Preparation and Characterization of Plasma-Polymerized Thiophene Films

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ABSTRACT: Plasma polymerization of thiophene was carried out in a tubular reactor using an rf source. Various substrates such as aluminum, glass, and NaCl crystal were used. The rate of deposition attained an equilibrium value of 0.35 μg cm^{-2} s^{-1}. Infrared spectra revealed the formation of polythiophene. The films were found to be highly crosslinked. The electrical conductivity was found to be very low (10^{-15}–10^{-10} S/cm). The mode of electrical conduction was found to be space charge-limited current. SEM studies showed that the films consist of globules, the size of which varied from 1 to 10 μ depending on the time of deposition. X-ray diffraction studies revealed the films to be highly amorphous. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 203–209, 1998

Key words: plasma polymerization; polythiophene; thin films; electrical conduction; morphology

INTRODUCTION

Conducting polymers have attracted the attention of physicists, chemists, engineers, and material scientists on account of their many newer properties and the possibility of their applications in emerging technologies. In addition to the normal chemical route of polymerization and electrochemical polymerization, the technique of plasma polymerization can be used for this purpose. Plasma polymerization today is gaining recognition as an important process for the formation of entirely new kinds of materials. This technique is used for preparing organic as well as inorganic thin solid films. The films obtained by plasma polymerization are significantly different from conventional polymers. They are generally of high quality, adherent, and pinhole free.[1] Polythiophene (PTh) is one of the conductive polymers, which is stable in air and can be easily processed. PTh films have been prepared by conventional methods like chemical synthesis[2] or electrochemical polymerization.[3] Recently, plasma has been used for the preparation of PTh.[4] Plasma-polymerized thiophene conducting films have been prepared away from the high rf flux density region in the reactor. An inert gas (Ar) is passed through the plasma zone and its excited species is used for initiating polymerization.[4] Semiconductive thin organic polymer films have been prepared by plasma polymerization of 1-benzothiophene.[5] Also, plasma-polymerized thiophene films have been evaluated as passivating layers on GaAs for metal insulator semiconductor (MIS) field-effect transistors.[6,7] Homogeneous plasma-polymerized films of 2-iodothiophene were obtained which showed good electrical conductivity of up to 10^{-1} S/cm.[8]

In the present investigation, we report the preparation of plasma-polymerized thiophene films in the high rf flux density region near the monomer inlet. The glow discharge was obtained at low pressure (0.5 Torr), using a 13.56 MHz rf source. The deposition rate was calculated for various periods of deposition. The morphology of the films was studied in relation to the deposition

periods. Electrical conductivity was measured by a two-probe method. The films were further characterized using the methods of IR spectroscopy and X-ray diffraction.

EXPERIMENTAL

Plasma polymerization was carried out in an inductively coupled tubular reactor. It consists of a reactor chamber (45 cm long, 3.8 cm diameter), rf power source (13.56 MHz), matching network, vacuum pump, and needle valve. The substrates were thoroughly washed with acetone in an ultrasonic cleaner. The starting material for film formation was a thiophene monomer obtained from Aldrich Chemicals (Milwaukee, Wisconsin, U.S.A.). The cleaned substrates (aluminum plate, glass microslide, and NaCl crystal) were placed near the monomer inlet. Initially, the system was evacuated to about 0.1 Torr and the monomer was injected through a precision needle valve so that vacuum decreased to 0.5 Torr. The deposition was carried out at 10 W of rf power. After the deposition for specific periods (2, 5, 10, 15, 25, 35, 45, and 60 min), the reactor was opened and samples were taken for characterization. The films were characterized by measuring the weight gain. The IR spectra were recorded using a PYE UNICAM Model PU 9512 infrared spectrophotometer. The morphology was investigated using a Philips SEM 515. The samples were tested for their crystallization behavior using a Philips X-ray generator PW 1729 and automatic diffractometer control PW 1710.

