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SYNTHESIS OF POLYANILINE IN PRESENCE OF LOW MAGNETIC FIELD, ITS STRUCTURE AND ELECTRICAL PROPERTIES

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Abstract. Polyaniline is synthesized chemically under the influence of low magnetic field of intensity 1KGauss. The effect of magnetic field during the synthesis process causes enhancement of electrical conductivity by two orders of magnitude. This increased electrical conductivity depends on the polymer chain ordering, as well as structure and morphology of the reported polymer.

Key words: polyaniline, chemical polymerization, low magnetic field, electrical conductivity

1. Introduction

The capability of conjugated polymers to act like inorganic semiconductors is broadly known. Many of semiconducting devices like p-n Diode, Schottky Diode, LED's and Photovoltaic Cell are constructed using these polymers. The efficiency of a device based on conjugated polymers is substantially lower and thus renders putting them into practical use impossible. Low efficiency of such devices is *inter alia* due to the lack of order in polymeric materials, which is necessary to obtain proper electrical conduction.

Magnetic field effect (MFE) on the kinetics of chemical reactions has been studied for a long time. The overall change of yield and kinetics of chemical and related physical processes due to the effect of a static magnetic field has been studied by few researchers. Mori *et al.* [1] found an increase of the initial rate and yield of radiation-induced polymerization of acrylonitrile when the reaction was carried out in an increasing magnetic field from 0 to 0.5 T at 77 K. Turro *et al.* [2] synthesized the styrene and methyl-methacrylate by dibenzyl ketones using emulsion polymerization. They concluded that this process was markedly influenced by an external magnetic field. Lin-Tao-Cai *et al.* [3] have studied MFE on polyaniline (PANI) film by *in situ* conductivity measurements and reported that the value of conductivity for the PANI ($B_p = 0.7$ T) film prepared parallel to electrodes surface increases threefold as compared to that of PANI prepared in the

absence of the magnetic field. H. Morika [4] reported the effect of magnetic field on the surface morphology and oxidation-reduction process in polypyrrole films.

Based on the literature survey it has been observed that the effect of low magnetic field during polymerization of aniline has been investigated with respect to change in morphology, UV spectrum, oxidation-reduction process *etc.* However, the effect of low magnetic field during polymerization of aniline has not been reported with respect to increased electrical conductivity. Since the changes in electrical conductivity depend on the structure and morphology of the polymer these properties have been investigated and reported in this work.

2. Experimental

2.1. Sample preparation

Chemicals: 1M H_2SO_4 , 0.5M aniline and 0.5 M potassium dichromate ($K_2Cr_2O_7$). Using the above chemicals aniline was polymerized according to the standard method [5] (**sample M0**). Polymerization was carried out in a glass beaker which was placed in between the pole pieces of electromagnet of field 1KGauss for one hour. (**sample M1**)

2.2. Analysis method

Elemental analysis of CHNS-O was performed on Vario EL III, (GmbH Germany).

Infrared spectra of samples were recorded in the range of 4000 - 400 cm^{-1} using "BRUKER" (model: vector 22) FTIR spectrophotometer.

An X-ray diffractometer (Philips Analytical X-Ray B.V., PW 1710) was used to examine PANI samples. The X-Ray beam was Cu Ka radiation from a sealed tube operated at 35 KV and 25 mA. The data were recorded from $2\theta = 1^\circ$ to 40° .

A scanning electron microscope (Philips SEM; Model 515) was used to examine PANI powder.

Electrical conductivity of the sample (M0 and M1) was measured at room temperature using four probes (SES-Model DEP-02) technique. Two-probe method, in which sample in the form of pellet was sandwiched between two copper electrodes, was also used for determining electrical conductivity.

3. Results and Discussion

The physical appearance of modified PANI designated as sample M1 (in powder form) was lustrous, silvery green, very smooth and fine as compared to sample M0.

Table 1 shows the percentage of C, H, N, S obtained by elemental analysis result.

Table 1

Results of elemental analysis

Sample	Designation	C, %	H, %	N, %	S, %
SO ₄ ²⁻ doped polyaniline (PANI)	M0	30.68	4.96	6.03	9.02
1KG magnetic Field applied during polymerization (SO ₄ ²⁻ doped PANI)	M1	21.23	6.93	4.06	10.08

Elemental analysis results show that in sample M1 hydrogen percentage has increased tremendously and percentage of sulphur introduced in polymer chain has also increased. This implies that more sites are exposed where doping of sulphur occurs. Thus in sample M1 it has been found that protonation has increased (higher percentage of hydrogen).

