

Synthesis and Characterization of Polyarylureas. I. Potentially Semiconducting Polymers

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ABSTRACT: Polyarylureas were synthesized from the reaction between phosgene with aromatic diamines. Depending on the pH, the polyarylureas presented different colors when the solvent used was pyridine. The polyarylureas were characterized by IR spectroscopy, elemental analysis, and X-ray photoelectron spectroscopy (XPS). To study the thermal stability of the polymers, a thermal degradation was performed between 35 and 700°C. The polyarylureas decomposed above 350°C. Without doping, polyarylureas are considered as semiconductors [$\sigma = 10^{-9} (\Omega\text{cm})^{-1}$]; after doping with I_2 , their electrical conductivity increases by several orders of magnitude. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 822–830, 2001

Key words: polyarylureas; semiconducting polymers

INTRODUCTION

The usage of organic polymers that present an electrically conducting structure has been uncommon. However, since Shirakawa et al. synthesized polyacetylene in 1977,¹ considerable attention has been directed to this field. Since then, many organic materials with conducting properties have been reported. One of them, polyaniline (PANI), which was synthesized a century ago,^{2–4} continues to attract extensive attention from scientists and engineers.

High electrical conductivity, processability, and stability in air have been the three major targets sought for conducting polymers. The sta-

bility of conducting polymers seems especially important for application of the material. It has been discovered, however, that most of the reported conducting polymers are unstable in air except those containing nitrogen or sulfur atoms in the polymer backbone.^{5–10}

Polymers based primarily on heterocyclic units can be used as semiconducting materials due to electron delocalization through the rings. A fundamental and still open scientific problem is the correlation between the structure and properties of these polymers. Some factors currently limiting the application and use of many of these materials are the lack of long-term stability and the need of low-cost techniques for easy processing.

In 1989, Ghander and Diab¹¹ reported the synthesis of a polymer formed by a Michael addition reaction between *p*-bis-*N*-sulfinyldiamine and *p*-phenyldiamine. The thermal stability of this polymer is up to 200°C, and it presents a conductivity of $10^{-6} (\Omega\text{cm})^{-1}$.

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Table I Polymerization: Conditions, Yields, and Colors of Obtained Products

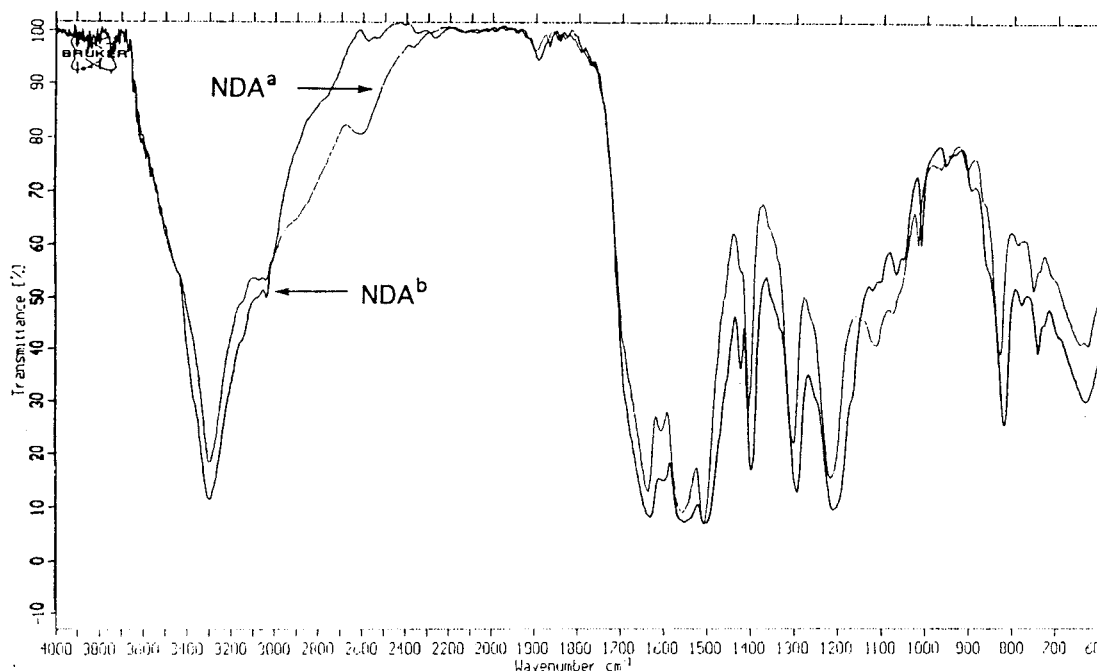
Polymer	Monomer	Solvent	Color	Yield (%)
FDA	1,4-Phenylendiamine	THF	Gray	96
FDA ^a	1,4-Phenylendiamine	Py	Pink	97
FDA ^b	1,4-Phenylendiamine	Py	Orange-yellow	96
NDA	1,5-Naphtalendiamine	THF	Black	69
NDA ^a	1,5-Naphtalendiamine	Py	Brown	70
NDA ^b	1,5-Naphtalendiamine	Py	Dark brown	69

