side groups. The polymers may be stored without change in solution at low temperature ($<0^\circ\text{C}$) in the absence of light and oxygen.

Synthesis of Cyclic Trimer 10. Compound 10 was prepared by the treatment of $[\text{NPCl}_2]_3$ 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.

Table III

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.

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-Bu₄NBF₄. 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 electrochemical oxidative polymerization of heterocyclic monomers.¹² Therefore, a constant current of 1 mA/cm² 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(ClO₄)₃ or FeCl₃ 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

Table IV

materials. In most cases, the conductivities did increase for the oxidized polymers. Indeed, the conductivities of polymers 3 and 9 increased by at least 4 to 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 $1 \times 10^{-4} \text{ S cm}^{-1}$,¹⁶ while the conductivity of oxidized 3 is $5 \times 10^{-5} \text{ S cm}^{-1}$. In addition, the conductivities of oxidized 3 and 9 are comparable to that of oxidized poly[bis-(pyrrolyl)phosphazene] ($10^{-6} \text{ S cm}^{-1}$).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, mis-linking of the heterocyclic units, or other reactions that generate non-conductive 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 a period of 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], $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$,^{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 $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$. Potential sweep experiments conducted in a variety of solvents (such as MeCN, PhCN and PhNO₂) with 0.2 M n-Bu₄NBF₄ 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(ClO₄)₃, FeCl₃, and I₂ resulted in no detectable interaction and the polymer could be re-isolated unchanged. Therefore, the phosphorus-nitrogen backbone in $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ 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 crosslinking could take place through the open 5-position on the thiophene ring, polymerization could not occur to yield a conjugated heterocyclic polymer. Only non-conductive 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 non-conjugated, and therefore non-conductive, 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 $\text{Fe}(\text{ClO}_4)_3$ as described below. Following anion exchange and drying, the conductivity was found to be $<10^{-10} \text{ S cm}^{-1}$. 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.

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 alpha-alpha bonded and that the constituent heterocyclic rings be oriented co-planar 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 alpha-alpha bonded alkyl-derivatized thiophene chains is 345 nm, 412 nm, 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 non-conjugated 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.

Figures 1a and 1b

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 non-conjugated 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 2

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

Figure 3

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 $\text{Fe}(\text{ClO}_4)_3$, and ion-exchange using BF_4^- . The atomic ratios of carbon, nitrogen and phosphorus are

Table V

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 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 to 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 to 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.^{3,4} 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, crosslinking 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 crosslinking may influence the degree of oxidation is by the way in which it affects polymer solubility. Even a low degree of crosslinking can render a polymer insoluble. Such lightly crosslinked materials generally swell, but do not dissolve in polar solvents. Moderate to heavy crosslinking 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 crosslinking 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 crosslinking 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 semi-conductive materials. A number of possible explanations exist for the relatively low conductivity values. These include the relatively large inter-chain hopping distance, the insolubility of the crosslinked 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 $20^\circ\text{C}/\text{min}$. 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 $n\text{-Bu}_4\text{NBr}$ 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.³³ 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 of films cast from solution onto quartz slides. Electrochemical measurements were made with the use of a EG & G PAR273 potentiostat. Platinum disk working electrodes were constructed for these studies.³⁴ 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 diethylether (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 $n\text{-Bu}_4\text{NBF}_4$ (Southwestern Analytical), Et_4NBF_4 (Aldrich), $\text{Fe}(\text{ClO}_4)_3$ and anhydrous FeCl_3 were used as received. Nitrobenzene was distilled under nitrogen before use. Gold paste (Pellco SEM, Ted Pella) was used for making electrical contacts. Potassium, sodium and $\text{Li}[\text{AlH}_4]$ (all Aldrich) 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 Aldrich) 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 1 and characterization data are listed in Tables I and II. Polymers 1-7 were all prepared in the same manner. Yields of 40 to 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 $[\text{NP}(\text{Cl})_2]_n$ (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 x) and from THF into hexanes (3 x). 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 $[\text{NP}(\text{Cl})_2]_n$ (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 x) and from THF into hexanes (3 x). Yield = 8.2 g (53%).

