

CHAPTER 1

CHEMICAL SYNTHESIS OF PEDOT NANOFIBRES USING DBSA AND APS OXIDENTS

INTRODUCTION:

The term ‘Nanotechnology and Nanoscience’ are often used synonymously. The literal meaning of nano is ‘dwarf’ or an abnormally short person, in scientific language one billionth part of unit scale i.e. nanometer or nanosecond etc. Nanotechnology includes small dimension materials usually in the range of 1 to 100nm. When at least one of the dimension of any type is reduced below $\sim 100\text{nm}$, its mechanical, thermal, optical magnetic and other properties change at some size characteristic of that material. Thus within the same material one can get range of properties.

Research in the field of (at least one dimension of less than 100nm) has led to the discovery that at this scale, dramatically different properties may be demonstrated with respect to bulk materials. (1). This has inspired recent efforts to synthesize nanostructures of various materials including conduction polymers like PEDOT as nano fibres, hollow tubes and spheres. (2)

Nano fibres are hollow and solid carbon fibres with lengths of the order of a few microns and width varying from some tens of nanometer to around 200nm. These materials have occasionally been referred to as nanotubes. Polymeric

nanofibers have very high surface area, remarkable surface and superior mechanical properties.

Nanofibers are some of the true nano materials engineered at the molecular level and they exhibit physical and electrical properties that are excellent. They show tensile strength to be in excess of some 60 times stronger than high grade steel. By some estimates, nanofibers narrower than the human hair might be able to suspend a semi-trailer. Nanofibers are not only the strongest material ever made, they are amongst the strongest materials it will be ever possible to make. Not only nanofibers are very strong but they are also light and flexible.

π Conjugated polymers (or conducting polymers) have been intensively studied in the field of fundamental and applied research, because of their one dimensional intrinsic properties and their potential for commercial applications. (3). With the development of Si-based nanotechnology, π -conjugated organic materials have been applied to many nanoscale devices and microelectronic devices (2,4). Nanoscale π -conjugated organic molecules and polymers can be used for biosensors (5), electrochemical devices, single electron transistors (6), nanotips in the field emission display (FED) (7) etc.

The physical properties of thenanofiber are striking enough, but their electrical properties may be even more exciting. Current theory holds that nanofibers act as either superconductors or semiconductors depending on the exact proportions of the fibre and the materials which are introduced into material such as dopants.

Nanofibers and nanowire research and manufacturing are hot topic for both scientists and industries. Several companies are taking effort to manufacture these materials and also finding ready market for their products. Engineers in thephaedonAvouris's group at IBM have usable transistors with properties exceeding those of pure silicon.

PEDOT Nanofibers have been the thrust area of research since last decades because of its electronic applications in PCB's LED's and in many electronic devices. Therefore, researchers have made efforts to synthesizePEDOT in nano regime [8] to improve the electronic as well as optical properties of these polymers so as to enhance their applicability. Thus, on this background the reports are available viz. wang et al. has prepared PEDOT nanoparticles by inverse micro emulsion polymerisation through ultrasound waves to overcome the problem of processibility and solubility [9]. On similar lines ,Seung et al. has also prepared PEDOT nanoparticles by usingDBSA as a dopant at

room temperature [10]. However, all these reports have given the focus on the solubility and processibility of the PEDOT.

It is well known that the properties of the material depend not only on their chemical structure but also on their morphologies e. g. nanoscale material possess unique properties on account of their finite size and have wide ranging application in a variety of area [8]. Thus, the synthesis of nanoscale material has become a thrust area of research. Therefore, attempts have been made to prepare in nanosize. Few reports are available on the synthesis of nanoparticles nanofiber synthesized by electrochemical polymerization using a scanning micro needle electrode or a micro porous membrane as a template [9-10]. One of the alternative method to synthesize in nano regime is the use of sulphonic acids [11] as they can play two way role i.e. dopant as well as surfactant [12]. Earlier also, these surfactants have been utilized to prepare water soluble PEDOT [13] by template synthesis. However, these methods bear several disadvantages such as formation of irregular or non-uniform particles, poor processibility, low yield etc. To overcome these limitations, one has to search for new methods of synthesis.

Therefore, using this knowledge as a key the present work reports the synthesis of PEDOT and nanofibers by using ultrasonic technique. Ultrasonic waves have been used for synthesis as high intensity ultrasound can accelerate the heterogeneous liquid-liquid chemical reaction and can break the aggregation thereby reducing the particle size. A set of surfactants such as CSA, HAS, PSA, CTAB, DTAB, DBSA were used as structure directing agents. The reaction was carried out under ambient conditions. Parameters such as concentration of monomer, surfactant and oxidizing agent along with the reaction time were optimized to obtain the polymers in the nano regime with fibrous morphology.

Details about the range of concentrations used for each of the polymers are given in the experimental section of chapter 2. After extensive experimentation and analysis the result showed that the formation of nanofibers giving homogenous sols was best in presence of DBSA as the surfactant in each of the cases and the reaction was seen to complete after 2h of sonication. Further, they were observed to be formed at a specific concentration or ratio of monomer to surfactant to oxidizing agent for each one being 1:0.3:1 and 1:5:0.5 for PEDOT respectively

CHAPTER 2

CHEMICAL SYNTHESIS OF PEDOT NANOFIBRES USING CSA AND PTSA OXIDENTS

Figure 1 shows the VU-V is spectra of PEDOTnanosols obtained in presence of different concentration of aniline. The spectra were recorded as a function of sonication time from zero to two hours. At each concentration the spectra shows a peak at ~400nm corresponding to the formation of polaron band of PEDOT. However, a comparison of the spectra reveal that the intensity of absorbance and sequential increase in absorbance is best at an PEDOT concentration of 0.01M. The colour of the nanosol is dark green and is observed to be homogenous at this concentration.

