

The Influence of Organic Solvents on the Polymerization of Polyaniline.

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Research Article

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ABSTRACT

During the polymerization of aniline in aqueous solution, different organic solvents such as DMF, DMSO and THF were added. The influence of organic solvents on the polymerization of polyaniline on the conductivity and elemental analysis were studied. These study had been investigated using FTIR and UV-Vis spectroscopy, which attest that the usage of organic solvents is helpful for the increase of the doping level of the resulting PANI. The rate of polymerization increased when THF was used as a solvent for polyaniline.

INTRODUCTION

Polyaniline (Fig.1), was first prepared in 1834 by the chemical oxidation of aniline as aniline black and it has been the subject of intensive research ever since [1]. After two decades, the electrochemical synthesis of polyaniline was reported by Ietcheby [2].

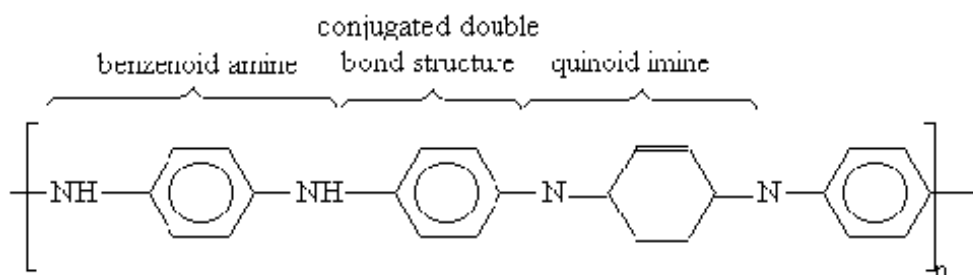


Figure 1: Structural formula of undoped PANI

In 1878 Nietski [3] used aniline black as a dye to color cotton fibers. Oxidative polymerization studies of aniline using mineral acids and oxidants such as persulfate, dichromate, chlorate, and the determination of the oxidation state of each constituent by redox titration using $TiCl_3$ were reported with the advent of conducting polymers, renewed interest was generated in polyaniline and in the 1980s the conductivity properties of polyaniline were recognized and the number of articles dealing with this polymer grew rapidly [1,4-7]. The treatment interest in polyaniline is rooted in its unique chemical structure and properties besides its stability, ease of synthesis and low cost of production which makes it commercially attractive [8-10]. The major disadvantage of polyaniline is its insolubility in common organic solvents and its infusibility. Considerable progress has been made in the last few years in the processibility of conducting polymers by the synthesis of polymer blends and composites [11,12], and soluble polyaniline derivatives and copolymers [13,14]. However, they have been found to be less conductivity than polyaniline even though they are more soluble. We report, in this paper, the influence of organic solvents on the polymerization of polyaniline using tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) as

organic solvents. The effect of these organic solvents on the resulting polyaniline have been investigated using FTIR , UV-Vis spectroscopy, conductivity measurements and elemental analysis.

Reagents

Different materials have been used in this work such as : Aniline (ANI) (ADWIC, Egypt), Ammonium persulfate (APS) (WINLAB, UK), Hydrochloric acid (HCl 32%), tetrahydrofuran (THF) , N,N-dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). All these materials were used as received without further purification.

Characterization

The FTIR spectra were recorded using FTIR- 8201 PC (SHIMADZU) instrument by KBr pellets, and UV-Vis absorption spectra were recorded in spectrophotometer (UV-1601 SHIMADZU). The electrical conductivity was measured at room temperature by using conductivity meter (CM-30V) and The C, H, N analysis was carried out using EA 1110 elemental analyzer.

Procedure

Synthesis of polyaniline

0.47g(0.1M) of aniline was dissolved in hydrochloride solution (1M). Then the organic solvent was dropped into the above solution under stirring. 5 min later, (0.1M) ammonium per sulfate (APS) dissolved in 50ml of hydrochloride solution (1M) was added into the mixture in a dropwise manner to initiate the polymerization of the aniline .The mixture was stirred at room temperature for 8h and the resulting precipitate was collected by filtration. After the product was washed by distilled water and ethanol continuously, the product was dried under vacuum at room temperature for 48h. The addition of different volumes of organic solvent to poly aniline is show in the Table ^[4]

