

Influence of Reaction Media on Pressure Sensitivity of Polyanilines Doped with DBSA

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ABSTRACT: The effect of the reaction medium on the final electrical performance of Pani doped with dodecylbenzene sulfonic acid (DBSA), Pani.DBSA, is analyzed in this manuscript. Pani.DBSA was synthesized through the one-step route in nonaromatic media, in accordance with a mixture experimental design. Polymer samples were analyzed by UV-vis and WAXS to characterize the differences among the many prepared Pani.DBSA samples and to explain the observed conductivity and compression sensitivity characteristics. Obtained results were modeled in ac-

cordance with a standard empirical modeling approach. Based on the obtained experimental data and on the proposed empirical models, it is shown that addition of acetone and isopropanol into the aqueous media during the one-step synthesis of Pani.DBSA materials must be encouraged. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2404–2413, 2008

Key words: polyaniline; DBSA; polymerization; reaction media; compression sensitivity; pressure sensors

INTRODUCTION

Polyaniline (Pani) has attracted much attention in the last 2 decades due to its potential usage in different electro/electronic applications. For instance, Pani has been used for fabrication of electrodes,¹ microelectronic circuits,² electrochromic displays,^{3,4} sensors,^{5,6} and electromagnetic shields.⁷ The advantages of Pani, when compared with other conducting polymers, are its easy chemical synthesis, its high stability toward environmental exposition and its special electronic properties, which can be reversibly controlled through charge transfer doping and protonation.⁸

Among the several methods available for preparation of Pani, the one-step *in situ* polymerization is perhaps the most attractive one.^{9,10} However, this method ordinarily uses organic solvents, such as toluene, which allows for easy dissolution of organic acids and aniline but also generates dangerous and harmful aromatic residues, increasing production costs. Pani can also be prepared through the one-step method in water.¹¹ However, dissolution of large amounts of organic acids, such as the dodecyl-

benzene sulfonic acid (DBSA), in water is inefficient. (Addition of DBSA improves the processibility of Pani, allowing for production of semiflexible Pani materials for pressure sensor applications.^{8–11}) Besides, the viscosity of the reaction medium can increase significantly along the reaction course, leading to diffusion limitations and low-quality polymer materials. These problems can be minimized if organic substances, such as isopropanol and acetone, are added to the aqueous phase. These oxygenated organic substances are much less dangerous and harmful than the aromatic substances (such as toluene) normally used for the one-step preparation of Pani, allowing simultaneously for cost reduction and improved environmental protection.

The main objective of this work is to analyze the effects of solvent compositions of different aqueous media on the final compression sensitivities of Pani samples prepared through the one-step method. It is very important to notice that the polymer materials prepared here are intended for manufacture of pressure sensors. For this reason, Pani samples are not required to present extremely high conductivities, as sensitivity of electrical properties to modification of certain operation variables (such as pressure) is usually more important than the overall conductivity of the final polymer piece. For this reason, extremely high conductivities are not pursued here and the analysis is focused primarily on the responses of pressure sensitivities.

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TABLE I
Experimental Design

Water, x_1	Isopropilic alcohol, x_2	Acetone, x_3
1	0	0
0	1	0
0	0	1
0.5	0.5	0
0.5	0	0.5
0	0.5	0.5
0.33	0.33	0.33

To reach the objective described above, Pani doped with DBSA (Pani.DBSA) was synthesized through the one-step route at different conditions, in accordance with a mixture experimental design. The samples were analyzed by ultraviolet–visible spectroscopy (UV–vis) and wide-angle X-ray scattering (WAXS) to characterize the differences among the many prepared Pani.DBSA samples and to explain the observed conductivity and compression sensitivity characteristics.

EXPERIMENTAL

Synthesis of Pani.DBSA

Pani.DBSA was synthesized through the one-step route in different reaction media, in accordance with a mixture experimental design (see Table I). In a typical procedure, 0.30 mL (0.0032 mol) of aniline (analytical grade from Vetec, Brazil), 1.06 g (0.0032 mol) of DBSA (commercial grade from Solquim LTDA, Brazil), and 0.73 g (0.0032 mol) of ammonium peroxydisulfate (APS, analytical grade from Vetec, Brazil) were dissolved into 15 mL of the analyzed medium under constant stirring. Water was distilled twice before use. Isopropanol and acetone were analytical grades provided by Vetec, and used as received. Reaction mixtures were kept at 0°C. After 12 h, the reaction medium was poured into ethanol (analytical grade from Vetec), filtered, washed several times with ethanol, and dried. All experiments were replicated at least three times.

Characterization

Samples used for measurement of volume resistivity were prepared by compression-molding as disks of 14 mm of diameter, using a force of 4.5 ton. ASTM D 257 procedure was used for determination of the volume conductivity, V_c . All measurements were performed with a multimeter Minipa ET-2907.

UV–vis spectral analyses were performed on a Varian UV–vis Spectrometer Model CARY 100. Samples were dissolved in toluene (analytical grade from Vetec) in a concentration of 5.5×10^{-5} g/mL.

