Synthesis and Characterization of Poly(pyridylurea) and Poly(pyridylthiourea), Potentially Semiconducting Polymers

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ABSTRACT: Poly(pyridylureas) and poly(pyridylthioureas) were synthesized by reacting 2,6-diaminopyridine with phosgene and thiophosgene, respectively, using THF and pyridine as solvent. The synthesized polymers were characterized by IR-spectroscopy, elemental analysis, and X-ray photoelectron spectroscopy. Thermal stability of the polymers was determined by thermal degradation between 35°C and 700°C .The 50% weight loss of polypyridylureas was above 400°C while for the polypyridylthioureas it was above 450°C. Undoped poly(pyridylureas) and poly(pyridylthioureas) behave as semiconductors, $\sigma = 10^{-9}$ (Ω cm)$^{-1}$. After doping with I_2 and SbF_5, the electrical conductivity increases several orders of magnitude, $\sigma = 10^{-7}(\Omega$ cm)$^{-1}$. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1344–1350, 2007

Key words: poly(pyridylureas); poly(pyridylthioureas); semiconducting polymers

INTRODUCTION

Very little attention had been paid to organic polymers that presented an electrically conducting structure until Shirakawa et al., in 1977, synthesized polyacetylene.[1] From then on, increasing interest was devoted to this field and many organic materials with conducting properties have been reported. Among conducting polymers, polyaniline (PANI), which was synthesized a century ago,[2–4] stands out because of its outstanding properties.

High electrical conductivity, processability, and stability in air have been the three major targets sought for conducting polymers. The material used as conducting polymer needs to have high stability in air; however, most of the reported conducting polymers are unstable in air except those containing nitrogen or sulfur atoms in the polymer backbone. Consequently, heteroatoms such as N, S, or Se might be beneficial to the stabilization of doped conjugated polymers.[5–10]

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.

Although much research has been carried out on the synthesis, characterization, and application of polyesters, polyamides, polyurethanes, and polyimides, little work has been reported regarding the synthesis of polyureas. This could be due to their low solubility and high melting points.[11] Polyureas have been used for many applications, including the encapsulation of pharmaceuticals, inks, dyes, and the modification of wool fibers by interfacial grafting techniques.[12]

In 1989, Ghander et al.[13] reported the synthesis of a polymer formed by a Michael addition reaction between *p*-bis-*N*-sulfinylendiamine and *p*-phenylendiamine. The thermal stability of this polymer is up to 200°C, and it presents a conductivity of 10^{-6} (Ω cm)$^{-1}$.

Other organic compounds that may be used as conducting polymers are thioureas (currently used as fungicides and arthropodicides[14]) and ureas whose high thermal stability is due to the presence of nitrogen and sulfur in their structure, a very important characteristic for a conducting polymer.
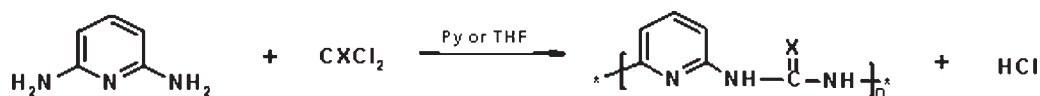
Scheme 1 Synthesis of poly(pyridilureas) and poly(pyridilthioureas).

Polymers based primarily on heterocyclic units can be used as semiconducting materials because of electron delocalization through the rings.

These characteristics encouraged our group to study thioureas as conductive polymers. In a previous article we have reported about the significant increase in conductivity of poly(aryilureas).[15] In the present work we describe the synthesis of poly(pyridylureas) and poly(pyridylthioureas) in different solvents. The polymers were characterized by IR spectroscopy, elemental analysis, and XPS. We also studied the stability and conductivity of the polymers before doping and doped with I_2 and SbF_5.

Undoped poly(pyridylureas) are considered semiconductors ($\sigma = 10^{-9}$ (Ω cm)$^{-1}$) but after doping with I_2 the electrical conductivity increases several orders of magnitude ($\sigma = 10^{-7}$ (Ω cm)$^{-1}$).

EXPERIMENTAL

Solvents were purchased from Aldrich, Merck, and Fluka and were purified according to standard procedures. The diamines were crystallized from ethanol. Commercial phosgene and thiophosgene were dissolved in toluol to give a 10% (w/w) solution.