Synthesis of 10. A solution of $\text{NaOCH}_2\overline{\text{CCHSCHCH}}$ (34.5 mmol, prepared as above) in THF was added to a solution of $[\text{NP}(\text{Cl})_2]_3$ (1.0 g, 2.9 mmol) in THF (50 mL) at room temperature. After the mixture had been stirred for one 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 $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{NCHCHCHCH}$ (3a). 1-Pyrrole-propionitrile (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 hours). The solution was cooled to room temperature and was then acidified to pH 5 using aqueous HCl. The product, 1-(2-carboxylic 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 $\text{Li}[\text{AlH}_4]$.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 calc: 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 HOCH₂CH₂OCH₂CH₂OCH₂CH₂Cl (16.9 g, 0.1 mol) in THF (50 mL). The mixture was stirred at room temperature for 2 hours and was then poured into distilled water (1000 mL). The solution was extracted several times with Et₂O. The organic extracts were combined and dried over MgSO₄. The oil obtained by removal of the solvent was introduced onto a silica gel column. Elution with Et₂O first yielded the elimination product, HOCH₂CH₂OCH₂CH₂OCH=CH₂, identified by ¹³C NMR analysis. Continued elution with Et₂O 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; ¹³C NMR: 120.8, 107.9, 72.3, 71.1, 70.4, 61.5, 49.2 ppm; MS calc: 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; ¹³C 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 calc: 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-pyrrole-propionitrile, respectively) using Li[AlH₄].³⁸ Both products

were purified by vacuum distillation from CaH_2 .

For 8a: ^1H NMR: 7.1 (m, 1H), 6.9 (m, 2H), 4.0 (t, 2H), 3.8 (t, 2H), 2.7 (s, 2H) ppm; ^{13}C NMR: 140.5 (s), 128.3 (d), 125.6 (d), 121.1 (d), 43.4 (t), 35.1 (t) ppm; MS calc: 127; Found (EI): 111 ($\text{M} - \text{NH}_2$)⁺.

For 9a: ^1H NMR: 6.6 (m, 2H), 6.1 (m, 2H), 3.9 (t, 2H), 2.6 (t, 2H), 1.8 (m, 2H), 1.1 (s, 2H) ppm; ^{13}C NMR: 120.0, 107.4 (both d), 46.6, 38.8, 34.6 (all t) ppm; MS calc: 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 $n\text{-Bu}_4\text{NBF}_4$ 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 In order 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 $\text{Fe}(\text{ClO}_4)_3$ 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 $\text{Fe}(\text{ClO}_4)_3$ 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 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 cm² 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).

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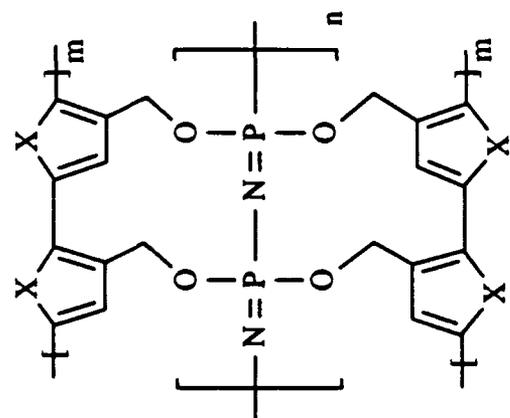
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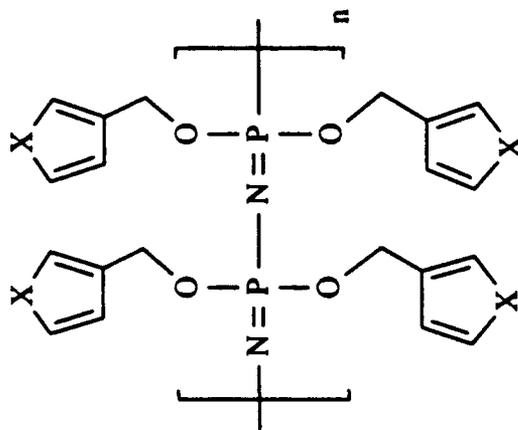
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Scheme I