In the present work, we describe the synthesis of polyarylureas, in different solvents. They were characterized by IR spectroscopy, elemental analysis, and X-ray photoelectron spectroscopy (XPS). We also studied the stability and conductivity without doping and with doping with I₂ and SbF₅.

EXPERIMENTAL

The solvents used during the process were obtained from Aldrich (Milwaukee, WI), Merck (Darmstadt, Germany), and Fluka (CH-9471, Buchs, Switzerland) and were purified according to standard procedures. The diamines were crystallized from ethanol. Commercial phosgene was dissolved in toluol at 10% weight.

Polymers were obtained according to the following procedure: In a round-bottom flask, the diamine (0.0139 mol of 1,4-phenylendiamine or 9.5×10^{-3} mol of 1,5-naphtalendiamine) was dissolved in 50 mL of tetrahydrofuran (THF) or pyridine (Py) with constant stirring. Phosgene was slowly added to this mixture. The molar ratio of diamine:phosgene was 3:2. The reactions were carried out at room temperature. After reacting for 30 min with stirring, when pyridine was used as a solvent, one batch of the polymer was washed with H₂O/HCl and the other with a H₂O/NaOH solution. On the other hand, the synthesized product in THF was washed with boiled water. The solids obtained by reaction in pyridine or THF were then filtered and washed several times with CH₃OH, CHCl₃, and diethyl ether and dried under a vacuum.

**Figure 1** IR spectra of NDA^a and NDA^b polymers.

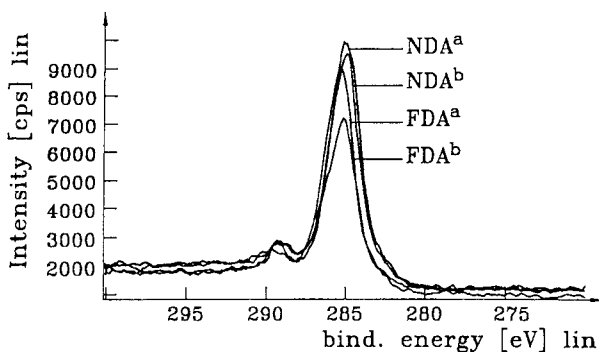


Figure 2 XPS spectra of C1s of the polymer.

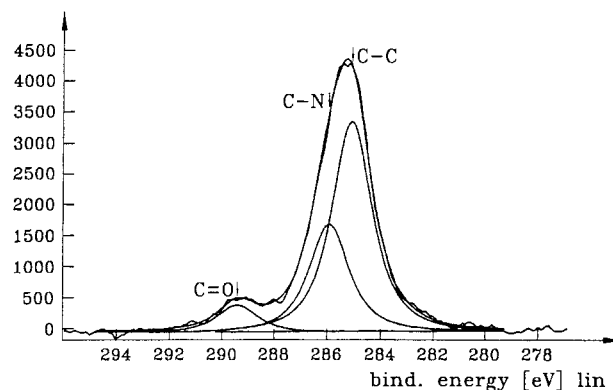


Figure 3 Curve-fitting of C1s peak of the polymer.

Elemental Analysis was performed on a C—H—N Heraeus Mikrostandar analyzer. IR spectra were obtained in KBr pellets in a Bruker Vector 22 spectrophotometer. Band positions are expressed in wavenumber (cm^{-1}).

