

# Structure and Effect of Pyrolysis on Plasma Polymerized Polyfuran Thin Films

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**ABSTRACT:** As part of our attempt to make semiconducting polymers from the plasma polymerized polymers, we have polymerized Furan and annealed the polymerized film under different annealing conditions. It is noted that the current density is increased by one order when the sample is annealed in the presence of air, and in the case of vacuum annealed sample, the current density decreased in comparison with the unannealed sample. The probable reason for this difference is also discussed. Comparative study of the infrared spectra of the monomer and polymer gives some hints regarding the structure of the polymer unit. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1176–1179, 2000

**Key words:** plasma polymerization; annealing; conductivity; activation energy; semiconducting

## INTRODUCTION

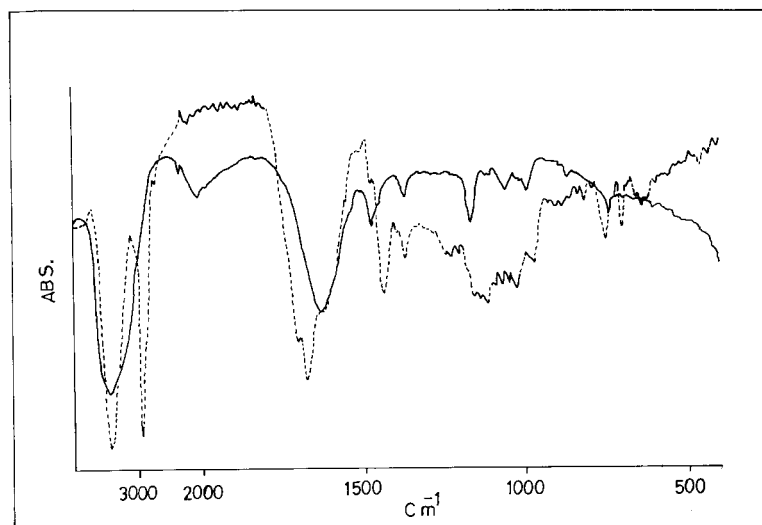
Plasma polymerization, the formation of polymers under the influence of plasma, yields materials that are vastly different from conventional polymers. Owing to their formations by a fragmental polymerization process in contrast to the molecular polymerization process used to synthesize conventional polymers, these materials show no crystallinity and are highly branched.<sup>1,2</sup>

Plasma polymerized organic films are in general dielectric materials with insulating properties.<sup>3</sup> An increasing number of applications are found for these films in a wide variety of fields. Among these applications, they are used as solar mirror protective coatings,<sup>4</sup> antireflection coatings, thin film capacitor materials, humidity sensors,<sup>5</sup> and so on. These films are subjected to different types of treatments such as Iodine doping,<sup>6</sup> annealing in different conditions, to enhance the conductivity and to make semiconducting and

even conducting materials. The aim of this paper is to discuss the structure of plasma polymerized Furan and its dependence of conductivity on thermal treatment under different conditions.

## EXPERIMENTAL

Plasma polymerized Furan films were obtained by polymerizing monomer Furan in radio frequency discharge plasma. The experimental set up consists of a long glass tube connected to a rotary pump for evacuation. To get radio frequency discharge, an oscillator that oscillates in the region 1–4.5 MHz was capacitively coupled to the system. Monomer Furan (AR grade) was polymerized in the radio frequency discharge plasma under monomer vapour pressure of 0.2 Torr and plasma current 20–80 mA. Polymer films in the thickness range 1000–6000 Å could be grown on very well-cleaned glass substrates under the above mentioned conditions with the time of polymerization varying from .5 to 2 h.



**Figure 1** IR spectra of monomer and plasma polymerized Furan. — Monomer Furan; --- Polymer Furan.

The IR spectra of monomer liquid and of polymer thin films were recorded from 400–4000  $\text{cm}^{-1}$  in a Shimadzu IR 470 under identical conditions. The polymer was scrapped from the glass substrate and was pelletized after mixing with KBr. These pellets were used to record the IR spectra.

For the studies of electrical conductivity we have prepared M-I-M structures of area  $0.25 \text{ cm}^2$  in the usual way. Aluminum was used as metal electrodes. Conventional vacuum coating unit under a pressure of  $2 \times 10^{-5}$  Torr was used for electrode coating. The films were annealed either for 1 h at  $150^\circ\text{C}$  in air or vacuum of 0.01 Torr, or unannealed before coating the second electrode.