Polymers were obtained according to the following procedure. In a round-bottom flask, the diamine (0.0136 mol of 2,6-diaminopyridine) was dissolved in 70 mL of tetrahydrofuran (THF) or pyridine (Py) with constant stirring. Phosgene (molar ratio diamine:phosgene 3:2) or thiophosgene (molar ratio diamine:thiophosgene 3:2) solution was slowly added to this mixture. The mixture was allowed to react at room temperature for 20 min with constant stirring. When pyridine was used as solvent, one portion of the polymer was washed with H_2O/HCl and the other with H_2O/NaOH solution. On the other hand, the product synthesized in THF was washed with hot water. The solids obtained in pyridine were filtered, washed several times with CH_3OH, $CHCl_3$, diethyl ether, and vacuum-dried. The solid obtained in THF was filtered, washed several times with H_2O, and vacuum-dried. The dried product was now washed with CH_3COCH_3, diethyl ether, and vacuum-dried.

Elemental Analysis was performed on a C-H-N Heraeus Mikrostandar Analyzer. IR spectra were obtained in KBr pellets on a Brucker Vector 22 Spectrophotometer. Dynamic thermogravimetric analyses were conducted on a Perkin-Elmer TGS-1 thermobalance using a Perkin-Elmer UV:1 temperature program control. Samples were placed on a platinum sample holder, and the thermal degradation measurements were performed between 35°C and 700°C at a heating rate of 20°C min^{-1} under N_2.

Electrical conductivity measurements were performed on an Elchema Electrometer, Model CM-508, using polymer pellets by the four-probe method.

Doping with I_2 was accomplished by placing samples of the polymers along with I_2 into a desiccator at room temperature. 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.[16]

Doping with SbF_5 was performed by exposing the polymers to SbF_5 vapor over its condensed phase at 60°C for 1 h. The product was washed with CH_3OH, and vacuum-dried.[17]

The resulting polymers were characterized by XPS analysis at the University of Nantes-CNRS on a Leybold LHS-12 spectrometer. The data was obtained with a magnesium source of radiation (1253.6 eV) operating at 10 kV and 10 mA, and the pass energy set at 50 eV. High resolution scans, with a good signal-to-noise ratio, were obtained in the C 1s, N 1s , O 1s, S 2p, and Cl 2p 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 studies were based on the determination of the C1s, N1s, O1s, S 2p, and Cl 2p peak areas using sensitivity factors 0.2, 0.36, 0.61, 0.44, and 0.58, respectively. The sensitivity factors were provided by the manufacturer. The vacuum in the analysis chamber was approximately 10^{-6} Pa. All spectra were recorded under identical conditions.

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

Polymer	Solvent	Color	Yield (%)
DAP	THF	Green-brown	23
DAP[a]	Py	Pink	74
DAP[b]	Py	Yellow-brown	66
DAP-S	THF	Red-yellow	35
DAP-S[a]	Py	Dark-brown	76
DAP-S[b]	Py	Brown-red	68

[a] Acidic.
[b] Basic.

TABLE II
Elemental Analyses of Poly(pyridilureas) and Poly(pyridilthioureas)

Polymers	C%		N%		H%		S%	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
DAP	42.0	42.4	24.5	27.3	3.5	4.4	–	–
DAP[a]	53.3	50.5	31.1	28.4	3.7	4.3	–	–
DAP[b]	53.3	52.0	31.1	29.7	3.7	3.9	–	–
DAP-S	47.7	47.1	27.8	28.8	3.3	3.7	21.2	19.3
DAP-S[a]	47.7	47.9	27.8	28.2	3.3	3.6	21.2	16.6
DAP-S[b]	47.7	47.6	27.8	28.5	3.3	3.9	21.2	11.8

[a] Acidic.
[b] Basic.

Deconvolution of the XPS peaks into their different components and the quantitative interpretation were performed after subtracting the background using Shirley's method.[18]

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 intensity of the contribution, to be performed. These parameters were optimized by a curve-fitting program to obtain the best fit.