Dynamic thermogravimetric analyses were conducted in a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UV:1 temperature-program control. Samples were placed on a platinum sample holder, and the thermal degradation measurements were carried out between 35 and 700°C at a heating rate of 20°C min^{-1} under a N_2 atmosphere.

The glass transition (T_g) values and the decomposition temperature (T_d) were determined in a Perkin–Elmer DSC-1B differential scanning calorimeter at 16°C min^{-1} under N_2 . The electrical conductivity measurements were performed with an Elchema electrometer Model CM-508 using polymer pellets by the four-probe method.

Conductivity measurements in a temperature domain were performed on pressed polymer pellets. The upper and lower faces of the pellets were metallized by thermal evaporation of gold under a

vacuum. Copper wires were stuck by silver paste to the gilt faces of the pellets. An Keithley electrometer Model 617 was used to measure the conductivity.

To dope with I_2 , samples of polymers in separate glass cups were placed in a desiccator with I_2 at room temperature and atmospheric pressure. Samples were periodically removed, weighed, and returned to the desiccator until no more I_2 was taken up. I_2 uptake was monitored by weighing.¹² To dope the polymers with SbF_5 , they were exposed to vapor over its condensed phase at 60°C for 1 h and then washed with CH_3OH , CHCl_3 , and diethyl ether and dried under a vacuum.¹³

The morphology of the grains of the polymer powder was observed using a field-effect scanning electron microscope JEOL 6400F. The resulting powders were characterized by XPS analysis at the University of Nantes–CNRS on a Leybold LHS-12 spectrometer. The data were obtained with a magnesium source of radiation (1253.6 eV) operating at 10 kV and 10 mA, and the pass

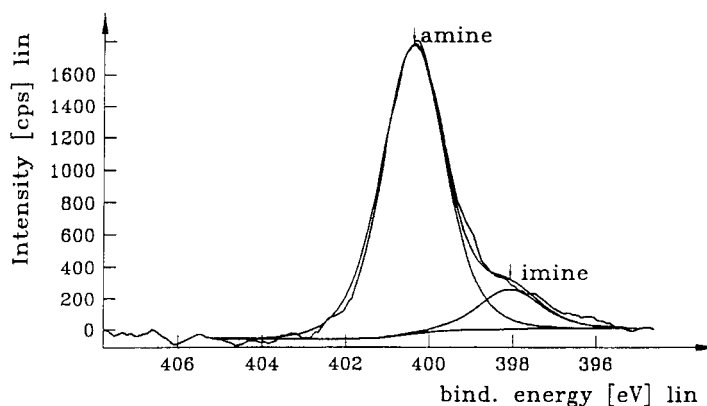


Figure 4 Curve-fitting of N1s peak of the polymer.