Electrical measurements were carried out on the sample film after loading the sample in a metal chamber. The current flowing through the films were measured using an electrometer amplifier (Keithley model 617). On applying voltage, the current initially obtained was found to decay with time. For each values of the applied voltages 1 h stabilization time was hence allowed, so that almost constant current values could be recorded. A copper constantan thermocouple mounted on the sample holder, with the fused end in contact with the polymer film, permitted temperature measurements using a APPA classic 108 digital multimeter. Thickness of the samples were measured using Tolensky technique.<sup>7</sup>

## RESULTS AND DISCUSSION

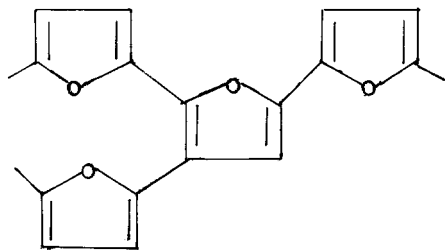
### Structural Characterization

Comparing the IR spectra of monomer and polymer Furan (Fig. 1), it is seen that the ring stretching vibrations are retained in both the spectra, which means the ring does not undergo any rupture in plasma polymerization. But in the polymer spectrum additional intense peaks ( $1120, 1136, 1200 \text{ cm}^{-1}$ ) were observed. These may be attributed to C—C stretching vibrations.<sup>8</sup> The three peaks may be due to Fermi resonance, when additional C—C bonds are created in the processes of polymerization. In electrochemically polymerized Thiophene also, C—C stretching vibrations have been reported in this region.<sup>9</sup> In the light of the above observations, it can be inferred that plasma polymerization of Furan has taken place by Hydrogen abstraction and a tentative structure of the plasma polymerized Furan may be predicted as shown in Figure 2.<sup>10</sup>

### Electrical Studies

The electrical resistance measurements were made between 303 K (room temperature) and 473 K under vacuum conditions. Annealing was done in such a way that at every step the temperature was steady for about 2 min. Every reading is performed by giving a bias voltage of 2 V to the sample.

According to Arrhenius the sheet resistance  $R_{sh}$  can be expressed as

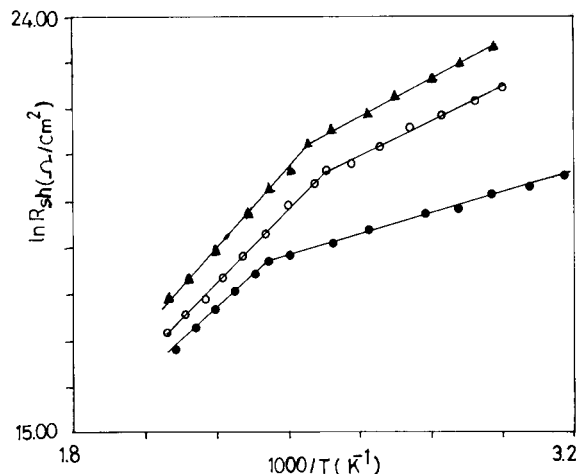


**Figure 2** Proposed structure of plasma polymerized Furan.

$$R_{sh} = R_0 \exp[-(E_{a1} + E_{a2} + E_{a3} \dots)/kT] \dots \dots \quad (1)$$

Where  $k$  is Boltzmann constant and  $E_{a1}, E_{a2} \dots$  etc. are different activation energies. Graphs are plotted for  $\ln R_{sh}$  versus  $1000/T$  in the case of unannealed samples (see Fig. 3), vacuum annealed samples (see Fig. 4), and air annealed samples (see Fig. 5). In Figures 3 and 4, it may be noted that there are two straight line segments with differing slopes for all the films. This means that there are two regions of differing activation energies, one for higher temperature region and the other for lower temperature region. But in the case of film annealed in air, there is only one straight line (Fig. 5), pointing out that there is only one activation energy.

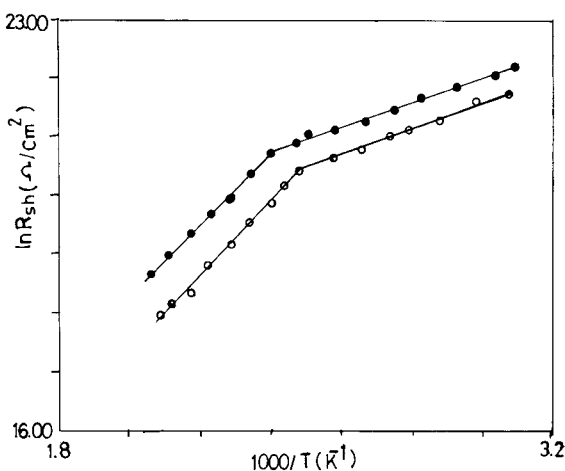
The activation energies obtained from Arrhenius plots of these samples are given in Table I for different thickness;  $A_1$  &  $B_1$  for unannealed samples,  $A_2$  &  $B_2$  for vacuum annealed samples, and



