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SYNTHESIS AND CHARACTERIZATION OF CONDUCTIVE POLYMERS WITH ENHANCED SOLUBILITY

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În cadrul lucrării, s-au studiat posibilităţile de sinteză ale polianilinei în prezenţa acidului dodecilbenzensulfonic (DBSA) şi a polivinilpirolidonei (PVP) în vederea îmbunătăţirii solubilităţii polianilinei (PANI) în apă. Monitorizarea progresului reacţiei de polimerizare şi caracterizarea compuşilor rezultaţi s-au efectuat cu ajutorul spectroscopiei UV-VIZ, FT-IR şi DSC/TGA. Prin utilizarea unor rapoarte molare PANI/DBSA adecvate se obţin soluţii solubile în apă, clare, transparente, verzi care se pot aplica direct pe diferite substraturi..

The polyaniline synthesis in the presence of dodecylbenzenesulphonic acid (DBSA) and polyvinylpirolidone (PVP) was studied in order to improve the solubility of polyaniline (PANI) in water. UV-VIS, FT-IR spectroscopy and DSC/TGA/MS have been used to characterize and monitor the progress of the polymerization. Using an adequate molar ratio PANI/DBSA it is possible to obtain water soluble, clear, green solution which can be directly applied on different substrates.

Keywords: polyaniline; conductive polymers; spectroscopy

1. Introduction

Polyaniline (PANI) is one of the most important conductive polymers due to its properties such as:

- High conductivity in doped state;
- High redox reversibility;
- Easy transformation in colored films;

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- High stability in the environment;
- Special electronic, optical, magnetic and mechanic properties allowing its use in a large number of applications.

Polyaniline could be used for batteries electrodes, electrochromic devices, photovoltaic cells, light emitting diode, biosensors, electronic sensors, electrorheological suspensions, protecting films against corrosion, gas separating membranes, catalysis for organic reactions, textile materials antistatisation and electromagnetic shields.

The polyanilines processability depends on synthesis methods and dopant ions type, thermal stability, viscosity, degree of crystallinity and molecular alignment, molecular structure and miscibility with other polymeric matrix, interactions with other additives, etc.

Due to its large area of application, many researches have been dedicated to the polyaniline synthesis. Polyaniline is generally synthesized by chemically [1,2] or electrochemically [3,4]. But, the electrochemical methods generate very low soluble polyaniline which is difficult to process and has restricted application. The chemical methods lead to low molecular weight polyaniline whit a low mechanical strength [5].

The effort of the last researches was directed to the development of new synthesis methods to obtain to polyaniline with a high conductivity, improved solubility and good mechanical properties [6-8].

The interest for this "synthetic metal" also generated some remarkable works in Romania [9,10].

This paper work presents the studies performed to increase the polyaniline solubility while maintaining the electrically conductivity and stability of the polymer against the loss of dopants by a novel polymerization process for the production of a polyaniline salt. The process comprises chemical polymerization of the polyaniline dissolved in an aqueous solution of DBSA, in the presence of the oxidant and a dispersing agent (PVP).

2. Experimental

A new method to synthesize doped polyaniline was established based on the scientific fundaments and a high number of experiments. By controlling the ratio DBSA/Aniline, the time necessary to add the oxidizing agent, the temperature during the polymerization stage, it is possible to obtain a high soluble polyaniline, useful in many applications.

It must be underlined that the efficiency of the process consists not only in the solubility of the polymers but also in the cost reduction: the polyaniline is not necessary to be filtered, washed with large quantities, expensive and pollutant organic solvents. The obtained solutions are stable for long time.

2.1 Materials

Aniline (Merck) was distilled under reduced pressure; DBSA (Aldrich), PVP (Merck) and AP (Aldrich) were used as received.