$$\xrightarrow{[O]}$$


X = N, S or O

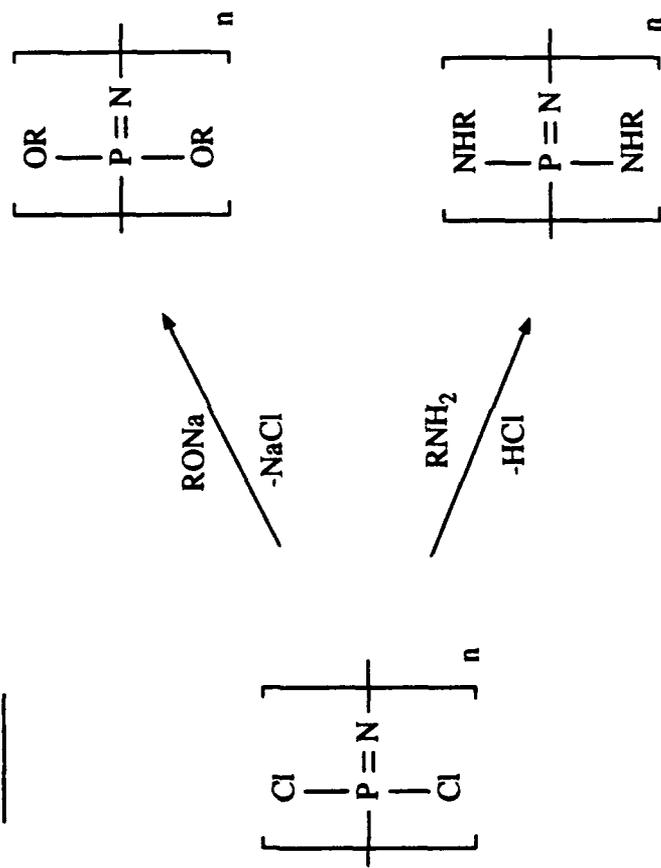
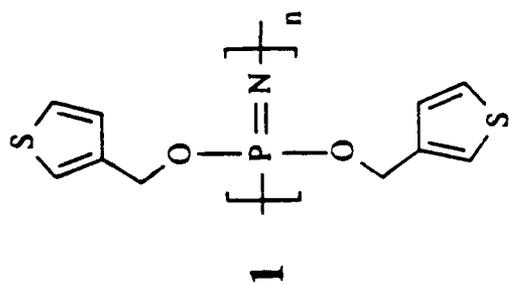
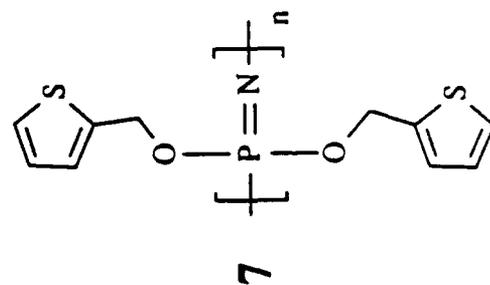
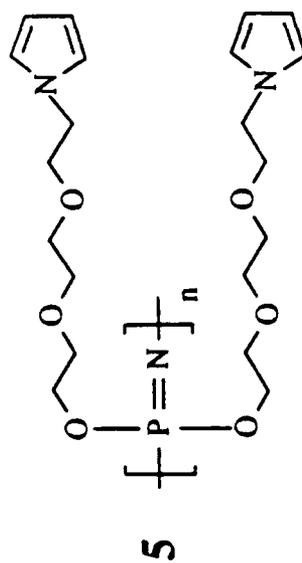
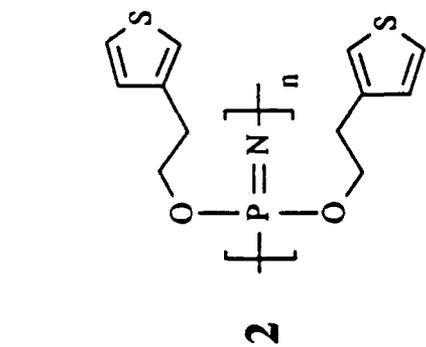
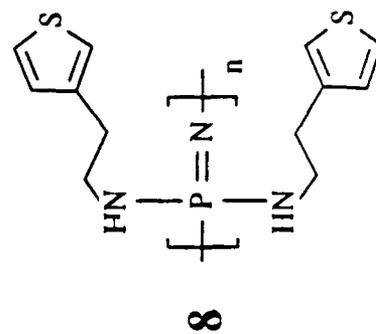
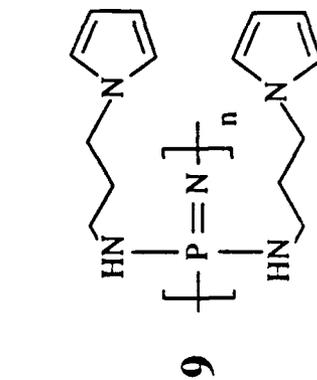
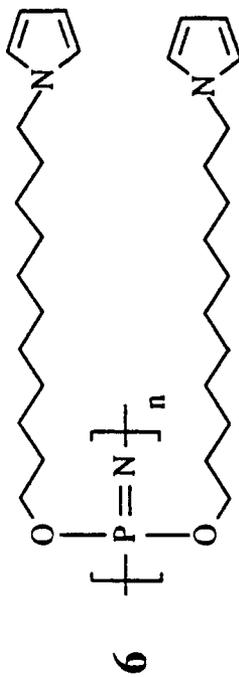
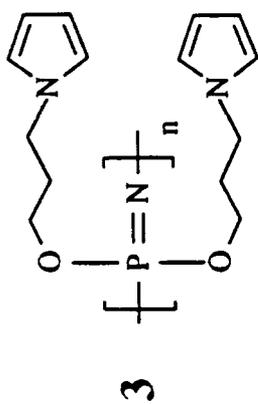
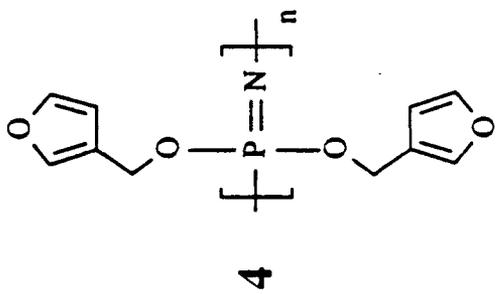
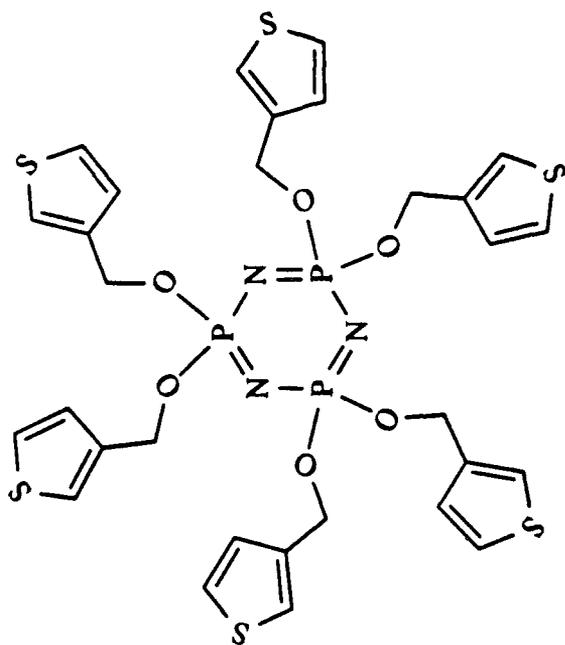
Scheme II