sample	Aniline(M)	Aps (M)	Org. solvent	HCL (ml)	conductivity
1	0.1	0.1	No solvent	50	0.026 S/m
2	0.1	0.1	DMF , 1ml	49	0.025S/m
3	0.1	0.1	DMF , 4ml	46	0.026 S/m
4	0.1	0.1	DMF , 8ml	42	0.020 S/m
5	0.1	0.1	DMF , 10ml	40	0.014 S/m
6	0.1	0.1	DMSO , 1ml	49	0.019 S/m
7	0.1	0.1	DMSO , 4ml	46	0.020 S/m
8	0.1	0.1	DMSO , 8ml	42	0.015 S/m
9	0.1	0.1	DMSO,10ml	40	0.013 S/m
10	0.1	0.1	THF , 1ml	49	0.012 S/m
11	0.1	0.1	THF , 5ml	45	0.015 S/m
12	0.1	0.1	THF , 8ml	42	0.012 S/m
13	0.1	.01	THF , 10 ml	40	0.014 S/m

Table 1: The addition of different volumes of organic solvents to polyaniline

FTIR spectra of the addition of organic solvents in PANI

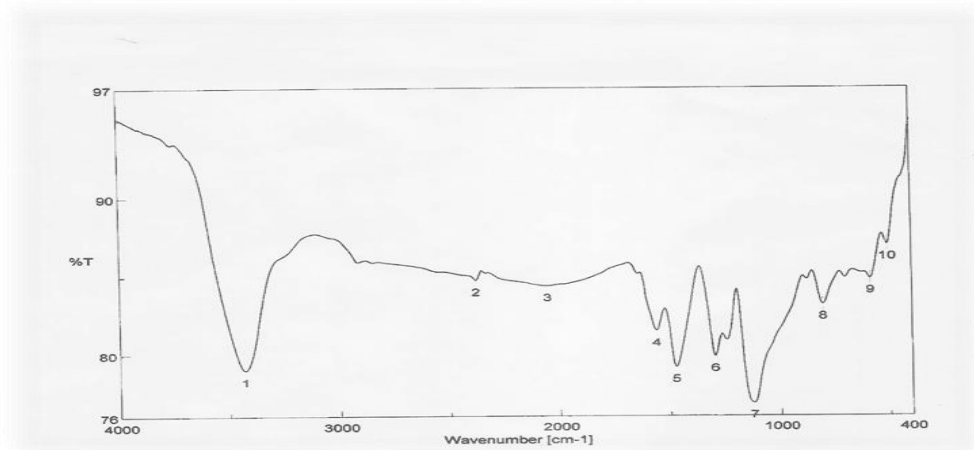


Figure 2: FTIR spectra of PANI obtained at no solvent.