Table 2

Electrical conductivity values at room temperature

Sample	Electrical conductivity, S/cm	
	Four probe	Two probe
M0	1.1·10 ⁻²	9·10 ⁻⁵
M1	1.2·10 ⁰	7.3·10 ⁻³

Electrical conductivity values determined using four probes and two-probe technique were tabulated.

M1 sample shows increase in electrical conductivity of two orders of magnitude as compared to M0. The effect of the temperature variation from room temperature to 423 K on electrical conductivity is shown in Fig. 1.

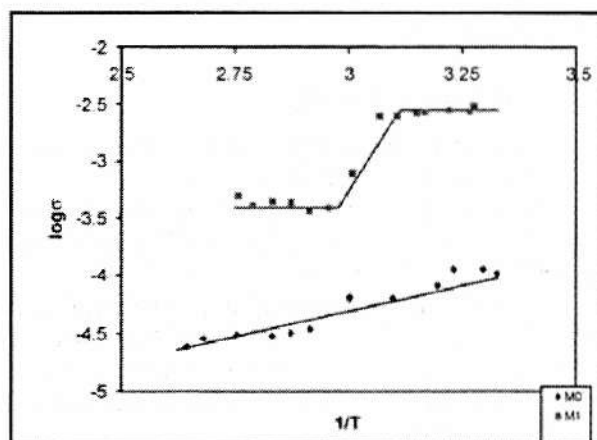


Fig. 1. Plot of $\log \sigma$ vs. $1/T \times 10^{-3}$ for sample M0 and M1

The curve for Sample M0, showing semiconducting behavior initially up to 423 K, thereafter shows metallic behavior. Sample M1 shows metallic behavior from room temperature onwards up to 323 K, thereafter conductivity suddenly decreases and again remains constant showing metallic behavior throughout the temperature range.

Fig. 2 shows the IR spectra recorded for samples M0 and M1. Various IR bands and their assignments are shown in Table 3.

As observed from IR scans as well as from Table 3, the band at 1493 cm⁻¹ due to benzenoid unit is not much shifted whereas the quinoid band (1599 cm⁻¹) after modification (samples M1) shifts towards low wave number side by 25 cm⁻¹. This indicates slight structure modification. The analysis of IR spectra shows that quinoid to benzenoid (intensity) ratio is almost constant for both samples, which is one of the parameters to explain the enhancement in electrical conductivity [6]. The region 1400–1240 cm⁻¹ is the C–N stretching region [6]. Sample M0 shows two peaks, medium absorption at 1302 cm⁻¹ and weak absorption at 1385 cm⁻¹. The peak at 1302 cm⁻¹ (medium) is strengthened enough and becomes strong as that of benzenoid and quinoid peak for sample M1. The weak absorption band at 1385 cm⁻¹ for M0 shows intensity growth in the order of increase in applied magnetic field during polymerization *i.e.* sample M1 has more intensity for this band as compared to M0. The increase in intensity of the two bands observed in this C–N stretching region in order of M0 and M1 suggests that the C–N group vibration in PANI is facilitated much, possibly due to greater promotion or degree of exposure. Boyer *et al.* [7] have observed and attributed the intensity of C–N stretching band to polymer chain length increase. They have treated this band as diagnostic of the chain length. From IR results, therefore the enhancement of intensity of C–N stretching band at 1385 cm⁻¹ indicates increase of continuous conjugation of polymer chain leading to exposure of hidden C–N groups.