Conductivity was measured using a two-probe method[9] in the temperature range of 30–150°C. The schematic diagram of the system used is shown in Figure 1(a). The system consists of a low-temperature cryostat, temperature control device, sample holder, and rotary pump. The sample holder consists of six terminals: two for the heater, two for the thermocouple, and two for the measuring current. The circuit diagram is shown in Figure 1(b). The digital picoammeter (EA 5600, of Electronics Corp. of India) measures the current in the range of 10^{-3}–10^{-11} amperes. The automatic temperature indicator/controller (type DTIC/S, Electronic Control Devices, Bombay) controls the temperature with an accuracy ±1°C. The regulated power supply gives the variable dc voltage upto 300 V. The voltage across the samples was measured with a digital multimeter.
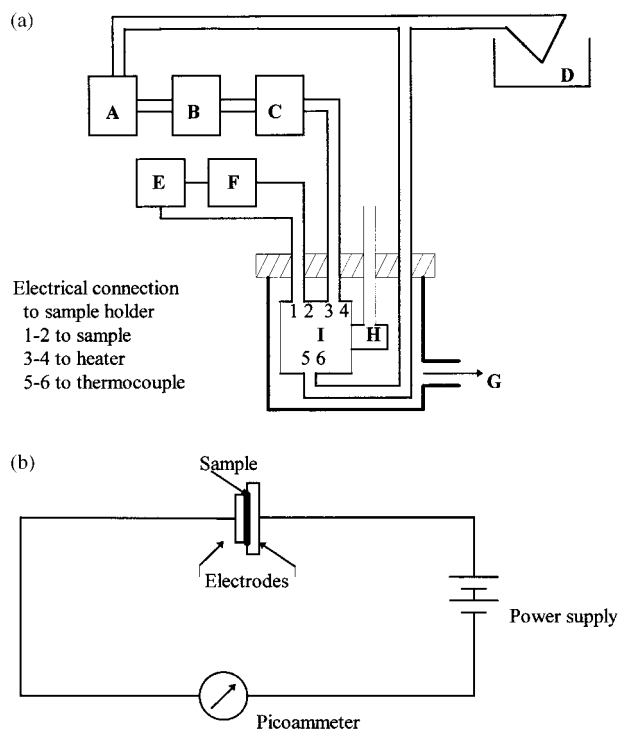

Figure 1(a) Set-up for conductivity measurement: (A) Digital temperature indicator, (B) programmable temperature controller, (C) DC power supply to heater, (D) reference temperature 0°C (ice), (E) digital picoammeter, (F) stabilized power supply, (G) to vacuum pump, (H) liquid nitrogen cylinder, and (I) sample holder. **(b)** Circuit diagram for I–V measurements.

The specimen was sandwiched between aluminum electrodes in the sample holder. The measurements were carried out in vacuum of 10^{-3} Torr. The voltage (V) across the sample was varied from 0 to 150 V and corresponding current (I) was read off from a picoammeter. I–V observations were carried out at temperatures 30–150°C with intervals of 10°C each.

RESULTS AND DISCUSSION

Deposition

It has been reported that the extent of polymerization and deposition depends on the position of the substrate in the reactor. Similarly, the deposition depends on the pressure in the chamber, power applied, rate of flow of the monomer, and addition of the carrier gas. In the present studies, it was thought interesting to place the substrate in the discharge zone and near to the monomer

