

## Effect of synthesis parameters in polyaniline: influence on yield and thermal behavior

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### Summary:

Influence of chemical polymerization conditions on the yield and thermal behavior of PANI doped Dodecylbenzensulfonic (DBS) was studied by means of a 2<sup>4</sup> factorial experimental design. These conditions included temperature, concentration of dopant, concentration of oxidant and stirring rate. It was found that the thermogravimetric behavior was not sensitive to any of the conditions tested. By contrast, the yield was dependent on three of the variables studied. For 10 mmol of aniline, the maximum yield was obtained when temperature, concentration of dopant, concentration of oxidant and stirring rate were 25 °C, 27 mmol, 11.5 mmol and 500 rpm, respectively. The most important effects on the yield are the main effect of oxidant (APS), the interaction dopant concentration-stirring rate and the three-factor interaction effect of dopant concentration-oxidant concentration-stirring rate. The prediction equation is:  
Mass PANI (g) = 1,5920 + 0,0477 DBS + 0,3496 APS + 0,1080 rpm + 0,0533 DBS\*APS + 0,2504 DBS\*rpm + 0,0959 APS\*rpm + 0,2333 DBS\*APS\*rpm

### Introduction

Intrinsically conducting polymers are materials relatively new which show several properties useful for technological applications. Among others, volume changes when are submitted to redox reactions, ability to store charge, color changes associated with their oxidation state, porosity changes, electronic and ionic conductivity, etc. These properties can be useful in the fabrication of actuator devices, polymeric batteries, smart windows, membranes, anticorrosion coatings, sensor devices, etc [1-5]. Each one of these applications is based on some property of conducting polymers. For example, the polymers available for smart windows show color changes, the anticorrosion coatings need good conductivity and dispersability of powders, the actuator devices require volume changes, etc. The end properties of an intrinsically conducting polymer depend greatly on synthesis conditions, therefore, a polymer can have properties very different according to these conditions. The synthesis of an intrinsically conducting polymer can be tailored [3].

Electrochemical synthesis and chemical oxidation are two major routes for preparing intrinsically conducting polymers. These methods produce materials with different

forms, chemical oxidation generally produce powders, while electrochemical synthesis leads to films. The electropolymerization is a complex process oversimplified where the electrode material, the solvent, the counterion, the monomer and the electrochemical conditions are the parameters most important that influence the nature of the processes occurring. The number of experimental variables available with chemical polymerization is greatly reduced because no electrochemical cell or electrodes are employed. Furthermore, chemical polymerization has the advantage of being a simple process capable of producing bulk quantities of these polymers on a batch basis. To date, it has been the major commercial method of producing conducting polymers, several companies producing bulk powders, dispersions and coated products<sup>3</sup>.

Among intrinsically conducting polymers, the polyaniline (PANI) is claimed to be one of the most versatile and to have one of the highest environmental stability. From an industrial point of view it would be useful to be able to thermally process this material into functional products using conventional processing techniques which generally are carried out at elevated temperatures. Somewhat surprisingly, relatively few studies have addressed the thermal stability of PANI. An enormous amount of research has focused on the influence of the polymerizing conditions on general properties of conducting polymers (chemical, electrochemical, physical, electrical, mechanical, morphological characteristics) [3,6]. Among others, the nature and concentration of the dopant, nature and concentration of oxidant, duration of the reaction and temperature of polymerization have a very significant effect on the end characteristics of intrinsically conducting polymers [6-9].

We consider interesting a systematic investigation aimed at establishing the relations between a wide range of synthesis variables and the characteristics of polyanilines obtained. In this paper we present results on the effects of the dopant concentration, oxidant concentration, stirring rate and synthesis temperature on the yield and thermal behavior. The former, we believe is of paramount importance for the manufacturing of high-quality polyaniline products, such as blended materials.

A  $2^4$  factorial design was used in this study to assess the contribution of the variables evaluated on both yield and thermal behavior of PANI doped with Dodecylbenzenesulfonic acid (DBS). The factorial experimental design is a powerful tool to realize the effects of some independent variables that significantly affect the experimental results [10].

## **Experimental**

### *Polyaniline synthesis*

*Reagents:* synthesis grade aniline and ammonium persulfate (APS), dodecyl benzenesulfonic acid (DBS), sodium chloride and ethanol. All reagents from Aldrich. Aniline was purified by distillation prior to use.