2.2 Synthesis of Polyaniline doped with DBSA (PANI-DBSA)

DBSA in controlled quantities and PVP were added to a certain volume of deionized water. The mixture is vigorously stirred at 80–90ºC until a homogeneous solution was obtained. The obtained solution was cold down at 15ºC, when the prescribed quantities of aniline were added to the above cold solution followed by dropping a 0.01M ammonium persulfate (AP) solution. The initially milky homogeneous solution turns blue and then dark green. The reaction mixture was kept under mechanical stirring for 6 hours. Finally a dark green homogenously solution is obtained (Table 1).

Table 1

Concentration of the reactants

Ex no.	Aniline [mol]	DBSA [mol]	AP [mol]	Water [ml]	[DBSA]/[Aniline] [M/M]	Aspect / Solubility
8	0.0150	0.026	0.0100	450	1.73/1	green, fluid, soluble in water
9	0.0225	0.026	0.0225	350	1.15/1	green dispersion, large particles
10	0.0300	0.026	0.0300	250	0.87/1	green dispersion, fine powder
11	0.03700	0.026	0.0370	200	0.70/1	2 layers, resinous powder
12	0.0200	0.100	0.0200	250	5.00/1	green highly viscous fluid
13	0.0200	0.100	0.0200	350	5.00/1	green viscous dispersion
14	0.0200	0.100	0.0200	450	5.00/1	green viscous fluid
15	0.0200	0.100	0.0200	500	5.00/1	green fluid
17	0.0300	0.100	0.0300	500	3.33/1	green fluid
20	0.0600	0.100	0.0600	500	1.67/1	green solution fine particles

2.2 Characterization

- UV-VIS spectra (190nm to 1100nm) were recorded on a Varian Cary 50 spectrophotometer;
- FT-IR spectra were recorded on CaF_2 windows and in KBr pellets using a Digilab spectrophotometer;
- DSC/TGA/MS were performed in a DSC/TGA Netzch STA 449 coupled with a QMS 403 Mass Spectrometer (MS). The samples were scanned from 0 to 800°C at a scanning rate of 20 °C/min under helium gas.

3. Results and Discussions

3.1. Solubility

The solubility of PANI is influenced by its basic thermodynamic properties [12] like unmoldability, unfavorable entropy of dissolution and the extremely high lattice energy (ca. 1,100 KJ/mol). The poor solubility of PANI [13] is due to the impossibility of the solvents to dissolve both the hydrophilic dopant part and the hydrophobic organic part of the polymer. It was found that two main parameters determine the solubility of PANI-DBSA complex: the ratio water/reactants and the molar ratio DBSA/Aniline. As the ratio water/reactants increases, the solubility of complex increases as well. For the same molar ratio aniline/oxidant and the same quantity of water, the polyaniline solution homogeneity increases with the increase of the DBSA quantity (exp. 9 and 13). The solutions are stable if the ratio DBSA/Aniline > 3. Under this ratio, the solution became very viscous, with dispersed particles. The solubility in other solvents is presented in table 2.

Table 2

The solubility of PANI-DBSA complex in organic solvents

Experiment	PANI-DBSA Solubility, [%]		
	Isopropyl alcohol	Toluene	Xilene
8	1.60	5.30	0.85
9	3.38	1.35	0.91
10	2.56	2.30	2.35
11	1.66	4.30	0.43

3.2. UV-VIS spectroscopy

The spectra of the polyanilines are very complex owing to multiple individual distribution of the quinoid and benzenoid ring along the polyaniline backbones, different final groups, minor substituents, different products resulted from possible side reactions, cyclizations, conformation effects and reduction in ring symmetry [14, 15].

3.2.1. Polymerization Process

UV-VIS spectra of the reaction mixture were recorded 30 minutes after the addition of the oxidant up to 5h of polymerization. The reaction mixture was transparent, during the induction period and the only band recorded was that of the DBSA (around 900nm). The induction time depends largely on reaction parameters: it is longer at low temperature and at higher molar ratio. After the addition of 3/4 of the ammonium persulfate, the reaction mixture turns from clear transparent to light blue. After the addition of all the oxidant, the mixture became dark blue and during reaction (3 hours), dark green [16,17].