The WAXS measurements were performed at the WAXS/SAXS beam line of the LNLS (Laboratório

Nacional de Luz Sincrotron – Campinas, Brazil), using monochromatic beam with wavelength of 1.7433 Å. The scattering intensity was recorded with a two-dimensional detector, using a sample-detector distance of 1641.5 mm. In the case of WAXS, 2 θ degree corrections were computed with the help of Al₂O₃ patterns. The scan range (2 θ) was in the interval 10°–60° and crystallinity calculations were performed with the Fityk—free peak fitting software.

The electrical–mechanical tests were performed in accordance with well-known published procedures,¹² allowing for evaluation of compression sensitivity and hysteresis of the polymer samples. Experimental measurements were performed in a multimeter Minipa ET-2907, connected to a “home made” sample compartment and coupled to an Instron Machine Model 5569. The maximum force used for characterization was equal to 2 kN and the test speed was set to 0.25 mm/s. The number of cycles in all cases was equal to 10. All tests were replicated at least three times.

Compression sensitivities

To correlate the data sets supplied by the Instron machine and the electrometer, a computer program was developed for process synchronization and data treatment.¹² The method can be summarized as follows:

1. The software selects data points (compression and conductivity values) that were recorded at similar sampling times (time difference $\Delta t = 0.01$ s).
2. Data obtained under low force ($F < 10$ N) are discarded.
3. The initial resistivity (R_0) is assumed to be equal to the resistivity value (R) obtained when $F = 10$ N.
4. The percentage variation of the sample conductivity ($\Delta\sigma$) is calculated in accordance with eq. (1).

$$\Delta\sigma = \frac{100 \times (R^{-1} - R_0^{-1})}{R_0^{-1}} \quad (1)$$

5. Experimental data obtained during compression (loading) and expansion (unloading) are treated separately.
6. The areas under compression and expansion diagrams ($\Delta\sigma$ vs. P) are calculated numerically, as a sum of discrete trapezoids.
7. The average hysteresis (\bar{h}) is calculated in accordance with eq. (2).

$$\bar{h} = \sum_{j=1}^n \frac{(A_{c(j)} - A_{d(j)})}{n} \quad (2)$$

where n is the number of compression and expansion cycles and $A_{c(j)}$ and $A_{d(j)}$ represent the areas obtained after the j th compression and expansion cycles, respectively.

8. The maximum compression sensitivities and respective pressures during the compression and expansion cycles are calculated, as described below.

The compression sensitivity (Scomp%) can be defined as

$$\text{Scomp}\% = \left(\frac{\Delta\sigma}{\Delta P} \right) \quad (3)$$

and can be computed for each data pair ($\Delta\sigma$ vs. P) during compression and expansion cycles. Maximum values (Scomp%_{Max}) and respective pressures (P_c , for compression, and P_e , for expansion) are recorded. As both P_c and P_e are orders of magnitude larger than the initial pressure obtained when $F = 10$ N, it is reasonable to write

$$\begin{aligned} \Delta P_c &= P_c \\ \Delta P_e &= P_e \end{aligned} \quad (4)$$

Finally, the average Scomp%_{Max} during the compression and expansion stages can be calculated as

$$\overline{\text{Scomp}}_{\text{MaxC}} = \sum_{j=1}^n \frac{(\Delta\sigma_{(j)}/P_{c(j)})}{n} \quad (5)$$

$$\overline{\text{Scomp}}_{\text{MaxE}} = \sum_{j=1}^n \frac{(\Delta\sigma_{(j)}/P_{e(j)})}{n} \quad (6)$$

RESULTS AND DISCUSSION

The main observed problem during Pani synthesis in pure water is foaming. Because of this problem, modification of reaction medium is necessary. Possible additives that can be used to modify the properties of the reaction medium and minimize the foam formation are oxygenated nonaromatic species, such as isopropanol and acetone. These chemicals are cheap, can be handled safely, and do not pose serious environmental risks. Isopropanol is completely miscible with water and readily soluble in a huge variety of common organic solvents (e.g., ethers, esters, acids, ketones, other alcohols). For this reason, it is used frequently as an interfacial agent for reduction of foaming in aqueous processes. Acetone is the first and most important member of the homologous aliphatic ketone series and is completely soluble in water. Pure acetone resists air oxidation under ambient conditions, although its chemical stability diminishes significantly in the presence of water. As ace-

tone is subject to typical carbonyl reactions, it can participate in a large number of chemical reaction mechanisms.¹³

Pani samples were prepared in accordance with the mixture design presented in Table I. Obtained samples were characterized by UV-vis, WAXS, electrical conductivity, and compression sensitivity analyses and the results are summarized in Tables II and III. Results are presented in terms of monomer conversion, extension of the doping process (Edp), volume conductivity (V_c), crystallinity (%), compression sensitivity (Scomp), and hysteresis.

To investigate the possible existence of correlations among the observed results, a standard correlation analysis was performed.¹⁴ Obtained results are presented in Table IV. Correlation matrices were calculated with Statistica[®]. Statistically significant results are obtained whenever the P -level is lower than the selected critical significance level, which was selected to be 5%. The P -level represents the probability of error when the observed result is assumed to be correct.¹⁵

Results presented in Table IV indicate the existence of some reliable correlations (in bold) among some of the analyzed properties. However, correlation values are usually small (smaller than 0.70), indicating that the distinct evaluated properties respond differently to modifications of the compositions of the reaction media. The exceptions are the strong correlations among maximum sensitivities during compression and expansion cycles and the hysteresis, as one might already expect, as the hysteresis is calculated from measured pressure sensitivities.