*Polymerization:* polyaniline powder was prepared by chemical oxidation based on the procedure by De Paoli et.al.[11]. Two solutions were prepared previously:

**Solution A:** aniline (10 mmol) and DBS were dissolved in 100 mL of 30% ethanol solution.

**Solution B:** APS and NaCl (24 mmol) were dissolved in 100 mL of 30% ethanol solution.

Solution B was added drop by drop into solution A, the temperature and the mechanical stirring were kept during the polymerization. After about 10 hours, the precipitated was collected, washed with ethanol and water to give a colorless filtrate. Then, the material was dried under vacuum for 48 hours.

For the purpose of studying the influence of four factors (independent variables): temperature, concentration of DBS, concentration of APS and stirring rate on the yield and the mass loss with temperature of polyaniline (dependent variables), we carried out a factorial design at two levels ( $2^4$ ) which includes 16 experiments. These experiments provide information on how the factors interact. Two levels, high (+) and low (-) were defined for each factor according to Table 1. In accordance with values of APS the ratios of APS /aniline studied were 0.7 and 1.15.

These experiments are thought to occur randomly in time such as is showed in the Table 2. The TGA was carried out in a STA 409 PC LUXX Netzch thermal analyzer from 30 °C up to 1100 °C at heat rate of 15 °C/min under nitrogen atmosphere.

Table 1. Variables evaluated on synthesis of PANI.

Independent Variables	Low level (-)	High level (+)
Temperature (°C)	1.2	25
Dopant, DBS (mmol)	27	45
Oxidant, APS (mmol)	6.9	11.5
Stirring rate (rpm)	500	1500

Table 2. Factorial design matrix for PANI polymerization.

Experiment	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
T (°C)	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+
DBS	-	-	+	+	-	-	+	+	-	-	+	+	-	-	+	+
APS	-	-	-	-	+	+	+	+	-	-	-	-	+	+	+	+
Stirring rate	-	-	-	-	-	-	-	-	+	+	+	+	+	+	+	+

## Results and discussion

The results are evaluated according to an analysis of variance for each dependent variable. For a start, a figure of normal probability of the effects was plotted, then an analysis of variance including the interactions with a big effect was carried out and finally, the diagnostic is verified with a model of regression. In the figure of normal probability of the effects are shown the factors with some effect on the reply, all effects on the straight line are insignificant while the major effects are on the outside of the line.

*Influence of independent variables on mass of PANI*

The factors have effects on yield of PANI are shown in the figure of normal probability (Figure 1).

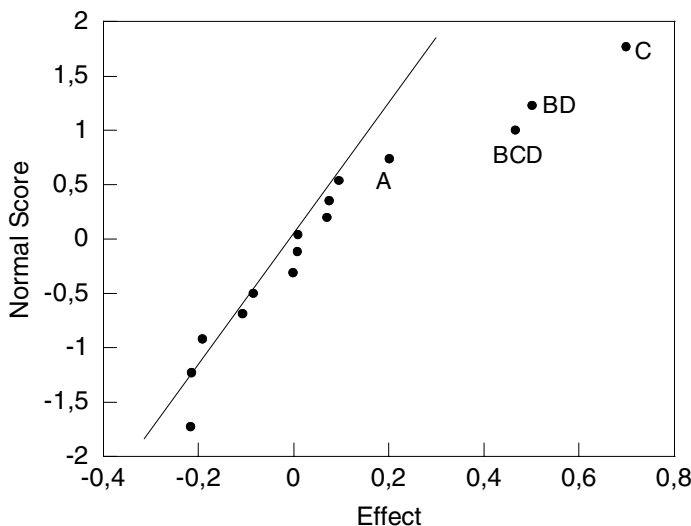


Figure 1. Normal probability of the effects. A: synthesis temperature, B: concentration of DBS, C: concentration of APS, D: stirring rate.

The Figure 1 indicates that the most important effects are the main effect of APS (C), the interactions of DBS\*rpm (BD) and the interaction of DBS\*APS\*rpm (BCD). The main effects are shown in the Figure 2, the most influential of them is the effect of APS which has the biggest influence when is at high level. We found that the PANI(DBS) yield by APS to be virtually independent of the temperature (Figures 1 and 2). However in other studies, it has been observed a slightly decrease in the yield with the temperature [12,13]. For example, Cao et. al. synthesized PANI at  $-10\text{ }^{\circ}\text{C}$  with a yield of 38% and at  $25\text{ }^{\circ}\text{C}$  with a yield of 37.7% [13]; C. Cheng obtained a yield of 78% at  $0\text{ }^{\circ}\text{C}$  and of 74% at  $40\text{ }^{\circ}\text{C}$  for PANI. These small variations in the yield happen because the overoxidative and the hydrolysis side reaction are stimulated by higher temperature [12].

