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Study on Infrared Spectra of Poly aniline Synthesized by Chemical Oxidation Method

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ABSTRACT

In this study infrared spectra of polyaniline prepared under different physical and chemical conditions are reported. The observed band assignments of various polymers under investigation are mostly identical with a few exception. Small variation in position of particular band among different polymers are observed.

Key words: Poly aniline, Chemical Oxidation and Infra red spectra.

INTRODUCTION

Infrared spectral analysis is an important and powerful tool of chemical identification of organic substances. The major advantages of infrared spectroscopic method over other methods of structural analysis are: (i) it gives useful information about the structure of molecule quickly without tiresome evaluation method. (ii) it requires very small amount of sample. As a result it is being widely used for the identification of different functional groups present in organic molecules. The basic principle of IR-spectra is based upon the fact that due to molecular vibration a chemical substance shows marked selective absorption in the infrared region. With the absorption of IR-radiation, the molecules of a chemical substance undergo vibration at different rates giving rise to closed packed absorption bands. These absorption bands are called infrared absorption spectrum which usually extends over a wide wavelength range. Absorption bands in the IR region at different wavelength correspond to the different characteristic functional groups and bonds present in a chemical molecule. Therefore, any structural change like addition or substitution of groups or atoms in a molecule results in a change in band position, appearance of a new band, change of intensity of absorption, splitting of a single peak into two or more peaks etc.

Thus inferred spectral analysis has been carried out in order to characterize polyaniline synthesized under three acids (HCl, H_2SO_4 & H_3PO_4) medium in this study.

EXPERIMENTAL

In this study, polyaniline sample were synthesized under three different acid (HCl, H_2SO_4 & H_3PO_4) conditions to obtained doped polyaniline. The bath compositions were as follows:

Sample	Monomer	Solvent composition and Molar ratio	Monomer: oxidant ratio Aniline : $(NH_4)S_2O_8$
1	Redistilled aniline	CH_3CN : H_2SO_4 ; 1:1	1 : 1
2	"	CH_3CN : H_2SO_4 ; 1:1	1 : 1.05
3	"	CH_3CN : HCl ; 1:1	1 : 1
4	"	CH_3CN : HCl ; 1:1	1 : 1.05
5	"	CH_3CN : H_3PO_4 ; 1:1	1 : 1
6	"	CH_3CN : H_3PO_4 ; 1:1	1 : 1.05

The mixtures were kept under constant stirring for 10 hours and at a constant temperature of ~2 °C (using ice and NaCl in thermostatic bath). During stirring the colour of the solvent gradually changes from colourless to greenish black via yellow, light brown, deep brown and greenish black. The greenish black precipitate was thoroughly washed with distilled water and then with ethanol. It was then dried at 65 °C under vacuum for about 24 hours. The dried mass were grounded and kept in a vacuum desiccator for further study.

The IR-spectra of different samples synthesized in this study were recorded in a IR-470 infrared spectrophotometer, Simadzu Corporation Japan, within a range from 400 cm^{-1} to 4000 cm^{-1} at room temperature (20°-22°C) using KBr pellet technique at the Department of Chemistry, BUET, Dhaka.

RESULTS AND DISCUSSION

A representative of infrared spectra of polyaniline prepared under different physical and chemical conditions is given in figure-1, while the band assignments of the spectra are cited in tables 1-6. The observed assignments of the spectra of various polymers under investigation testify that the sequence of functional groups attached to the polymer are mostly identical with a very few exception. Small variation in position of particular absorption band among the polymers is due to difference in condition of polymerization. The observed bands at 3500 cm^{-1} in S_1-PANI, 3000-3500 cm^{-1} in H_1-PANI, 3600 cm^{-1} in P_1-PANI, 3500 cm^{-1} and 3300 cm^{-1} in H_2-PANI, 3400-3600 cm^{-1}in S_2-PANI, 3400-3580 cm^{-1} in P_2-PANI are due to stretching of aromatic amine system[1,2]. C-H

Table 1: Infrared absorption bands of polymer S_1-PANI

Frequency (cm^{-1})	Band Assignment
(a) 3500 (vs)	υ (N-H) stretching band
(b) 3050 (s)	C-H stretching band
(c) 1500-1700 (b,m)	C=C skeletal mode of benzene ring δ (N-H) i.e. N-H in plane bending
(d) 1300- (w) 1380 (m)	C-N stretching
(e) 1100-1200 (m)	C-H in plan deformation of benzene ring
(f) 750 (vs), 800 (w),850 (m) 900 (w).	C-H out of plane deformation vibration of benzene ring.

(vs = very strong, s = strong, m = medium, b = broad, w = weak, vw = very weak & vvw = very very weak)

Table 2: Infrared absorption bands of polymer H_1-PANI

Frequency (cm^{-1})	Band Assignment
(a) 3500 (s), 3300 (s)	υ (N-H), stretching band two bandsappeared due to N-H asymmetric and N-H symetric stretch
(b) 3000 (w)	C-H stretching band
(c) 2100 (m)	Overtone of benzene ring
(d) 1500- 1600 (b,m)	C=C skeletal mode of benzene ring δ (N-H) i.e. N-H in plane bending
(e) 1300 (m), 1400 (w)	C-N stretching
(f) 1100 (m), 1200 (s)	C-H in plane deformation vibration of benzene ring.
(g) 950(w), 900(w) 750 (vs)	C-H out of plane deformation vibration of benzene ring

