ELECTRICAL PROPERTIES OF POLYANILINE DOPED WITH DBSA PREPARED IN NON AROMATIC AQUEOUS MEDIA[1]

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Abstract
Polyaniline (Pani) is one of the most versatile and cheapest conductive polymers. For this reason, 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 non aromatic media, in accordance with a mixture experimental design. The samples were analyzed by UV-Vis, and WAXS, in order to characterize the differences among the many prepared Pani.DBSA samples and to explain observed conductivity characteristics.
Key words: Polyaniline; DBSA; Polymerization; Reaction media; Experimental design.

PROPRIEDADES ELÉTRICAS DE POLIANILINA DOPADA COM DBSA PREPARADA EM MEIO AQUOSO NÃO AROMÁTICO

Resumo
A polianilina é um dos mais versáteis, baratos e interessantes polímeros condutores. Por isso, neste trabalho o efeito do meio reacional sobre a condutividade elétrica da polianilina dopada com ácido dodecilbenzenossulfônico, DBSA, é estudado. A polianilina dopada com DBSA, PAni.DBSA, foi sintetizada em única etapa, usando meios aquosos não aromáticos, seguindo um planejamento experimental. As amostras obtidas foram estudadas por UV-Vis e por WAXS, o que permitiu a compreensão das características condutivas destes materiais.
Palavras-chave: Polianilina; DBSA; Polimerização; Meio reacional; Planejamento experimental.

[1] *Technical Contribution to the 62st International Congress of the ABM, July 23-27 2007, Vitória – ES – Brazil.*
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1 INTRODUCTION

In front of other conductive polymers, polyaniline presents some advantages like its easy chemical synthesis, its high stability towards environmental exposition and its special electronic properties, which can be reversibly controlled through charge transfer doping and protonation.[1] Pani has been used for fabrication of electrodes,[2] microelectronic circuits,[3] electrochromic displays,[4,5] sensors[6,7] and electromagnetic shields.[8]

Among others, the one-step in situ polymerization is perhaps the most attractive method available for preparation of Pani.[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 risks and 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 dodecylbenzene sulfonic acid (DBSA), in water is inefficient. 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 compounds, such as isopropanol and acetone, are added to the aqueous phase. These oxygenated organic compounds are much less dangerous and harmful than the aromatic compounds normally used for the one-step preparation of Pani, being helpful to reduce costs and protect environment.

The main objective of this work is to analyze the effect of different media on the electrical conductivity of polyaniline samples prepared through the one-step method, allowing for obtaining useful and cheapest material in an easy way, reducing costs and time in the preparation of polymeric semi conductive materials. In order to reach this objective, polyaniline 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), in order to characterize the differences among the many prepared Pani.DBSA samples and to explain observed conductivity and compression sensitivity characteristics.

2 MATERIALS AND METHODS

Pani.DBSA was synthesized through the one-step route in different reaction media, in accordance with a mixture experimental design (Table 1). In a typical procedure, 0.30 mL (0.0032 mol) of aniline (analytical grade from Vetec, Brazil), 1.06g (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 appropriate medium under constant stirring. Water was distilled twice before use. Isopropanol and acetone were analytical grades provided by Vetec, Brazil, and used as received. Reaction mixtures were kept at 0º C. After 12 h, the reaction medium was poured into ethanol, filtered, washed several times with ethanol and dried. All experiments were made in triplicates.

Ultraviolet-visible spectral analyses were performed on a Varian UV-Vis Spectrometer Model CARY 100. Samples were dissolved in toluene 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 Sincroton – Campinas, Brazil), by 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. Needed 2θ degree corrections were computed with the help of Al2O3 patterns. The scan range was in the interval 10º< 2θ < 60º and crystallinity calculations were performed with the Fityk - free peak fitting software.

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 D257 procedure was used for determination of the volume conductivity, Vc. All measurements were performed with a multimeter Minipa ET-2907.