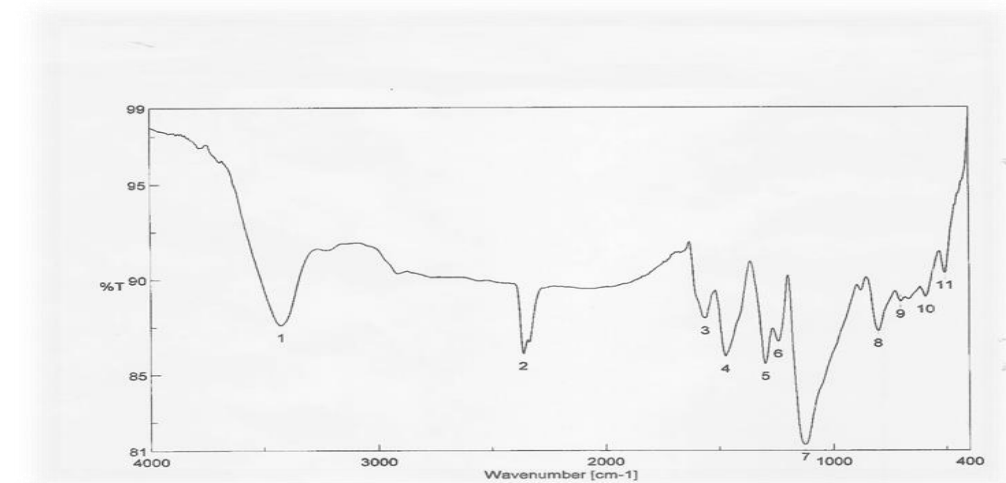


Figure 3: FTIR spectra of PANI obtained at 8 ml DMF

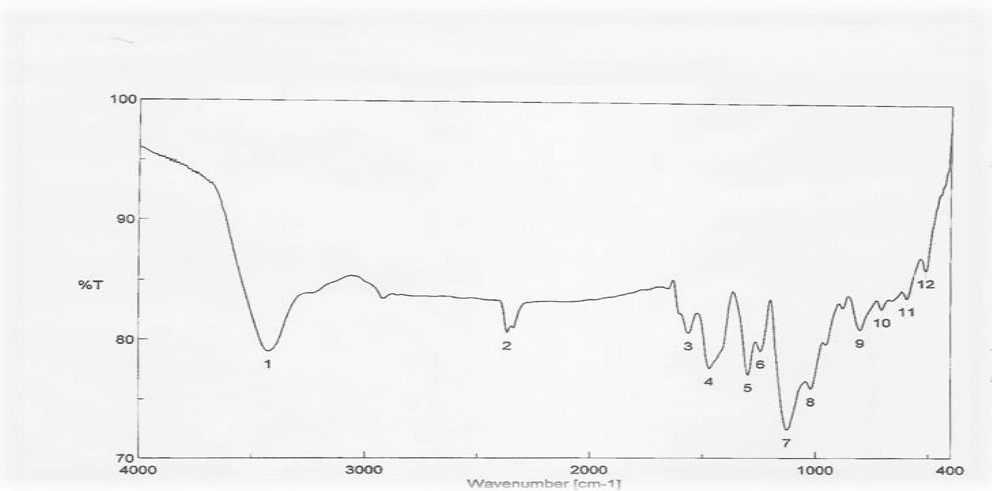


Figure 4: FTIR spectra of PANI obtained at 8 ml DMSO

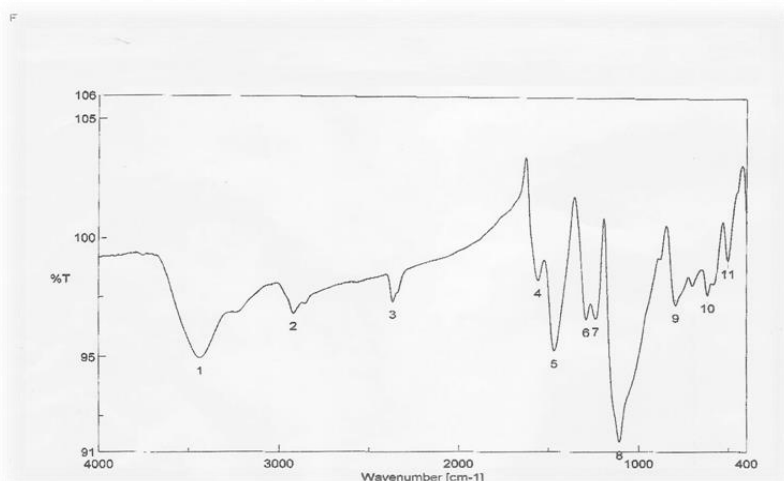


Figure 5: FTIR spectra of PANI obtained at 8 ml THF

Figs (3-5) show FTIR spectra of PANI obtained by the addition of 8 ml of DMF, DMSO and THF respectively. The spectra at 1561 cm^{-1} are assigned to C=C stretching of the quinoid and benzenoidrings respectively. The spectra observed at 1294 cm^{-1} is related to the C-N stretching vibration of the benzenoidring. The band which fall in 800 cm^{-1} is identified with the out-of-plane bending of C-H bond in the 1,4-disubstitued ring. The peak at 1111 cm^{-1} represents the C-H aromatic in-plane bending and is often related to the doped structure. One can find the peak at 1111 cm^{-1} red shifted to about 1021 cm^{-1} when 8ml of DMSO are added into the system. However, excess addition of the organic solvents led the peak to the wave number as that of the PANI obtained by conventional method, this means that appropriate usage of organic solvents is helpful for the increase of the doping level of the resulting PANI.

UV-Vis spectra of the addition of organic solvents in PANI : A typical absorption peaks at 320 nm and 604 nm respectively are shown in Fig.6.