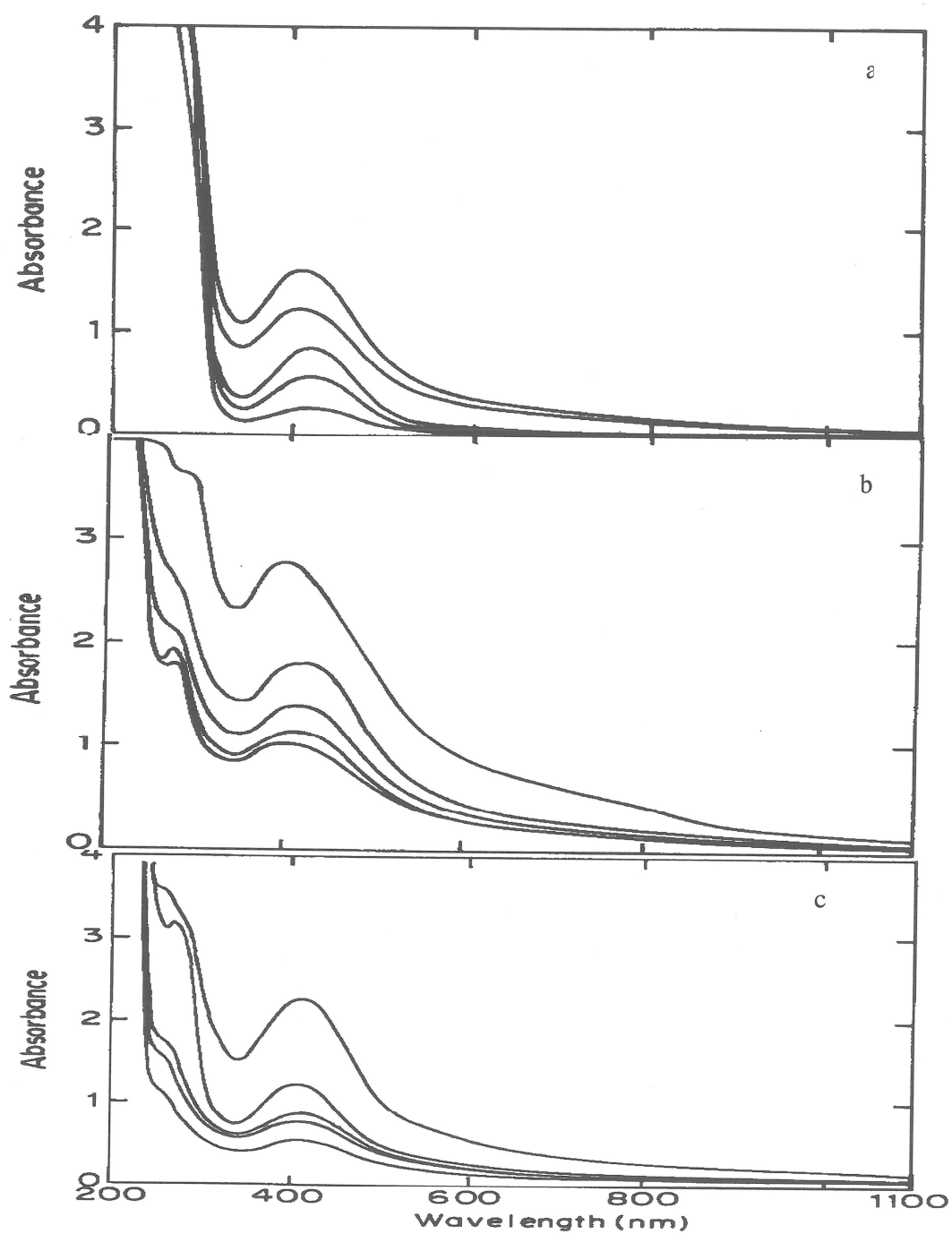


Fig.1: UV- Visible Spectra of PEDOT Nanofibers at Different Monomer Concentrations,a)0.001 b)0.01 and c) 0.1M.

On the other hand, at 0.001M concentration the reaction is observed to progress gradually and after 90 min of sonication precipitation is observed. At higher concentration of 0.1M aniline, though PEDOT formation occurs the process is accompanied by precipitation after 30 min of sonication.

Similarly, Figs. 2 and 3 depict the UV-V is spectra of the nanosols prepared by varying the concentration of DBAS and APS respectively. The results show that at each concentration PEDOT is formed as the UV-V is spectra exhibit a sharp peak at $\sim 400\text{nm}$. However, only at a concentration of 0.005 M DBSA and 0.01 M APS fibre formation and homogenous sol is obtained. At other concentrations, precipitation is seen occur.