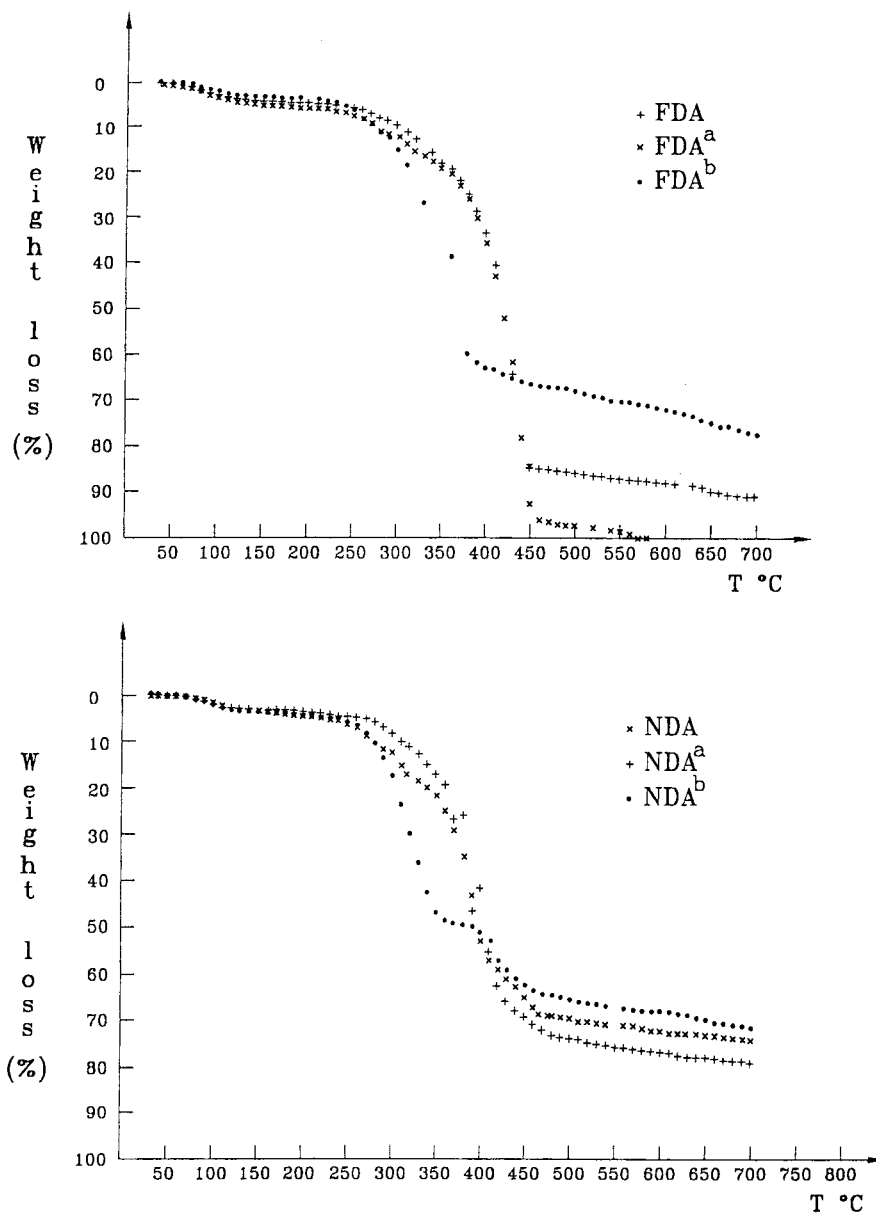


Figure 5 Thermogravimetric analysis of the polymers.

energy was set to 50 eV. High-resolution scans with a good signal-to-noise ratio were obtained in the C1s, N1s, O1s, and Cl2p regions of the spectrum. To decrease the charge effect, the powders were fixed to the substrate holder by pressing the polymer powder onto a sheet of indium.

The quantitative analysis was based on the determination of the C1s, N1s, O1s, and Cl2p peak areas with sensitivity factors of 0.2, 0.36, 0.61, and 0.58, respectively. The sensitivity factors of the spectrometer were provided by the manufacturer. The vacuum in the analysis cham-

ber was approximately 10^{-6} Pa. All spectra were recorded under identical conditions. The decomposition of the XPS peaks into different components and the quantitative interpretation were made after the subtraction of the background using the Shirley method.¹⁴

The developed curve-fitting programs allow the variation of parameters such as the Gaussian/Lorentzian ratio, the full-width at half-maximum (fwhm), and the position and the intensity of the contribution. These parameters were optimized by a curve-fitting program to obtain the best fit.

Table II Elemental Analyses of the Polyarylureas

Polymers	C (%)		N (%)		H (%)	
	Calculated	Found	Calculated	Found	Calculated	Found
FDA	62.7	61.1	20.9	21.1	4.5	5.3
FDA ^a	62.7	60.7	20.9	21.0	4.5	4.7
FDA ^b	62.7	62.0	20.9	20.0	4.5	4.5
NDA	71.7	70.9	15.2	14.9	4.3	4.7
NDA ^a	71.7	69.2	15.2	15.4	4.3	5.0
NDA ^b	71.7	71.4	15.2	14.4	4.3	4.7

RESULTS AND DISCUSSION

It is known that when phosgene¹⁵ is treated with an excess of a primary or secondary amine symmetrical ureas are produced with high yields. The reaction is usually carried out in the presence of an acid acceptor such as sodium hydroxide,^{16–18} sodium carbonate, or pyridine.¹⁹

In the present work, new polyarylureas were obtained from the reaction of phosgene with some aromatic diamines, using pyridine or THF as solvents, as shown in Scheme 1. When the solvent used was pyridine, the polymers presented different colors, depending on the pH (a = acid, b = basic; Table I). This did not occur when THF was the solvent.