The band at 740 nm (originating from polaron transitions) is an indicator of the progress of the reaction (Fig. 1, Table 3). Initially, it shows a batochromic shift indicating an increase in conjugation length of the polymer backbone and a high protonation.

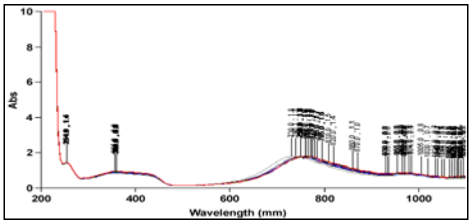

Fig. 1. UV-VIS patterns of PANI-DBSA at different reaction times (exp. 15)

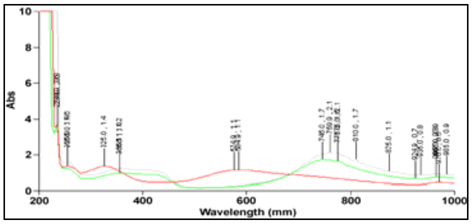

Fig. 4. UV-VIS patterns of PANI-DBSA, exp. 15 (green pH=1, grey pH=3, red pH=9)

Table 3

UV –VIS spectra of PANI at different reaction times

Time, min	λ, nm	Absorption	Time, min	λ, nm	Absorption
30	730	1.80	150	765	1.68
40	740	1.80	240	765	1.60
60	750	1.79	270	770	1.60
90	760	1.72	310	770	1.60
120	760	1.72	-	-	-

The band in the region of 730-795 nm attains a constant position (770 nm) approximately 3 hours after the addition of AP, indicating the completion of the polymerization.

Electronic absorption spectra of all the solutions (pH = 1) show three bands: 750-770 nm (the shifting of electron from benzenoid ring to quinoid ring), 430 nm (π*←π transition in polaron/bipolaron) and 350-360 nm (π*←π transition of the benzenoid rings) [21] indicating that the polymer is in its emeraldine salt form [18] (Table 4).

Table 4

Polyaniline UV-VIS spectra

Exp.	Wavelength, nm	Exp.	Wavelength, nm	Exp.	Wavelength, nm
7	350, 430, 765	10	360, 430, 765	13	360, 430, 760
8	355, 430, 760	11	355, 430, 765	14	360, 430, 760
9	350, 430, 770	12	355, 430, 750	15	355, 430, 765

The band at 770 nm is sensitive to changes in the concentration of the dopant. For example, the increase of the DBSA concentration determines a hypsochromic shift of this band as it could be seen in experiment 9 (0.028M DBSA – λmax = 790 nm) and experiment 12 (0.1 M DBSA – λmax = 780nm). Normally, an increase of the DBSA concentration decreases the pH of the medium thereby decreasing the band gap due to higher protonation. Yin and Ruckenstein [19] suggested that an increase in the amount of dopant in the polymer increases the compact coil conformation of the polymer, leading to a hypsochromic shift. The effect was observed also for PANI-DBSA dissolved in chloroform [20].

3.2.2. Effect of pH on polyaniline UV-VIS Spectra

The pH influences the protonation-deprotonation equilibrium of conducting emeraldine salt and non-conducting emeraldine base forms of polyaniline. Emeraldine base has two bands at 550–600 ($\pi^* \leftarrow n$ transitions – quinone-imine groups – exciton transition of the quinoid rings), and 315–330nm ($\pi^* \leftarrow \pi$ transitions) [21]. Fig. 4 shows UV-VIS absorption spectra of PANI– experiment 15 - recorded at pH = 1, 3 and 9.

The position and the absorbance of the band at 350 nm are unaffected when the pH < 8. Further increase in the pH increases the absorbance of this band exhibiting a blue shift because of the emeraldine salt-to-emeraldine base transformation in this pH range. The band at 420 nm, assigned to the polaron transition, disappears at pH > 9. The decrease of the band situated around 775nm as the pH increases is attributed to the decrease in protonation of the polymer backbone which in turn decreases the number of polarons. At pH > 9 an increase of the conjugation length and a decrease of the band gap take place. This demonstrates the transformation of protonated benzoid structures into unprotonated quinoid structures in this pH range [21].