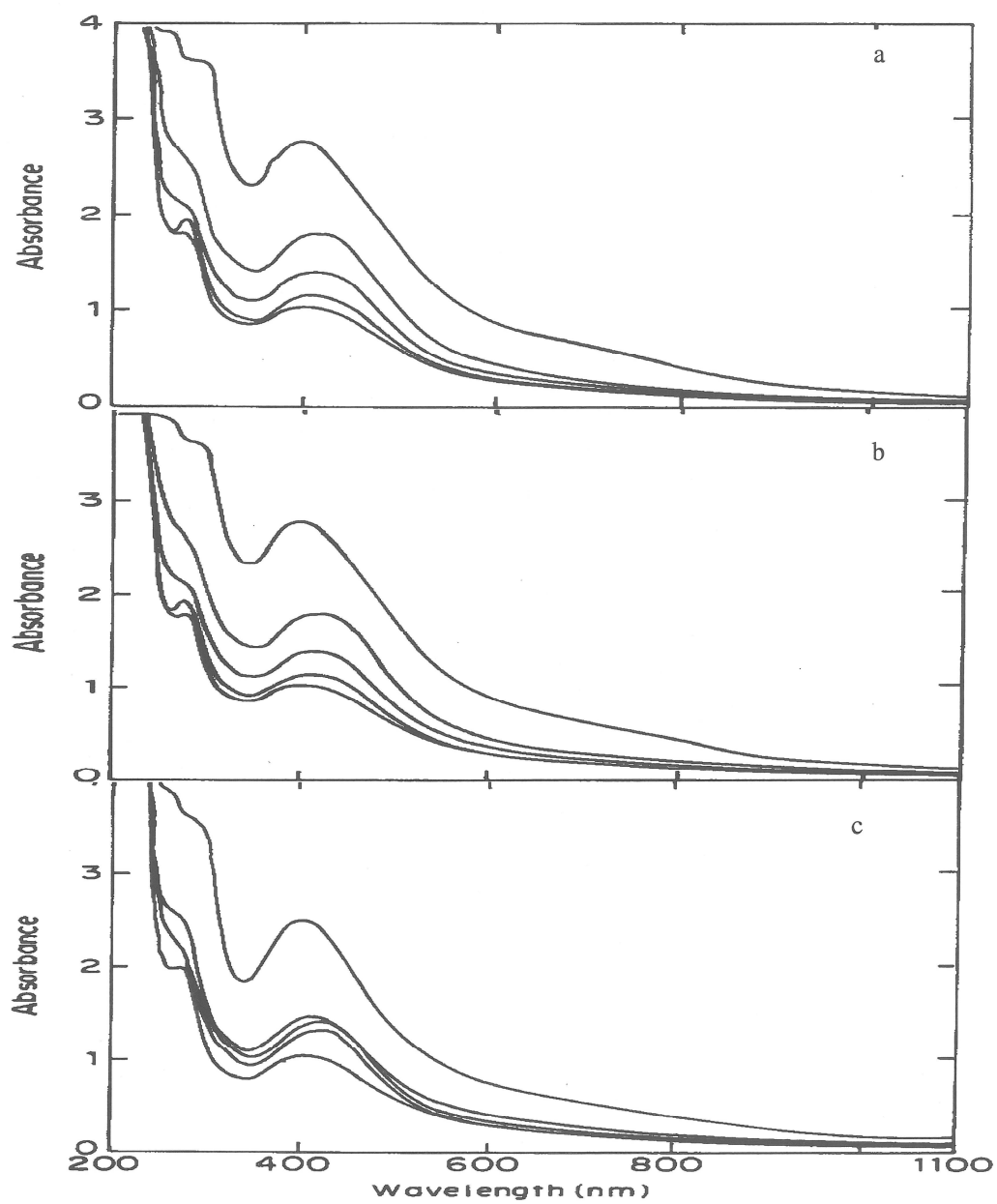


Fig.2: UV- Visible Spectra of PEDOT Nanofibers at Different DBSA Concentrations,a)0.001 b)0.01 and c) 0.1M .

