

Electrochemical polymerization and Optical Vibrations of Polyaniline Films

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Abstract: Polyaniline films were electrochemically synthesized of aniline in a two-electrode cell. It was observed that the doping influences the color of PANI thin films, which passes from blue to dark green color. Characterizations were made using FT-IR (Fourier transform spectroscopy) and a group theory analysis. A complete assignment of the fundamental infrared modes ($400\text{-}4000\text{ cm}^{-1}$) of polymer is proposed. Experimental spectra were compared with that calculated by AM1, PM3, RM1, and MNDO. Results indicated that, for aniline, bianiline, and polyaniline, PM3 and RM1 calculated frequencies are in good agreement with experimental data. The geometry and vibrational calculations of four-ring unit (emeraldine base, EB) are believed to be a good representation of polyaniline.

Keywords: Polyaniline, Electro-Polymerization, Vibrational modes, Infrared Spectroscopy.

I. INTRODUCTION

Electrochemical Polymerization is one of the excellent methods to synthesize conducting polymers because their area and thickness can be controlled. Polypyrrole (PPP), Polythiophene (PT) and Polyaniline (PANi) all contain conjugating (π) electron system i.e. they are members of the same class of polymers, and have been intensively studied from both experimental [1-5] and theoretical [6-8] points of view. Polyaniline is one of the most potentially conducting polymers, due to its easy synthesis, high conductivity, and unique redox properties [9-12]. PANi has attracted attention due to its stability in air in the oxidized state, which can be reversibly doped in aqueous medium from a semi conducting state ($\sigma \approx 10^{-8}\ \Omega^{-1}\text{cm}^{-1}$) to a conducting state ($\sigma \approx 10^2\ \Omega^{-1}\text{cm}^{-1}$) [13]. Conducting polyaniline, on account of its excellent optical and electronic properties is promising in many fields, in electronics. During the last years, conducting polymers have conjured great interest in the world of research due to their various physical, chemical properties and their numerous possible applications [14]. Conducting polymer PANi attracted much attention because of its physical and chemical characteristics which make it interesting material for applications in different areas such as Light-weight batteries [15-18], capacitors [19], electrochromic devices [20, 21], photoelectric cell [22, 23], light emitting diodes [24], biosensors [25], sensors [26], switchable membranes [27], anti-corrosive coatings on metals [28].

The microstructure of conductive PANi can vary greatly with the preparing methods and processing conditions. Sazon et al reported polyaniline coating on stainless steel by potentiodynamic and potentiostatic deposition [29]. Zhang et al prepared a series of polyaniline/Carbon nanotube array composite electrodes by cyclic voltammetry electrode position, to improve the capacitive performance of PANi/CNTA Composites [30]. Wu et al recently studied the PANi counter electrode coated on conductive glasses using a chemical synthesis method [31].

The present work is conducted to study the polymerization of aniline by electrochemical method and using attenuated absorption Fourier-transform infrared spectroscopy. The experimental spectra are compared with calculated frequencies spectra using (hyperchem 8 packages)

II. EXPERIMENTAL

An amount of 0.1 and $5 \times 10^{-2}\text{M}$ aniline were added to 0.1M of electrolytic medium consisted of Lithium tetrafluoroborate and acetonitrile, the mixture was placed and stirred in a cell (All chemicals and materials were

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obtained from Sigma-Aldrich chemical Co.). The solution was degassed by argon bubbling; because the presence of oxygen affects the quality of the prepared conducting polymers. The polymer thin films formed on gold electrode, but other electrode materials such as Pt, SnO₂, In₂O₃ are also suitable for this purpose, when the potential value > 4v the current increases sharply, and stabilized after about three minutes. The Au surface was then covered by a blue, highly adhesive deposit, it's high conductivity allowed a fast growth of the film of many μm thickness. The color of the solution was observed during reaction, it was opaque blue at the beginning and it became dark green and viscous at the end of the reaction. The thickness of films can be easily controlled by the Polymerization time as reported in our previous paper [32].