inlet. To measure the depositions, the samples were weighed using a Mettler AE 240 precision balance with an accuracy 1×10^{-5} g. The substrates used were glass microslides of dimensions 1.8×1.8 cm having a weight of 0.15134 g. Alternately, aluminum plates of dimensions 2×2 cm having a weight of 0.08345 g were also used. The amount of PTh deposited on the substrate was determined from the gain in the weight per square centimeter. Although the thickness of the deposition varies as per the position of the substrate in the reactor, in the present investigation, we feel that the deposited film is homogeneous as only a small area was used for measurement. A few measurements at the edges of the depositions using an interference fringe method shows that the variation in the thickness is 10%. A plot of the amount of the deposition per centimeter squared with respect to the time of the polymerization is depicted in Figure 2. It shows that the amount of deposition increases more or less linearly except during the initial 5–10 min. Therefore, it was thought interesting to find the rate of deposition. The deposition rate was calculated by finding weight gain per unit area per second, that is, μg $cm^{-2} s^{-1}$ and is plotted in Figure 3. It can be seen that the rate of deposition is quite high initially, which decreases and then steadily increases,
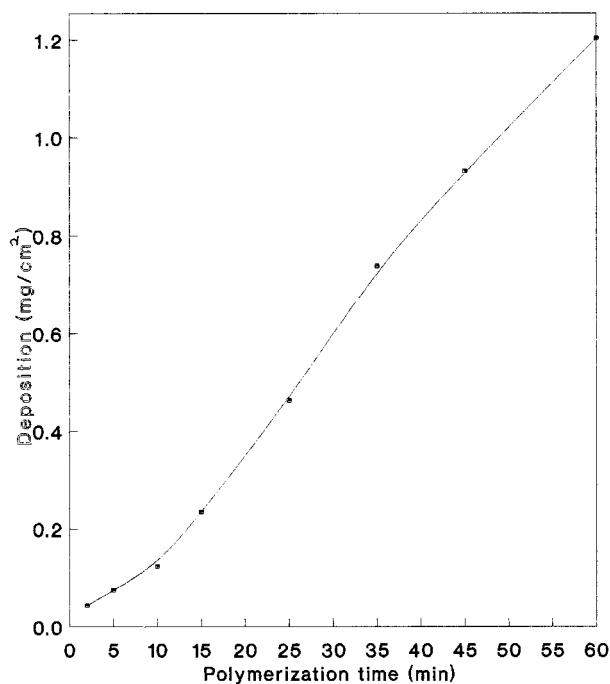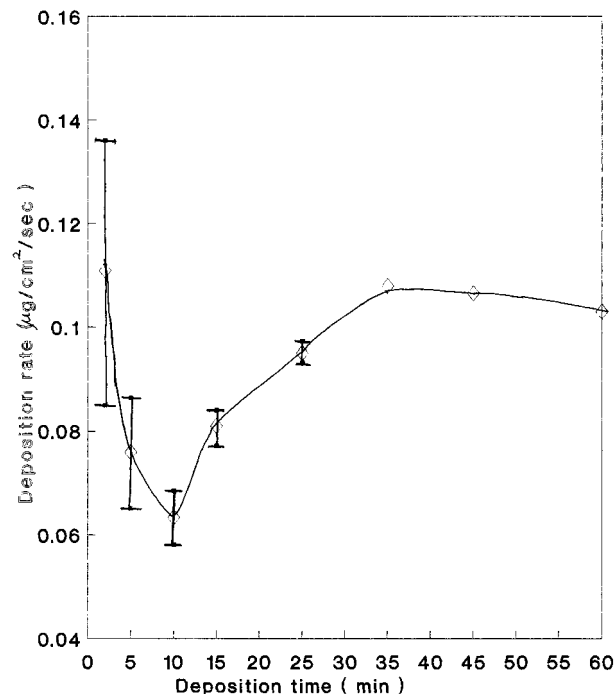

Figure 3 Rate of deposition versus deposition time.

reaching an equilibrium after about 30 min. The error involved in these measurements can be large in the initial stages as the total increase in the weight is much smaller in comparison to the weight of the substrate (40 μg for substrate weight of 0.15134 g). As the time of deposition increases, the weight uptake is higher and thus the error diminishes. This has been indicated by insertion of an error bar in Figure 3. There is sufficient overlap of error for the first two or three points and thus the data expressed will have less reliability for the first two points. However, it does indicate qualitatively that the initial deposition is higher. The high rates of deposition in the initial stage can be understood as due to the adsorbed layer of the monomer on the substrate. This causes increased concentration of the monomer at the inception of glow discharge, so that the deposition rates are high. At a later stage of up to 10 min, although deposition occurs, the competitive ablation process also comes into the picture and, therefore, the deposition rate decreases. After a period of 15 min, the deposition rate increases further. The rate of ablation and deposition then reaches an equilibrium after about 30 min.