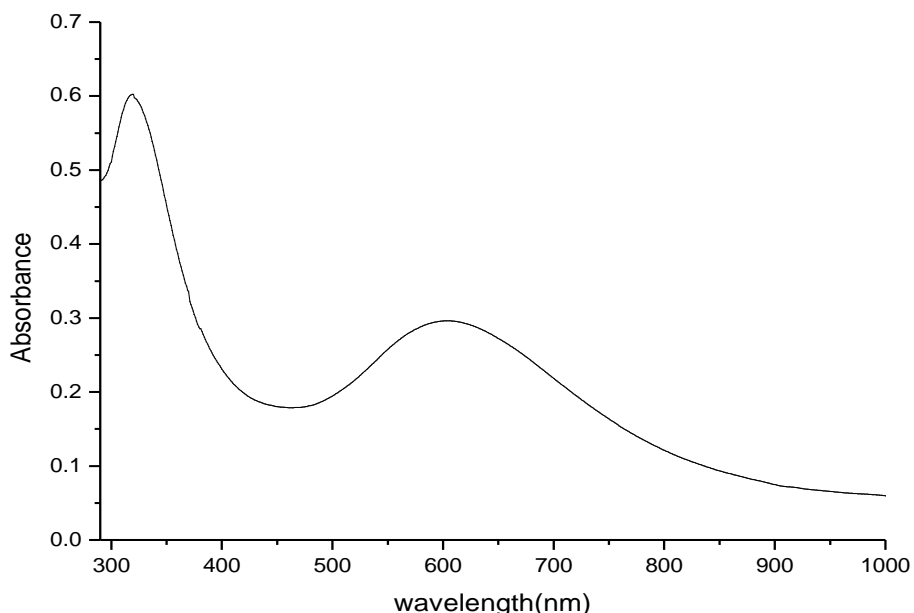


Figure 6: Uv-Vis- spectra of PANI obtained at no solvent

The peak at 320 nm arises from the $\pi-\pi^*$ electron transition within benzenoid segments and the peak at 604nm is related to the doping level and formation of polaron. The UV-Vis. Spectra of PANI obtained by the addition of different volumes of DMF, DMSO and THF are represented in Figs (7-9).

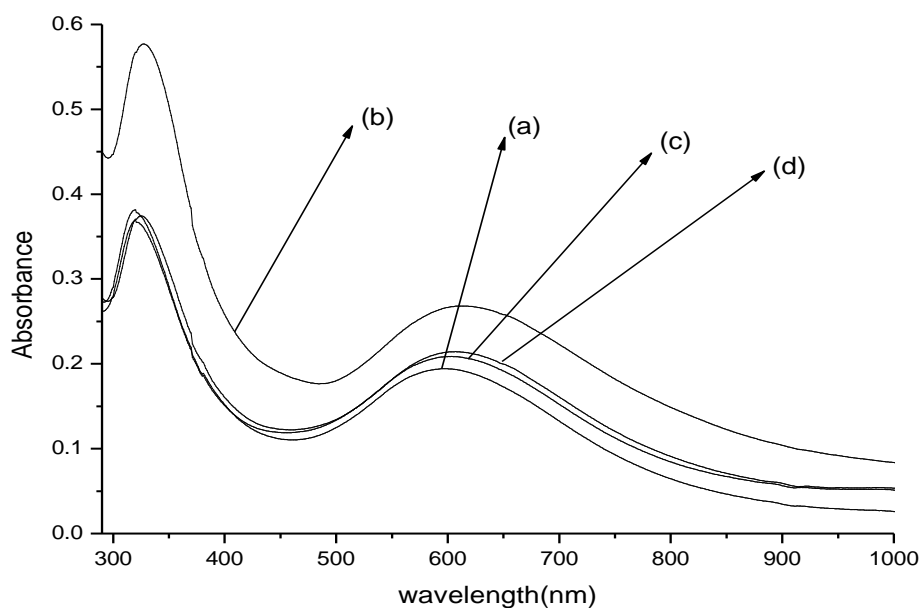


Figure 7: Uv-Vis- Spectra of PANI obtained from different solvent of DMF

(a . 1 ml , b . 4 ml , c . 8 ml , d . 10 ml)