Table 3: Infrared absorption bands of polymer P_1-PANI

Frequency (cm^{-1})	Band Assignment
(a) 3600 (b,s)	υ (N-H), stretching band
(b) 3000 (w)	C-H stretching band
(c) 2000 (m)	Overtone of benzene ring
(d) 1700- 1800 (b,m), 1550 (s), 1450 (w)	C=C skeletal mode of benzene ring δ (N-H) i,e. N-H in plane bending
(e) 1300 (m)	C-N stretching
(f) 1100 (w), 1200 (m)	C-H in plane deformation vibration of benzene ring.
(g) 900 –1000(w) 700 (s)	C-H out of plane deformation vibration of benzene ring

Table 4: Infrared absorption bands of polymer H_2-PANI

Frequency (cm^{-1})	Band Assignment
(a) 3500(vs,b) 3300 (m,b)	υ (N-H), stretching band
(b) 3000 (m)	C-H stretching band
(c) 1700-1850 (b,m), 1550 (vs)	C=C skeletal mode of benzene ring δ (N-H) i. e. N-H in plane bending
(d) 1400 (m) - 1300(m)	C-N stretching band
(e) 1200 (vs), 1100 (m), 1050 (w)	C-H in plane deformation vibration of benzene ring
(f) 950 (b,m), 850 (b,m), 700 (b,m)	C-H out of plane deformation vibration of benzene ring.

Table 5: Infrared absorption bands of polymer S_2-PANI

Frequency (cm^{-1})	Band Assignment
(a) 3400- 3600 (b,m)	υ (N-H), stretching band
(b) 1700 – 1800 (b,m) 1530 (s,m) 1450 (w)	C=C skeletal mode of benzene ring δ (N-H) i.e. N-H in plane bending
(c) 1350 (m)	C-N stretching band
(d) 1200 (m) - 1100(w)	C-H in plane deformation vibration of benzene ring
(e) 1000 –900 (w) 700 (vs)	C-H out of plane deformation vibration of benzene ring.

Table 6: Infrared absorption bands of polymer P_2-PANI

Frequency (cm^{-1})	Band Assignment
(a) 3400- 3580 (b,m)	υ (N-H), stretching band
(b) 3100 (w) 3200 (vs)	C-H stretching band
(c) 2200 (b,m)	Overtone of benzene ring
(d) 1800-2000 (b,m), 1600 (s)	C=C skeletal mode of benzene ring δ (N-H) i.e. N-H in plane bending
(e) 1400 – 1300 (s,m)	C-N stretching band
(f) 1200(s), 1100(s), 1050(m)	C-H in plane deformation vibration of benzene ring.
(g) 900(b), 800(b), 700 (sm)	C-H out of plane deformation vibration of benzene ring

stretching band of the polymer are found within a range of 3000 - 3200 cm^{-1}. It may be assumed that intensity of band absorption depends on the mode of preparation of polymer. C=C skeletal mode of benzene ring and d (N-H) i.e., N-H in plane bending[3] vibration observed at 1500-1800 cm^{-1}. C-N stretching[4] in aromatic system is found at 1340-1250 cm^{-1}. But incase of these polymers the absorption bands are found at 1300 cm^{-1} and 1380 cm^{-1} for S_1-PANI, 1300 cm^{-1} and 1400 cm^{-1} for H_1-PANI, 1300 cm^{-1} in P_1-PANI, 1300 cm^{-1} and 1400 cm^{-1} in H_2-PANI, 1350 cm^{-1} in S_2-PANI, 1300-1400 cm^{-1} in P_2-PANI. C-H in plane deformation vibration of benzene ring[5,6] of various polymers are found within the range of 1100 – 1200 cm^{-1}. C-H out of plane deformation[7] vibration band of aromatic system is found at 700 – 1000 cm^{-1}. The intensity of bands varied and depends on the condition of preparation of polyaniline as mentioned in the following tables.

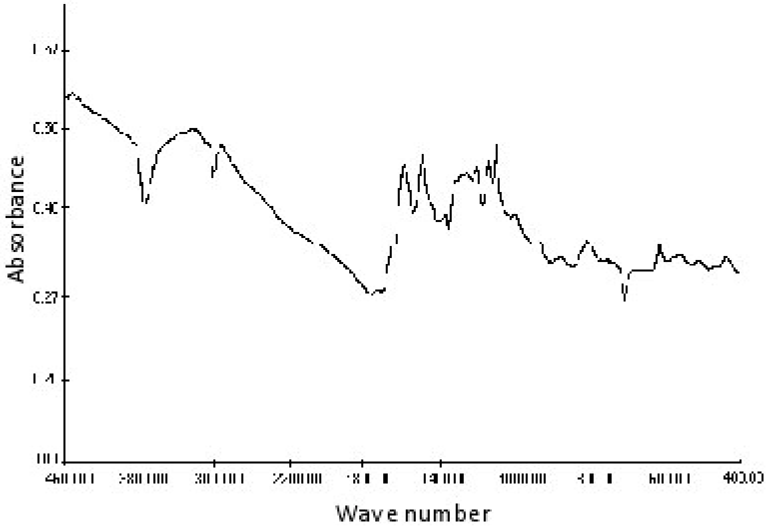

Fig. 1: Infrared spectra of polyaniline (S_1-PANI) synthesized at 20°C, monomer ($C_6H_5NH_2$): oxidant [$(NH_4)_2S_2O_8$] ratio 1:1 and solvent (CH_3CN: H_2SO_4) Ratio 1: 1.

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