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OFFICE OF NAVAL RESEARCH

Contract N00014-82K-0612

Task No. NR 627-838

TECHNICAL REPORT NO. 72

Effect of Synthesis Temperature in the Structure, Doping Level and Charge-Transport Properties of Polypyrrole

by

Wenbin Liang, Junting Lei and Charles R. Martin

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

Prepared for publication

in

Synthetic Metals
May 8, 1992

EFFECT OF SYNTHESIS TEMPERATURE ON THE STRUCTURE, DOPING LEVEL AND CHARGE-TRANSPORT PROPERTIES OF POLYPYRROLE

Wenbin Liang, Junting Lei and Charles R. Martin*
Department of Chemistry
Colorado State University
Fort Collins, CO 80523

* To whom correspondence should be addressed

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Abstract

Polypyrrole perchlorate was chemically synthesized at various temperatures and the resulting polymers were investigated by elemental analysis, fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and conductivity measurements. A correlation between conductivity, doping level and synthesis temperature was observed. The doping level of the polymer is higher when the synthesis is conducted at lower temperature. In addition, polypyrrole synthesized at lower temperature exhibits longer conjugation length, fewer structural defects, higher charge carrier hopping frequency and higher conductivity. Furthermore, the results of this study indicate that the positive charges of doped polypyrrole are preferentially localized on the nitrogen atoms which are adjacent to the doping anions, as opposed to being uniformly delocalized along the polymer backbone.

Introduction

Polypyrrole (PPY) is one of the most extensively studied of the conductive polymers[1-3]. This polymer is of interest because it exhibits both high conductivity and good environmental stability. Furthermore, some new applications of this polymer, such as in biosensors[4,5] and microelectronic devices[6,7], have recently been explored. Polymers with well defined chemical, optical and electronic properties are essential for most of these applications. The properties of the polymer, in turn, depend upon the synthetic conditions employed such as reactant concentration, reaction temperature, reaction time, pH of the system, and nature of incorporated counterions.[8,9] Unfortunately, the effects of these various synthetic parameters on the chemical and electronic properties of the resulting polymer have been investigated only sporadically;[8-11] hence, there is a lack of systematic correlation between the synthetic conditions used and the properties of the polymer obtained.

We have recently initiated a series of investigations aimed at systematically exploring the effects of synthetic conditions on the structure and properties of conducting heterocyclic polymers.[10-12] For example, we recently investigated the effects of concentrations of the monomer and oxidant used in the polymerization on the chemical and electronic properties of the resulting polymer.[10] We have since turned our attention to the effect of synthesis temperature on the properties of the resulting polymer. These studies have focused on chemically-synthesized polypyrrole. We have explored the effects of synthesis temperature on doping level, conjugation length, nature and extent of chemical defect sites, and charge distribution in the resulting polymer. We report the results of these investigations in this paper.

Experimental

Polypyrrole syntheses. Pyrrole (Aldrich) was purified by fractional distillation and stored under argon at -15 °C. Ferric perchlorate (Mallinkrodft) was used without further purification. Distilled water was further purified by passage through a Millipore milli-Q cartridge system. This water was used as the solvent for all solutions. Polypyrroles were synthesized by mixing solutions of pyrrole with solutions of ferric perchlorate.[10-12] The monomer solution was 0.1 M pyrrole and the concentration of $Fe(ClO_4)_3$ was 1.0 M. Both solutions were degassed twice by the freeze-pump-thaw technique and kept under argon prior to use. The syntheses were carried out in the absence of air at temperatures of 0^o, 27^o and 45 °C. An excess of oxidant (molar ratio of $Fe(ClO_4)_3$: pyrrole = 5 : 1) was employed for all syntheses to ensure complete consumption of pyrrole monomer.

In a typical experiment, 40 ml of the degassed pyrrole solution was transferred under argon into a 250 ml, 2-neck round bottom flask equipped with an argon gas inlet. The solution was kept at the desired temperature using a constant temperature bath. To the pyrrole solution were added 20 ml of 1.0 M $Fe(ClO_4)_3$ solution (also at the desired temperature) via a double tipped syringe. The mixture was stirred magnetically and the polymerization was allowed to proceed for 2 hr. The mother liquor was removed by vacuum filtration. The polypyrrole precipitate was washed (under argon) with copious amounts of degassed millipore water and then dried under vacuum overnight.

X-ray photoelectron spectroscopy (XPS). XPS measurements were performed using a Hewlett Packard 5950 ESCA spectrometer with monochromatized Al K_α radiation. The energy resolution was 0.9 eV. The spectrometer was calibrated with graphite using the C_{1s} line at 284.6 eV. The pressure inside the spectrometer analyzer was maintained in the low 10^{-9} torr range by ion pumps. The polypyrrole samples were taken to the measuring chamber directly without exposure to air. Samples were mounted onto copper sample holders using double-sided adhesive tape (Scotch, 3M). The flood gun was not used during the XPS measurements on these doped polypyrroles since these samples are sufficiently conductive to prevent electrostatic charging.