Independent of the solvent, solubility tests showed that polymers were insoluble in all common organic solvents and inorganic acid. This insolubility does not allow one to specify the molecular size of the polymers.

The polymers were characterized by IR spectroscopy, elemental analysis (Table II), and XPS analysis (Table III–IV). The results were consistent with the proposed structures. When the polymers were synthesized using pyridine and washed with H₂O/HCl, the IR spectra show (Fig. 1) some N⁺ groups at 2600–2700 cm⁻¹. However no shoulder attributed to N⁺ was observed when

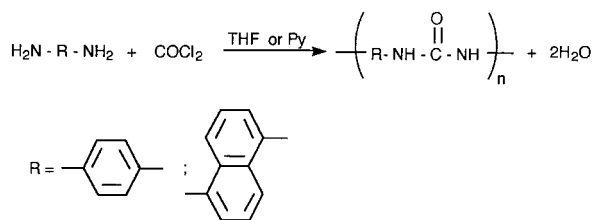
the polymers were synthesized using pyridine and washed with the H₂O/NaOH solution.

These results corroborate what was shown in the XPS spectra; when the polymer was synthesized using THF or pyridine-H₂O/HCl, a small shoulder appeared at 402.2–402.3 eV in the XPS spectra attributed to N⁺. Also, a small peak was observed at 198.8 eV, which corresponds to chloride as the counterion.

XPS quantitative analysis of polymers relative to the constituents are presented in Table III. It can be seen that there is oxygen contamination at the surface of the samples. No other contaminating element was detected in any of the samples.

The carbon–carbon bond present in the polymers was taken as the reference to estimate the charge effect. Briggs and Seah showed²⁰ that this bond has a well-defined position at 285 eV. It can be seen in Figure 2 that there is some charge effect, which is due to the small conductivity of the polymer. Therefore, the charge effect must be subtracted from the binding energies of the experimental curves.

Figures 3 and 4 show that the C1s and N1s peaks exhibit shoulders and large fwhm for all

**Scheme 1****Table III** XPS Surface Quantitative Analyses of Polymers Relative to the Constituents: C, N, O (at %)

	At % C	At % N	At % O
FDA theoretical	70	20	10
FDA	72	12	16
FDA ^a	74	17	9
FDA ^b	72	16	12
NDA theoretical	78.6	14.2	7.2
NDA	81	9	10
NDA ^a	81	11	8
NDA ^b	78	13	9

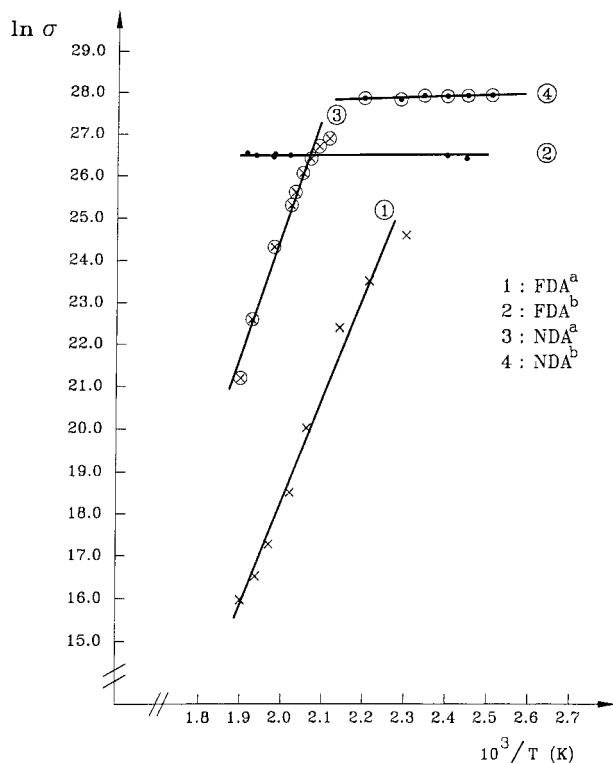


Figure 6 $\ln \sigma$ versus $10^3/T$ (K) of the polymers synthesized in pyridine.