Infrared Spectroscopy

During the plasma process, numerous different fragments, radicals, ions, etc., are generated

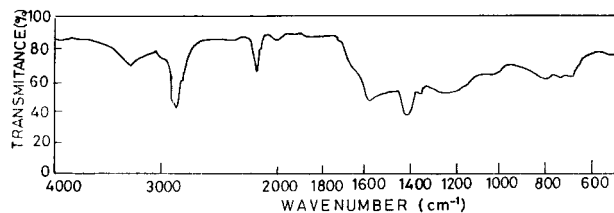**Figure 2** Amount of deposition versus time of polymerization.

Figure 4 Infrared absorption spectrum of plasma-polymerized thiophene.

which form the plasma polymer. They build up an amorphous structure with a high degree of crosslinking. Each molecular structure is embedded in different molecular surroundings. Therefore, IR bands are shifted as compared to their spectral position in conventional polymers and broadened asymmetrically. The films deposited on the NaCl crystal were used to record the IR spectra. In Figure 4, the IR spectra of the plasma-polymerized thiophene deposited for 35 min is given. The following peaks can be assigned for monomer fragmentation and thiophene coating: The absorption peak at 2910 cm^{-1} can be assigned to the stretching mode of methyl and methylene groups. The threefold C—C bond of a fragment from the thiophene ring can be found at 2200 cm^{-1}.[5] This shows that a considerable amount of monomer fragmentation takes place in plasma polymerization. The characteristic absorption of poly-2,5-thiophene can be seen at 1440, 1050, and 700 cm^{-1}. The IR spectra show weak absorption bands at 830 and 750 cm^{-1} which can be assigned to poly-2,4-thiophene. This clearly shows that the film contains molecular groups due to the fragmentation of the monomer ring, α,α'-coupling, and a small amount of α,β'-coupling. Thus, the plasma-polymerized material is a mixture, the major part being normal PTh and minor parts from other reactions.

Conductivity

The electrical conductivity of the films deposited on aluminum plates (2 × 2 cm) were measured using the two-probe method in a sandwiched configuration as shown in Figure 1(b). Thus, what is measured is the bulk conductivity (rather than surface conductivity). Aluminum plates were chosen as the substrate as it would serve as one electrode in contact with the deposited film. The second electrode of aluminum (1 × 1 cm) then could be pressed against the upper surface of the film. Peeling off the deposited film from the glass

substrate is not feasible for such measurements and, therefore, deposition of aluminum plates was used. Thus, the effective area of the sample over which measurement is made is 1 cm^2. The conductivity was measured from 30 to 150°C. The I–V characteristics were studied for all samples polymerized for different durations of time. Since conductivity showed little variation for different samples, films polymerized for 35 and 45 min are discussed in this report. The thicknesses of the films deposited for 35 and 45 min were 3.99 and 6.5 μm, respectively. The conductivity was measured between 0 and 150 V. A typical plot for current versus voltage is depicted in Figures 5 and 6 for temperatures of 60 and 110°C, respectively. It can be seen that in the region of the low field the variation of the current is linear. However, in the region of the high field, the I–V characteristics show nonlinearity. The nonlinearity in the high-field region shows that the mechanism of conduction is not ohmic.

This was further analyzed by plotting a graph of log I versus log V. The graphs for temperatures 60 and 110°C are depicted in Figures 7 and 8, respectively. It can be seen that two separate lines could be drawn. The slopes of these lines are given in Table I. For a temperature of 60°C, the slope of the line changed at around 70 V and that corresponding to 110°C changed at around 100 V.
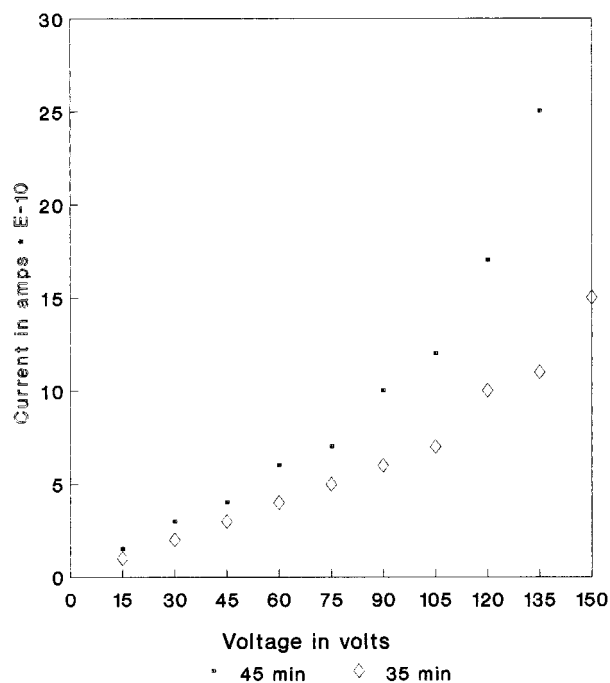