3.2.3. Fourier Transform Infrared (FTIR) Spectroscopy

Formation of the polymers, presence of a functional group on the polymer backbone or change in the protonation-deprotonation equilibrium of emeraldine can be deduced from the presence of corresponding bands in the FTIR spectrum [20]. The presence of the imine and amine bands is an indication of the polyaniline in emeraldine state (EB). The vibration frequencies specific for polyaniline PANI-EB [22] are: 1590, 1495, 1305, 1165 and 830 cm^{-1}. The vibration frequencies of the major infrared bands and their assignment for some of our experiments are summarized in table 5.

Table 5

The vibration frequencies of the complex PANI-DBSA

Vibration frequencies, cm^{-1}				
Exp. 8	Exp. 9	Exp. 11	Exp. 15	Assignment
3464	3471	-	3489	Asymmetric NH_2^+ stretching
2826	2173	3029	2928;	Symmetric $–CH_2–$ stretching (DBSA)
-	1640	1637	1628	C=N stretching
1520	1444	1446	1458	Aromatic C–C stretching
1298	1269	1305		C–N stretching and ring stretching vibration
-	1180	1183	1177	C–H bend; DBSA
1098	1094	1094	1090	C–H in plane bending 1,4-disubstituted benzene
844	867	867	870	Out of plane C–H bending 1,4-disubstituted benzene (ES)

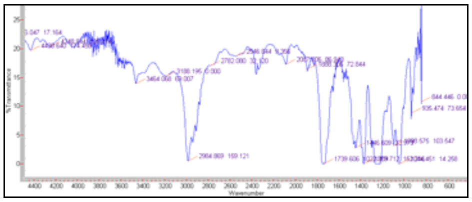

Fig. 5. PANI-DBSA Exp. 8: dry layer

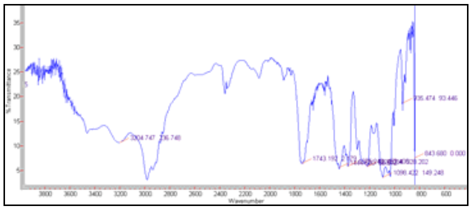

Fig. 6. Exp. 8: de-doped PANI, basic medium (ammonia), emeraldine base, blue layer

All the spectra display benzenoid and quinoid ring vibrations. The main bands are situated around 860 cm^{-1} (C–H out-of-plane bending vibration in the 1,4-disubstituted ring), around 1180 cm^{-1} (C–H bending), in the range of 1298 - 1305 cm^{-1} (C–N stretching of the aromatic secondary amines), around 1444 -1520 cm^{-1} (benzenoid stretching) and around 1628 - 1640 cm^{-1} (quinoid stretching). The results show that obtained polyaniline contain 1,4-para-disubstituted linear chains.

3.4 DSC/TGA/MS

One of the most important properties associated with the polyanilines processability is represented by the thermal stability. The samples were studied as such, without any processing.

Generally, to eliminate the humidity influence, the samples are dried under vacuum, at 45°C, during 3 days.

The degradation took place in many stages, as it is shown in the recorded thermograms, the most important being the stage in which the degradation is due to the dopants release and the second, that in which the polymer is hardly degraded due to the polymer chain break.

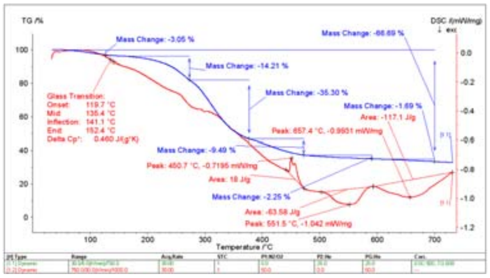

Fig. 7. DSC/TGA thermogram of PANI-DBSA

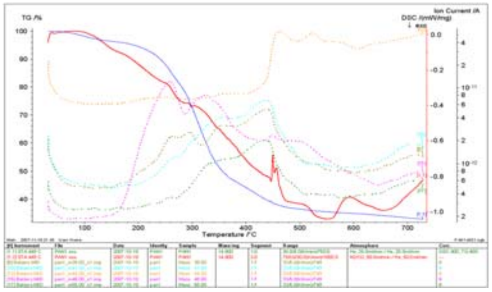

Fig. 8. PANI-DBSA (m/z = 39 to 55)