Prior XPS investigations have shown that simple gaussian-shaped peaks are never observed for polypyrroles.[13,14] The complex XPS peaks were deconvolved into component gaussian peaks using the "automatic fitting" program provided with the XPS spectrometer.[15] Information about the chemical structure and composition of the polymer can be obtained from the positions and relative intensities of these component gaussians.[10] The elemental compositions of the polypyrroles were determined from the areas under the total C_{1s}, N_{1s}, Cl_{2p}, and O_{1s} peaks for the various polypyrrole samples. Instrumental sensitivity factors for these elements were first determined by conducting XPS analyses on Bu_4NCl_4, a reference compound with known stoichiometry.[16] Details of this XPS method for determining the chemical compositions can be found in.[10-12] We have shown that compositions obtained via this XPS method agree with compositions obtained via conventional elemental analysis.[10,11]

Infrared spectroscopy. Infrared measurements were performed using an IBM IR/30 fourier transform infrared spectrometer. Pressed pellets of the PPY powder samples were ground with KBr powder (Aldrich, IR grade) and used for the IR data acquisition. The spectral resolution was set at 4

cm^{-1} and the signal-to-noise ratio was increased by averaging the signal over 256 scans for each sample.

Conductivity measurements. Room temperature conductivities were measured via the four-point method on pressed rectangular pellets (1x1x10 mm) of the various PPY powder samples. The pellets were pressed under a pressure of 6.5 ton/cm^{-2} for 2 min. These samples were also used for variable temperature conductivity measurements. In this measurement, a PPY pellet was mounted onto a 4-lead probe with a thermocouple in close proximity to the sample (ca. 3 mm away from sample). The probe was inserted in a long (30 cm) Schlenk tube and sealed under vacuum. The sample was cooled with methanol/liquid nitrogen to -98 °C in a dewar and allowed to warm up gradually (approximately 0.5 °C/ min.). The electrical resistance of the sample was monitored during this warming process using the four-point method. The sample was held under a dynamic vacuum of 10^{-3} torr during data acquisition.

Results and Discussion

I. Chemical composition and doping level. The results of the XPS determination of elemental composition[10-12] for the various PPY samples are shown in Table I. The carbon and nitrogen stoichiometries are in good agreement with that expected for polypyrrole. The doping level (ρ), expressed as the perchlorate content in the PPY samples, increases by almost 50%, from $\rho = 0.24$ at the highest synthesis temperature (45 °C) to $\rho = 0.35$ at the lowest temperature (0 °C). Thus, the data in Table I demonstrate that the doping level of polypyrrole can be varied over a moderate range by varying the polymerization temperature.

We have recently proposed an alternative XPS-method for determining the doping level in polypyrrole.[10,11] Figure 1 shows a typical

N_{1s} spectrum for one of our polypyrrole samples. According to Kang[13] and Inganas[17], the N_{1s} XPS spectrum can be deconvolved into three component gaussians indicating that three distinct types of nitrogen exist in these polypyrrole samples. The high binding energy component at 401.5 eV has been assigned to positively charged pyrrolylium nitrogen cations.[13,18,19] Each positively charged nitrogen (N^+) must be compensated by a negatively charged counterion in order to maintain charge neutrality in the polymer. If this is true, the component with a binding energy of 401.5 eV should be equivalent to the doping level of the polymer.[10]

In order to test this premise, the area under the gaussian at 401.5 eV was ratioed to that of the total N_{1s} peak area to give the fraction of positively charged N atoms designated the N^+/N ratio in Table II. Again, if the arguments presented above are correct, this ratio should be equivalent to the doping level. Table II compares the N^+/N ratio with the doping level as determined by the XPS-based elemental analyses.[10,11] As can be seen in Table II, the agreement between these two methods for determining the doping level is very good. We have observed analogous results in our previous investigation.[10,11]

The correlation between the fraction of N's that are positively charged (401.5 eV component in Figure 1) and the doping level has interesting and important implications for distribution of charge along the polymer chain. This correlation suggests that rather than being distributed uniformly across all of the molecular units in the chain, the positive charge is preferentially localized on the nitrogen atoms adjacent to the doping anions. The fact that several forms of nitrogen exist in PPY also support this conclusion. Analogous conclusions have also been reached by Kang et al.[13] and by Eaves et al.[18]

A final point is worth making about the elemental analysis data in Table I. These data show that excess amounts of oxygen exist in all of the PPY samples. Excess oxygen has been widely observed in PPY samples prepared chemically and electrochemically.[10,13,20,21] Various explanations for this excess oxygen have been proposed. For example, it has been suggested to arise from a surface oxidation reaction, such as formation of a charge transfer complex with oxygen.[21-23] Since the samples investigated here were synthesized in the complete absence of air, the excess oxygen found here is not due to reaction of the polymer with molecular oxygen. Furthermore, the samples were transferred to the XPS chamber without exposure to oxygen and these samples were evacuated to a high vacuum (10^{-9} torr) prior to measurements. Again, this strongly suggests that the oxygen present in these samples is not from air. We will discuss the origins and nature of this excess oxygen in a later section of this paper.