RESULTS AND DISCUSSION

Babad and Zeiler[19] reported that for the synthesis of ureas, when phosgene is treated with an excess of a primary or secondary amine, symmetrical ureas are produced in high yields. The reaction is conducted in the presence of an acid acceptor such as sodium hydroxide,[20–25] sodium carbonate, or pyridine.[26]

In the present work, novel poly(pyridylureas) and poly(pyridylthioureas) were obtained by reacting phosgene or thiophosgene with 2,6-diaminopyridine, using pyridine or THF as solvent, according to scheme 1.

Polypyridylureas (DAP) and polypyridylthioureas (DAP-S) obtained in pyridine as solvent, were insoluble in all common organic solvents and in the commonest inorganic acids. 0.1 mol L^{-1} HCl and NaOH solutions were employed to precipitate the polymer.

The color of the precipitated polymer is pH-dependant of the solution utilized for the precipitation of the polymer. (Table I) This insolubility prevented us, again, from determining the molecular size of the polymers.

This behavior was not observed when THF was employed as solvent. These polymers synthesized in THF as solvent were soluble in polar solvents, such as dimethyl sulfoxide, N,N-dimethylacetamide, N,N-dimethylformamide, N-methylpyrrolidone, therefore their characterization by ^{1}H-MNR should be possible. However, a chemical reaction between the polymer and the solvent occurred. This finding was corrobo-

rated by a blackening of the solution and subsequent precipitation. The precipitate was filtered and characterized by IR spectroscopy, which confirmed polymer decomposition and, consequently, in these conditions the molecular size could not be determined.

All polymers were characterized by IR spectroscopy, elemental analysis (Table II), XPS surface quantitative analysis (Table III), and XPS analysis (Table IV). The results are consistent with the proposed structures. In Table II the lower values for DAP compared to those obtained for DAP[a] and DAP[b] are because DAP possesses a shorter chain, which is also responsible for the abovementioned solubility of this compound in polar solvents. Unfortunately, decomposition of the product in different solvents prevents an evaluation of its molecular magnitude.

IR spectra of polymers, with or without S in their polymeric chain, synthesized in THF or pyridine washed with a H_2O/HCl mixture showed a shoulder ascribed to some N^+ groups at 2600–2700 cm^{-1} (Fig. 1). However, no N^+ band was observed when the polymers were synthesized in pyridine and washed with a H_2O/NaOH solution.

The protonated nitrogen of pyridine can be observed at 2743 cm^{-1} in 2,2'-bipyridinium pentachlorooxomolybdate(V)[27]

TABLE III
XPS Surface Quantitative Analyses of Polymers Relative to the Constituents C, N, O, S, and Cl (at %)

Compounds	C	N	O	S	Cl
DAP theoretical	60.0	30.0	10.0	0.0	0.0
DAP	69.5	15.0	12.0	0.0	3.5
DAP[a]	65.0	22.5	10.5	0.0	2.0
DAP[b]	69.0	18.7	12.0	0.0	0.3
DAP-S theoretical	60.0	30.0	0.0	10.0	0.0
DAP-S	64.0	15.0	15.5	4.0	1.5
DAP-S[a]	68.5	15.0	9.0	6.0	1.5
DAP-S[b]	67.0	17.0	12.0	4.0	0.0

[a] Acidic.
[b] Basic.

TABLE IV
XPS Analyses after Decomposition of the Peaks

	C 1s				N 1s		S 2p			O 1s		Cl 2p
	C—C	N—C=N	X=C—N	C_{ox}	N—CX—N	N^+	S=C	S^+	S_{ox}	N—CO—N	C—OH	Cl^-
DAP	285	287.5	289.3	–	399.6	401.0	–	–	–	532.0	533.8	198.0
	75	21	4	–	60	40	–	–	–	75	25	100
DAP[a]	285	287.0	289.2	–	399.3	400.3	–	–	–	531.8	–	198.0
	60	27	14	–	41	59	–	–	–	100	–	83
DAP[b]	285	287.0	289.0	–	399.3	–	–	–	–	531.6	533.4	–
	61	27	12	–	100	–	–	–	–	81	19	–
DAP–s	285	286.7	287.5	289.2	398.5	399.6	161.3	164.1	–	529.8	531.6	197.2
	71	10	15	4	49	51	77	23	–	34.5	65.5	100
DAP–S[a]	285	286.0	287.0	288.4	398.5	400.4	161.2	163.4	–	530.7	532.8	196.5
	34	22	36	7.7	80	20	38	62	–	41	59	100
DAP–S[b]	285	285.4	286.6	288.9	399.5	–	162.2	164.4	168.2	531.0	532.6	–
	52	28	17	3	100	–	40	45	14	60	40	–

First line: binding energy e.V. Second line : relative atomic percentage (%). X = O,S.
[a] Acidic.
[b] Basic.