The electrochemical dedoping is carried out by shortening the external circuit of the electrolysis cell to obtain a neutral PANi films, the resulting film contained some traces of dopant. A compensation treatment was needed by immersing it in methanol for about 48 hours followed by drying in vacuum. These procedures resulted in an extremely low conductivity PANi Film less than 10⁻⁹ Ω⁻¹cm⁻¹ [33]. This film can be easily doped again by either chemical or electrochemical means, by exposing the film to iodine or bromine gas, and applying appropriate voltage across the electrodes of the electrolytic cell which was then rinsed in acetone to compensate trace amount of dopant. The conductivity of conductive PANi thin films was measured using the standard four-probe technique; the measured conductivity of our films was about 10 Ω⁻¹cm⁻¹. We have also obtained a dark green powder of PANi in the viscous solution, to extract a powder sample we wetted a glass substrate with some of the resulting solution. The solution was let to settle for 24 hours at room temperature and then dried at 60 °C for 10 hours; the powder was then peeled out the glass substrate.

III. GROUP THEORY ANALYSIS

This part presents the calculation of number of modes of chain vibrations for the monomer and polymer. The general formula for Aniline and calculated structure is shown in fig.1.

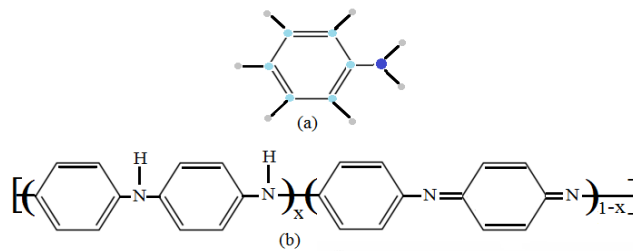


Fig. 1 General Formulas for both aniline (a), and the conductive polyaniline (emeraldine form (b))

The application of group theory to monomer presents C_{2v} symmetry, the calculation shows that we have 32 modes of vibrations, which are active in both I.R and Raman and 4 modes are Raman active as seen from eqs.1 & 2 respectively

$$\Gamma_{1\text{vibration}} = 13A_1 + 7A_2 + 4B_1 + 12B_2 \quad (1)$$

$$\Gamma_{2\text{vibration}} = 4B_1 \quad (2)$$

The 36 modes of vibrations of aniline consist of: five Stretching modes (ν_{C-H}) situated around 3050 to 3078 cm⁻¹, five deformation modes (δ_{C-H}) in plane situated around 1300cm⁻¹, and five bending modes out of plane (γ_{C-H}) situated around 700 to 1000 cm⁻¹. We also have two stretching modes (ν_{N-H}) situated around 3250 to 3300 cm⁻¹, two deformation modes in plane (δ_{N-H}) situated around 1650 to 1580 cm⁻¹, and two deformation modes out of plane (γ_{N-H}) situated around 660 to 900 cm⁻¹. For the vibration of C-N, we have one mode stretch (ν_{C-N}) situated around 1335 to 1250 cm⁻¹, One mode of bending (δ_{C-N}) situated around 1000 cm⁻¹, One mode of deformation out of plane (γ_{C-H}) situated around 500 cm⁻¹. There are also 12 modes of ring vibrations that consist of four Stretching modes, four bending and four out of plane vibration modes.

The polymerization of aniline monomer can be found in one of three idealized oxidation states: Leucoemeraldine-white clear, emeraldine-green or blue, pernigraniline-blue/violet. These three types are different in the degree and nature of

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polymerization. The emeraldine form of PANi is the most symmetric. Emeraldine base (EB) is also regarded as the most useful form of PANi due to its high stability and good electrical conductivity.