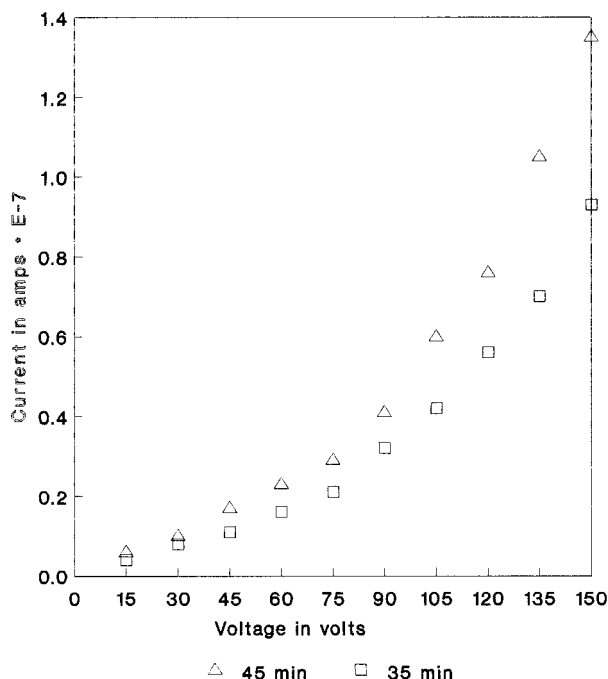**Figure 5** A plot of I versus V at temperature 60°C.

Figure 6 A plot of current versus voltage at temperature 110°C.

In the low-field region, the slopes of all the lines are near to unity, and those in the high-field regions are slightly greater than 2. This shows
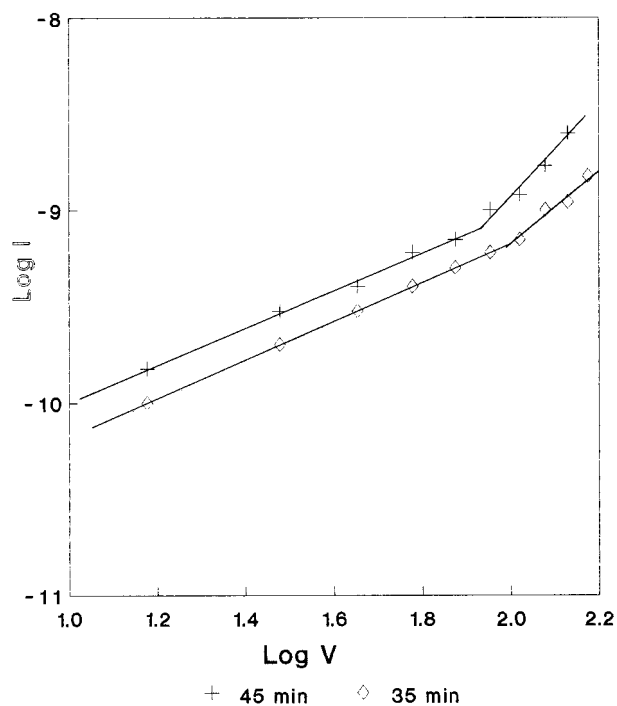