the polymers; therefore, they have decomposed. The C1s peak can be decomposed into three peaks (Fig. 3). The first corresponds to the carbon-carbon and hydrocarbon bonds. The second can be attributed to the C-N bonds, and the third peak may be attributed to the carbonyl bond.²¹

When the polymer was synthesized using THF or pyridine washed with H_2O/HCl , the N1s peak can be decomposed into two peaks (Fig. 4) and a small shoulder at 402.3 eV was attributed to N^+ . The two peaks obtained after decomposition of N1s could be attributed to $N=$ and $N-$ bonds (Fig. 4), except for an FDA^a compound which does not have an imine group.

The DSC analyses of the polymers showed no glass transition temperature. Furthermore, polyarylureas did not melt. However, they decomposed at temperatures above 350°C, as verified by the IR spectra.

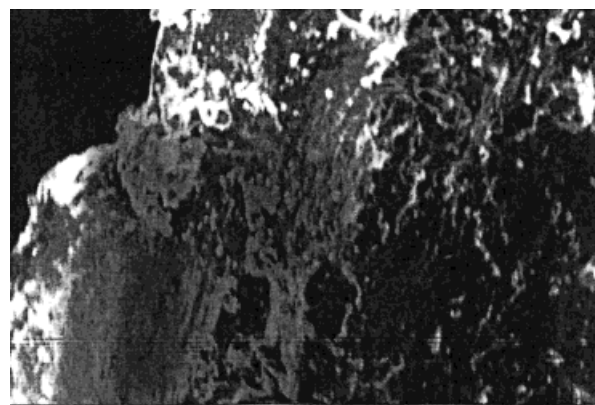
To study the thermal stability of the polymer, a thermal degradation study was performed under the same conditions for all the compounds. Figure 5 represents the weight loss of the material between 35 and 700°C. According to this figure, the polymers present similar behavior with a one-stage thermal-degradation process, except for the

NDA^b compound, which decomposes in a two-stage process (Fig. 5).

For the compound obtained in basic medium, a weight loss was observed: at 350°C, 38% for FDA^b and 47% for NDA^b . Under acidic conditions and in THF, a lower percentage of weight loss was seen, which could be due to the H-links formed that give more stability to the polymers.

Table V shows the data obtained for the heating curve. Polymers with one aromatic ring in the structure presented a greater weight loss at 450°C (Table V) than did those with a second ring in the polymeric chain (phenyl or naphthyl) which produces stabilization of the system, as was proved by Marvel.²²

The XPS analysis shows that the high weight loss of FDA^a at 450°C is due to the absence of imine groups in the polymer. This fact is confirmed by the presence of only amine bands. These results are in accordance with the work reported by D'Alelio et al.²³



a) FDA.



b) NDA.

Figure 7 Microphotography of the polymers: (a) FDA; (b) NDA.