The obtained results encourage the development of independent statistical analysis for the distinct analyzed properties. (The exceptions are the compression and expansion sensitivities and the hysteresis, which can be grouped and analyzed simultaneously, as a single process response.) To analyze the effects of system compositions on the characterized properties, a standard empirical modeling approach is used. It is assumed that the process response can be modeled as

$$y_n = \sum_{i=1}^N \alpha_i^{\mu} x_i + \sum_{i=1}^N \sum_{j=i+1}^N \beta_{ij}^{\mu} x_i x_j + \sum_{i=1}^N \sum_{j=i+1}^N \sum_{k=j+1}^N \gamma_{ijk}^{\mu} x_i x_j x_k \quad (7)$$

where y_k is an experimental response, x_i ($i = 1, \dots, N$) is an experimental design variable and α_i^{μ} , β_{ij}^{μ} , and γ_{ijk}^{μ} ($i = 1, \dots, N$; $j = 1, \dots, N$; $k = 1, \dots, N$) are model parameters. α_i^{μ} represents the linear effects, while β_{ij}^{μ} and γ_{ijk}^{μ} represent the nonlinear synergistic effects.

Tables V–IX present the parameter estimates for eq. (7) (and respective confidence levels) for the dif-

TABLE II
Characterization of Pani Samples

Water, x_1	Isopropilic alcohol, x_2	Acetone, x_3	Conversion, y_1 (%)	Edp B2/B1, ^a y_2	Volume conductivity, y_3 (S/cm)	Crystallinity, y_4 (%)
1	0	0	34.00	1.19	5.68 E -02	7.3
1	0	0	36.62	1.08	5.56 E -02	8.0
1	0	0	35.00	1.13	5.71 E -02	7.5
0	1	0	28.68	1.35	1.79 E -02	6.7
0	1	0	21.45	1.23	1.79 E -02	7.0
0	1	0	27.22	1.29	1.80 E -02	6.7
0	0	1	28.86	1.00	6.21 E -02	10.7
0	0	1	29.80	0.96	5.95 E -02	10.0
0	0	1	31.79	0.92	6.29 E -02	11.2
0.5	0.5	0	36.85	1.38	1.12 E -01	13.6
0.5	0.5	0	33.55	1.44	1.05 E -01	15.1
0.5	0.5	0	39.55	1.32	1.14 E -01	14.0
0.5	0	0.5	53.40	1.30	4.65 E -02	11.2
0.5	0	0.5	54.01	1.19	5.26 E -02	10.9
0.5	0	0.5	50.02	1.24	4.88 E -02	10.8
0	0.5	0.5	12.44	0.28	4.66 E -03	9.5
0	0.5	0.5	17.20	0.27	4.65 E -03	9.0
0	0.5	0.5	18.85	0.26	4.55 E -03	10.0
0.33	0.33	0.33	37.10	0.96	5.01 E -05	6.6
0.33	0.33	0.33	36.80	0.91	4.13 E -05	7.1
0.33	0.33	0.33	32.90	0.86	7.29 E -05	6.4

^a Edp – estimative of the extension of the doping process, computed as the ratio between polaronic (B2) and π - π^* (B1) absorptions in the UV-vis spectrum of polyaniline.

ferent analyzed process responses. Based on Tables V-IX it is possible to discriminate the most influential composition effects on the analyzed responses and to observe whether important nonlinear (synergistic) effects are present. Whenever P becomes

larger than 0.05 in Tables V-IX, it may be said that the related experimental effect is not significant within the 95% confidence level, which means that the considered experimental effect may be discarded from the analysis.

TABLE III
Electromechanical Properties

Water, x_1	Isopropilic alcohol, x_2	Acetone, x_3	Scomp compression, ^a y_6 (%/MPa)	Scomp expansion, ^b y_7 (%/MPa)	Hysteresis, y_8 (% \times MPa)
1	0	0	4.29 E +02	4.74 E +02	8.61 E +03
1	0	0	5.12 E +02	5.71 E +02	8.55 E +03
1	0	0	3.45 E +02	3.77 E +02	8.67 E +03
0	1	0	6.82 E +03	9.30 E +03	6.67 E +04
0	1	0	8.03 E +03	1.07 E +04	5.80 E +04
0	1	0	5.61 E +03	7.94 E +03	7.53 E +04
0	0	1	4.61 E +03	4.56 E +03	9.12 E +03
0	0	1	6.17 E +03	5.70 E +03	1.30 E +03
0	0	1	3.04 E +03	3.42 E +03	1.69 E +04
0.5	0.5	0	1.77 E +03	1.94 E +03	1.46 E +04
0.5	0.5	0	2.07 E +03	2.26 E +03	2.67 E +04
0.5	0.5	0	1.48 E +03	1.62 E +03	2.40 E +03
0.5	0	0.5	1.23 E +04	1.41 E +04	7.11 E +04
0.5	0	0.5	1.56 E +04	1.79 E +04	7.75 E +04
0.5	0	0.5	9.06 E +03	1.02 E +04	6.47 E +04
0	0.5	0.5	4.44 E +01	4.90 E +01	2.12 E +02
0	0.5	0.5	4.99 E +01	5.50 E +01	2.35 E +02
0	0.5	0.5	3.89 E +01	4.31 E +01	1.89 E +02
0.33	0.33	0.33	3.13 E +04	3.43 E +04	1.92 E +05
0.33	0.33	0.33	3.44 E +04	3.85 E +04	1.70 E +05
0.33	0.33	0.33	2.83 E +04	3.00 E +04	2.15 E +05

^a Compression sensitivity along compressive semicycle.