2 RESULTS AND DISCUSSION

The foam formation in pure water medium was the first problem fronted to achieve the main objective, which is to obtain easily as possible a reasonably conductive material in a cheap and reproducible way. Mainly due this problem, modification of reaction medium, pointing foam reduction, is a very necessary pathway. Among possible additives that can be used to modify the properties of the reaction medium are oxygenated non-aromatic species, such as well known isopropanol and acetone. These chemicals are cheap, can be handled safely and do not present 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, and 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. Pure acetone resists air oxidation under ambient conditions, although its chemical stability diminishes significantly in the presence of water. As acetone is subject to typical carbonyl reactions, it can participate in a large number of chemical reaction mechanisms.[13]

Several tests, like UV-Vis, WAXS and electrical conductivity were performed on synthesized materials. Most important results as conversion; extension of the doping process (Edp); crystallinity (%) and volume conductivity (Vc); are shown in Table 1. In all cases, main effect analysis was performed with the help of an empirical cubic model with the general form:

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

where y_k is an experimental response, x_i (i = 1, …, N) is an experimental design variable and α_i^{μ}, β_{ij}^{μ} and γ_{ijk}^{μ} (i = 1, …, N; j = 1, …, N, k = 1, …, N) are model parameters.

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 1.

Table 1. Experimental data.

Water (x_1)	Isopropilic Alcohol (x_2)	Acetone (x_3)	Conversion (%) (y_1)	[a] Edp B2 / B1 (y_2)	Crystallinity (%) (y_3)	Volume conductivity (S/cm) (y_4)
1	0	0	34.0	1.2	7.3	5.7E-02
1	0	0	36.6	1.1	8.0	5.6E-02
1	0	0	35.0	1.1	7.5	5.7E-02
0	1	0	28.7	1.4	6.7	1.8E-02
0	1	0	21.5	1.2	7.0	1.8E-02
0	1	0	27.2	1.3	6.7	1.8E-02
0	0	1	28.9	1.0	10.7	6.2E-02
0	0	1	29.8	1.0	10.0	6.0E-02
0	0	1	31.8	0.9	11.2	6.3E-02
0.5	0.5	0	36.9	1.4	13.6	1.1E-01
0.5	0.5	0	33.6	1.4	15.1	1.1E-01
0.5	0.5	0	39.6	1.3	14.0	1.1E-01
0.5	0	0.5	53.4	1.3	11.2	4.7E-02
0.5	0	0.5	54.0	1.2	10.9	5.3E-02
0.5	0	0.5	50.0	1.2	10.8	4.9E-02
0	0.5	0.5	12.4	0.3	9.5	4.7E-03
0	0.5	0.5	17.2	0.3	9.0	4.7E-03
0	0.5	0.5	18.9	0.3	10.0	4.6E-03
0.33	0.33	0.33	37.1	1.0	6.6	5.0E-05
0.33	0.33	0.33	36.8	0.9	7.1	4.1E-05
0.33	0.33	0.33	32.9	0.9	6.4	7.3E-05

[a] Extension of the doping process; [b] radius of gyration, Compression sensitivity along [c] compressive and [d] expansive semi-cycles

Main effect analysis of obtained conversion values performed with Equation (1) led to correlation of 0.9583 among calculated and observed data. Obtained results are shown in Table 2.

Table 2. Main effect analysis for conversion **(y_1)**.

Factors and synergisms	Coeff.	Std.Err.	P
A (α_1^1)	35.21	1.52	0.00000
B (α_2^1)	25.78	1.52	0.00000
C (α_3^1)	30.15	1.52	0.00000
AB (β_{12}^1)	24.63	7.47	0.00530
AC (β_{13}^1)	79.19	7.47	0.00000
BC (β_{23}^1)	-47.22	7.47	0.00002
ABC (γ_{123}^1)	-28.85	52.56	0.59165

Obs.: A – Water; B – isopropanol; C – Acetone; AB, AC, BC and ABC – Synergisms.

Obtained model parameters (water (A); isopropanol (B); acetone (C)) indicate that water is the most important chemical constituent in the reaction mixtures. However, Table 2 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 probably due to the increase of the polarity of the reaction media and to the relatively lower competition by the oxidant species (when compared to isopropanol, as acetone is less susceptible to oxidation process). Thus, the oxidant power of water / acetone media seems to be 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.

Ultra-violet spectroscopy is a very useful tool for characterization of Pani.[14-18] 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.[17-19] The peak placed at higher wavelengths is related to the doping level and formation of polarons.[20] The extent of doping can be estimated from the ratio between the observed absorbance intensity at 750–800 nm (π-polaron) and the observed absorbance intensity at 350 nm (π–π^* transition).[14,16] These data are shown in Table 1 (Column: Edp - B1 / B2). All spectra displayed π–π^* absorption peaks placed at 369 nm and two polaronic bands placed at 450 and 779 nm, confirming the synthesis of Pani.DBSA.[14]

Main effect analysis of obtained ratios between polaronic (B2) and π-π^* (B1) bands was performed with Equation (1) and led to correlation of 0.9863 among calculated and observed data. The results are summarized in Table 3.