II. Structural defects. XPS is an effective tool for elucidating structural defects in polypyrrole and other conductive polymers.[19] We have shown in the previous sections that the N_{1s} core-level XPS spectra are asymmetric, and that this spectrum can be deconvolved into several components (Figure 1). The carbon 1s peak is also asymmetric and can likewise be deconvolved into its components (Figure 2). Therefore, Figures 1 and 2 show that there are structural irregularities and defects involving C and N atoms in the polymer. We identify and quantitate a number of these chemical defect sites below.

A. Deprotonated nitrogen. There is a clearly resolved low binding energy shoulder at 397.5 eV in the N_{1s} XPS spectra (Figure 1). This shoulder has been attributed to deprotonated, uncharged, imine-like nitrogens (>C=N-).[13,14,17] The percentage of N atoms present as this imine-like nitrogen can be obtained by ratioing the area under the 397.5 eV gaussian to the area under the entire N_{1s} peak. These data are shown in Table III. As indicated in Table III, the quantity of this defect site increases with synthesis temperature. Furthermore, the quantity of this defect site is very small (3% of the total N) in the materials synthesized at 0 °C. The concentration of this defect site is important because these defects interrupt conjugation.[14] The data in Table III suggest that the polymer synthesized at 0 °C should be more conductive than the materials synthesized at higher temperatures. As we shall see, this is, indeed, the case.

B. Carbonyl. Another type of structural defect in PPY is carbonyl.[11,24-26] Carbonyls can be formed by over-oxidation of polypyrrole[24,25] or as the product of chain termination by nucleophillic attack by H_2O on the pyrrole rings;[11,26] thus, carbonyl defects may exist at β-carbon positions in the middle of a chain or at the chain ends. In both cases it is obvious that the conjugation is disrupted at pyrrole rings which contain carbonyl defects. The infrared spectrum of the polypyrrole sample synthesized at the highest temperature (45 °C) shows a weak absorption at 1710 cm^{-1} (Figure 3a); this band has been attributed to carbonyl.[24,27] This band is completely absent in the spectrum for the material synthesized at 0 °C (Figure 3b). These data suggest that the quantity of carbonyl defects incorporated into the polymer varies with synthesis temperature. This relationship between quantity of carbonyl defects and synthesis temperature is corroborated and quantified by the XPS data.

A typical C_{1s} XPS spectrum was shown in Figure 2. As indicated in Figure 2, the asymmetric C_{1s} peak can be deconvolved into four component gaussians. As discussed in detail in our previous papers,[10-12] the predominant part of the highest binding energy component (288.0 eV) in the C_{1s} spectra can be attributed to carbonyl carbons.[28,29] Thus, by ratioing the area under the 288.0 eV gaussian to the total C_{1s} area, an estimate[10,11] of the quantity of carbonyl defects can be obtained (Table III). As shown in Table III, the percentage of carbonyl defects increases from 5.5% for polypyrrole synthesized at 0 °C, to 9.2% for PPY synthesized at 45 °C. Again, because carbonyl interrupts conjugation, these data (and the analogous IR data) suggest that the material synthesized at lower temperature should be more conductive.

C. Hydroxyl. The data presented above clearly show that carbonyl groups are present in these polypyrrole chains. However, the concentrations of these defect sites (5-9%, Table III) cannot account for the large quantities of extraneous oxygen seen in the elemental analysis data (Table I). Hence, there must be another O-containing functionality in these polymers. We have recently carried out a series of infrared spectroelectrochemical investigations aimed at understanding the source and identity of this extraneous oxygen in polypyrrole.[30,31] We have found that this excess oxygen exists predominantly as -OH groups that are covalently bonded to the pyrrole rings.[30] These -OH groups result from the reaction of the nascent PPY chains with water present in the solvent.

In order to see the absorption bands associated with -OH in the infrared spectrum for polypyrrole, the polymer must be electrochemically undoped.[30] We accomplished this in our previous investigations[30] by electrochemically-synthesizing ultrathin films of the polymer on an IRtransparent electrode. It would, however, be very difficult to accomplish this electrochemical reduction with the chemically-synthesized polypyrrole powders investigated here. However, XPS can be used to confirm that -OH is present in these polymers. Furthermore, the XPS data can provide an estimate of the concentrations of these -OH defects.

As indicated above, the C_{1s} XPS spectra were deconvolved into four component gaussians (Figure 2). In addition to the carbonyl C's at 288.0 eV and the α and β ring carbons at 283.8 and 284.9 eV,[13,15,20,21,32] there is an additional component with a binding energy of 286.5 eV. This component can be attributed to a combination of carbon atoms which are adjacent to a positively-charged N atom[18,19,33] and carbon atoms which are sigma-bonded to oxygen[14]. This 286.5 eV component accounts for about 20% of the total C_{1s} area. Furthermore, the contribution from the carbons bonded to positively-charged nitrogens can be accounted for via the N_{1s} XPS data in Table II. After this correction is made, we find that 5-10% of the carbon atoms in these samples are sigma-bonded to oxygen. If the amount of the carbon atoms existing as carbonyls is also taken into account (Table II), the combined amount of carbon atoms which are bonded to oxygen (as carbonyls or as sigma-bonded) is about 10-15%. This estimate of excess oxygen (about 0.4 to 0.6 oxygen per ring) is in reasonable agreement with the elemental analysis data shown in Table I. Therefore, in agreement with our previous studies, these data indicate that the majority of the extraneous oxygen found in polypyrrole is present as covalently-bound hydroxyl.