^b Compression sensitivity along expansive semicycle.

TABLE IV
Correlation Matrix for Observed Values

	Conversion, y_1 (%)	Edp B2/ B1, ^a y_2	Volume conductivity (S/cm)	Crystallinity, y_4 (%)	Scomp compression, ^b y_6 (%/MPa)	Scomp expansion, ^c y_7 (%/MPa)	Hysteresis, y_8 (% × MPa)
Conversion, y_1 (%)	1.00	0.64	0.40	0.27	0.34	0.34	0.29
Edp B2/B1, ^a y_2	0.64	1.00	0.60	0.21	0.05	0.07	0.10
Volume conductivity (S/cm)	0.40	0.60	1.00	0.79	-0.47	-0.48	-0.51
Crystallinity, y_4 (%)	0.27	0.21	0.79	1.00	-0.40	-0.42	-0.48
Scomp compression, ^b y_6 (%/MPa)	0.34	0.05	-0.47	-0.40	1.00	1.00	0.95
Scomp expansion, ^c y_7 (%/MPa)	0.34	0.07	-0.48	-0.42	1.00	1.00	0.96
Hysteresis, y_8 (% × MPa)	0.29	0.10	-0.51	-0.48	0.95	0.96	1.00

Marked correlations are significant at $P < 0.05000$.

^a Estimative of the extension of the doping process.

^b Compression sensitivity along compressive semicycle.

^c Compression sensitivity along expansive semicycle.

Information about monomer conversion is frequently neglected in most publications in the field, although monomer conversion is a very important factor for cost estimation. Very different conversion values were obtained in the analyzed experimental region. Maximum and minimum values of 52.5 wt % and 16.2 wt % were obtained in water/acetone (1 : 1) and isopropanol/acetone (1 : 1) media, respectively. All calculated values are shown in Table II. Main effect analysis of obtained conversion values performed with eq. (7) led to correlation of 0.9583 among calculated and observed data. Obtained results are shown in Table V.

Obtained model parameters (water (A); isopropanol (B); acetone (C)) indicate that water is the most important chemical constituent in the reaction mixtures. However, Table V shows very clearly that there is a strong synergism between water and acetone (AC), which leads to increase of monomer conversion when small amounts of acetone are present. This may be regarded as a beneficial effect, as higher monomer conversions can be attained in the presence of acetone. This is possibly due to the increase of the polarity of the reaction media—once acetone (2.91D) possesses a higher dipole moment than isopropanol (1.66D)—and to the relatively lower com-

petition by the oxidant species (when compared with isopropanol, as acetone is less susceptible to oxidation). Thus, the oxidant power of water/acetone media is larger than the oxidant power of water/isopropanol mixtures, when similar amounts of the organic constituent are added to water. This leads to increase of the number of propagating chains and consequently to increase of monomer conversion. On the other hand, there is a significant negative synergism between isopropanol and acetone, which causes significant decrease of monomer conversion when both organic constituents are added to the reaction mixture. This may be due to complex combination of both monomer solubility and oxidant capability effects. Thus, if the increase of the conversion values is the main objective, obtained results indicate that the simultaneous addition of acetone and isopropanol to the reaction medium should be avoided.

Ultraviolet spectroscopy constitutes a very useful tool for characterization of Pani.^{16–20} The spectrum of protonated (conducting) Pani normally presents three characteristic absorption peaks. The peak placed at 350 nm is normally ascribed to π - π^* transition of the benzenoid rings. The peaks placed at 400–420 and 750–800 nm are attributed to polaron- π^* transition and π -polaron transitions, respectively.^{19–21} The peak placed at larger wavelengths is related to the doping level and formation of polarons.²² Furthermore, the peaks placed at 400–420 and 750–800 nm can be related to the doping level and formation of polarons.^{22–26} For this reason, the ratio between the absorbances observed at 750–800 nm (π -polaron) and 350 nm (π - π^* transition) can be roughly related to the extension of the doping process (or simply doping level) of the Pani sample,^{16,18,19,23} as illustrated in Figure 1 for Pani.DBSA samples synthesized in pure water, isopropanol, and acetone. The obtained ratios are shown in Table II for different

TABLE V
Main Effect Analysis for Conversion (y_1)

Factors and synergisms	Coeff.	Std. Error	P
A (α_1^1)	35.2063	1.52480	0.000000
B (α_2^1)	25.7836	1.52480	0.000000
C (α_3^1)	30.1505	1.52480	0.000000
AB (β_{12}^1)	24.6270	7.46994	0.005296
AC (β_{13}^1)	79.1894	7.46994	0.000000
BC (β_{23}^1)	-47.2201	7.46994	0.000019
ABC (γ_{123}^1)	-28.8532	52.55568	0.591652

A – water; B – isopropanol; C – acetone; AB, AC, BC, and ABC – synergisms.