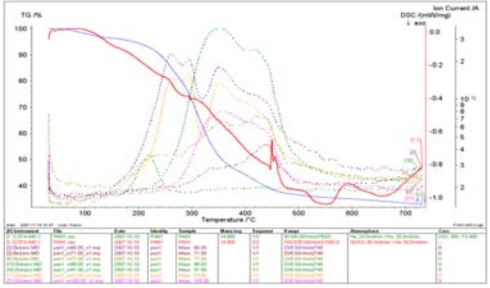

Fig. 9. PANI-DBSA (m/z = 66 to 105)

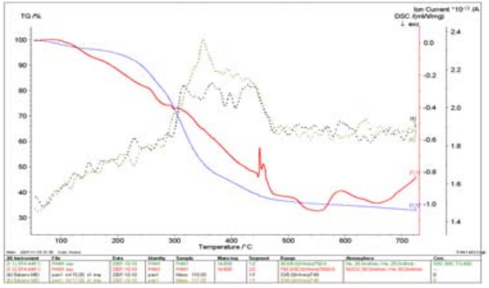

Fig. 10. PANI-DBSA (m/z = 115 to 117)

Some authors found a three step decomposition process of PANI doped by acids [23]. They suggest that the initial stages of weight loss are due to the volatilization of water molecules and oligomers, as well as unreacted monomer elimination. Then, at higher temperatures the dopant acid is lost and finally at more extreme temperatures the polymer chain break can lead to production of gases such as acetylene and ammonia.

Unlike them we found, in our experiments, five stages of thermal decomposition of the PANI doped with DBSA:

- The first stage is situated between 119.7 to 152.4ºC. It is considered that this is the initial stage of dehydrating (the only fragment is m/z=18). After the dehydration stopping, a 2nd order transition situated at Tg = 141°C is found. The transition point (Tg) of pure PANI-DBSA, was reported to be around 130°C, lower than the Tg of undoped PANI (over 200°C). This is the result of plasticization effect of the DBSA dopant [24]. As it is shown in diagram 1, the DSC curves for PANI-DBSA showed endothermic peaks around 135.4°C. These endothermic transitions are related to the water excess existing in the PANI lattice, influencing the conductivity and crystal structure of PANI.
- The second stage involves the beginning of PANI-DBSA degradation at temperatures around 250°C. According to literature, pure DBSA shows one sharp weight loss process starting at 160ºC. The weight losses at 250ºC are related to DBSA degradation when mixed with PANI.

- The following stages (the 3rd situated at 450.7ºC; the 4th at 551.5ºC and the 5th at 657.4ºC) involve the polymer chain break.

As general aspect, the first degradation stages are characterized by the elimination of many small fragments, with m/z < 60 accompanied by aromatic fragments (m/z = 77; 78). In the following stages, the fragments with m/z = 88 - 91 are prevalent, representing substituted aromatic fragments.

A particular aspect is the evolving of the fragment with m/z = 44 (CO_2) at temperatures over 500°C, due to the decarboxylations in extended aromatic structures. The sample leads to a high residue (around 40–50% coke at 700°C), decomposing in continuous stages until graphitization.

4. Conclusions

Doping of PANI with DBSA in the presence of PVP not only improves the solubility but also leads to a good yield of PANI. Stable PANI-DBSA solutions are obtained at a molar ratio higher than 3. The UV-VIZ and FTIR spectroscopy evidence the formation of polyaniline structure containing 1,4-*para*-disubstituted linear chain.

PANI doped with DBSA shows a relatively low thermal stability, the decomposition process starting around 250°C.

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