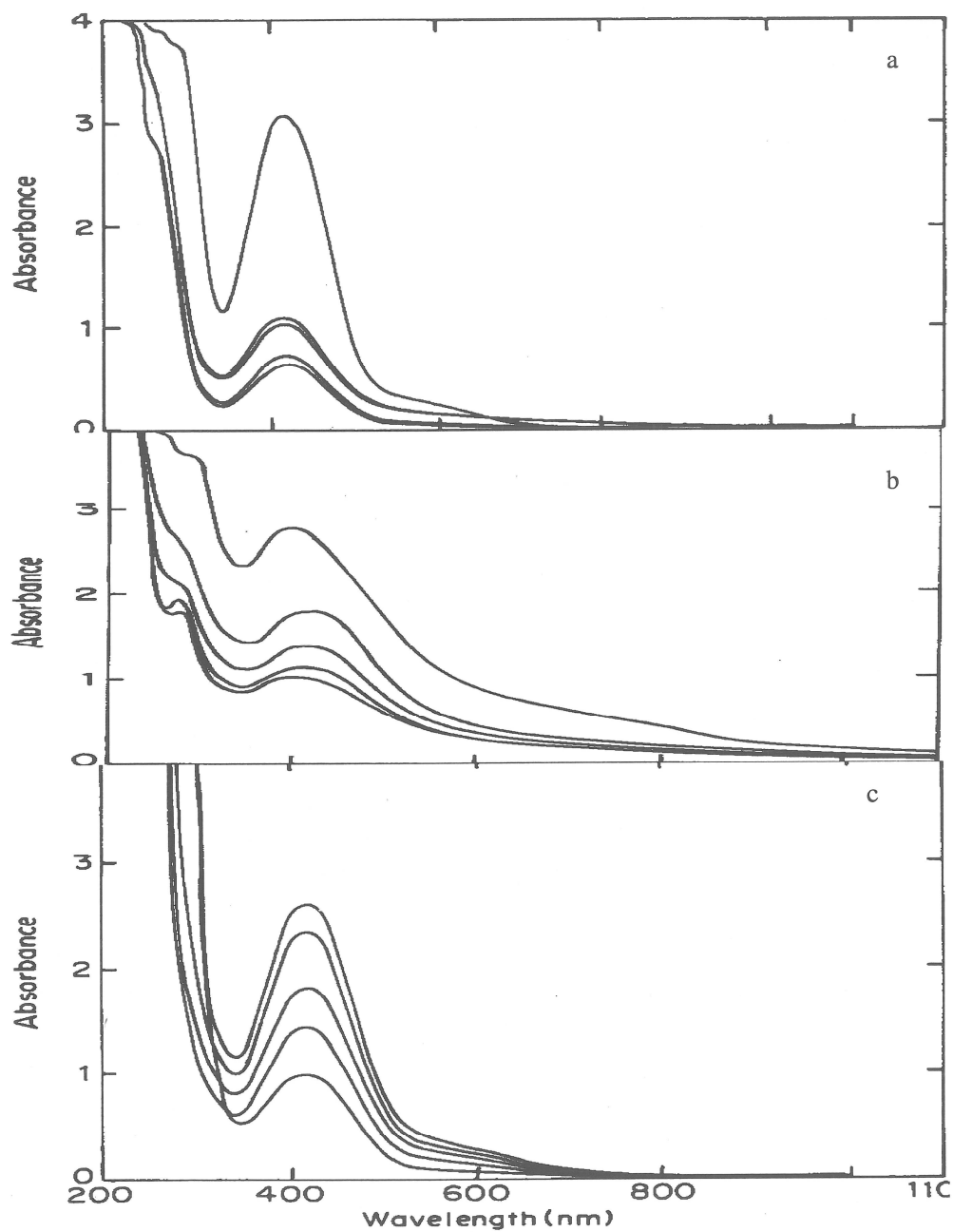


Fig.3: UV- Visible Spectra of PEDOT Nanofibers at Different APS Concentrations,a)0.001 b)0.005 and c) 0.01M

The X-ray diffractograms (Fig.4) of the nanosol having fibrous morphology were recorded at different time intervals i.e. before sonication(Fig. 4 a) and after 1 and 2h sonication (Fig.4 b, c). Significant differences were noted in the diffractograms when compared. The intensity of the peaks in the 2θ range of $\sim 10-40^\circ$ is observed to be increasing as the sonication time increases. Before sonication (Fig.4 a) only peaks at $\sim 14.70, 22.40$ corresponding to the planes (010), (001) reflections of PEDOT were appeared and after sonication all the reflections that correspond to PEDOT were seen clearly in the X- ray diffractogram (Fig. 4 b and c). Fig. 4 b is the intermediate stage of PEDOT formation at this phase some peaks of unreacted DBSA are also present.