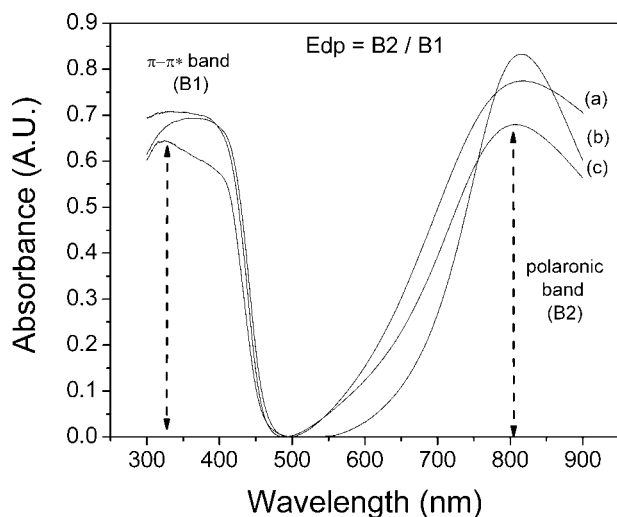


Figure 1 Average UV-vis spectrum of Pani.DBSA prepared in (a) water, (b) isopropanol, and (c) acetone.

Pani samples ($Edp = B1/B2$). All spectra displayed typical $\pi-\pi^*$ absorption peaks placed at 369 nm and two polaronic bands placed at 450 and 779 nm, confirming the production of Pani.DBSA.¹⁶

Main effect analysis of obtained ratios between polaronic (B2) and $\pi-\pi^*$ (B1) bands was performed with eq. (7) and led to correlation of 0.9863 among calculated and observed data. The results are summarized in Table VI. The strongest positive effect is obtained when isopropanol is present in the reaction medium, while the strongest negative effect is the synergism between isopropanol and acetone. Obtained results indicate that doping is more effective when isopropanol is present and that acetone causes the inverse effect, as the linear coefficients are respectively larger and smaller than the linear coefficient of water. However, observed differences are not very large, which means that doping is not affected very much by addition of the organic substances. However, if concentrations of isopropanol and acetone increase, the nonlinear synergisms indicate that doping can be severely affected because of large negative effects. This certainly is a consequence

TABLE VI
Main Effect Analysis for Estimative of the Extension of the Doping Process (η_2)

Factors and synergisms	Coeff.	Std. Error	P
A (α_1^2)	1.13494	0.028480	0.000000
B (α_2^2)	1.29080	0.028480	0.000000
C (α_3^2)	0.96209	0.028480	0.000000
AB (β_{12}^2)	0.67841	0.139522	0.000251
AC (β_{13}^2)	0.76836	0.139522	0.000077
BC (β_{23}^2)	-3.42137	0.139522	0.000000
ABC (γ_{123}^2)	-0.03784	0.981627	0.969793

A – water; B – isopropanol; C – acetone; AB, AC, BC, and ABC – synergisms.

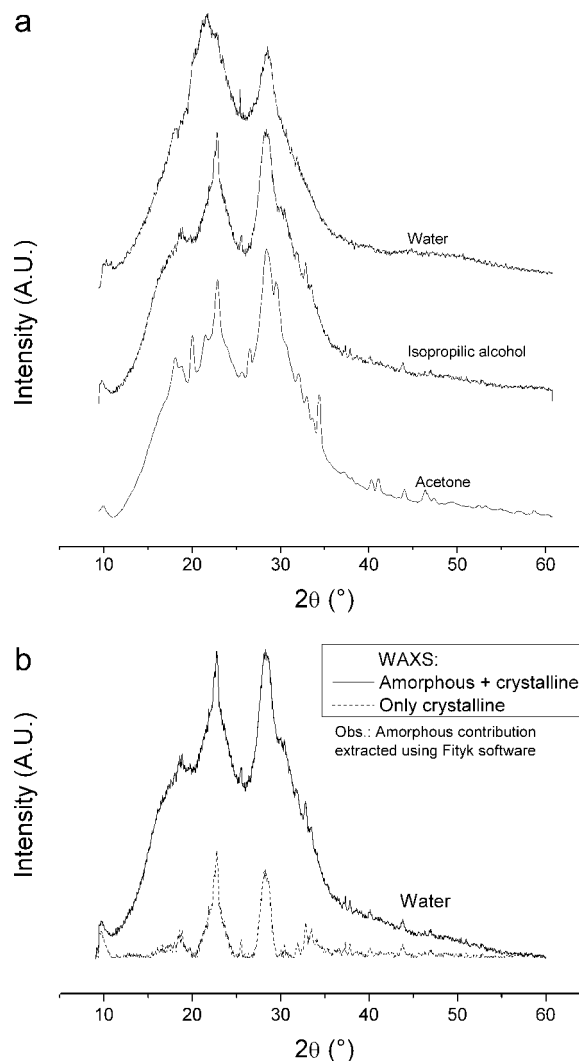


Figure 2 WAXS of Pani.DBSA prepared in water, isopropanol, and acetone media (a) and deconvolution of the crystalline contribution, as performed for calculation of crystallinity (b).

of the reduction of the polar nature of the reaction media, indicating that organic concentrations should not be increased arbitrarily.