The O_{1s} XPS data corroborate these C_{1s} spectral assignments and the assessment of the extraneous oxygen in polypyrrole. A typical O_{1s} core-level XPS spectrum is shown in Figure 4. As indicated in Figure 4, the

O_{1s} XPS spectra can be deconvolved into two component gaussians. However, the main component has a peak width at half height (pwhh) of 1.9 eV. This is significantly wider than a typical gaussian XPS peak. (Typically 1.3 to 1.5 eV, e.g. the O_{1s} peak in Bu_4NClO_4 has a pwhh of 1.4 eV.) This broad, main component at 531.5 eV can be assigned to an overlap of the carbonyl oxygens and the oxygens from the perchlorate doping anions.[33,34] The minor component, with a binding energy of 534.0 eV, can be attributed to the oxygens sigma-bonded to carbons (i.e. carbons bonded to -OH).[14,34] The ratio of the area of this 534.0 eV component to the total O area is 0.13 for PPY_{45C}, 0.15 for PPY_{27C}, and 0.16 for PPY_{0C}. These data translate to 4.5, 5.6, and 7.5% of the C atoms being sigma-bonded to O. This estimate of the -OH content is in excellent agreement with the estimate obtained from the C_{1s} spectra (see above).

III. Conjugation Length. Tian and Zerbi have recently used the "effective conjugation coordinate" theory (ECCT) to calculate the vibrational spectra of pristine and doped PPY.[35,36] They show that ECCT can be used to predict the effects of variation in the extent of delocalization along the polymer chain on the positions and intensities of the infrared bands in PPY. The ECCT analysis of PPY suggests that the relative intensities of the infrared bands at 1550 and 1470 cm^{-1} (highlighted in Figure 3) are particularly sensitive to extent of delocalization.

We have shown that by ratioing the integrated absorption intensities of the bands at 1550 and 1470 cm^{-1} (Figure 3), a qualitative measure of conjugation length can be obtained.[10] We call this ratio I_{1550}/I_{1470}; we have shown that the magnitude of I_{1550}/I_{1470} is inversely proportional to the conjugation length.[10-12] This FTIR method for assessing the conjugation length in polypyrrole was applied to polymers synthesized here. I_{1550}/I_{1470} ratios of 3.3, 4.9 and 7.0 were obtained for the samples synthesized at 0, 27, and 45 °C, respectively. These data show that the conjugation length is longer in the materials synthesized at lower temperatures. Yamaura et al reached the identical conclusion concerning the effect of synthesis temperature on conjugation length in electrochemically-synthesized PPY.[37] This conclusion is also supported by the various assessments of quantity of conjugation-interrupting defect sites (Table III). The material synthesized at the lowest temperature has fewer of these defect sites and thus has extended conjugation.

IV. Conductivity.

A. Room-Temperature Conductivity. We have demonstrated that polypyrroles synthesized at lower temperatures have higher doping level. fewer structural defects and longer conjugation lengths. This suggests that the materials synthesized at lower temperature will be more conductive. Room temperature conductivity data are shown in Table IV. As expected, the material synthesized at the lowest temperature is significantly more conductive. This inverse relationship between synthesis temperature and conductivity is also observed in our "template-synthesized" polypyrrole fibers[12] and in electrochemically-synthesized polypyrrole film.[37,38] Again, the data presented above help to explain this synthesis-temperature-dependent conductivity.

B. Variable temperature conductivity. Polarons and bipolarons are believed to be the charge carriers in PPY.[1-3,12] Polaron or bipolaron are localized charges on the PPY chain that constitute a boundary between two segments corresponding to different molecular wave-functions.[39,40] The temperature dependence of conductivity in such a system can be described by the variable-range hopping (VRH) model for which the conductivity σ can be represented by[39-41]

$$\sigma = \sigma_0 T^{-1/2} \exp(-T_0/T^{1/4}) \qquad (1)$$

where $\sigma_0 = 0.39e^2 v_0 \,(N(E_F)/\alpha k_B)^{1/2}$ and $T_0 = 1.66[\alpha^3/k_B\, N(E_F)]^{1/4}$. Here, $N(E_F)$ is the density of states at the Fermi level, α^{-1} is the decay length of a localized state, v_0 is the hopping attempt frequency, and k_B and e are Boltzmann's constant and the charge on the electron, respectively. The density of states is closely related to the doping level of the sample and the decay length of a localized state is related to the conjugation length. Samples with longer conjugation lengths (fewer defects and higher degree of structural order) and higher doping level are expected to have larger σ_0 and smaller T_0 values. Therefore, an analysis of the temperature dependence of conductivity can provide useful information about the conduction mechanism, the density of charge carriers, and the conjugation length of the polymer system.