The main effects of DBS and rpm were not significant on yield of PANI(DBS) (Figures 1 and 2). The incorporation of dopant molecules (DBS) into the intrinsically conducting polymers is related to the yield [14]. We found that the range of DBS concentrations employed in this study have not caused a notorious variation in the yield. Therefore, the doping grade was not changed notably. D. Han et. al. studied the synthesis of DBS-PANI nanoparticles and found that the highest yield was obtained when the ratio  $\text{DBS}/\text{An}=2$ . With the increasing of DBS/An more and more DBS has doped into the backbone of PANI which results in the increasing of yield. But when  $\text{DBS}/\text{An}>2$ , excessive DBS may aggravate the glutinosity of the system and

directly induce difficulties to separation and washing [15]. We employed DBS/An ratios of 2.7 and 4.3 in the polymerizations. In some cases we noticed agglutinations, however, the washing with ethanol made easier the filtration. In some experiments, the aniline did not react completely since oxidation products were observed in the filtrate (reddish coloration), these samples represented to the lower yields. The filtrate was colorless for those polymers giving the higher yields. In this last case, we believe that the dopant did not interfere with the polymerization of aniline by agglutination.

The stirring rate has not considerable main effect on the yield, however, it has second and third-order effects. Few studies have considered the influence of stirring on the conducting polymer synthesis. One of these evaluated the synthesis of PANI-nanorods under different conditions and found that the oxidant and stirring conditions have influence on average length of the PANI chains. The length of chains decreases with the stirring [16]. The longer chains are more stable and are not removed during the washing at the end of the synthesis. In this study the highest yield was obtained when: temperature was at high level, DBS at low level, APS at high level and stirring rate at low level.

About interaction of DBS\*rpm, the effect is biggest when both rpm and DBS are at low level. Therefore, the highest yield is obtained when both rpm and DBS are at low level and APS at high level. About oxidant concentration, our results are according with those obtained by De Paoli et. al. They evaluated the influence of some variable on the synthesis of poly(o-methoxyaniline) and found that the yield increases with the oxidant amount [11]. Increasing the amount of oxidant in the reaction medium the concentration of radical cations will be higher and consequently the polymerization will occur faster. However, other studies point out that this behavior depend on ratio APS/aniline, when this ratio is greater than 1.15 the PANI undergoes an overoxidation with a concomitant decrease in the yield [12,15,17]. In this study, the evaluated ratios APS/aniline were 0.7 and 1.15. Therefore, we didn't expect that the polymer was degraded by overoxidation. The APS concentration affects the chemical oxidative polymerization of aniline directly. Then, the APS concentration has more influence on the yield of PANI(DBS) than the concentration of DBS. The interaction of APS with other variables in our study is given by the equation of the design which is shown below.

The effect of temperature was discarded because it was not significant. Therefore, the design was converted to a factorial design of three factors with three replicates. The only replicate of the  $2^4$  design is projected to a  $2^3$  design with two replicates. Then, the model for PANI mass obtained is:

$$\text{Mass PANI (g)} = 1,5920 + 0,0477 \text{ DBS} + 0,3496 \text{ APS} + 0,1080 \text{ rpm} + 0,0533 \text{ DBS*APS} + 0,2504 \text{ DBS*rpm} + 0,0959 \text{ APS*rpm} + 0,2333 \text{ DBS*APS*rpm}$$

Therefore, in this study the maximum yield (2.96 g) was obtained when rpm and DBS are at low level (500 rpm and 27 mmol respectively) and APS at high level (11.5mmol) The worst yield was achieved when all variables were at their low level (1.01 g).