Regardless the analyzed reaction medium, WAXS diffractograms of all Pani.DBSA samples always presented several sharp reflections on a large amorphous halo [see Fig. 2(a)]. The most important ones are placed at $2\theta = 18.3, 21.6, 25.9, 28.4,$ and 33.2 , which are related with an orthorhombic cell.^{27–30} Crystallinity calculations followed traditional procedures proposed by Guinier³¹ and Kakudo and Kasai³² using the Fityk software, which also allows for deconvolution of the crystalline contribution of the scattering signal, as illustrated in Figure 2(b).

Crystallinity values are shown in Table II. Samples synthesized in water/isopropanol showed the largest crystallinity values, while the lowest crystallinity values were observed for samples prepared in water/

isopropanol/acetone mixtures. Main effect analysis of crystallinity was performed as described previously and led to correlation of 0.9783. Results are summarized in Table VII. The most important observed effects are the synergisms between water/isopropanol and water/isopropanol/acetone, which exert the higher positive and negative effects over crystallinity, respectively. It is important to observe that the crystallinity is increased when the organic concentrations increase, because of the large positive synergisms between the organic constituents and water. Again, this may be caused by the smaller solubilities obtained when the organic concentrations increase. However, as observed in the previous cases, there is a strong negative synergism between isopropanol and acetone, indicating once more that large organic concentrations should be avoided.

Volume conductivity results are shown in Table II. Main effect analysis of volume conductivity was performed with eq. (7) and led to correlation of 0.9975 among calculated and observed data. The results are summarized in Table VIII. The largest positive effect, associated with higher conductivity values, is related to the interaction between water and isopropanol, indicating that the addition of isopropanol may be beneficial for conductivity. This can be related to the improved crystallinity and doping obtained when isopropanol is added to the system.

It is well known that the polarity of a solvent greatly influences the energies of the electronic states and the photophysical properties of substances dissolved in aromatic systems.³³ In addition, electrical conductivity of Pani is linked to its oxidation state. The most conductive form is the half-oxidated form, named emeraldine. Emeraldine has basic character and is the ground state or lowest energy state of Pani. The emeraldine salt (protonated emeraldine) corresponds to the excited state of Pani, which is characterized by existence of charge transfer. The equilibrium between ground and excited states depends on solvent polarity and temperature. High solvent polarity favors the ground state.³⁴ Despite the possible existence of nonlinear effects, it is reasonable to assume that mixing of a polar species

TABLE VII
Main Effect Analysis for Crystallinity Values (y_4)

Factors and synergisms	Coeff.	Std. Error	P
A (α_1^4)	7.619	0.266834	0.000000
B (α_2^4)	6.763	0.266834	0.000000
C (α_3^4)	10.655	0.266834	0.000000
AB (β_{12}^4)	28.223	1.307214	0.000000
AC (β_{13}^4)	7.375	1.307214	0.000061
BC (β_{23}^4)	3.024	1.307214	0.036434
ABC (γ_{123}^4)	-160.385	9.197067	0.000000

A – water; B – isopropanol; C – acetone; AB, AC, BC, and ABC – synergisms.

TABLE VIII
Main Effect Analysis for Conductivity Values (y_3)

Factors and synergisms	Coeff.	Std. Error	P
A (α_1^3)	0.05651	0.001268	0.000000
B (α_2^3)	0.01792	0.001268	0.000000
C (α_3^3)	0.06151	0.001268	0.000000
AB (β_{12}^3)	0.29282	0.006210	0.000000
AC (β_{13}^3)	-0.03880	0.006210	0.000021
BC (β_{23}^3)	-0.14039	0.006210	0.000000
ABC (γ_{123}^3)	-1.56286	0.043693	0.000000

A – water; B – isopropanol; C – acetone; AB, AC, BC, and ABC – synergisms.

with a second less polar substance will cause the global decrease of the polarity of the medium. Thus, it can be expected that the polarity of aqueous media modified with isopropanol will decrease with the increase of the alcohol content. This decrease of polarity can lead to the formation of more ordered (crystalline) Pani materials, and consequently more conductive Pani samples. Table IV confirms that there are moderate correlations among volume conductivity, doping extent, and crystallinity. On the other hand, the largest negative effects are obtained when the concentrations of acetone and isopropanol are increased simultaneously, indicating once more that the organic concentrations should be kept below an optimum value for obtainment of improved responses.

Compression sensitivity values and hysteresis obtained for tests performed with the produced samples are shown in Table III. Main effect analysis is presented in Table IX. Results are similar for the three process responses due to the strong correlations among these variables, as already explained. Maximum values were obtained with Pani.DBSA samples synthesized in water/isopropanol/acetone media, while minimum values were obtained for Pani.DBSA samples synthesized in isopropanol/acetone media. This indicates once more that addition of small amounts of isopropanol and/or acetone can be beneficial, because of the increase of the crystallinity and extent of doping of the final samples, which also lead to improved electrical responses. One should observe, however, that the arbitrary increase of the acetone and/or isopropanol concentrations (removal of water) can be very deleterious, as the secondary synergism between these two variables indicates.