The temperature-dependent conductivity data for the samples synthesized at 0 and 27 °C are plotted as $\ln(T^{1/2} \times \sigma)$ vs. $T^{-1/4}$ (Equation 1) in Figure 5. Clearly, $\ln(T^{1/2} \times \sigma)$ is linearly related to $T^{-1/4}$ (correlation coefficients ≥ 0.992). Thus, charge transport in both PPY_{0C} and PPY_{27C} is amenable with the 3-D VRH conduction mechanism. The σ_0 and To data obtained from these plots are presented in Table IV.

As shown in Figure 5 and Table IV, the T_0 value for PPY_{0C} is significantly larger than T_0 for PPY_{27C}. The lower T_0 value for the sample synthesized at lower temperature suggests that PPY_{0C} possesses a higher density of states $N(E_F)$ and/or a longer conjugation length (α^{-1}). Both the doping level data and the infrared assessment of conjugation length (see above) support this conclusion. PPY_{0C} also shows a larger σ_0 value than PPY_{27C} (Table IV). This larger σ value can be attributed to a higher hopping-attempt frequency in PPY_{0C}, *a direct result of the higher doping* level in the sample.

Conclusions

Polypyrrole perchlorates have been synthesized under inert atmosphere at various temperatures. The doping level of the polymer is found to increase with decreasing synthesis temperature. FTIR, XPS and variable temperature conductivity data indicate that polypyrroles synthesized at lower temperature have longer conjugation length as well as fewer structural defects. The XPS data suggest that the positive charges are not uniformly distributed along the polymer chain. These studies have also shown that the excess oxygen frequently observed in PPY is reduced only slightly by carrying out the synthesis in anaerobic atmosphere; thus the solvent (H_2O), and not O_2, is suggested to be the main source of this extraneous oxygen.[30] The extraneous oxygen is present predominantly as covalently-bound hydroxide.[30] It is interesting to note that a hydroxide covalently bound to a pyrrole ring is an enol. This enol might be expected to tatonmerize to the corresponding ketone. We have suggested that this tatonmerization is suppressed because formation of the ketone interrupts conjugation.[30,31]

Finally, the observation that polymers synthesized at higher temperatures contain high concentrations of defect sites is not surprising. These defect sites are introduced as a result of unwanted side reactions; these reactions are essentially occurring in competition with the desired reaction, α-α coupling of oxidized monomer units to produce a defect-free polymer chain. At very low temperatures the rates of these unwanted reactions become much slower relative to the rate of the desired reaction. As a result we produce more highly defect-free polymer chains at lower temperature.

Acknowledgments

This work was supported by the Office of Navel Research and by the Air Force Office of Scientific Research.

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Table I. **Chemical composition of polypyrrole perchlorate samples synthesized at various temperatures**

Synthesis Temperature (°C)	Designation	Composition[a]
0	PPY_{0C}	$C_{4.00}N_{0.95}(ClO_4)_{0.35}O_{0.48}$
27	PPY_{27C}	$C_{4.00}N_{0.94}(ClO_4)_{0.27}O_{0.43}$
45	PPY_{45C}	$C_{4.00}N_{0.92}(ClO_4)_{0.24}O_{0.48}$

a. As determined via XPS. See text.

Table II. Comparison of the doping level with the N^+/N ratio

Sample	ρ[a]	N^+/N ratio[b]
PPY_{0C}	0.35	0.31
PPY_{27C}	0.27	0.24
PPY_{45C}	0.24	0.22

a. Doping level as determined via XPS-based elemental analysis. See text.

b. The ratio of the 401.5 eV component to the total area of the N_{1s} peak. See text.

Table III. Percentages of deprotonated nitrogens and carbonyl carbons as determined by XPS[a]

Sample	>C=N-	>C=O
PPY_{0C}	3.0	5.5
PPY_{27C}	4.5	7.0
PPY_{45C}	8.0	9.2

a. Determined by ratioing the gaussian at either 397.5 eV (N) or 288.0 eV (C) to the total peak area. See text.

Table IV. Charge Transport Data for Polypyrrole Samples

Sample	σ_{RT} (S/cm)	σ^{a} (x 10^{4})	T_{0}^{a}
PPY_{0C}	22.3	2.0 ± 0.2	16.5 ± 0.4
PPY_{27C}	5.9	1.2 ± 0.1	20.0 ± 0.4
PPY_{45C}	4.8		

a. Obtained from plots of $\ln(T^{1/2} \times \sigma)$ vs. $T^{-1/4}$.