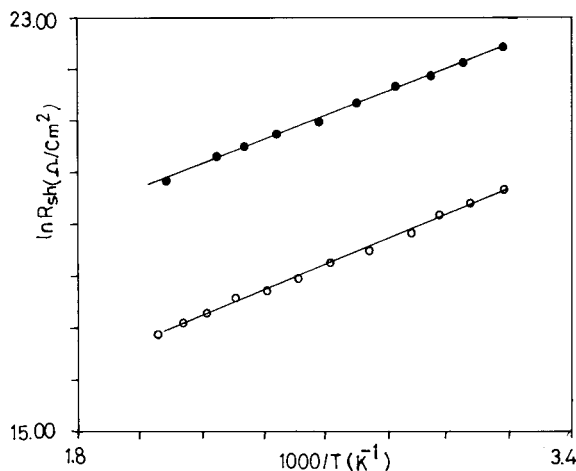
**Figure 4** Plot  $\ln R_{sh}$  versus  $1000/T$  for vacuum annealed polymer Furan.  $\blacktriangle$ -3250 Å;  $\circ$ -1650 Å;  $\bullet$ -1050 Å.

$A_3$  for air annealed samples. From Table I it may be observed that the activation energy (both at high temperature  $B_1$  &  $B_2$  and at low temperature  $A_1$  &  $A_2$ ) decreases with increase in thickness. A similar behavior is reported in other materials also.<sup>11,12</sup> But in the case of vacuum annealed samples, the activation energy increases with the increase in thickness.

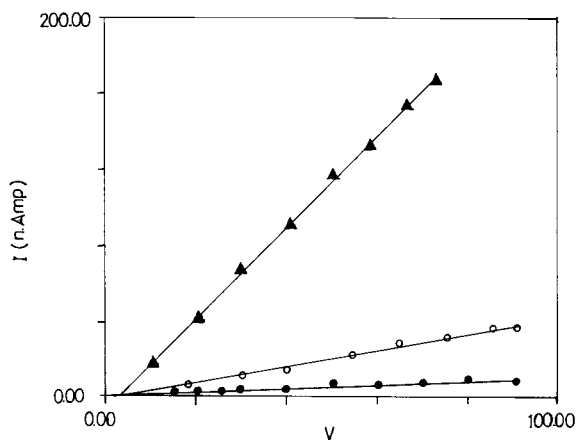
The V-I characteristics of these differently treated samples of thickness 3250 Å is shown in Figure 6. From the figure it may be observed that there is a linear relationship between voltage and current. It may be noted that the current density of the air annealed samples increases by one or



**Figure 3** Plot  $\ln R_{sh}$  versus  $1000/T$  for unannealed polymer Furan.  $\bullet$ -3250 Å;  $\circ$ -1650 Å.



**Figure 5** Plot  $\ln R_{sh}$  versus  $1000/T$  for air annealed polymer Furan.  $\bullet$ -3250 Å;  $\circ$ -1650 Å.



**Figure 6** Plot V-I relationship of differently treated polymer Furan of thickness 3250 Å. ▲-air annealed; ○-unannealed; ●-vacuum annealed.

der compared with that of the unannealed sample. But the current density decreases in the case of vacuum annealed samples with respect to the unannealed samples.

Comparatively low value of activation energy of the air annealed samples with respect to unannealed samples, the increase in the current density, and the single activation energy curve of air annealed samples can all be explained by the process of the diffusion of chemically adsorbed oxygen into the thin film when it was heated in the presence of air.<sup>12,13</sup> The decrease in the current density and increase in the activation energy of the vacuum annealed samples from that of the unannealed samples may be due to the expulsion of oxygen from the trapping sites and removal of impurity levels.<sup>12-14</sup>

**Table I** Activation Energy of Unannealed ( $A_1, B_1$ ), Vacuum Annealed ( $A_2, B_2$ ), and Air Annealed ( $A_3$ ) Samples for Different Thickness

Thickness (Å)	Activation Energy (eV)				
	$A_1$	$B_1$	$A_2$	$B_2$	$A_3$
1050			0.63	0.18	
1650	0.55	0.18	0.68	0.33	0.27
3250	0.53	0.17	0.72	0.36	0.21

## CONCLUSION

The electrical conductivity studies in the range 300 K and 473 K on unannealed, vacuum annealed, and air annealed polymer samples show that the activation energy decreases when annealing takes place in open air, and the conductivity increased by one order. This may be due to the oxygen incorporation from the air. By proper optimization of the plasma polymerization and annealing treatment the conductivity may be enhanced further. The work is progressing in this direction.

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