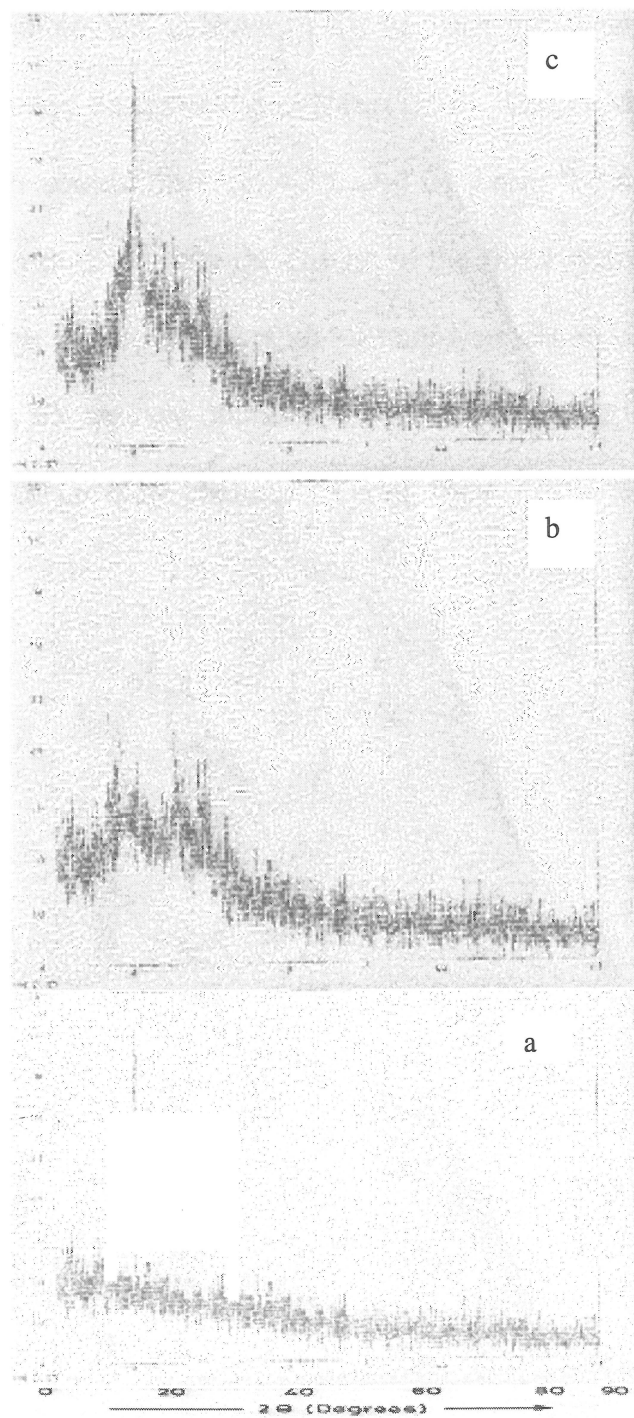


Fig.4: XRD Patterns of PEDOT Nanosols Recorded after
a) 0, b) 1 and c) 2 h of Sonication

The morphological analysis of the nanosol was done by observing it under Transmission Electron Microscope (TEM). The TEMs were recorded before and after sonication (Fig.5 a and b). From the micrographs it is clear that after sonication only the growth of the fibers were started whereas before sonication small particles with ~30 nm were observed in the sol. The nanofibers with the average diameters of ~35 nm with the length extending greater than ~1500nm were obtained by sonication.

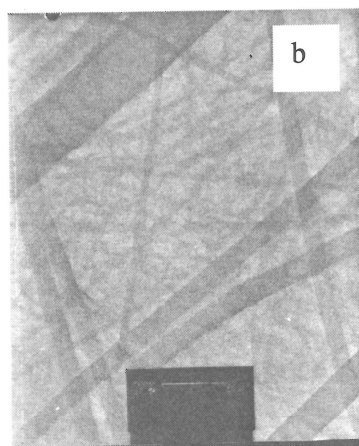
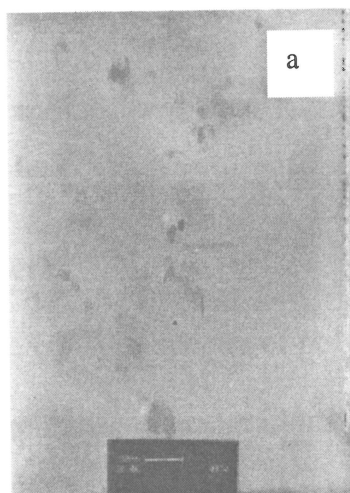


Fig.5: TEM Micrographs of PEDOT Nanofibersafter a) 0 and b) 2h of sonication.

Nanofibers of PEDOT have been successfully prepared by using ultrasonic technique.

2. PEDOTNanofibers:

Fig.6 shows the UV-VIS spectra of PEDOTnanosols obtained in presence of varying monomer concentrations after 2 h of sonication. A comparison of the spectra reveals the presence of a peak at $\sim 490\text{nm}$ in case of nanosol formed at 0.01 M monomer concentration which can be attributed to the polaron band of polymer and the nanosol is observed to be homogeneous with dark green colour. Similar peak is observed at a monomer concentration of 0.1 M but the sharpness is relatively less, though the overall absorbance is higher due to higher monomer concentration and precipitation is observed at this particular concentration.

On the other hand, absence of peak at $\sim 490\text{nm}$ indicates that polymerization does not seem to occur in the solution containing 0.001 M pyrrole monomer (Fig.6, curve A).

Further, the curves of absorbance vs. sonication time (inset of Fig. 6) show that in case of the nanosol prepared using 0.001M as monomer concentration the absorbance increases gradually and saturation is observed after ~ 150 min whereas, at 0.1 M concentration measurable absorbance is

Observed only after ~ 50 min which increase rapidly with a subsequent saturation after ~ 120 min From these result, it could be concluded that 0.01M monomer concentration is optimum, yielding product.