The bianiline form presents C_{2v} symmetry also; the calculations show that we have 61 modes of vibrations that are active in both I.R and Raman as given in eq.3, while 11 modes are Raman active as given in eq.4.

$$\Gamma_{1\text{vibration}} = 25A_1 + 24B_2 + 12A_2 \quad (3)$$

$$\Gamma_{2\text{vibration}} = 11B_1 \quad (4)$$

The PANi backbone was assumed to be planar for the calculations, and have C_s point group symmetry as shown in Fig.1b. The empirical formula for our polymer is $C_{24}H_{20}N_4$, there are 138 calculated genuine internal vibrations spanning the irreducible representations as seen in eq.5, and all fundamentals are active in both IR and Raman spectra.

$$\Gamma_{1\text{vibration}} = 93\dot{A} + 45\ddot{A} \quad (5)$$

TABLE 1
COMPARISON OF THE EXPERIMENTAL WAVE NUMBER (cm^{-1}) OF MODES IN RAMAN AND FT-IR SPECTRA AND THEORETICAL HARMONIC FREQUENCIES, F (cm^{-1}) WITH CALCULATED EIGEN VALUES OF VIBRATIONS USING RM1 METHOD/FORCE FOR ANILINE

No	Fr	Expt	Fr ^a	Expt ^b	Expt ^c	Sym	Assignment
1	95		217	217 ^d	179 ^e	1B1	ν_{C-N}
2	386		289	277 ^f		1A2	ν_R
3	427		377	390 ^g	386	1B2	δ_{C-N}
4	466		410	415 ^g		2B1	ν_R
5	524		489	501 ^g	442	2A2	ν_{N-H}
6	525		525	526 ^g	519	3B1	ν_{N-H}
7	547		541	541 ^h	652	1A1	δ_R
8	623		626	619 ^g	582 ^f	4B1	ν_R
9	637		689	688	622	2B2	ν_{C-H}
10	800	791	752	755	785	5B1	ν_{C-H}
11	861	825	816	812		3A2	ν_{C-H}
12	897	850	819	822	814 ^f	2A1	δ_R
13	923	881	873	875	913	6B1	ν_R
14	986	995	951	957 ^g		4A2	ν_{C-H}
15	1016		966	958 ^g		7B1	ν_{C-H}
16	1079		996	996	982 ^f	3A1	δ_{C-H}
17	1116	1026	1031	1028	993	3B2	δ_{N-H}
18	1134	1057	1043	1054 ^g		4A1	δ_R Breathing
19	1169	1127	1115	1115 ^g	1107	4B2	δ_{C-H}
20	1198	1153	1163	1152 ^g	1171	5B2	δ_{C-H}
21	1248	1175	1183	1176	1188 ^f	5A1	δ_{C-H}
22	1252	1277	1280	1272	1385 ^f	6B2	δ_R
23	1313	1312	1323	1324 ^g	1360	7B2	δ_{C-H}
24	1444	1335	1349	1340 ^g	1351	6A1	ν_R
25	1507	1499	1508	1503	1434	8B2	ν_R
26	1595	1601	1599	1594	1483	7A1	δ_{N-H}
27	1666	1620	1617	1608	1594 ^f	8A1	δ_R
28	1705					9B2	ν_R
29	1805					9A1	ν_{C-N}
30	3053	3010	3021	3025 ^g		10A1	ν_{C-H}
31	3057		3022			10B2	ν_{C-H}
32	3064	3036	3038	3037 ^g		11A1	ν_{C-H}
33	3069	3096	3044	3050 ^g	3076	11B2	ν_{C-H}
34	3078	3071	3060	3072 ^g	3080	12A1	ν_{C-H}
35	3277	3352	3430	3422 ⁱ	3391	13A1	ν_{N-H}
36	3308	3428	3526	3508 ⁱ	3488 ⁱ	12B2	ν_{N-H}

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^aTheoretical harmonic frequencies calculated by the B3LYP(UB3LYP) method for aniline from Ref. [34], ^bExperimental wave number Ref. [35],^c Experimental wave number Ref. [36], ^d Experimental wave number Ref. [37], ^e Experimental wave number Ref. [38], ^f Experimental wave number Ref. [39], ^g Experimental wave number Ref. [40], ^h Experimental wave number Ref. [41], ⁱ Experimental wave number Ref. [42].

TABLE 2
CALCULATED EIGENVALUES OF VIBRATIONS MODES IN RAMAN AND FT-IR SPECTRA USING PM3, RM1, MNDO AND AM1 METHODS/FORCE FOR BIANILINE, FREQUENCIES (cm⁻¹).