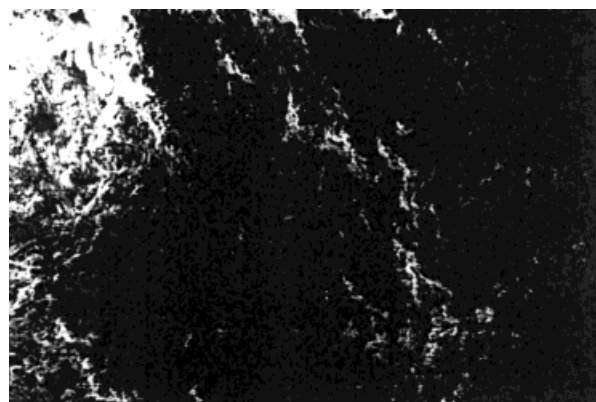
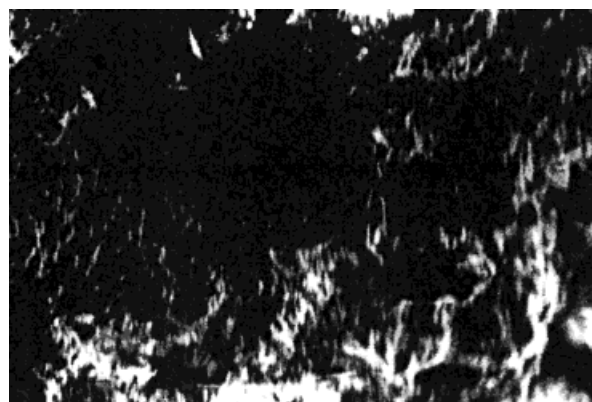
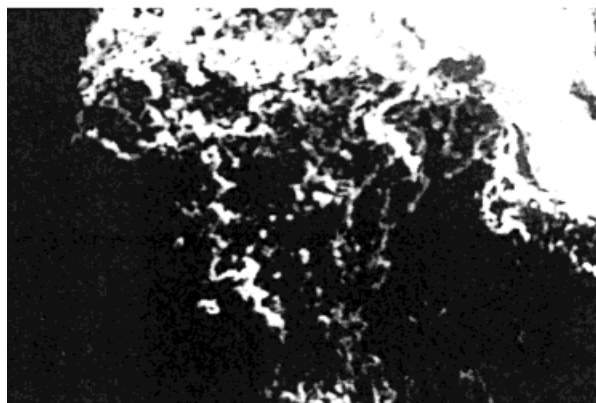
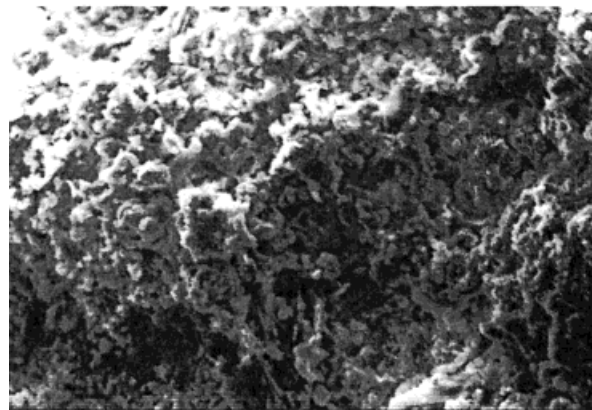
a) FDA^a. 10 μma) FDA^b. 10 μm.a) NDA^a. 10 μma) NDA^b. 10 μm.

Figure 8 Microphotography of the polymers: (a) FDA^a; (b) NDA^a.

Figure 9 Microphotography of the polymers: (a) FDA^b; (b) NDA^b.

Table IV XPS Analyses After Decomposition of the Peaks

	C1s Relative At %			N1s Relative At %			Cl2p Relative At %
	C—C	C—N	C=O	N=	N—	N+	Cl ⁻
FDA	285.0 61	286.0 31	289.9 8	398.1 12	400.4 88	402.3	200.4
FDA ^a	285.0 85	286.8 9	289.2 6	—	400.1 100	402.2	201.0
FDA ^b	285.0 69	286.1 21	289.2 10	398.3 12	400.4 88	—	—
NDA	285.0 67	285.6 25	289.0 8	397.5 13	399.8 87	402.3	198.8
NDA ^a	285.0 62	285.7 29	289.4 9	398.3 11	400.2 89	402.2	199.0
NDA ^b	285.0 61	285.8 31	289.6 8	398.5 11	400.3 89	—	—

First line: binding energy eV; second line: relative atomic percentage.

Table V Weight Loss Percent of Polymers at Different Temperatures (°C)

Polymers	Weight Loss (%)		
	100°C	350°C	450°C
FDA	2.9	18	85
FDA ^a	3.4	19	93
FDA ^b	2.0	38	66
NDA	1.9	23	66
NDA ^a	2.0	17	70
NDA ^b	2.3	47	62

Conductivity measurements at room temperature of compounds without dope and doped with I₂ and SbF₅ of the powdered samples are summarized in Table VI. The conductivity values of the polymers without doping indicates that they behave as semiconductors.

The synthesized polymers in THF or pyridine-HCl conditions present the amine group protonated in the polymeric chain, and the charge would be more localized. On the other hand, the conductivity values increase after doping with I₂, by at least 5 orders of magnitude, when the polymers were synthesized using pyridine as the solvent and washed with a H₂O/NaOH solution.