To provide an overall view of the process responses, response surfaces are presented in Figure 3. As a whole, optimum weight fractions are roughly equal to 50 wt % of water, 25% of acetone, and 25% of isopropanol. These compositions allow for maximization of pressure sensitivities, without significant reduction of monomer conversions, in spite of the poorer electrical responses.

TABLE IX
Main Effect Analysis for Compression Sensitivity (y_6 and y_7) and Hysteresis (y_8)

	Factors and synergisms	Coeff.	Std. Error	P
Compression (y_6)	A (α_1^6)	4.29 E +02	1.07 E +03	0.693800
	B (α_2^6)	6.82 E +03	1.07 E +03	0.000017
	C (α_3^6)	4.61 E +03	1.07 E +03	0.000704
	AB (β_{12}^6)	-7.40 E +03	5.22 E +03	0.178246
	AC (β_{13}^6)	3.92 E +04	5.22 E +03	0.000003
	BC (β_{23}^6)	-2.27 E +04	5.22 E +03	0.000676
Expansion (y_7)	ABC (γ_{123}^6)	7.12 E +05	3.67 E +04	0.000000
	A (α_1^7)	4.74 E +02	1.31 E +03	0.722087
	B (α_2^7)	9.30 E +03	1.31 E +03	0.000005
	C (α_3^7)	4.56 E +03	1.31 E +03	0.003567
	AB (β_{12}^7)	-1.18 E +04	6.40 E +03	0.086466
	AC (β_{13}^7)	4.62 E +04	6.40 E +03	0.000004
Hysteresis (y_8)	BC (β_{23}^7)	-2.75 E +04	6.40 E +03	0.000727
	ABC (γ_{123}^7)	7.75 E +05	4.50 E +04	0.000000
	A (α_1^8)	8.61 E +03	6.29 E +03	0.192493
	B (α_2^8)	6.67 E +04	6.29 E +03	0.000000
	C (α_3^8)	9.12 E +03	6.29 E +03	0.168980
	AB (β_{12}^8)	-9.23 E +04	3.08 E +04	0.009656
	AC (β_{13}^8)	2.49 E +05	3.08 E +04	0.000001
	BC (β_{23}^8)	-1.51 E +05	3.08 E +04	0.000238
	ABC (γ_{123}^8)	4.41 E +06	2.17 E +05	0.000000

A – water; B – isopropanol; C – acetone; AB, AC, BC, and ABC – synergisms.

The response surface of Edp is shown in Figure 3(a), indicating graphically that the doping process is less efficient when isopropanol and acetone are added simultaneously into the reaction medium and that the doping process is more efficient when water and isopropanol are mixed. This may be regarded as a beneficial effect, as more efficient doping occurs in the presence of isopropanol. The observed behavior may be related to the nucleophilic character of acetone, which may lead to removal of protons from the DBSA molecules. This may cause the reduction of the extent of protonation of the Pani chains and, consequently, reduction of the Edp. Therefore, addition of acetone causes the increase of the reaction rates, but also causes undesired deleterious effects on the electrical properties of the final polymer product.

Crystallinity surface response is shown in Figure 3(b), indicating graphically that the lowest degrees of crystallinity are obtained for mixtures of acetone/isopropanol and water/acetone/isopropanol. On the other hand, as observed for Epd, the largest crystallinity values are observed for reaction media containing water and isopropanol. Thus, according to the surface response analysis, water/isopropanol media produce large amounts of polarons and leads to improved organization of the polymer chains. As explained previously, this is caused both by the smaller solubilities of the monomer in the reaction system (and vice-versa) and the deleterious acetone effects on protonation. The response surface of conductivity is shown in Figure 3(c). The similarity with the response surface of crystallinity is obvious, indi-

cating that crystallinity exerts the most important effect on the final conductivities of the polymer samples.^{16,18,23}

Response surfaces for Scomp along compression and expansion semicycles and hysteresis are shown in Figure 3(d–f). The best values are obtained around the central point. This clearly indicates that pressure sensitivity is not correlated only to the electrical properties of the final polymer material. As a matter of fact, the smaller crystallinities of the polymer samples may significantly contribute with the pressure sensitivity, as the distance among polymer chains and crystallites can be significantly modified through usage of external forces. For this reason, although the central point provides Pani samples with low Edp, crystallinity, and conductivity values, this medium produces Pani with very high compression sensitivities, as desired for the manufacture of pressure sensors.

From a practical point of view, it may be said that addition of acetone affects the degree of protonation of Pani chains, causing the simultaneous and undesired decrease of the Edp, crystallinity, and conductivity of the Pani, while addition of isopropanol in water is able to produce better structured Pani chains, characterized by higher Edp, higher degree of crystallinity, and higher conductivity, due to solubility effects. However, as the obtainment of lower crystallinities may improve the pressure sensitivity, it is recommended that 25 wt % of acetone and 25 wt % of isopropanol be added to the aqueous phase for manufacture of pressure sensors with improved performance.