PM3	RM1	MNDO	AM1	Sym	Assignment
342	370	258	255	4A2	Y _{Ring}
343	381	326	327	4B1	Y _{Ring}
467	470	454	487	3A1	δ _{Ring}
502	511	495	529	2B2	δ _{Ring}
	556	635	627	6A2	Y _{N-H}
676				6A2	Y _{C-N}
772				7B1	Y _{C-N}
	792	703	728	7B1	Y _{N-H}
787.8	793	702	721	8A2	Y _{N-H}
788	802	792	807	8B1	Y _{C-H}
	913	889		10A2	Y _{C-H}
855			850	10A2	Y _{N-H}
923	982	973	887	11A2	Y _{C-H}
1021	1028	1072	1079	6B2	δ _{C-H}
1071	1046	1113	1121	7B2	υ _{C-C}
	1191	1238	1203	9A1	υ _{C-C}
1136				9A1	υ _{C-C}
1143	1242	1268	1213	10B2	Breathing
1426	1362	1449	1425	13A1	C-C inter chain
1571	1532	1699	1669	14B2	δ _{N-H}
1765	1708	1794	1804	17A1	υ _{C=C}
1827	1754	1838	1854	18A1	υ _{C=C}
3176	3041	3477	3315	19B2	υ _{C-H}
3194	3063	3487	3328	23A1	υ _{C-H}
3263	3256	3493	3332	24A1	υ _{N-H}
	3288	3509	3327	22B2	υ _{N-H}
3263				23B2	υ _{N-H}

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TABLE 3
CALCULATED EIGENVALUES OF VIBRATIONS MODES IN RAMAN AND FT-IR SPECTRA USING PM3, RM1, MNDO AND AM1 METHODS/FORCE FOR POLYANILINE, FREQUENCIES (cm⁻¹).

PM3	RM1	MNDO	AM1	EXP	Assignment
3331	3278	3516	3365	3400(3370)	ν_{N-H} Ring 4
3247	3272	3540	3359		ν_{N-H} Ring 3
3200	3070	3493	3334		ν_{C-H} Ring 1
3199	3076	3484	3340		ν_{C-H} Ring 2
3189	3068	3487	3333		ν_{C-H} Ring 3
3176	3064	3487	3338		ν_{C-H} Ring 4
3171	3025	3359	3148		ν_{C-H} Ring 1,2,3
3125	3009	3334		3062(3050)	ν_{C-H} Ring 1,2,3,4
1770	1674	1762	1802	1600	$\nu_{C=N}$ Ring 1,2
1723	1705	1825(1822)	1833	1660	$\nu_{C=N}$ Ring 1,2
1678	1534	1724	1764		$\nu_{C=N}$ Ring 3
1497	1443	1537	1525		ν_{C-N} Ring 1,2
1473	1425		1636		ν_{C-N} Ring 3
1445	1398	1544	1488	1340	ν_{C-N} Ring 1,2
1307	1318	1398	1384	1296	ν_{C-N} Ring 1
1312	1241	1256	1282	1239	ν_{C-N} Ring 4
789	723	723	770		γ_{C-N} Ring 1,2,3,4
1185	1171	1262	1282	1120	δ_{C-H} Ring 4
1150	1210	1230			δ_{C-H} Ring 1,2
972	814	779	728	744	γ_{C-H} Ring 1
949	883	1009	923		γ_{C-H} Ring 2
903	905	955	885		γ_{C-H} Ring 3
921	862	986	901		γ_{C-H} Ring 4
836	844	849	905		δ_{N-H} Ring 3
490	493	431	562		γ_{N-H} Ring 3
633	504	603	628		γ_{N-H} Ring 4
1036	1013	1050	1092	1037	Breathing Ring 1
948	981	1015	1057	1024	Breathing Ring 2,3,4
947	972	1014	1043		Breathing Ring 4,3,2
1625	1592	1750	1728	1500	$\nu_{C=C}$ Ring 4
1615	1540	1632	1656		$\nu_{C=C}$ Ring 1