Sakai et al.²⁴ reported that when polymers with nitrogen in their structure are doped with I₂ the nitrogen becomes coordinated with the dopant agent, leaving the polymeric chain with negative charge density, which is the reason for the increase in the conductivity values. In this case, iodine introduced into the polymeric chains fluctuates between 28 and 40% of weight for polymers having one aromatic ring, as in the case of FDA, and between 40 and 47% for polymers with two aromatics rings, as in the case of NDA.

In previous studies, it was found that a very strong dopant such as chlorine damages the poly-

mer while a weaker dopant such as iodine causes an increase in conductivity. Since SbF₅ is a stronger dopant agent than is iodine, it could cause the polymeric chain to result in cleavage; therefore, a considerable increase in the conductivity is not observed.²⁵⁻²⁷ The conductivity values remained almost unchanged for products doped with SbF₅; however, I₂ is more effective as a dopant for these polymers.

Polymers prepared in pyridine were studied as to the behavior of the conductivity under different temperature conditions. The results are represented by an Arrhenius plot.

The relationship between conductivity (σ) and temperature (T) is given by the expression²⁸

$$\sigma = \sigma_0 \exp(E_A/kT)$$

E_A = activation energy

$$k = \text{Boltzman constant} = 8.625 \times 10^{-5} \text{ eV/K}$$

T = Kelvin temperature

where E_A is the activation energy; k , the Boltzman constant = 8.625×10^{-5} eV/K; and T , the Kelvin temperature. A straight line was obtained by plotting $\ln \sigma$ versus $1/T$ (Fig. 6). The activation energy (E_A) is given by the slope of this line. In all the conditions studied, the increase in temperature generates an increase in conductivity. The values for the polymer prepared in pyridine and basic medium were not reproducible; therefore, they were omitted from the plot.

Using Figures 7-9, it is possible to observe that the reaction medium not only originates a difference in polymers colors, but also originates a difference in the morphology of each polymer. Although every polymer presents a not well-defined granulate morphology, which is possible to ob-

Table VI Conductivities at Room Temperature and Pressure (σ) ($\Omega \text{ cm}$)⁻¹ of Compounds Before Doping and After Doping with I₂ and SbF₅

Sample	σ Without Doping ($\Omega \text{ cm}$) ⁻¹	σ Doping with I ₂ ($\Omega \text{ cm}$) ⁻¹	σ Doping with SbF ₅ ($\Omega \text{ cm}$) ⁻¹
FDA	1.25×10^{-9}	7.40×10^{-7}	2.48×10^{-9}
FDA ^a	1.34×10^{-9}	1.14×10^{-6}	3.25×10^{-9}
FDA ^b	1.43×10^{-9}	2.78×10^{-4}	3.19×10^{-9}
NDA	1.75×10^{-9}	7.14×10^{-6}	3.45×10^{-9}
NDA ^a	1.81×10^{-9}	1.88×10^{-6}	3.12×10^{-9}
NDA ^b	1.87×10^{-9}	2.95×10^{-3}	3.20×10^{-9}

serve in Figures 7–9, corresponding to neutral, acidic, and basic medium, respectively, it is possible to observe a difference in each picture. This fact corroborates that the change of morphology is also associated with the reaction medium.

CONCLUSIONS

The color of the polymers synthesized in the presence of pyridine depends on the pH. The imine groups stabilize the polymeric chain.

Under acidic conditions and in THF, a low percentage of weight loss was observed, which could be due to the H-links formed that give more stability to the polymers. The compounds prepared with pyridine and washed under basic conditions presented a higher weight loss at 350°C.

Conductivity values of the polymers without doping increases in the presence of the aromatic rings in the chain. When the number of aromatic rings in the polymer chain is increased, the amount of dopant introduced into the compound and the conductivity also increased.

When SbF_5 was used as a dopant agent, no change was observed in the electrical behavior of the polymers. When the polymers were synthesized using pyridine as a solvent and washed with the $\text{H}_2\text{O}/\text{NaOH}$ solution, doping with I_2 increased the conductivity values 5 orders of magnitude. The morphology of the polymers is a not well-defined granulate.

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