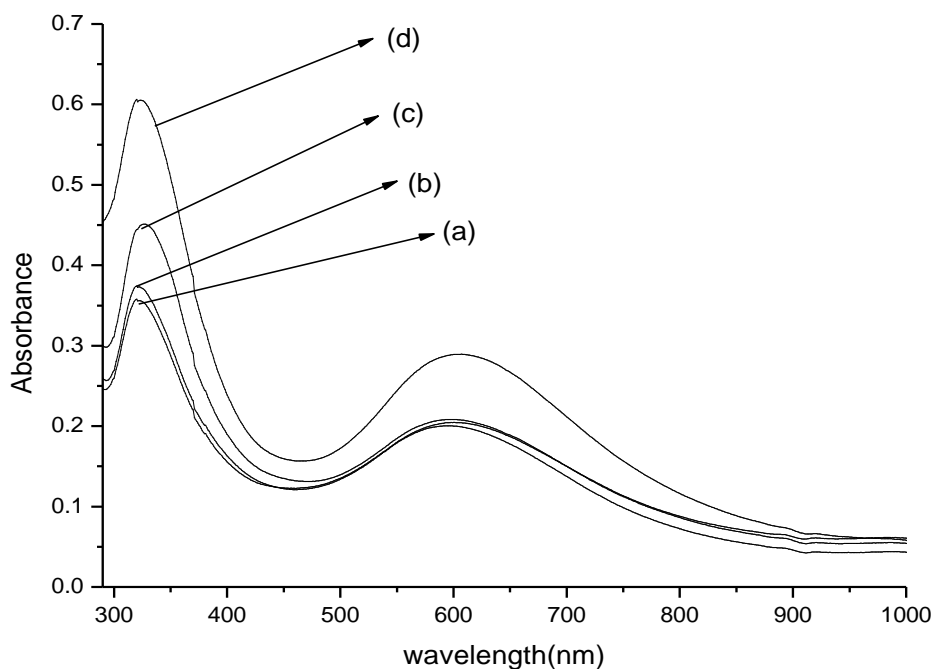


Figure 8: Uv-Vis- Spectra of PANI obtained from different solvent of DMSO

(a . 1 ml , b . 4 ml , c . 8 ml , d . 10 ml)

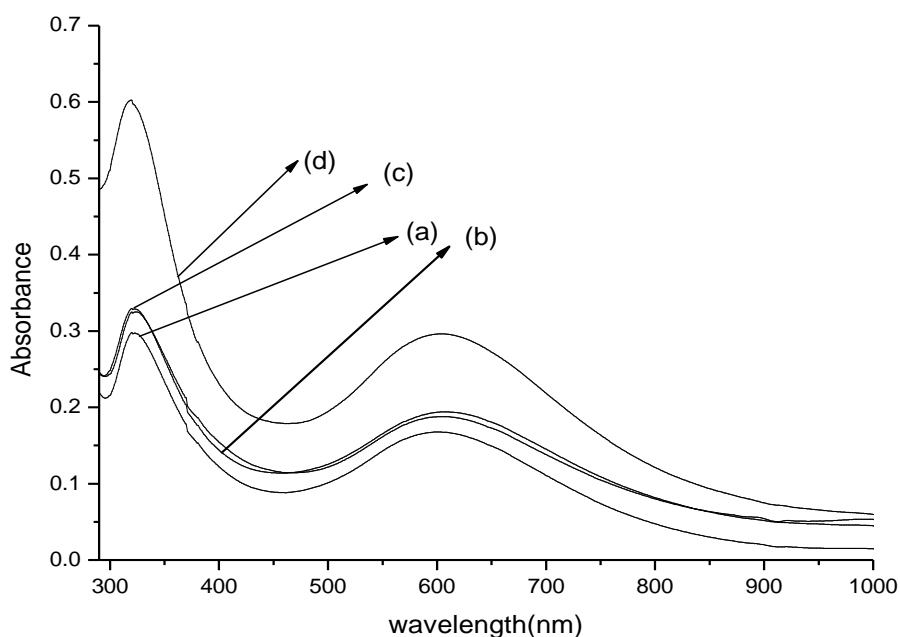


Fig.9.Uv-Vis- spectra of PANI obtained from different solvent of THF

(a . 1 ml , b . 5 ml , c . 8 ml , d . 10 ml)

Figs. (7 -9) are Based on the quantitative analysis of the UV-vis absorption of the samples, We found the dispersity of the PANI synthesized in the presence of 1ml DMF , DMSO and THF in Figs (7a) , 8(a) and 9a) at absorption peaks at 320,604- 324,607- 327,605 respectively. Which is bit better than that the sample without addition of organic solvent Fig.6. Addition of THF to the reaction system resulted in worst dispersity of the corresponding PANI. This may be originating from the fact the more uniform the PANI is, the better dispersity it has. On the other hand, THF has the strongest interaction with PANI among the other solvents. When for example the volumes of THF were changed, we found addition of 5, 8 and 10ml of THF all resulted in poor dispersity of PANI in water. We think appropriate usage of THF is helpful for the dispersity of PANI in water because THF has weak H-bond interaction with PANI and it can be partly dissolved in water. However, when more THF is added into the reaction system the interaction between THF and PANI becomes stronger.