IV. RESULTS AND DISCUSSION

To study the I.R spectra of both aniline and polyaniline, we need precise assignment of vibrational modes. This is achieved by a comparison of the band positions and intensities observed in I.R spectra with frequencies and intensities from the calculations of the molecular model used in our study of aniline. For this purpose, the hyperchem 8 package employed for theoretical calculations of the vibration modes active in I.R and Raman, this program uses the semi-empirical (RM1, PM3, MNDO, AM1) methods for electronic molecular structure modeling. These calculations were performed in order to determine the vibrational and rotational eigenvalues of aniline, bianiline and polyaniline. These calculated values were used to interpret the experimentally obtained of I.R absorption bands. Some frequencies of these modes are listed in tables 1, 2 and 3.

The FTIR spectrum of aniline is shown in fig.3 it shows the presence of C-NH₂ stretching vibrations at 3352 and 3428 cm⁻¹ [34]. The C-H stretching vibrations of benzene derivatives generally appear above 3000 cm⁻¹. In our I.R Spectrum of the titled compound, the bands at 3071, 3096, 3036, and 3010 cm⁻¹ are assigned as C-H stretching vibrations [43-45]. From the above discussion, this is clear that experimental and theoretical C-H stretching vibrations are nearly in agreement with each other. The three bands the main one at 995 cm⁻¹, and the two weak ones at 791 and 725 cm⁻¹ in fig.3 are C-H out of plane-bending modes [34-36]. The in-plane bending vibrations modes are situated at 1127, 1153,

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1175 and 1312 cm^{-1} [34-36], [42, 46, 47]. For the stretching vibrations of N-H in aniline, we have the bands at 3352 and 3428 cm^{-1} [34-36, 42]. The package of bands 1693, 1776, 1800, 1933, 2380, 2653 and 2785 cm^{-1} came from overtone combinations [45]. The ring carbon-carbon stretching vibrations occur at 1620, 1601 and 1466 cm^{-1} and assigned to C-C stretching vibrations. Our data shows good agreement with Varsanyi [48].

A close examination of fig.4a, b reveals that the spectra contain all the main characteristics of polyaniline bands i.e. the vibration frequencies of the broad band at 3400 cm^{-1} fig.4a is attributed to the characteristic free N-H stretching vibration which indicates the presence of secondary amino groups (-NH-) [49]. The weak bands at 2924 and 3036 cm^{-1} arise from the aromatic C-H stretching vibrations. The spectrum also exhibits main bands at 1500 and 1567 cm^{-1} corresponding to the benzenoid (C=N) and quinoid (C=C) rings stretching frequencies respectively [50-53, 47]. These bands are very weak in the case of polyaniline powder as shown in figure 4b. The absorption band at 1293 cm^{-1} fig.4a is related to C-N stretching vibration of secondary aromatic amine [54-56], this band shifted to 1288 cm^{-1} as shown in fig.4b. The band, which appeared at 1161 cm^{-1} in fig. 4a is assigned to the rings 1, 2, 3, 4 of PANI film [53]. In the case of Polyaniline powder, this band disappeared as shown in fig.4b. The 1120 cm^{-1} band can be assigned to the vibration of C-H mode, which is attributed to protonation [57-62], the broadness of this peak is owing to the high degree of electron delocalization [63], which is expected because of the greater degree of oxidation. The two bands at 1037 and 952 cm^{-1} represent the aromatic ring deformation and quinoid ring plane deformation respectively [64]. The C-H out of plane bending vibration band of 1, 4- distributed benzene rings appears at 744 cm^{-1} [65].