Table 3. Main effect analysis for extension of the doping process ($\mathbf{y_2}$).

Factors and Synergisms	Coeff.	Std.Err.	p
A (α_1^2 **)**	1.13	0.03	0.00000
B (α_2^2 **)**	1.29	0.03	0.00000
C (α_3^2 **)**	0.96	0.03	0.00000
AB (β_{12}^2 **)**	0.68	0.14	0.00025
AC (β_{13}^2 **)**	0.77	0.14	0.00008
BC (β_{23}^2 **)**	-3.42	0.14	0.00000
ABC (γ_{123}^2 **)**	-0.04	0.98	0.96979

Obs.: A – Water; B – isopropanol; C – Acetone; AB, AC, BC and ABC – Synergisms.

The most important effect is related to the isopropanol concentration in the reaction medium. Once more, a strong negative synergism is observed between isopropanol and acetone. Obtained results indicate 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 seems to occur in the presence of isopropanol. The observed behavior may be related to the oxidant capability 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, to reduction of the Edp. Therefore, addition of acetone seems to increase the reaction rates, but also seems to cause undesired deleterious effects on the final product properties.

WAXS scattering patterns obtained for all samples were very similar and indicated the existence of several diffraction picks on a large amorphous halo. Crystallinity calculations were performed with the standard Fityk software, which allowed for splitting of the crystalline contribution of the scattering signal, as illustrated in Figure 1.

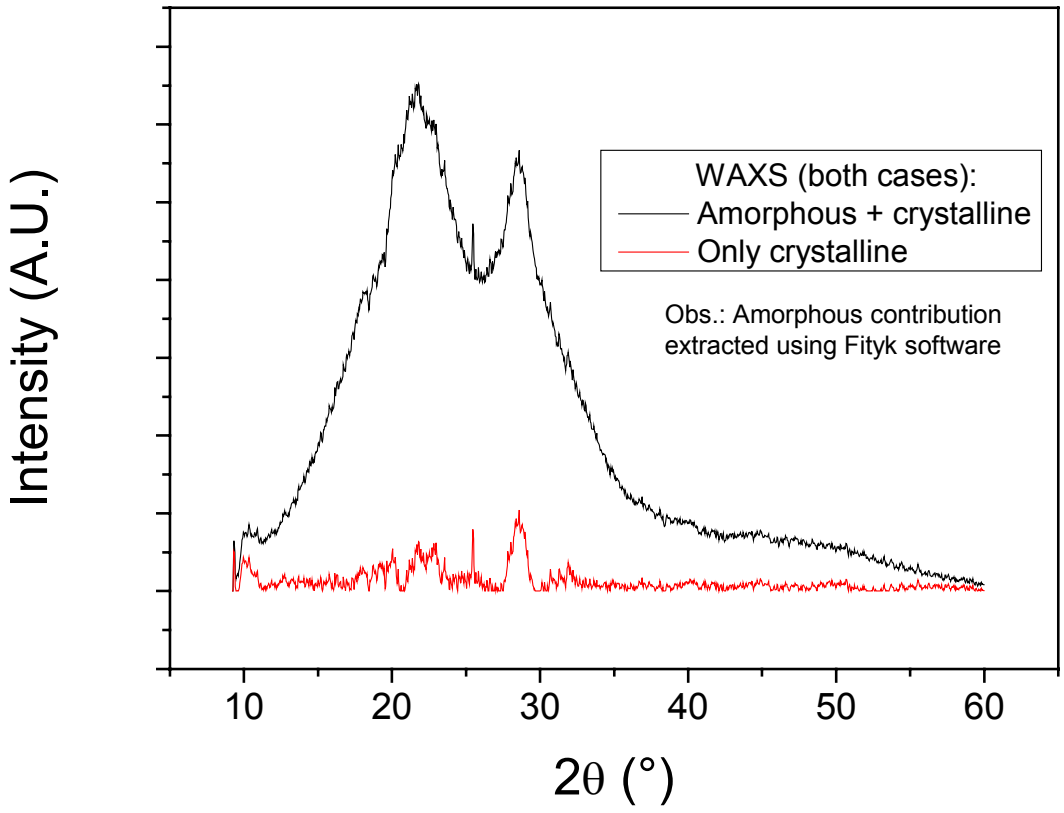

Figure 1. WAXS pattern of Pani.DBSA prepared in acetone.