Figure Captions:

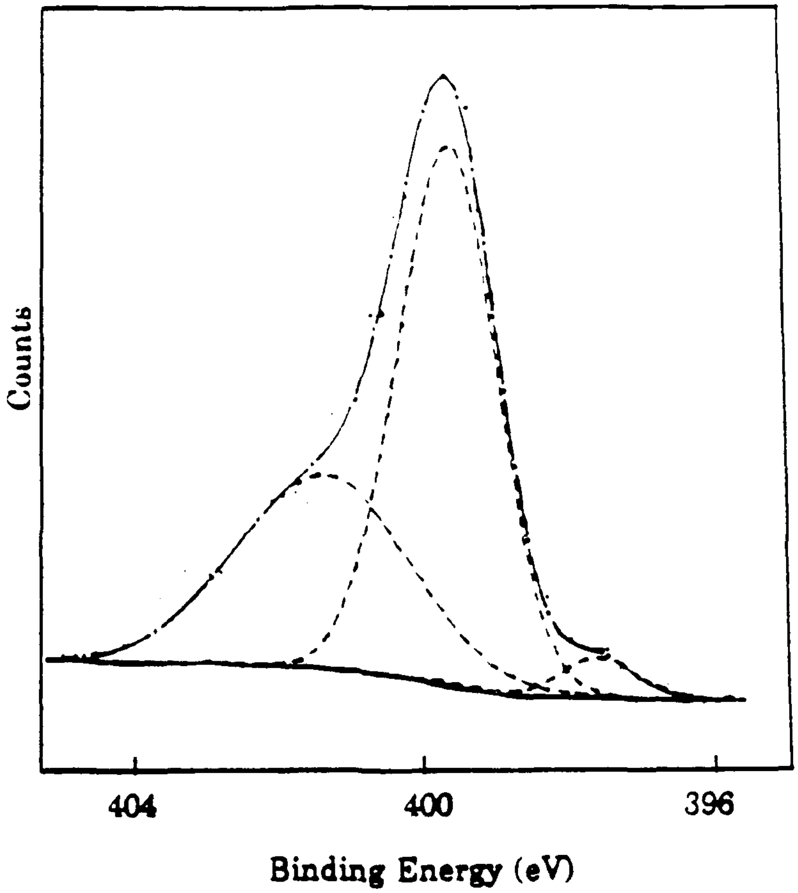
Figure 1. N_{1s} XPS core level spectrum of the polypyrrole perchlorate sample synthesized at 0 °C (PPY_{0C}).

Figure 2. C_{1s} XPS core level spectrum of PPY_{0C}.

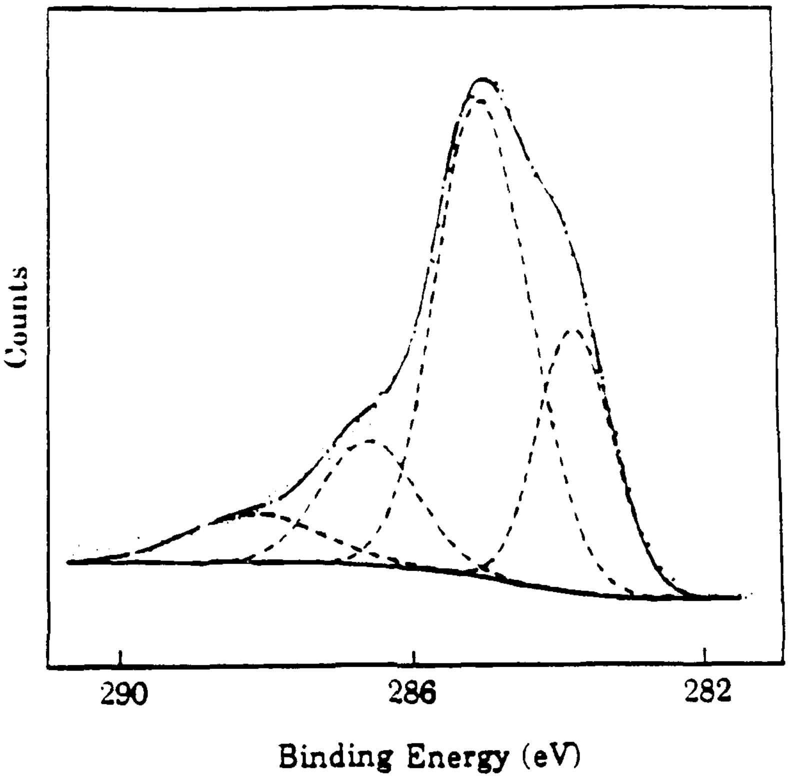
Figure 3. IR spectra of polypyrrole samples. (A): PPY_{45C} and (B): PPY_{0C}.

Figure 4. O_{1s} XPS core level spectrum of PPY_{0C}.

Figure 5. Plots of $\ln(T^{1/2} \times \sigma)$ vs. $T^{-1/4}$ for A: PPY_{0C} (◆) and B: PPY_{27C} (□).