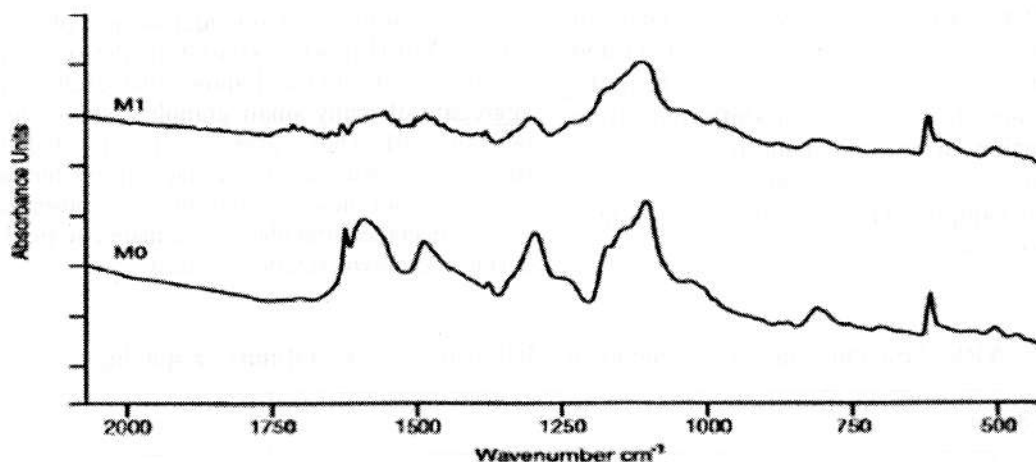


Fig. 2. IR spectra for samples M0 and M1

Table 3

Various IR bands and their assignment

Sample	Q, cm ⁻¹	B, cm ⁻¹	Q/B ratio	C-N, cm ⁻¹	N-H, cm ⁻¹	Charge delocalization peak, cm ⁻¹	C-H In plane, cm ⁻¹	C-H out plane, cm ⁻¹
M0	1599	1493	1.07	1302, 1385	1706	1112, 619	1156	816
M1	1576	1489	1.03	1306, 1385	1716	1117, 618	1170	817

As suggested by Genies and Laprowaski [8], Harada *et al.* [9] and Ray *et al.* [10] the relative concentration of various N-moieties: NH, +NH₂, N=, +NH=, C-N+ - in polyaniline depends on the nature and percentage of doping which in turn may affect the population of charge defect centers (polarons and bipolarons) and ultimately the electrical conductivity. The N-H stretching band, which is observed at 1706 cm⁻¹ for sample M0, gets shifted to higher wave number side for M1 with increase in intensity. In this case there is also a tremendous intensity increase for C-N, and NH bands which may affect the population of charge defect centers or there might be increased percentage of dopant (SO₄⁻²) introduced in PANI backbone for sample M1 as compared to M0.

The charge delocalization peaks appearing at ~ 1114 cm⁻¹ and 618 cm⁻¹ which have direct correlation with conductivity [11] also show pronounced increase in M1. This suggests a greater *p*-electron delocalization in PANI material and thereby explains enhanced electrical conductivity. The band at about 1160 cm⁻¹ is most likely to be due to in-plane C-H bending mode of aromatic rings. In sample M1 it is well resolved in intensity. The band at 816 cm⁻¹ is assigned to the out-of-plane C-H bending mode for SO₄⁻² doped polyaniline (M0). After modification, *i.e.* in samples M1 the band is observed at the same position, only its intensity has increased tremendously.

Figure 3 shows wide angle X-Ray diffraction pattern for samples M0 and M1. Percentage crystallinity of the sample is calculated using Manjunath's formula [12].

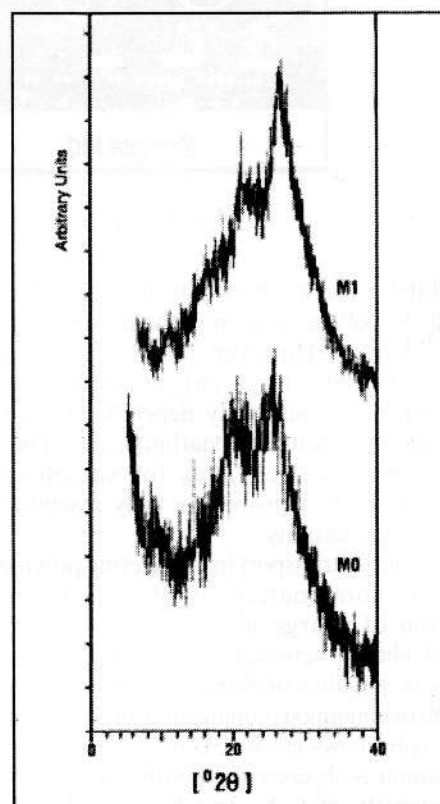


Fig. 3. Wide angle X-ray diffraction pattern for sample M0 and M1

The XRD pattern for M0 shows broad peaks at $2\theta = 20^\circ$ and at 25.8° corresponding to (0, 0, 1) and (1, 1, 0) reflections of PANI respectively [13]. The peaks obtained for sample M1 show slight shifts indicating slight modification in crystal structure (Table 4). Percentage crystallinity is approximately the same for sample M0 and sample M1. The d spacing slightly decreases in case of sample M1.