Crystallinity values are shown in Table 1. 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 4.

Table 4. Main effect analysis for crystallinity values ($\mathbf{y_4}$).

Factors and Synergisms	Coeff.	Std.Err.	P
A (α_1^4)	7.62	0.27	0.00000
B (α_2^4)	6.76	0.27	0.00000
C (α_3^4)	10.66	0.27	0.00000
AB (β_{12}^4)	28.22	1.31	0.00000
AC (β_{13}^4)	7.38	1.31	0.00006
BC (β_{23}^4)	3.02	1.31	0.03643
ABC (γ_{123}^4)	-160.39	9.20	0.00000

Obs.: A – Water; B – isopropanol; C – Acetone; AB, AC, BC and ABC – Synergisms.

The most important observed effect is the synergism between water and isopropanol, which exerts a significant positive effect over crystallinity. As it has been discussed in the literature, lower crystallinity values may lead to lower conductivity responses [21]. These results also indicate that addition of isopropanol may be helpful for production of better structured polyaniline chains, which are characterized by high degrees of crystallinity.

Volume conductivity results are shown in Table 1. Main effect analysis of volume conductivity was performed with Equation (1) and led to correlation of 0.9975 among calculated and observed data. The results are summarized in Table 5 and the response surface is presented in Figure 2.

Table 5. Main effect analysis for conductivity values ($\mathbf{y_3}$).

Factors and Synergisms	Coeff.	Std.Err.	p
A (α_1^3)	0.057	0.001	0.00000
B (α_2^3)	0.018	0.001	0.00000
C (α_3^3)	0.062	0.001	0.00000
AB (β_{12}^3)	0.293	0.006	0.00000
AC (β_{13}^3)	-0.039	0.006	0.00002
BC (β_{23}^3)	-0.140	0.006	0.00000
ABC (γ_{123}^3)	-1.563	0.044	0.00000

Obs.: A – Water; B – isopropanol; C – Acetone; AB, AC, BC and ABC – Synergisms.

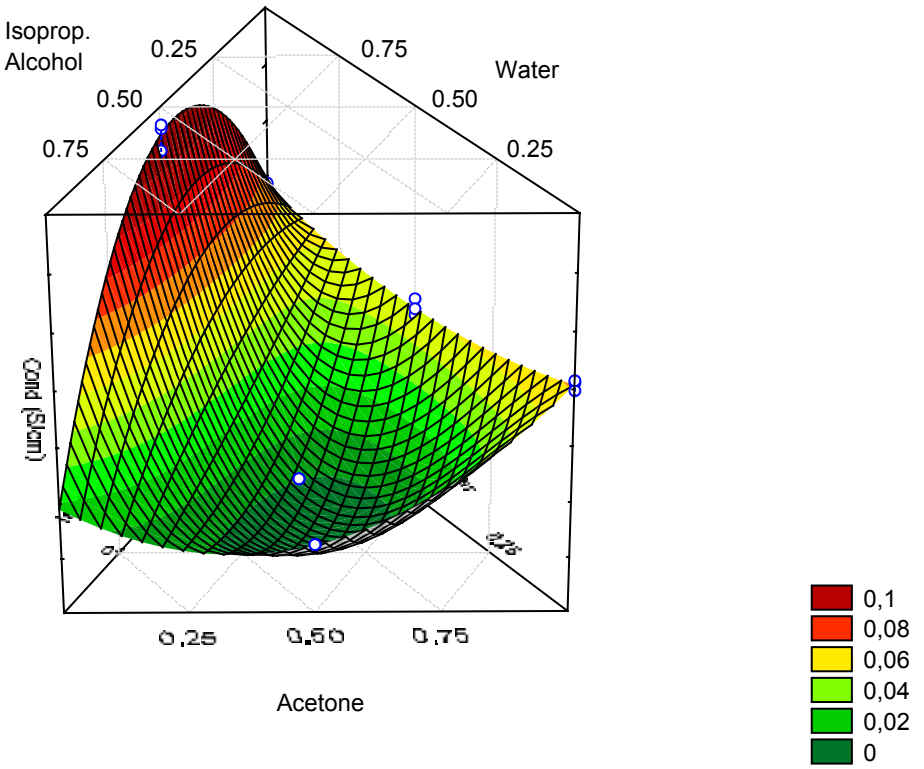

Figure 2. Fitted surface of the volume conductivity (y_3).