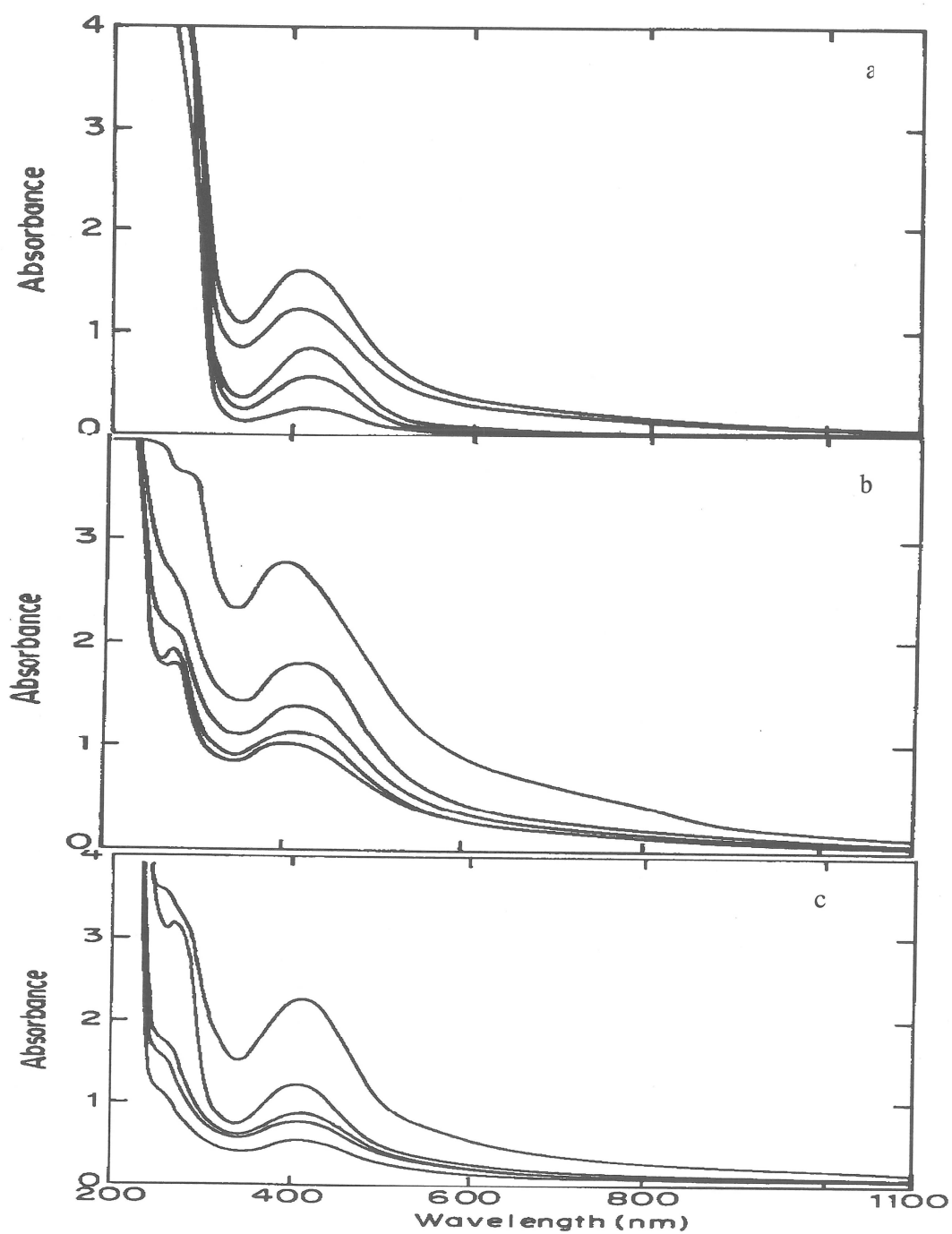


Fig.6: UV- Visible Spectra of PEDOT Nanofibers at Different Monomer Concentrations,a)0.001 b)0.01 and c) 0.1M.

In a similar way, experiments were performed to optimize the DBSA as well as APS concentrations. Figures 7 and 8 demonstrate the UV-Visible spectra of PEDOTnanosol obtained in the presence of varying the concentrations of DBSA and APS respectively. The spectra are recorded as a function of sonication time at each concentration. As seen from the figures a peak is noticed at a $\lambda_{\text{max}} \sim 490\text{nm}$ in each case, but sequential growth in absorbance i.e. reaction is observed at 0.05M (Fig. 7 a) and 0.005M APS (Fig. 8 c). Contrary to this, a slow growth as well as precipitation is observed at other concentrations.