Chart I





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Table I. Characterization data for $[\text{NP}(\text{OR})_2]_n$ and $[\text{NP}(\text{NHR})_2]_n$

compound	M_n	M_w	$T_g(^{\circ}\text{C})$	EA calc.	EA found
$[\text{NP}(\text{OCH}_2\text{CCHSCHCH})_2]_n$ (1)	1.2×10^5	2.0×10^6	-29	C 44.28 H 3.69 N 5.17 Cl 0	43.91 3.64 4.93 0.05
$[\text{NP}(\text{OCH}_2\text{CH}_2\text{CCHSCHCH})_2]_n$ (2)	9.8×10^4	8.5×10^5	-37	C 48.16 H 4.68 N 4.68 Cl 0	47.88 4.81 4.84 0.24
$[\text{NP}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{NCHCHCHCH})_2]_n$ (3)	8.9×10^4	3.2×10^6	-35	C 57.34 H 6.83 N 14.33 Cl 0	57.64 6.65 14.64 0.03
$[\text{NP}(\text{OCH}_2\text{CCHOCHCH})_2]_n$ (4)	7.6×10^4	1.9×10^6	-44	C 50.21 H 4.18 N 5.86 Cl 0	52.33 4.14 5.82 0.05
$[\text{NP}(\text{O}(\text{CH}_2\text{CH}_2)_3\text{NCHCHCHCH})_2]_n$ (5)	4.4×10^4	1.9×10^6	-48	C 54.42 H 7.26 N 9.52 Cl 0	54.48 7.28 9.42 0.04
$[\text{NP}(\text{O}(\text{CH}_2)_{11}\text{NCHCHCHCH})_2]_n$ (6)	4.5×10^4	1.7×10^6	-36	C 69.63 H 10.06 N 8.12 Cl 0	68.98 10.11 7.49 <0.4
$[\text{NP}(\text{OCH}_2\text{CH}_2\text{CSCCHCHCH})_2]_n$ (7)	6.7×10^5	1.4×10^6	-41	C 48.16 H 4.68 N 4.68 Cl 0	45.97 5.00 4.83 0.44
$[\text{NP}(\text{NHCH}_2\text{CH}_2\text{CCHSCHCH})_2]_n$ (8)	2.9×10^5	3.2×10^6	1	C 48.48 H 5.39 N 14.14 Cl 0	47.67 5.49 14.02 0.61
$[\text{NP}(\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NCHCHCHCH})_2]_n$ (9)	1.3×10^5	4.1×10^6	-8	C 57.75 H 7.56 N 24.05 Cl 0	56.32 7.53 23.67 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(1H), 6.9(1H) 6.8(1H), 4.9(2H)
(2)	-8.3 (s)	138.5(s), 128.5(d), 125.1(d) 121.4(d), 65.5(t), 31.1(t)	7.1(1H), 6.82(1H), 6.80(1H) 4.0(2H), 2.7(2H)
(3)	-7.7 (s)	120.3(d), 108.3(d), 62.8(t) 45.4(t), 32.0(t)	6.5(2H), 6.1(2H) 3.7(4H), 1.8(2H)
(4)	-7.5 (s)	142.8(d), 140.7(d), 121.9(s) 110.2(d), 59.5(t)	7.2(m, 2H), 6.2(1H) 4.7(2H)
(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 2H) 3.6(m, 4H), 3.4, 3.5 (both 2H)
(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 2H) 3.8(4H), 1.7(2H) 1.5(2H), 1.2(16H)
(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 1H) 4.0, 2.9(both 2H)
(8)	2.3 (s)	140.1(s), 128.2(d), 125.3(d) 120.8(d), 42.1(t), 32.6(t)	7.1(1H), 6.7(2H), 3.3(1H) 3.0(2H), 2.6(2H)
(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 2H), 3.0(1H), 2.6, 1.7(2H)