Scanning electron microscopy photograph for sample M0 (Fig.4) is similar to the one reported by S. Chen *et al.* [14] and shows that each particle is an aggregate of many small granules (shown by circle in micrograph). These granules are divided into small particles as observed in the micrograph for sample M1 (Fig 4). From these micrographs it is observed that the surface becomes smoother as the magnetic field is applied during the polymerization process.

Table 4

XRD data showing various peaks in XRD scans, % crystallinity, d spacing

Sample	$2\theta, ^\circ$	Xc, %	d space, A°
M0	8.8, 20, 25.8	61.4	3.4503
M1	9.2, 19.8, 26	64.81	3.4242

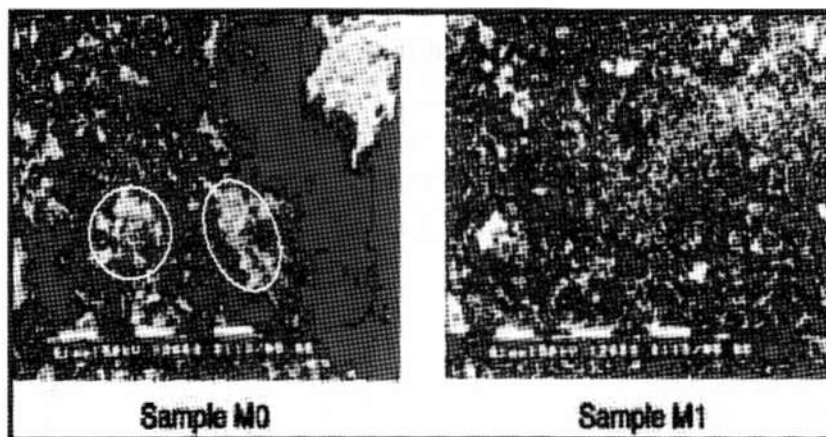


Fig 4. Scanning electron micrographs for samples M0 and M1

All these results show that there is slight structural change due to polymerization in the presence of magnetic field (sample M1). However, the electrical conductivity measurements show large enhancement. Some of the factors electrical conductivity depends on are Q/B ratio (from IR measurement), crystallinity, *etc.* These factors show only marginal changes for samples M1, and therefore, can be responsible for only marginal increase in electrical conductivity.

The charge transport in conducting polymers occurs through the combination of two mechanisms [15] propagation of charge along the polymer chain and hopping of charge between the neighboring chains.

The propagation of charge along the chain is improved if the length of continuous conjugation along the chain increases. M1 sample shows enhancement in the length of continuous conjugation as observed through the analysis of IR spectra (higher intensity of C-N stretching band at 1385cm^{-1}). Further high electrical conductivity in sample M1 can be attributed to higher number of dopant species entering the chain of sample M1 (elemental analysis supports this result).

4. Conclusions

Application of low magnetic field during chemical polymerization process of aniline give smooth, lustrous, silvery green, fine powder with two-order increase in electrical conductivity.

Thus the increased electrical conductivity in sample M1 is probably due to the slight increase in crystallinity with increase in chain (conjugation) length and increase in number of the dopant species.

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**СИНТЕЗ ПОЛІАНІЛІНУ
В НИЗЬОЧАСТОТНОМУ МАГНІТНОМУ ПОЛІ,
ЙОГО СТРУКТУРА ТА ЕЛЕКТРИЧНІ
ВЛАСТИВОСТІ**

Анотація Під дією низькочастотного магнітного поля інтенсивністю 1КГаус синтезовано поліанілін. Показано, що під час синтезу магнітне поле підвищує електропровідність на два порядки. Електропровідність залежить від впорядкованості ланцюга, структури і морфології вказаного полімеру.

Ключові слова: поліанілін, хімічна полімеризація, низькочастотне магнітне поле, електрична провідність.