These results are in good agreement with XPS spectra. Poly(pyridylthiourea), Fig. 2, is a good example of this behaviour. The peak deconvolution allows for a positive charge on nitrogen to be assumed (Fig. 3). This is confirmed by a small peak at 198.0 eV, corresponding to chloride as counter-ion (Fig. 4).

Because of protonation of the polymer, DAP microanalysis gives a high percentage of hydrogen. A percentage of ionic chloride was found in XPS, confirming our previous statement, i.e., the presence of Cl^- counter-ions (Fig. 4).

XPS quantitative analysis of the polymers, relative to the constituents, is listed in Table III. The data of composition is presented as a percentage of the referred element in relation to the tota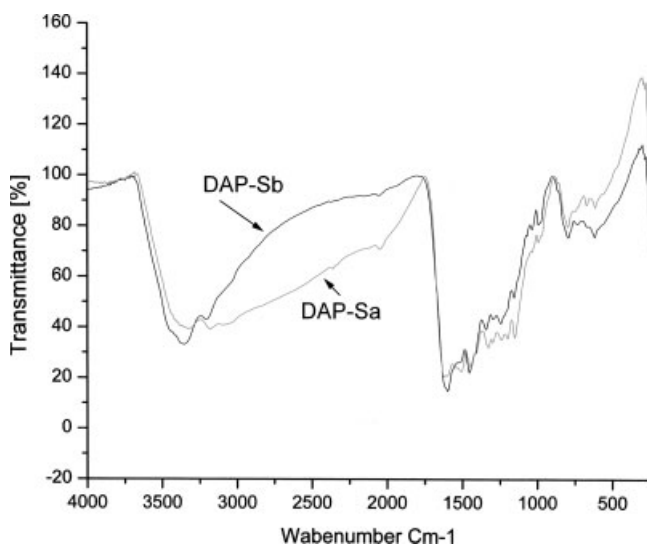l amount. An excess of carbon can be appreciated that may be related to surface contamination, as shown by the presence of oxygen, which is also associated to this contamination.

The carbon–carbon bond present in the polymers has been taken as reference to estimate the charge effect. Briggs and Seah[28] have shown that this bond has a well-defined position at 285 eV. As seen in Figure 5, 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.

The C1s peak of polypyridylureas can be deconvolved in 3 peaks (Fig. 6). The first corresponds to carbon–carbon and hydrocarbon bonds. The second can be attributed to C—N bonds, and the third peak may be assigned to O=C bond.

The C1S peak of polypyridylthioureas can be decomposed in 4 peaks (Fig. 7). The first corresponds to carbon–carbon and hydrocarbon bonds. The second can be associated to C—N bonds, the third peak has been assigned to S=C bond, and the fourth peak is due to Cox contamination.[29]

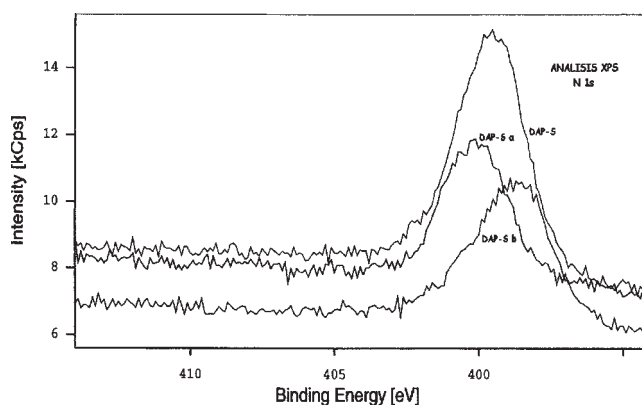

Figure 1 IR Spectra of DAP-S[a] and DAP-S[b] polymers.