Table III. Characterization Data for $[\text{NP}(\text{OCH}_2\text{CCHSCHCH})_2]_3$ (10)

^{31}P NMR, ppm	^{13}C NMR, ppm	^1H NMR, ppm	MASS SPEC.
+17.8 (s)	137.7(s), 127.0(d) 125.9(d), 123.4(d) 62.9(t)	7.3-7.2(m, 2H) 7.1(s, 1H), 5.0(s, 2H)	Calc: 813 Found (EI): 768 (M - HCS) ⁺ Found (FAB): 814 (MH) ⁺

Table IV. Conductivities of Oxidized 1-10.

<u>Polymer</u>	<u>Conductivity</u>
1 ^{a, b}	5 X 10 ⁻⁷ , 4 X 10 ⁻⁷
2 ^c	7 X 10 ⁻⁷
3 ^c	5 X 10 ⁻⁵
4 ^a	2 X 10 ⁻⁷
5 ^c	1 X 10 ⁻⁷
6 ^c	4 X 10 ⁻⁹
7 ^d	< 10 ⁻¹⁰
8 ^d	2 X 10 ⁻⁷
9 ^{b, d}	1 X 10 ⁻⁶ , 2 X 10 ⁻⁶
10 ^e	4 X 10 ⁻¹⁰

- a) Polymer was swollen with methylene chloride, oxidized with Fe(ClO₄)₃.
- b) First value is two point measurement; second value is four point measurement.
- c) Polymer was swollen with benzonitrile, oxidized with Fe(ClO₄)₃.
- d) Polymer was dissolved in benzonitrile, oxidized with Fe(ClO₄)₃.
- e) Cyclic trimer was dissolved in methylene chloride, oxidized with FeCl₃.

Table V. Elemental Analysis of Oxidized Polymer 3^a

<u>Atom</u>	<u>Elemental Analysis(%)</u>	<u>Atomic Ratio^b</u>	<u>Theoretical Atomic Ratio</u>
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 $\text{Fe}(\text{ClO}_4)_3$, then ion exchanged with BF_4^- (see text for details).
- b) Calculated from elemental analysis assuming a ratio of one for phosphorus.

List of Figures

Figure 1. UV-Visible absorption spectra of polymer 1 in methylene chloride. a) As-synthesized polymer. b) Polymer oxidized with $\text{Fe}(\text{ClO}_4)_3$.

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

Figure 3. UV-Visible absorption spectra of polymer 3. a) As-synthesized polymer. b) Polymer after oxidation with $\text{Fe}(\text{ClO}_4)_3$.