Liang/Lei/Martin .... Figure 1



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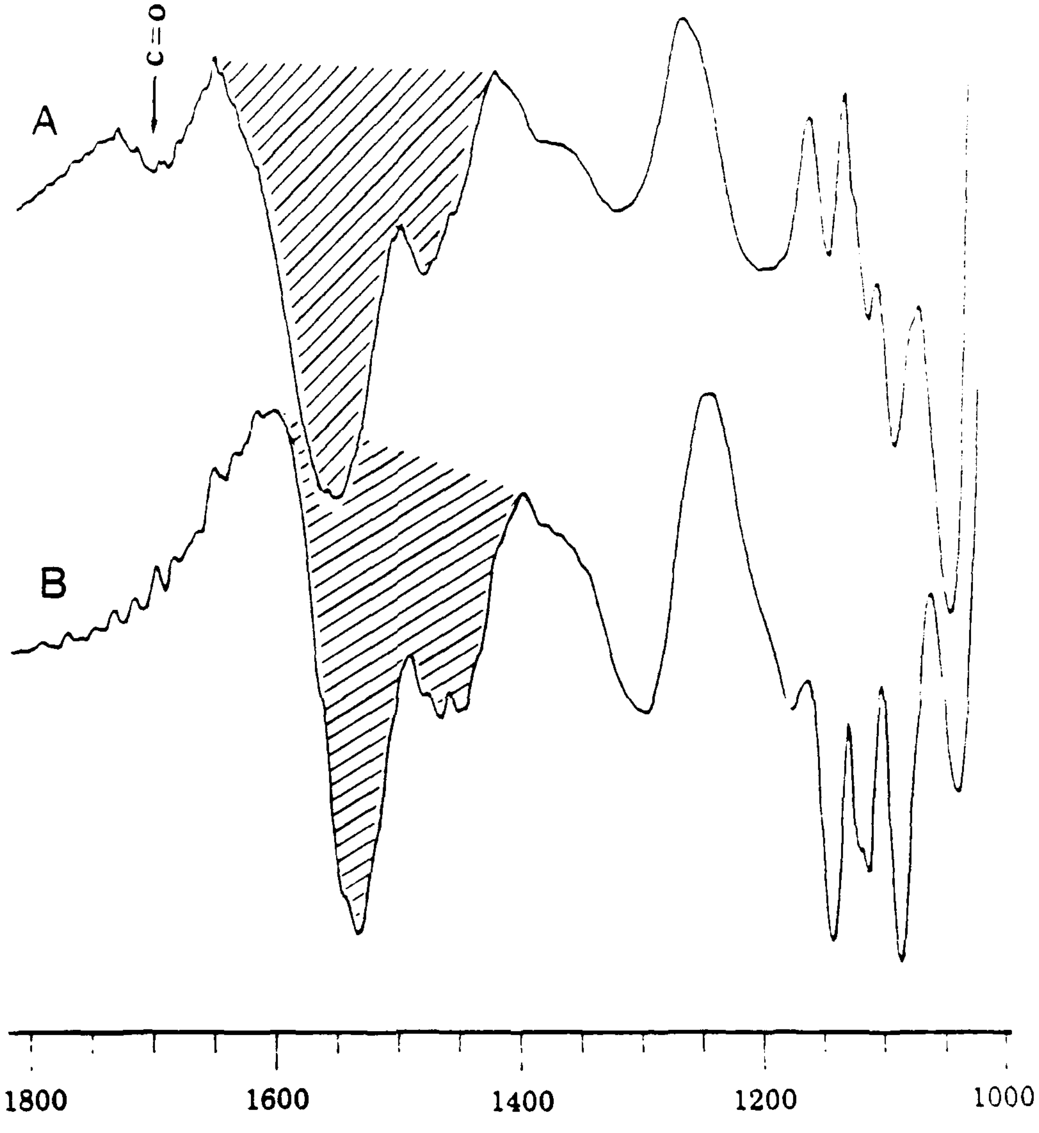

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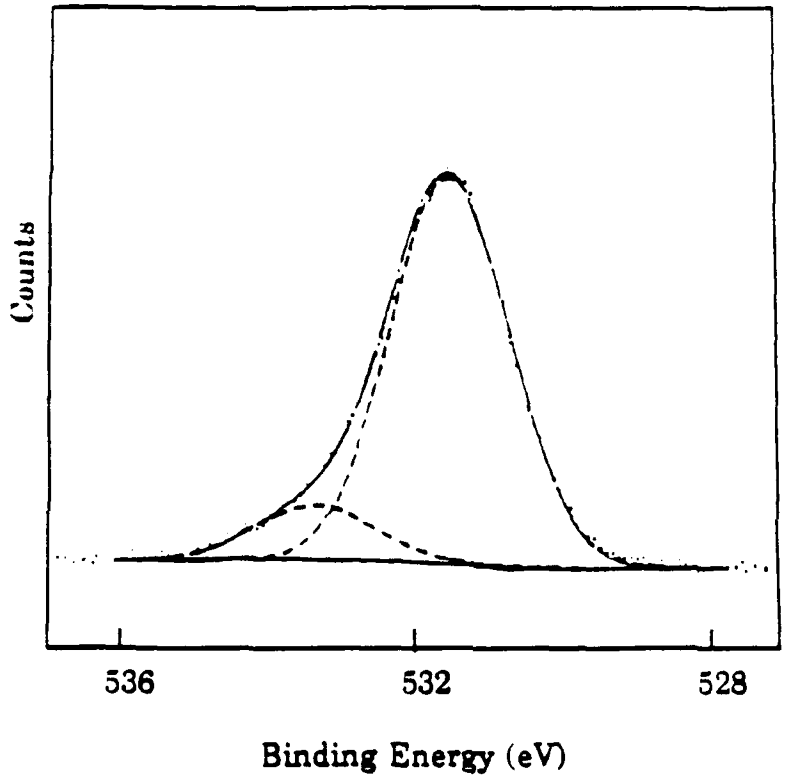