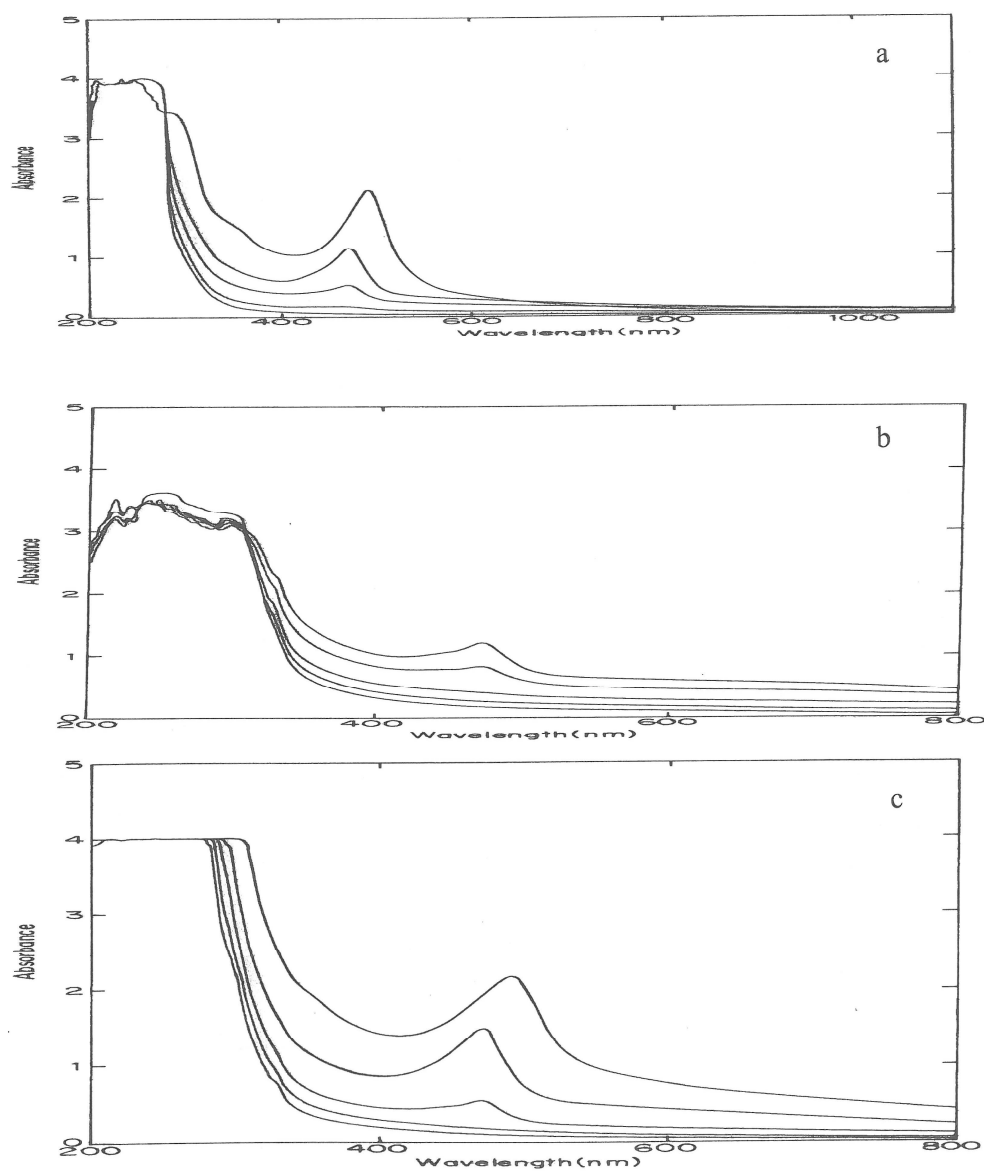


Fig.7: UV- Visible Spectra of PEDOT Nanofibers at Different CSA Concentrations, a) 0.05 b) 0.1 and c) 0.2M.

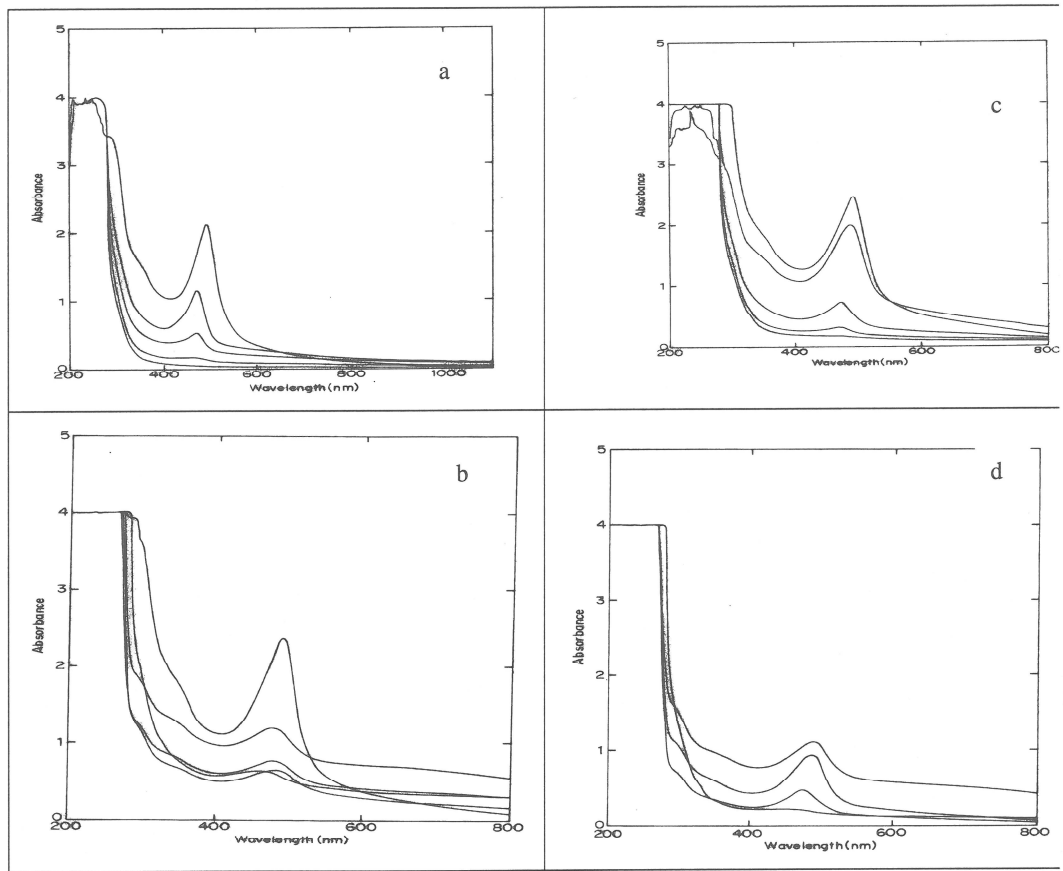


Fig.8:UV- Visible Spectra of PEDOT Nanofibers at Different PTSA Concentrations,a)0.0075 b)0.005 and c) 0.01 and d)0.02M

These results were further supplemented by TEM, SEM and XRD analysis. Figure.9 shows the TEM micrographs of the nanosol (optimum concentrations- 0.01 M PEDOT, 0.05 M DBSA and 0.05 M APS) recorded at different time of intervals, a) nanosol formed after complete addition of the oxidizing agent b) after 2h sonication and c) after aging the sample for eight days. Fig.9a shows the presence of particles (size $\sim 13\text{nm}$) as well as fibers (diameter $\sim 13\text{nm}$ and length $\sim 21\text{ nm}$) indicating that the fiber formations is initiated before sonication. After sonication, as the reaction progresses the size of the fibers in seen to increase with the length extending up to $\sim 35\text{ nm}$ and diameter $\sim 17\text{ nm}$. On aging the nanosol up to eight days, the length of the fiber was found to increase further to $\sim 1536\text{nm}$, however, the diameter of the nanofibers did not seem to change indicating growth only in longitudinal direction. The same sample when observed after a period of ~ 60 days under transmission electron microscope, the fibers could not be visualized to their fullest length. Therefor, the sample was analyzed under SEM (Fig .10) where the length is seen to extend beyond $\sim 1700\text{nm}$.