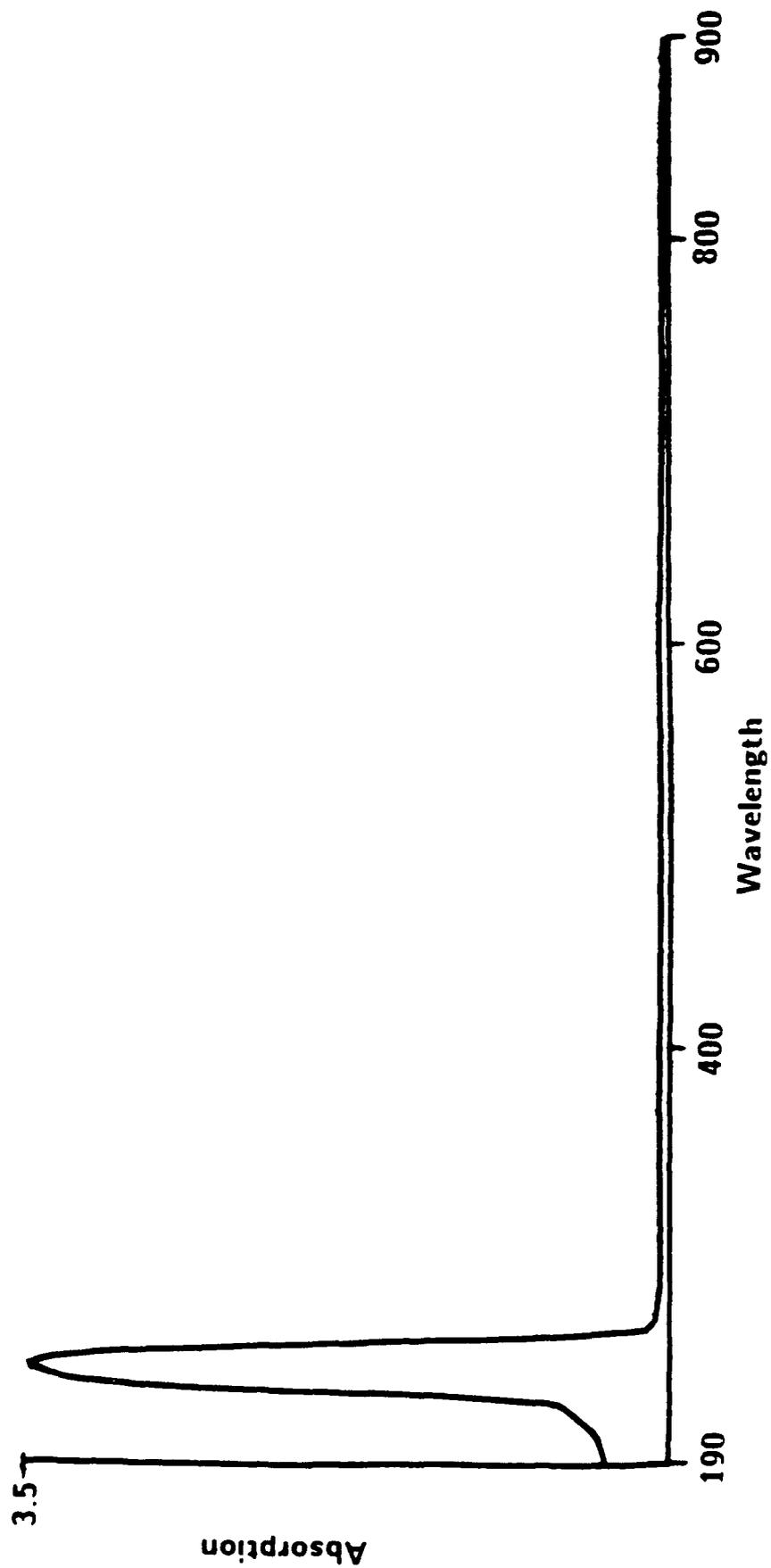


Figure 1a