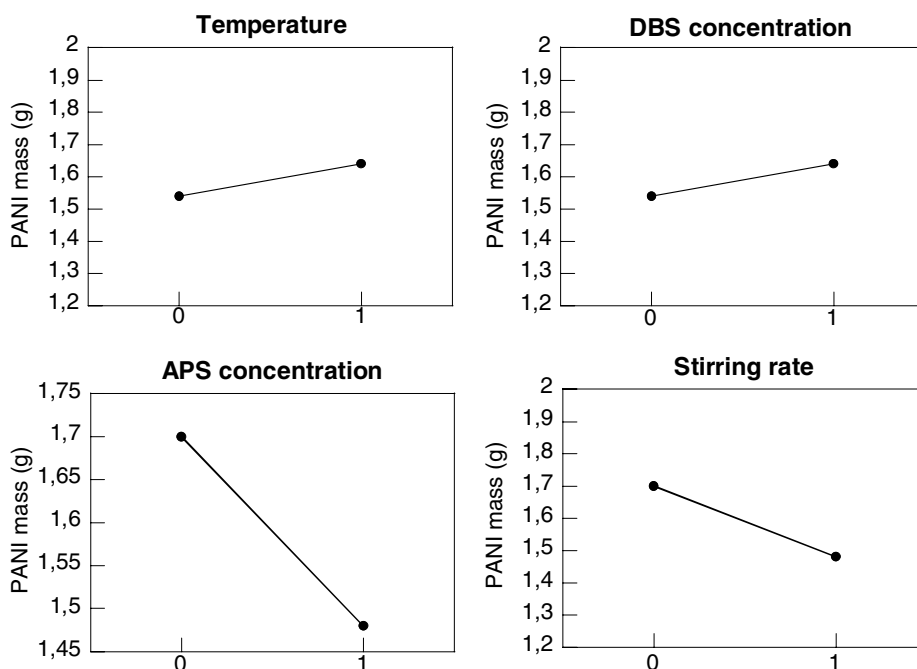


Figure 2. Relationship between main effects (temperature, DBS concentration, APS concentration and stirring rate (rpm)) and PANI mass.

### Thermogravimetric Analyses

Two forms of thermal behavior of PANI salts are reported in the literature. One of these indicates a two step mass loss process in which, initially, water is liberated from the polymer, followed by thermal degradation of the PANI salt [18,8]. The other form shows a three step mass loss process wherein water escapes followed by the dopant presents in the polymer, and finally complete degradation of the polymer results [19-21]. Three stage decomposition pattern also has been observed in poly(o-toluidine) and poly(o-anisidine) doped with different molecules including p-toluensulfonic acid [22-25]. The influence of type of dopant on the mass loss has been demonstrated by synthesizing of PANI with both organic and inorganic acids [20, 21].

In the present study, a two step mass loss process was observed and the analysis of the results is described next. Thermogravimetric behavior of the PANI(DBS) was very similar for all samples tested. Some thermograms of PANI(DBS) are shown in the Figure 3. The spectra showed a small mass loss below 150 °C (on average 5.4%). This initial mass loss is due to mainly release of moisture and other volatiles [29]. About 285 °C, a further mass loss begins and continues in the temperature range of 285 – 550 °C. The mass loss in this step was on average 68.6%. This loss is due to the decomposition of polymer by the dopant loss after 400 °C and to the thermal degradation of PANI chains [11,30]. Above 600 °C, the results obtained are associated with the polymer residues. Mass losses are conspicuous and rapid. By comparing with other results, the stability thermal is lower under these synthesis conditions. For

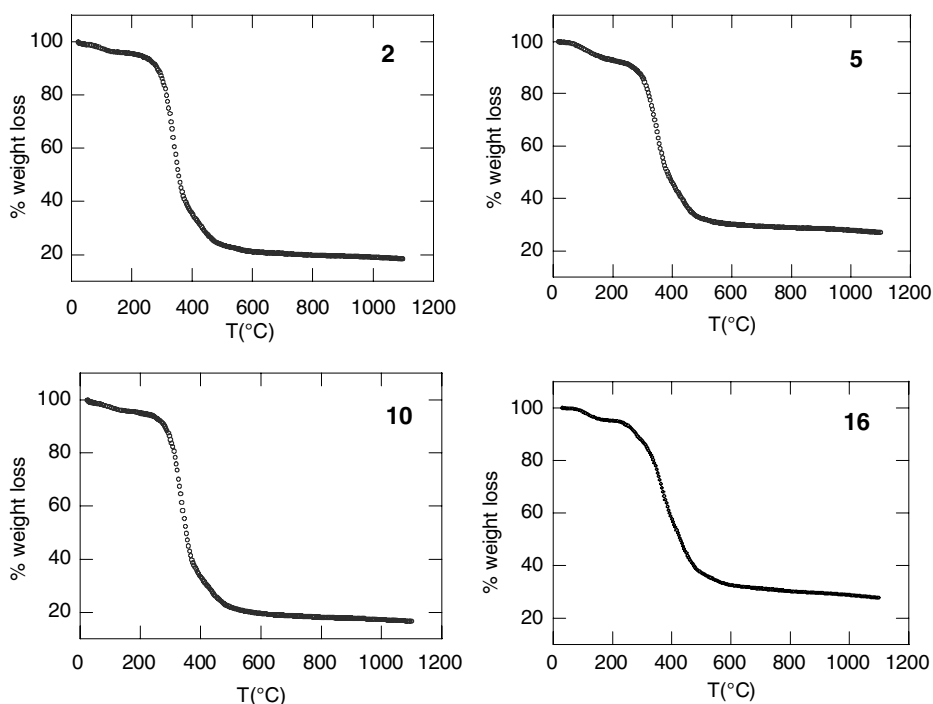


Figure 3. Thermograms of PANI(DBS). Experiments: 2,5,10,16 (see table 2 for polymerization conditions and table 3 for % mass loss). All polymers showed similar behavior.