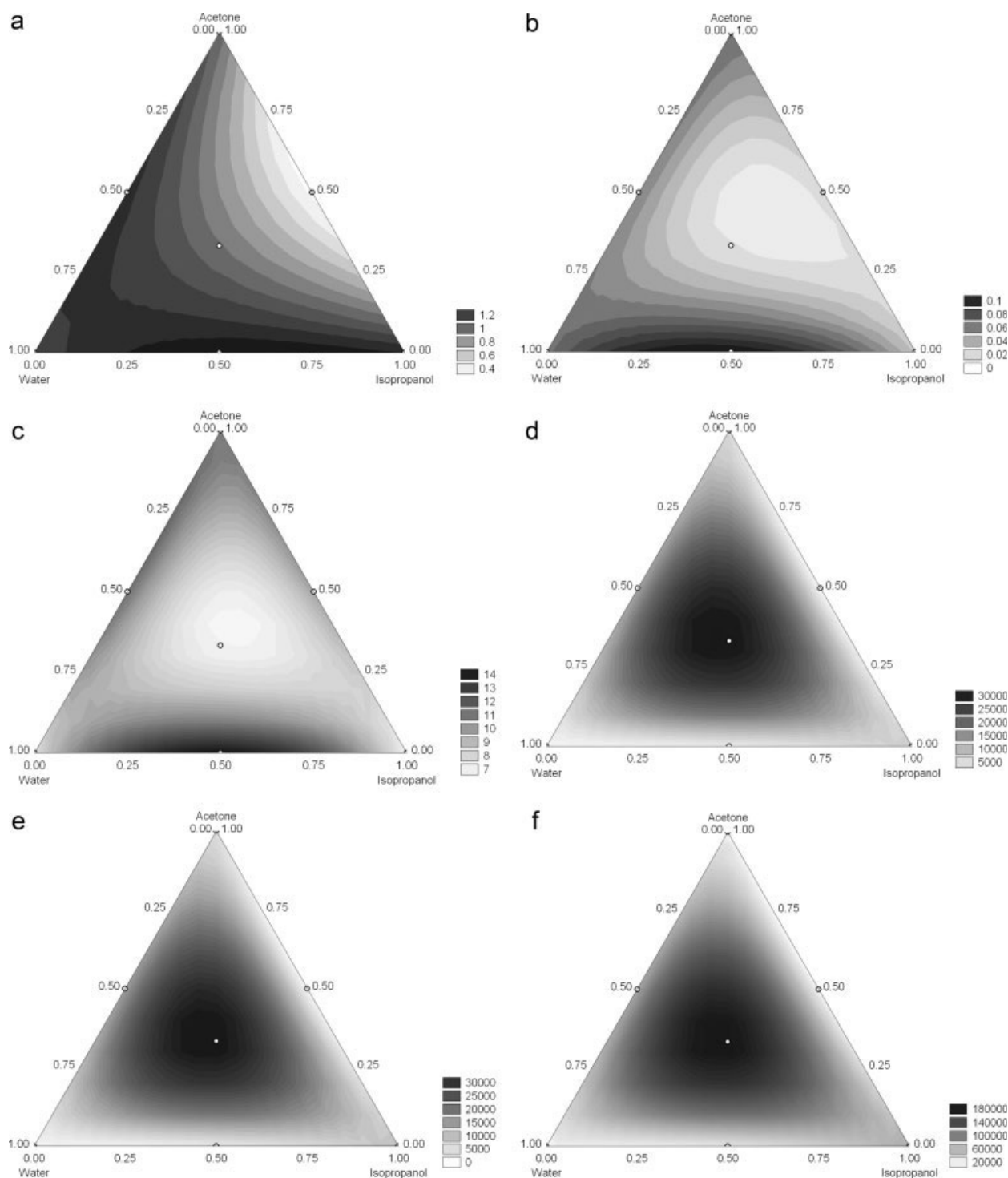


Figure 3 Surface responses for extension of doping (a), volume conductivity (b), crystallinity (c), compression sensitivity along compression (d), compression sensitivity along expansion (e), and hysteresis (f).

CONCLUSIONS

Different Pani.DBSA samples were prepared in aqueous media containing different amounts of acetone and isopropanol, according to the one-step process. Based on the obtained experimental results and on the proposed empirical models, it can be con-

cluded that the addition of isopropanol to water can be very beneficial for production of Pani.DBSA materials during the one-step method in water. This allows for reduction of foaming, decrease of the system viscosity, and improvement of the conductivity of the final polymer samples. Addition of acetone and isopropanol to water can also be beneficial if

one is interested in improving the compression sensitivity of the final polymer material, at the expense of reducing the final electrical conductivity. An additional benefit of acetone is the increase of the monomer conversion. It is believed that observed beneficial effects are related to the modification of the polarity and oxidative power of the reaction media. The proposed empirical models indicate that the final properties of the polymer samples respond nonlinearly to modifications of the composition of the reaction medium, so that optimum performances for pressure sensor applications are obtained when the isopropanol and acetone concentrations are around 25 wt %.

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