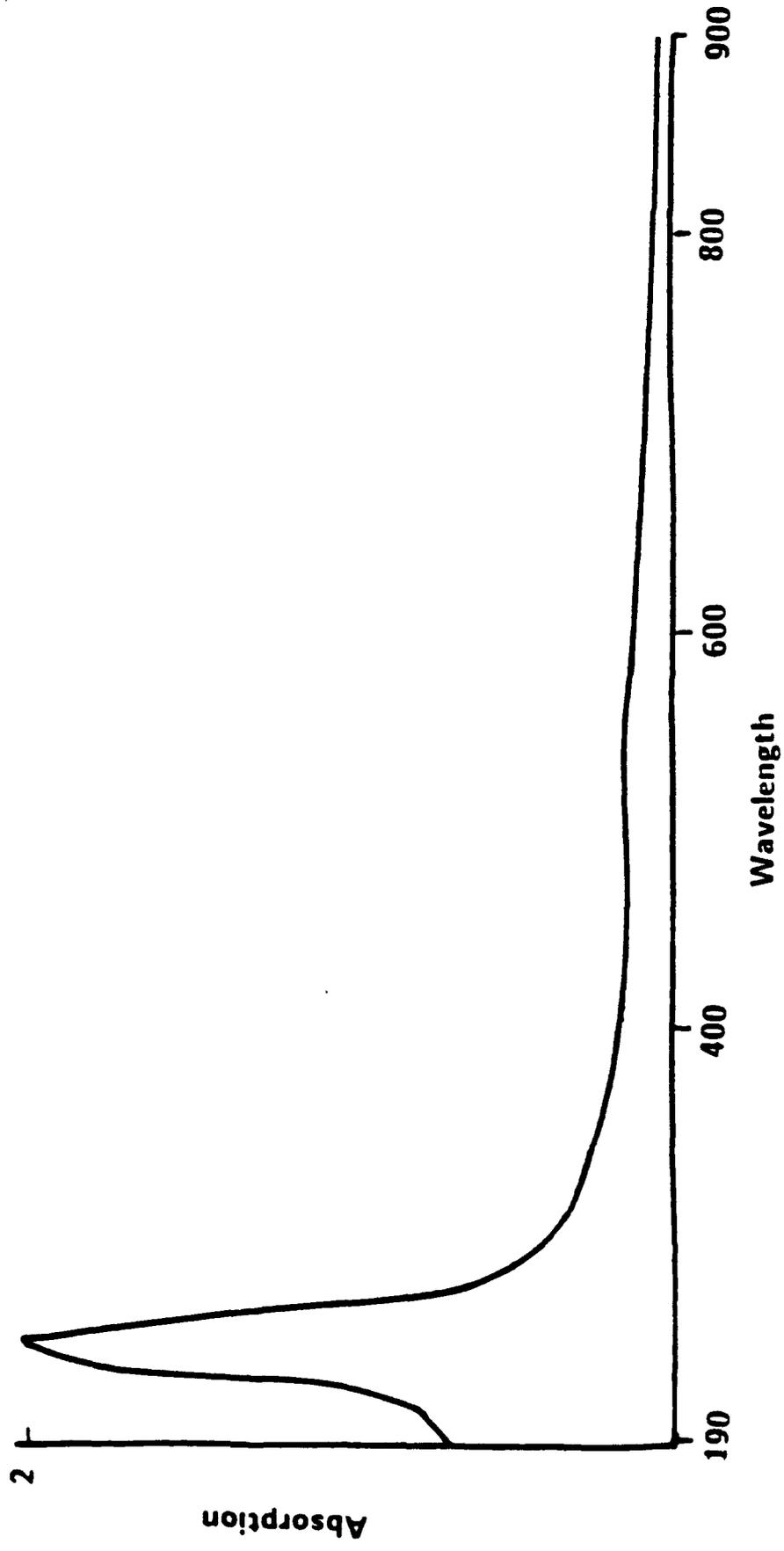


Figure 1b

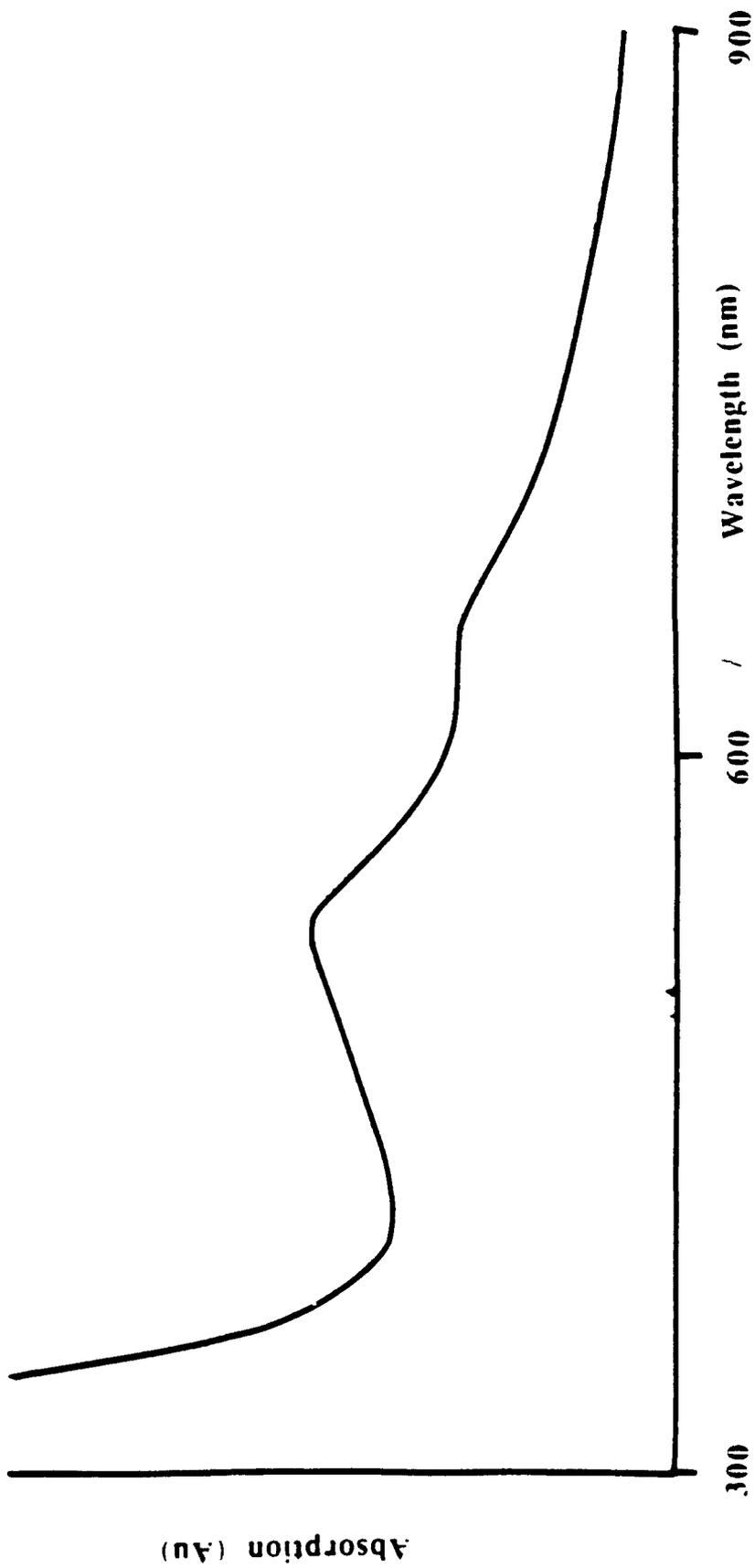