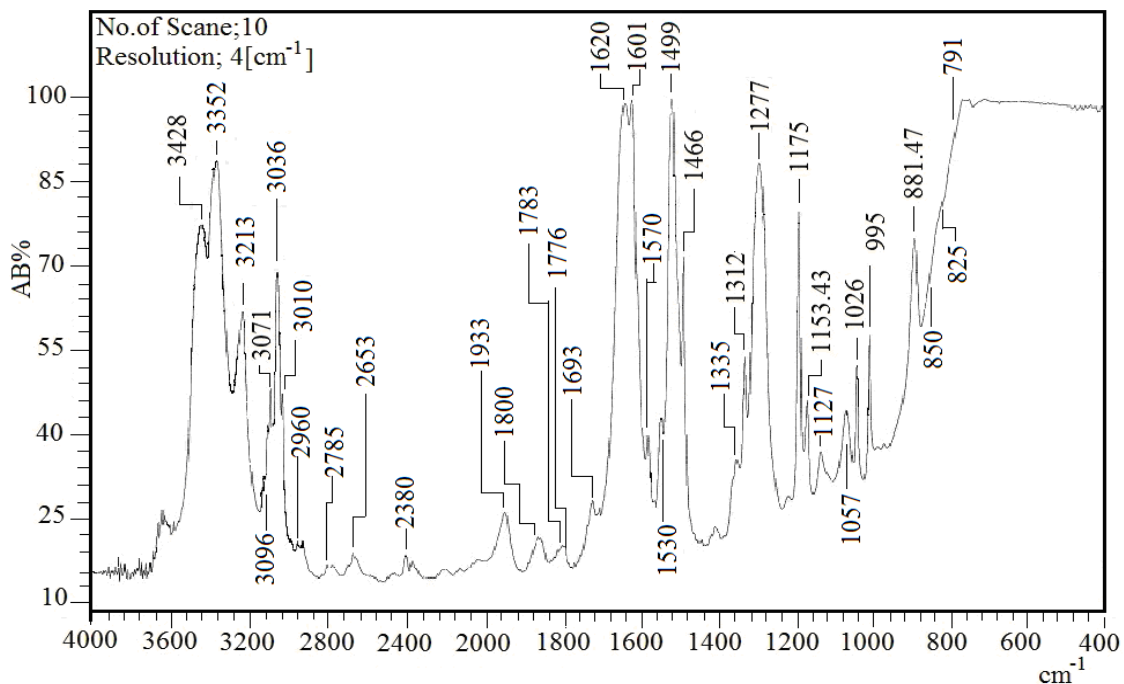


Fig.2 FTIR of Aniline

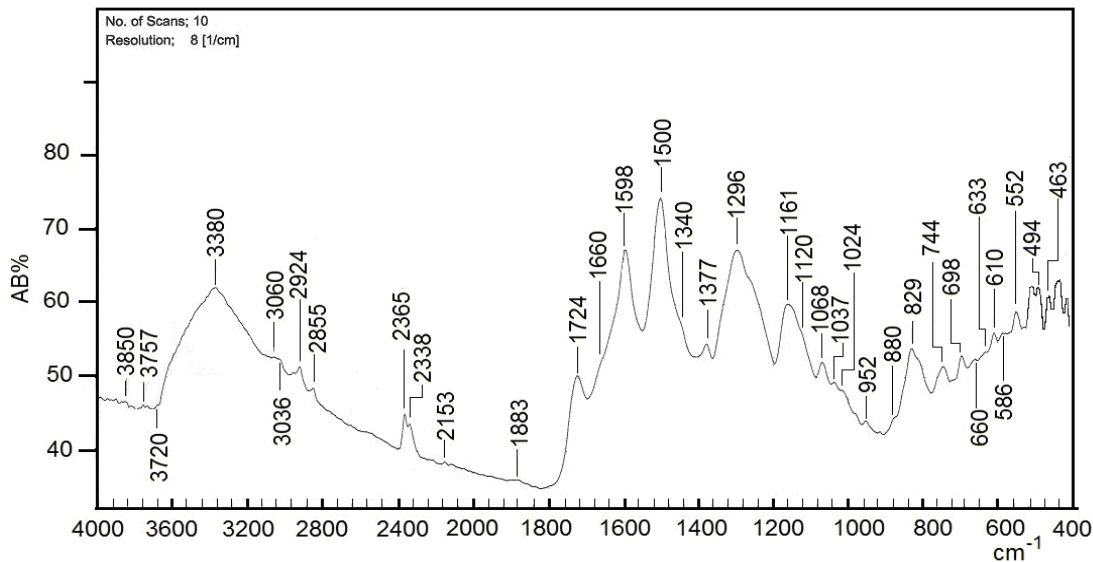


Fig.3a FTIR of a film of polyaniline

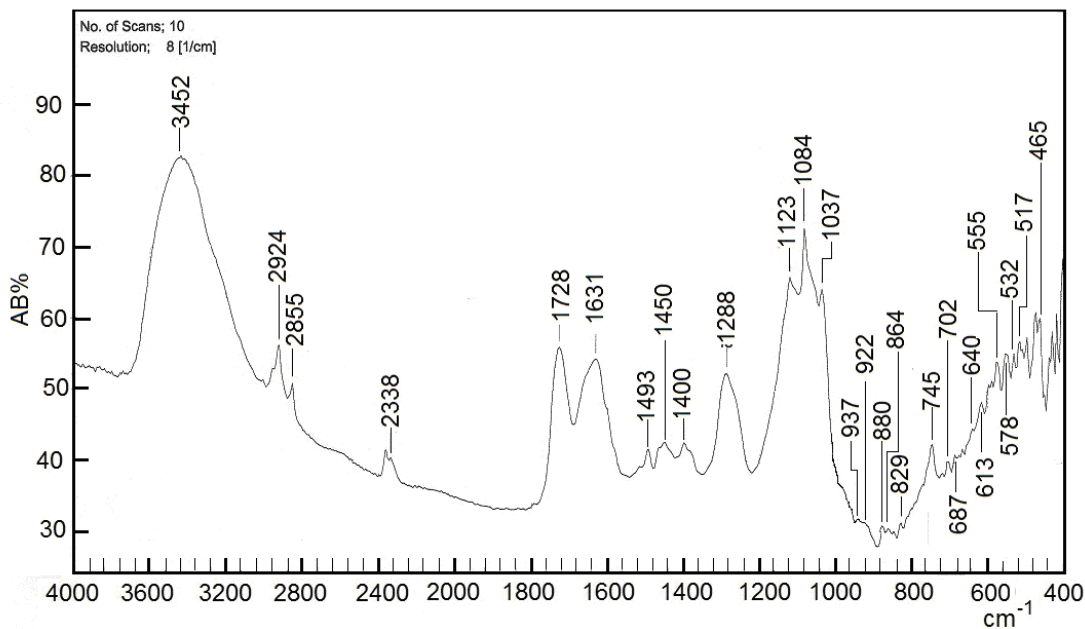


Fig.3b FTIR of a powder of polyaniline

V. CONCLUSION

Thin films of PANI conducting polymer can be successfully synthesized by electrochemical polymerization of aniline. FTIR spectroscopy is a powerful tool to investigate the spectral properties of these polymers, from these investigations we hope to obtain a better understanding these highly conducting polymer materials. Our results have been consolidated from vibrational bands spectrum analysis, which showed that most of these bands are attributed to C-N, C-C, and C-H stretching, in plane bending and out of plain vibrations as well as N-H modes of vibrations. From the

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(An ISO 3297: 2007 Certified Organization)

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comparison of both experimental and calculated frequencies, it is concluded that the results using PM3 and RM1 calculations are more accurate than those obtained from MNDO and AM1, these calculated frequencies are in good agreement with experimental frequencies for both monomer and polymer.

The characteristics of PANI films have been examined with respect to the samples prepared with different concentrations of monomer and different applied voltage, it is probably that the electronic properties of PANI films prepared with higher concentrations of monomer and higher applied voltage are poor compared with those prepared at lower monomer concentration and applied voltage. From comparison of PANI powder spectra with those of thin films, we conclude that the frequency bands intensities, which characterize the PANI powder in the region between 1400 and 1500 cm^{-1} are lower than in the thin film case; this can be used as an indicator of a lower degree of polymerization.

ACKNOWLEDGEMENTS

The author thanks the college of science for women, university of Baghdad for financial support.

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International Journal of Innovative Research in Science, Engineering and Technology

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