Figure 7 A plot of log I versus log V at temperature 60°C.
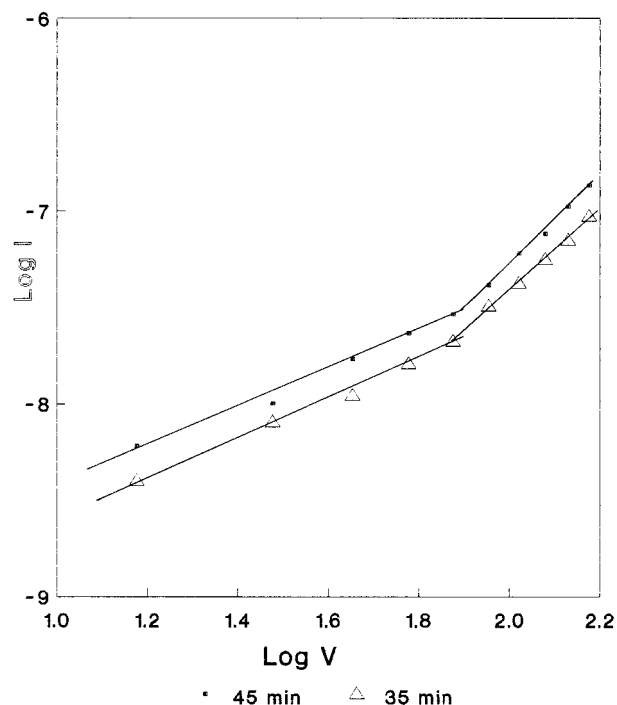

Figure 8 A plot of log I versus log V at temperature 110°C.

that the current in the high-field region is space charge-limited.

The data of electrical conduction was further analyzed by plotting log σ versus $1/T$. The conductivity was calculated from the I–V plots. Because of nonlinearity in the range of voltages used, it was decided to calculate the conductivity in two different voltage regions. The first region is 0–90 V, where the I–V is linear. The other region is 90–150 V, but the slope was taken at that part which is more or less linear. Therefore, in the plot of log σ versus $1/T$ (Fig. 9), we drew two curves, one for each voltage region. The slope of the line can be used for the calculation of the activation energy. The activation

Table 1 Slopes of log I versus log V Plots

	Temperature			
	60°C		100°C	
		Fields		
	Low	High	Low	High
Sample		Slopes		
35 min	1	2.33	1	2.08
45 min	1	2.70	1	2.40

Figure 9 A plot of log σ versus $1/T$.

Figure 10 Electron micrograph of film deposited on glass plate for 45 min.
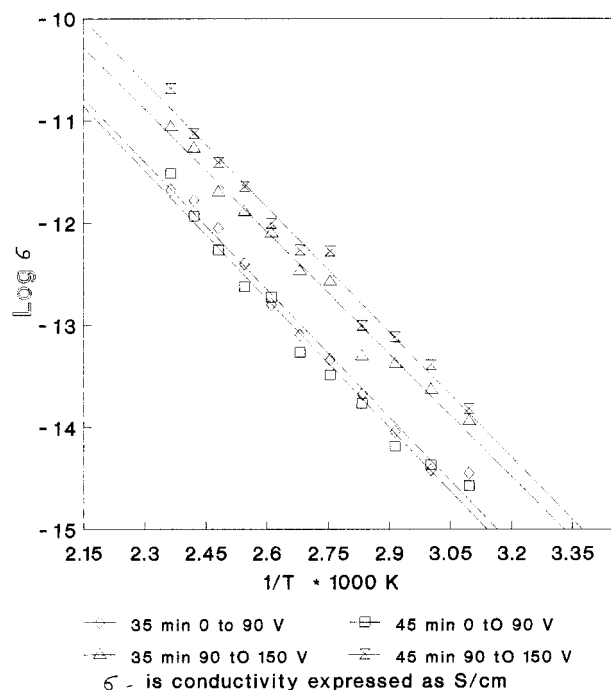
energies were calculated for different samples and are given in Table II. These values seem to be rather high, showing that the film is not a good conductor, contrary to the expectation that PTh has good conductivity. This is possibly due to the higher crosslinking and that the film is in the undoped state. To enhance the conductivity, doping is essential and attempts in that direction are being made. However, our immediate concern for this investigation was aimed at the modification of membranes by plasma treatment rather than by the conduction process.