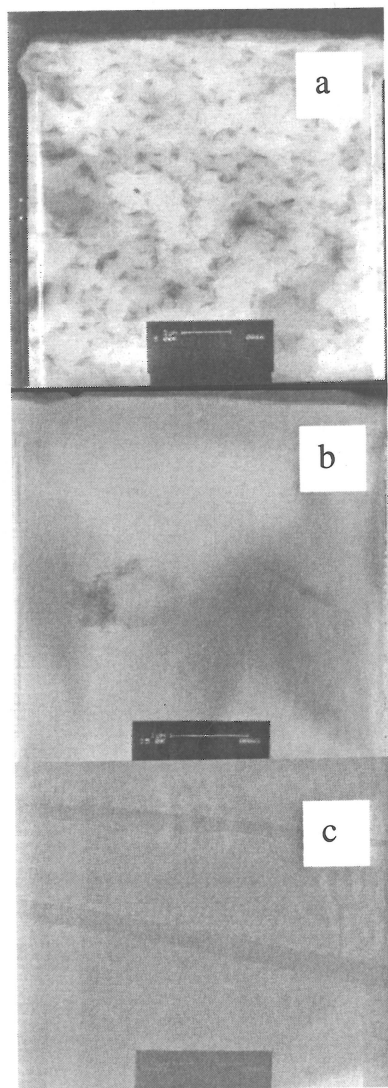


Fig.9: TEM Micrographs of PEDOT Nanofibers a)0 h, b)2 h, c) 8 day's aging

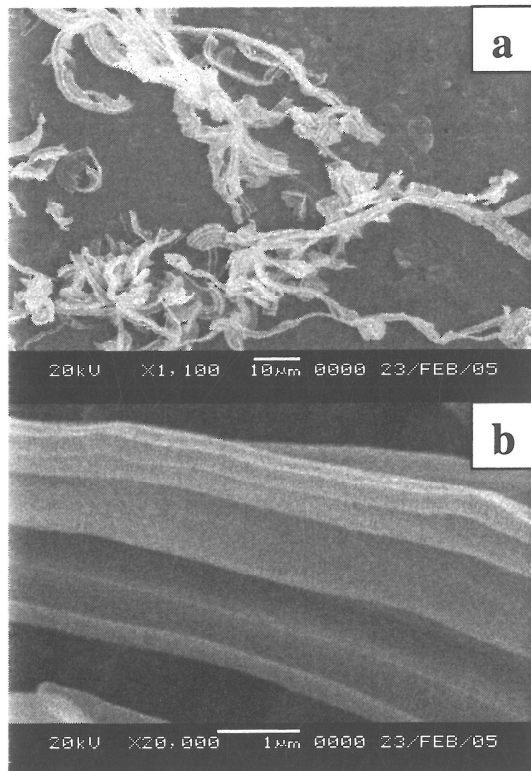


Fig.10:SEM of PEDOT Nanofibers at different magnifications. a) 100 x and 20000x.

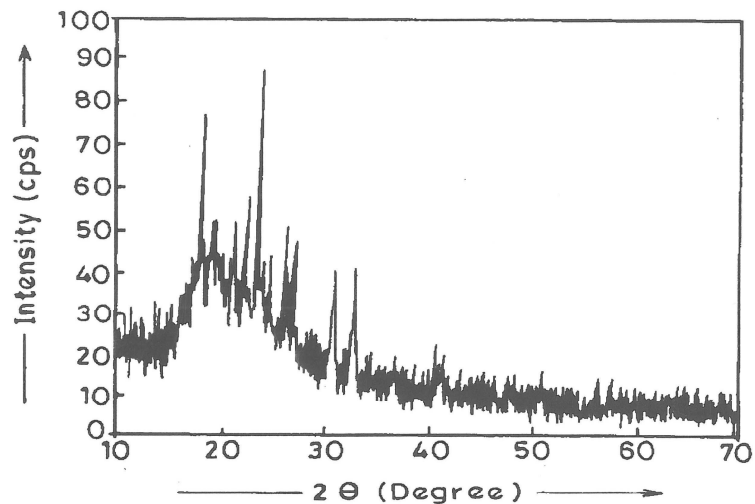


Fig.11: X-Ray diffractogram of PEDOT Nanofibres

The X- ray diffractogram of the sample (8 days, Fig 11) exhibits a broad peak in the range of $\sim 10\text{-}30^\circ$ and two sharp peaks at 2θ values of ~ 31 and 32° confirming the formation of PEDOT. However, no differences were observed in the XRD pattern taken at varying time intervals.

PEDOT and PEDOT nanofibers were successfully prepared at room temperature using ultrasonic technique. In future it is proposed to test these for sensor applications for chemical vapours.

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