Figure 2 XPS spectra of N 1s of poly(pyridilthiourea)

Figure 3   Curve fitting of N 1s peak of poly(pyriydilurea).

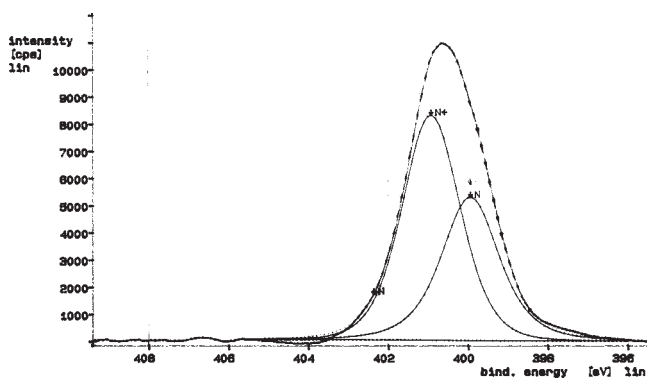**Figure 5**   XPS Spectra of C 1s of poly(pyridilthiourea).

A broad band for S 2p is seen in Figure 8. This behaviour is different from that observed for the polymer synthesized in basic medium. Table IV contains the data obtained from peak S 2p deconvolution.

In sulfurated polymers, prepared in THF or in acid media, the S 2p peak can be decomposed in 2 peaks (Fig. 9). The first corresponds to C=S bond. The second can be attributed to S$^+$, Table IV.

To study the thermal stability of the polymer, thermal degradation was investigated under the same conditions for all the compounds. Figure 10 depicts the weight loss of the material between 35 and 700°C. According to this figure, the polymers, polypyridylureas, Fig. 10a, and polypyridylthioureas, Fig. 10b, exhibit similar behavior with a one-step thermal-degradation process.

Table V shows the data obtained for the heating curve. Thermal decomposition temperature (TDT) of the polymer was taken as the temperature at which the polymer looses 10% of its weight.[30] No great variation in the TDT was observed and this small variation could be attributed to their different molecular sizes. Although the TDT are very similar, Table V, for the different polymers, as the temperature increases a higher stability of the thio- compound was observed.
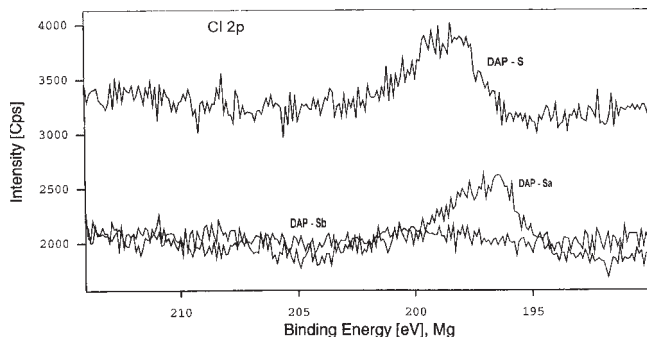
According to Marvel[31] the introduction of a heterocyclic unit in the polymeric chain gives more stability to the system; this is confirmed by the fact that the percentage of weight loss at 450°C is much lower for polypyridyl than for polyphenyl and polynaphtyl urea, as previously reported.[15]

The compounds bearing sulphur in their structures exhibited greater thermal stability than the compounds without sulphur in the polymeric chain. This has been previously corroborated,[32] and it has been attributed to cross-linking established among the chains of this kind of compounds.

XPS analysis, where the sulphur of these compounds presented positive charge density, corroborates the previous statement.

At 450°C, the weight loss of polythiopyridyls is much less than for polypyridyl's. At 350°C, the weight loss of DAP prepared in alkaline medium was 28%.

In THF and acid conditions, a lower percentage of weight loss is observed, which might be due to H-bonds that lend more stability to the polymers.