Figure 2

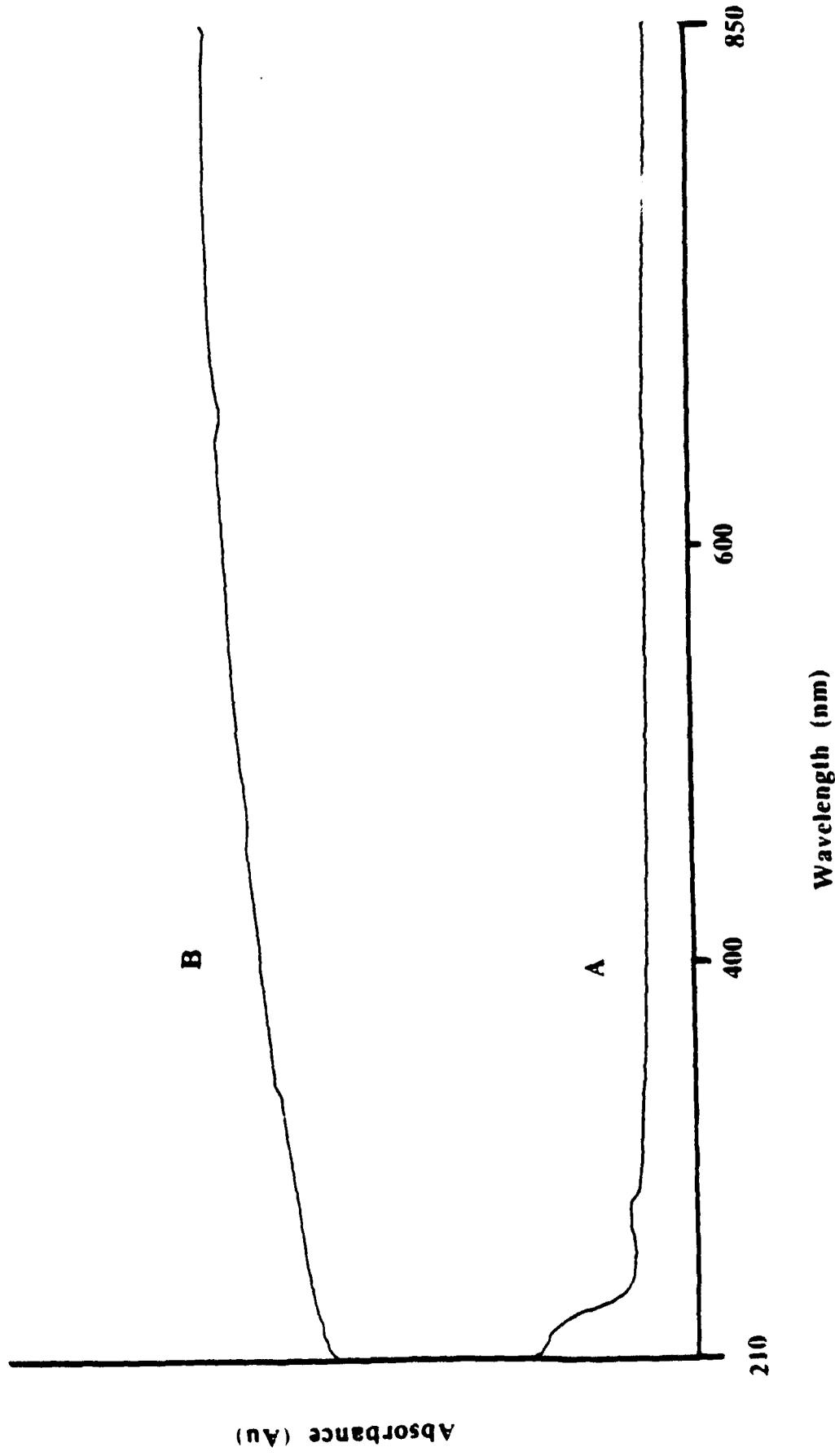


Figure 3