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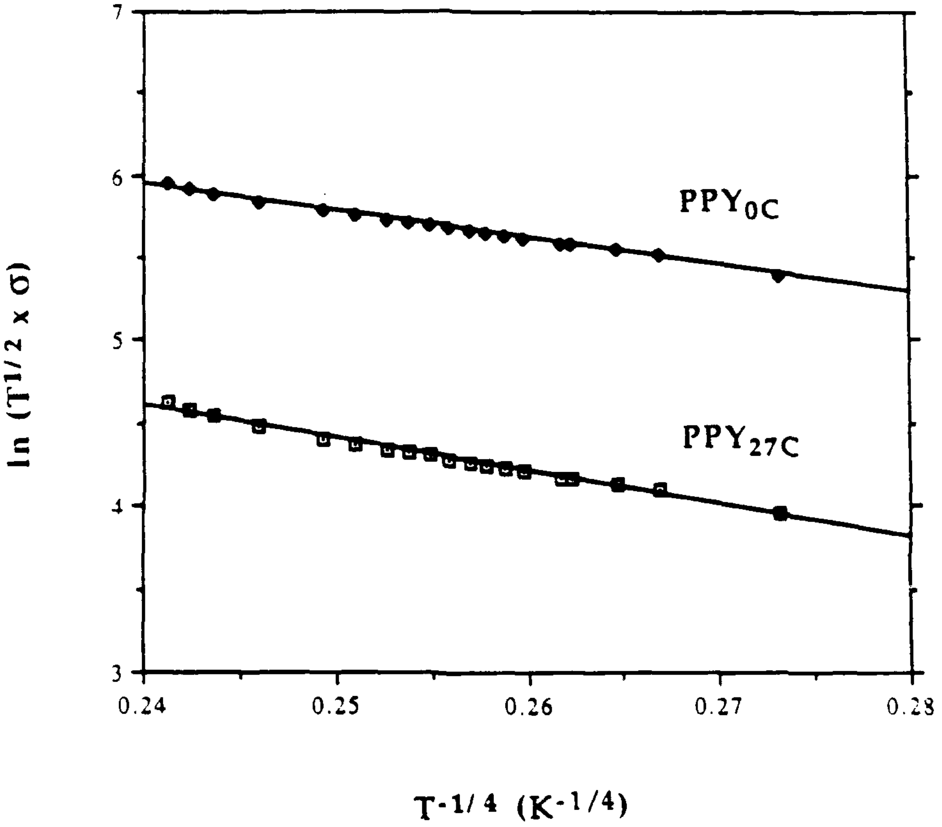

Liang/Lei/Martin .... Figure 5

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
APPROVED FOR PUBLIC DISTRIBUTION,
DISTRIBUTION UNLIMITED.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
ONR TECHNICAL REPORT #72

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Dr. Charles R. Martin
Department of Chemistry

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
Colorado State University
Ft. Collins, CO 80523

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Street
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Contract # N00014-82K-0612

8c. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Street
Arlington, VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO

11. TITLE *(Include Security Classification)*
Effect of Synthesis Temperature in the Structure, Doping Level and Charge-Transport Properties of Polypyrrole

12. PERSONAL AUTHOR(S)
Wenbin Liang, Junting Lei and Charles R. Martin

13a. TYPE OF REPORT
Technical

13b. TIME COVERED
FROM ________ TO ______

14. DATE OF REPORT *(Year, Month, Day)*
1992, 5, 8

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Polypyrrole, conductive polymers

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Polypyrrole perchlorate was chemically synthesized at various temperatures and the resulting polymers were investigated by elemental analysis, fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and conductivity measurements. A correlation between conductivity, doping level and synthesis temperature was observed. The doping level of the polymer is higher when the synthesis is conducted at lower temperature exhibits longer conjugation length, fewer structural defects, higher charge carrier hopping frequency and higher conductivity. Furthermore, the results of this study indicate that the positive charges of doped polypyrrole are preferentially localized on the nitrogen atoms which are adjacent to the doping anions, as opposed to being uniformly delocalized along the polymer backbone.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL
Dr. Robert Nowak

22b. TELEPHONE *(Include Area Code)*
(202) 696-4410

22c. OFFICE SYMBOL

DD Form 1473, JUN 86 *Previous editions are obsolete.* SECURITY CLASSIFICATION OF THIS PAGE