Conductivity measurements at room temperature of undoped and dope with I_2 and SbF_5 compounds

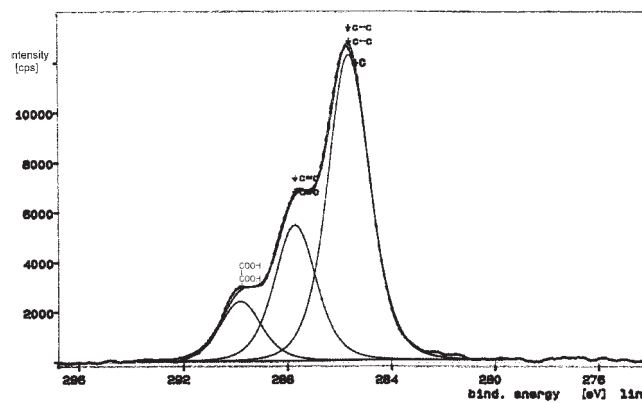**Figure 4**   Spectra of Cl 2p of poly(pyridilthiourea).

Figure 6   Result curve fitting of C 1s peak of the poly(pyridilurea).
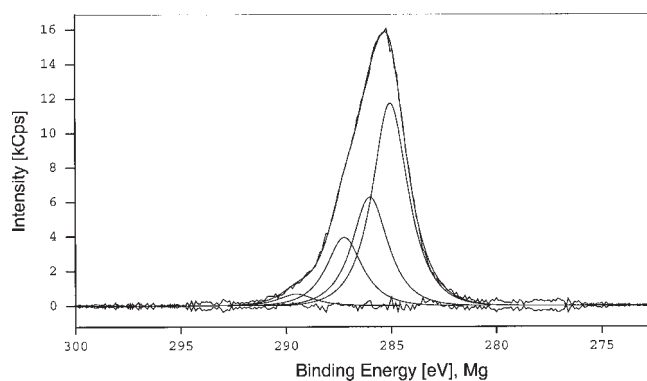
Figure 7 Result curve fitting of C 1s peak of poly(pyridilthiourea).

are summarized in Table VI. The conductivity of undoped polymers indicates that they behave as semiconductors.

Sakai et al.[33] have reported that when polymers with nitrogen in their structure are doped with I_2, the nitrogen becomes coordinated with the dopant agent, leaving the polymeric chain with negative charge density, which is the reason for the increase in conductivity.

This has been confirmed by the results obtained in basic medium for the polymer with and without sulphur in its polymeric chain.
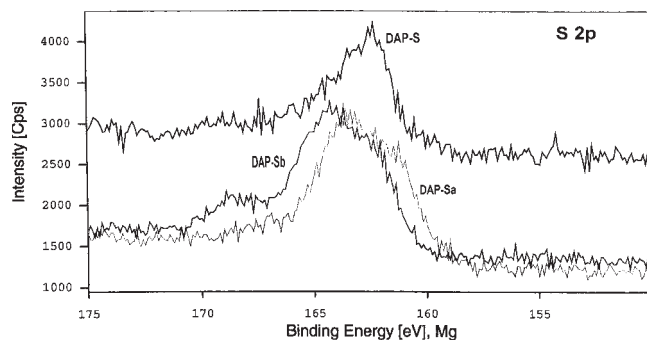