Conductivity Measurements

The conductivity of the samples lies in two aspect: microscopic and macroscopic conductivity. The microscopic conductivity depends on the doping level, conjugation length and chain length, whereas the macroscopic conductivity is related to some external factors, such as the compactness of the samples ^[15].

From Table ^[2], the conclusion can be confirmed the samples synthesized in the presence of 1 ml of THF, DMSO and DMF show relatively high conductivity values of 0.012, 0.019 and 0.025 S/m, respectively while the conductivity of the system without organic solvent is 0.026 S/m. Also we observed the excess addition of solvents to the reaction solution lead to decrease the values of the conductivity. On the contrary he interaction between THF and water is weakened , a poor water -dispersity is obtained in that case .

Elemental Analysis:

The elemental analysis was carried out in order to know the composition of the polymer. Table ^[3] shows the values of elemental composition of polyaniline which were prepared using different volumes of solvents. The contents of C, N, and H of polyaniline with different volumes of THF are relatively higher than

that of polyaniline prepared without solvent and with other solvents, which could be attributed to a higher rate of polymerization when THF was used as solvent.

Table [2] Absorption maxima and conductivity of addition of organic solvents in PANI

sample	Org. solvent	HCL (ml)	conductivity
1	No solvent	50	0.026 S/m
2	DMF , 1 ml	49	0.025 S/m
3	DMF , 4 ml	46	0.026 S/m
4	DMF , 8 ml	42	0.020 S/m
5	DMF , 10 ml	40	0.014 S/m
6	DMSO , 1 ml	49	0.019 S/m
7	DMSO , 4 ml	46	0.020 S/m
8	DMSO , 8 ml	42	0.015 S/m
9	DMSO , 10 ml	40	0.013 S/m
10	THF , 1ml	49	0.012 S/m
11	THF , 5ml	45	0.015 S/m
12	THF , 8 ml	42	0.012 S/m
13	THF , 10 ml	40	0.014 S/m

Table [3] Elemental composition of addition of organic solvents in PANI.

Sample	Org.Solvent	C %		H %		N %		S %
		Found	Cal.	Found	Cal.	Found	Cal.	Found
1	No solvent	49.65	66.06	5.89	4.85	9.77	12.84	2.71
2	DMF, 1ml	47.76	66.06	5.76	4.85	9.63	12.84	3.11
3	DMF, 4ml	49.26	66.06	7.63	4.85	9.29	12.84	4.72
4	DMF, 8ml	32.18	66.06	4.37	4.85	5.67	12.84	10.27
5	DMF, 10 ml	27.12	66.06	4.88	4.85	4.23	12.84	11.33
6	DMSO, 1ml	49.60	66.06	5.70	4.85	10.12	12.84	2.81
7	DMSO, 4ml	33.33	66.06	6.15	4.85	8.53	12.84	3.19
8	DMSO, 8ml	43.26	66.06	6.56	4.85	9.95	12.84	3.02
9	DMSO, 10ml	47.27	66.06	5.56	4.85	10.04	12.84	2.86
10	THF, 1ml	53.01	66.06	6.55	4.85	10.24	12.84	1.86
11	THF, 4ml	52.07	66.06	4.79	4.85	10.32	12.84	2.79
12	THF, 8ml	53.90	66.06	9.51	4.85	10.53	12.84	1.95
13	THF, 10ml	43.42	66.06	6.66	4.85	10.38	12.84	2.22

CONCLUSION

Different kinds of organic solvents such as DMSO, DMF and THF were added into the reaction systems during the polymerization of aniline in aqueous solution. The excess addition of solvents to the reaction solution leads to decrease the values of the conductivity. The contents of C, N and H of polyaniline with different volumes of THF are relatively higher than that of PANI without solvent and with other solvents, which could be attributed to a higher rate of polymerization when THF was used as solvent. The FTIR spectra certify that the usage of organic solvents is helpful for the increase of the doping level of the resulting PANI, and the UV-Vis spectra indicate that the more THF is added into the reaction system, the

interaction between THF and PANI becomes stronger. We conclude that THF is the best solvent for PANI among the other solvents, but in general the solubility of PANI can be modified by substitution one or more hydrogens by an alkyl, an alkoxy, an aryl hydroxyl, an amino group, or halogen in an aniline nucleus [16-19].

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