example, Tsocheva et.al. reported a mass loss of 32% by heating of PANI doped with DBSA up to 350 °C. Kulkarni et.al synthesized p-toluene sulfonic acid-doped PANI which retained 40% of the original weight above 800 °C [26]. Other authors present results similar to ours, a mass loss about 60% after 300 °C in PANI(DBSA) [27]. Several studies show that PANI doped with organic acid having long alkyl chain shows increased thermal stability [28]. All these results underline the importance of studying the simultaneous influence of the synthesis variables on end properties of conducting polymers.

The Table 3 shows the mass loss corresponding to each sample in the two steps. The Figure 4 shows the normal probability of the effects for the second mass loss. All points are on the straight line or very close to it and therefore prove that the four variables have not influence on the mass loss.

According to above results, the evaluated DBS concentration range has not influence on the yield and therefore does not modify the doping grade of PANI(DBS) notably. The second mass loss of PANI(DBS) is related to both DBS molecules loss and polymeric chains degradation. In this study, a constant doping grade ensured that the mass loss is practically constant for all samples. Besides, a significant difference in the degradation of the chains during the heating was not observed. It would be interesting to verify the little variability in the doping grade with a chemical characterization of the polymers.

Table 3. Weight loss of PANI(DBS) when it is heated from 30 to 700 °C, step 1: below 150 °C, step 2: from 285 to 550 °C.

Experiment	Weight loss % (step 1)	Weight loss % (step 2)
1	5.4	69.3
2	4.3	74.9
3	4.7	68.0
4	3.7	73.7
5	6.7	63.5
6	4.9	72.7
7	5.0	70.3
8	5.6	70.1
9	6.2	66.0
10	4.6	76.2
11	5.1	68.4
12	7.4	59.3
13	6.6	66.0
14	5.2	70.9
15	5.5	71.3
16	5	63.2

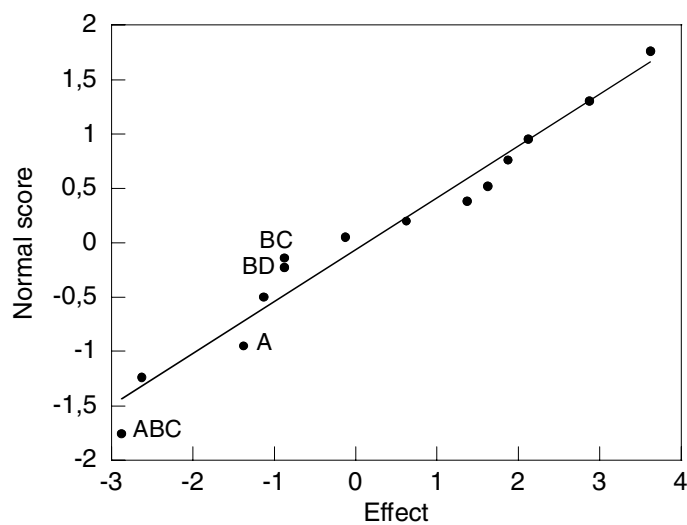


Figure 4. Normal probability of the effects on thermal behavior (mass loss). A: synthesis temperature, B: concentration of DBS, C: concentration of APS, D: stirring rate.

### Conclusions

The factorial design allowed us to study the influence of the concentration of dopant, the concentration of oxidant, temperature and stirring rate on the yield of PANI(DBS) and on its thermal behavior (TGA). By means a  $2^4$  design we found that the highest yield was obtained when both rpm and DBS are at their low level (500 rpm and



27 mmol respectively) and APS at high level (11.5mmol), these values correspond to ratios of DBS/aniline=2.7 and APS/aniline= 1.15. The range of DBS concentrations employed in this study have not caused a significant variation in the yield. Another side, the synthesis temperature doesn't influence on the yield and thermal behavior. The total mass loss during the thermal analysis was on average about 74% with a first loss about 150 °C (5.4%) and a second above 285 °C (68.6%) for all samples. The constant mass loss could be related to a constant doping grade. After these preliminary 2<sup>4</sup> experiments, those factors that prove of interest will need much closer study.

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