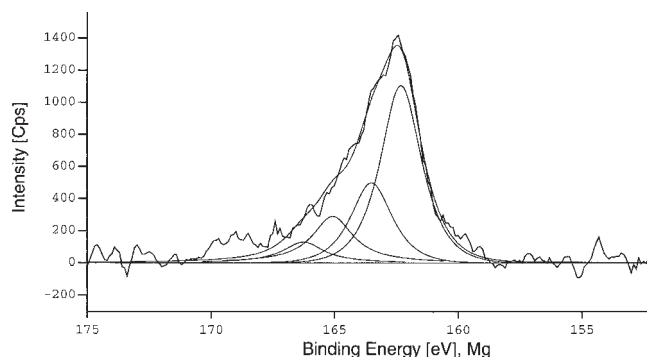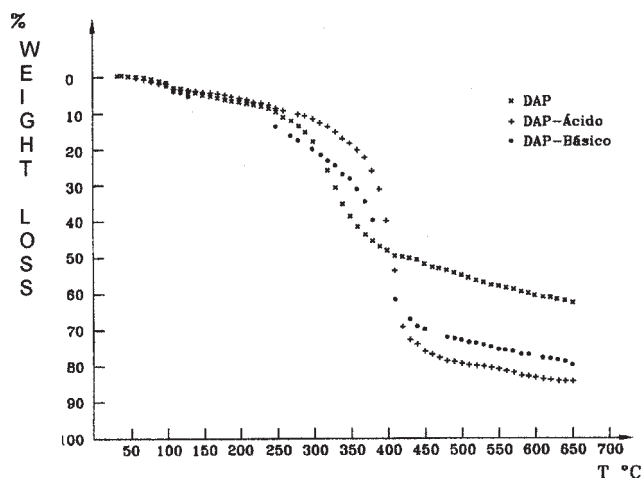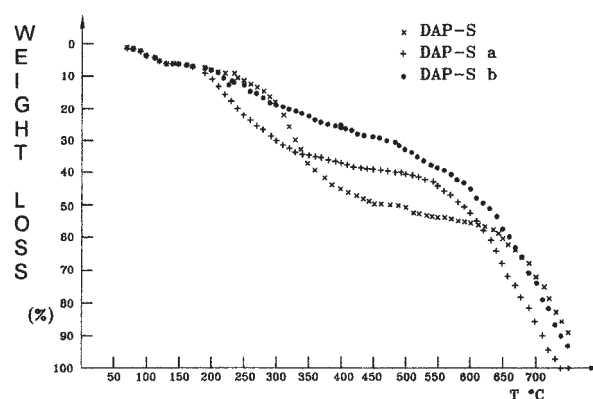
Figure 8 XPS Spectra of S 2p of poly(pyridilthiourea).

Figure 9 Curve fitting of S 2p peak of the poly(pyridilthiourea) (DAP-S).

Figure 10 Thermogravimetric analysis of polymers: (a) poly(pyririlurea); (b) poly(pyridilthiourea).

In previous studies it was found that a very strong dopant such as chlorine damages the polymer while a weak dopant such as I_2, increases the conductivity. Since SbF_5 is a stronger dopant agent than I_2 it may cause a cleavage of the polymeric chain; therefore a considerable increase in conductivity is not observed.[34–36] The conductivities remained almost unchanged for products doped with SbF_5; however, I_2 is a more efficient dopant for these polymers.

TABLE V
Results Study of Weight Loss Percent of Polymers at Different Temperatures (°C)

Polymers	TDT (°C)	Weight loss (%)	
		350°C	450°C
DAP	250	40	52
DAP[a]	270	19	76
DAP[b]	240	28	70
DAP-S	220	37	49
DAP-S[a]	235	34	39
DAP-S[b]	240	22	29

[a] Acidic.
[b] Basic.

TABLE VI
Conductivities at Room Temperature (σ) (Ω cm)$^{-1}$ of Compounds before Doping and Doped with I$_2$ and SbF$_5$

Compounds	Conductivities (10^9) (Ω cm)$^{-1}$		
	Undoped	Doped with I$_2$	Doped with SbF$_5$
DAP	27.2	530	28.0
DAP[a]	2.10	750	3.0
DAP[b]	2.00	910	2.9
DAP-S	8.10	610	660
DAP-S[a]	7.00	730	746
DAP-S[b]	2.00	800	640

[a] Acidic.
[b] Basic.

From Table VI, it follows that polypyridylthioureas exhibit greater conductivity than polypiridilureas when SbF$_5$ is employed as dopant.

CONCLUSIONS

Poly(pyridylureas) and poly(pyridilthioreas) were synthesized and characterized. The introduction of a heterocyclic unit in the polymeric chain gives more stability to the system. This was confirmed by the fact that the percent of weight loss at 450°C is much lower for polypyridyl- than for polyphenyl- and polynaphtyl-urea.[15]

Sulphur bearing materials exhibited greater thermal stability than the compounds without sulphur in the polymeric chain. This is due to cross-linking generated among the chains of this kind of compounds. XPS analysis showed that the sulphur of this compound has positive charge density, which corroborates the previous statement. Poly(pyridyl) thiourea)s present this effect at 450°C.

Polymers synthesized in basic medium using pyridine as solvent exhibited greater conductivity when doped than the rest. Undoped polymers present isolant characteristics, but after doping with I$_2$ their conductivities increased up to three orders of magnitude, becoming semiconductors. I$_2$ proved to be a better doping agent than SbF$_5$.

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