The larger positive effect is linked to the interaction between water and isopropanol, showing that it is the better medium to obtain higher conductivity values. On other hand, the larger negative effect was obtained in medium composed by water, isopropilic alcohol and acetone, indicating that it is the worst medium to conductivity. In addition, all synergisms where acetone is present showed negative values, indicating that acetone causes a reduction of electrical conductivity. It is very interesting to observe that, in spite differences, acetone does influence the degree of protonation of Pani chains and the crystallinity, causing the simultaneous and undesired decrease of the Edp, crystallinity degree and of the conductivity of the polymer material.

4 CONCLUSIONS

The main objective of this work, which was to analyze the effect of different media on the electrical conductivity of polyaniline samples prepared through the one-step method, was reached. It was demonstrated that the addition of isopropanol to water can be very beneficial for production of Pani.DBSA materials during the one-step method in water, allowing for reduction of foaming and improvement of the conductivity of the final polymer samples.

Acknowledgements

The authors thank CNPq - Conselho Nacional de Desenvolvimento Científico e Tecnológico for the financial support and the scholarships (CNPq – PDJ - 151616/2006-0). The authors also thank Laboratório Nacional de Luz Síncrotron for the technical support on the SAXS/WAXS (LNLS-D11A-SAXS1 # 5332/06) experiments.

REFERENCES

1 Kancko M, Nakamura H, J. Chem. Soc. Commun. 1985;346.
2 Chen SA, Fang Y, Synthetic Metals 1993; 60: 215.
3 Jelle BJ, Hagen G, J. Electrochem. Soc. 1993;140: 3560.
4 Jelle BJ, Hagen G, Sunde S, Synth Met 1993;54: 315.
5 Grant, L., Guernion, N., Ratcliffe, N. M. and Teare, C.; The surface analyses and responses of highly sensitive polypyrrole sensors. Materials Chemistry Conference; 2001 Bangor, Abstracts, P62.
6 Lee JK, Yoo DS, Handy ES Rubner MF, Applied PhysicsLetters 1996; 69: 1686.
7 Malinauskas A, Polymer 2001;42: 3959.
8 Souza Jr., F. G., Sirelli, L., Michel, R. C., Soares, B. G., Herbst, M. H.; JAPS 2006, 102, 535–541
9 Souza Jr., F. G., Soares, B. G, Mantovani G.L., Manjunath A., Somashekarappa H., Somashekar R. and Siddaramaiah; Polymer 47 (2006) 2163–2171.
10 Souza Jr., F. G., Soares, B. G. and Pinto, J. C.; Macromol. Mater. Eng. 2006, 291, 463–469
11 Malinauskas A, Polymer 2001;42: 3959.
12 Souza, Jr, F. G.; Michel, R. C. and Soares, B. G.; Polymer Testing, 24, 8, 2005: 998
13 ULLMANN'S ELECTRONIC ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY; 6th Edition; 1998.
14 Souza, Jr, F. G. and Soares, B. G.; Polymer Testing, 25, 4, 2006: 512
15 B.G. Soares, G.S. Amorim, F.G. Souza Jr., M.G. Oliveira and J.E. Pereira da Silva, Synth. Met. 156, 2006: 91
16 Z.X. Abdiryim, Z.X. Gang and R. Jamal, Mater. Chem. Phys. 90 (2005), 367.
17 H.S. Xia and Q. Wang, J. Nanoparticle Res. 3, 2001: 401
18 A.J. Epstein, J.M. Ginder, F. Zuo, R.W. Bigelow, H.S. Woo, D.B. Tanner, A.F. Richter, W.S. Huang and A.G. MacDiarmid, Synth. Met. 18, 1987, 303
19 Y. Wei, F.K. Hsuech and G.W. Jang, Macromolecules 27, 1994: 518
20 A.G. MacDiarmid and A.J. Epstein, Synth. Met. 65, 1994: 103
21 Abdiryim, T.; Xiao, G. Z. and Jamal, R.; Materials Chemistry and Physics 90: 2005, 367
22 Z. Bu, S. Koide And D. M. Engelman; Protein Sci. 7, 1998: 2681