Morphology

The morphology of the films deposited on glass plates for various periods of deposition was evaluated by SEM. The films have globular struc-

tures. The size of the globules increases with the time of deposition. The films deposited for 10 min showed a globular size ranging from 1 to 1.2 μ, whereas those deposited for 45 min revealed variation from 8 to 10.2 μ. In addition, the number of globules observed were higher (Fig. 10). The morphology of the films deposited on aluminum plates was also studied. The aluminum plate has some machine marks in the form of parallel grooves. The deposition therefore was found to grow along these lines in the form of globules (Fig. 11). When the deposition was carried out for a longer time, one could see the globular structure along with a parallel fiberlike appearance (Fig.
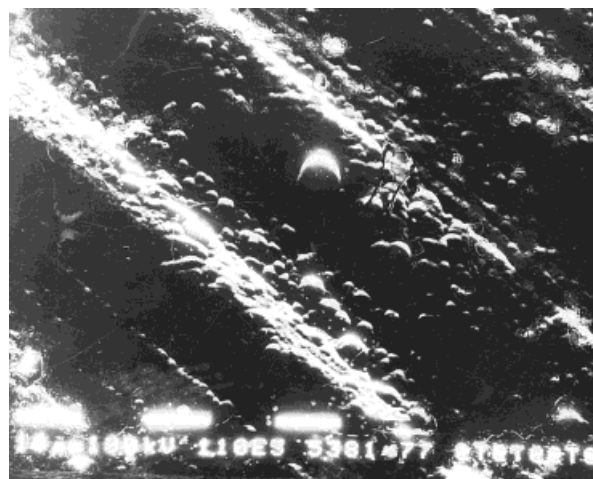
Table II   Activation Energies of Two Samples in Two Voltage Regions

Sample	Activation Energy (eV)	
	0–90 V	90–150 V
35 min	0.85	0.81
45 min	0.85	0.82

Figure 11 Electron micrograph of film deposited on aluminum plate for 25 min.
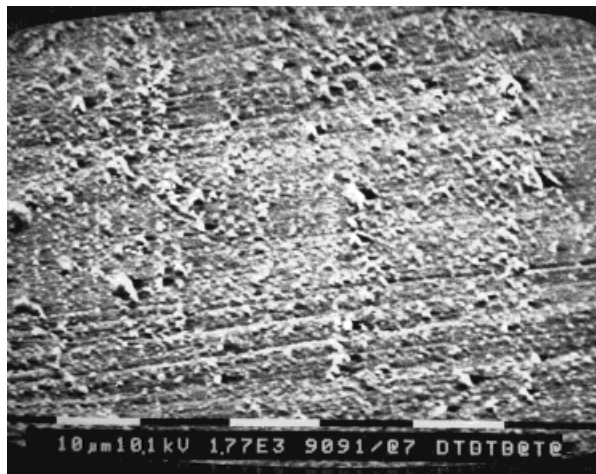
Figure 12 Electron micrograph of film deposited on aluminum plate for 60 min.

12). Incidentally, it may be added that the morphological features of PTh prepared by an electrochemical method also shows globular structure.[10]

All the polymerized thiophene films were studied by the method of X-ray diffraction to obtain more insight into the structure and morphological features. It shows a broad hump with a maximum intensity at around 18° to 19°. This reveals that the material is predominantly amorphous. This supports our microscopic observation of globular formation and IR spectroscopic results, indicating a mixture of different forms which results in an amorphous nature.

CONCLUSIONS

This work thus indicates that thin films of PTh can be prepared by the method of plasma polymerization. IR spectral studies indicate that the major polymerization is through α–α' coupling of the ring, although some α–β' coupling seems to be present. Films of various thicknesses can be prepared by increasing the time of deposition. The morphology of these films seems to be globular. The electrical conductivity of plasma-polymerized thiophene is rather low as compared to other methods of preparation. This can be due to higher crosslinking and that it is in an undoped state. By suitable doping, the conductivity can be increased. Thus, these studies for the control over the electrical conduction process in thin film is interesting and can be useful in the field of thin-film electronics.

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