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Effects of Monomer Flow Rate, Flow Configuration, and Reactor Geometry on the Rate of Plasma Polymerization

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Effects of Monomer Flow Rate, Flow Configuration, and Reactor Geometry on the Rate of Plasma Polymerization

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ABSTRACT

The effects of flow rate on the plasma polymerization of ethylene in an rf discharge were investigated using both a tubular and a bell-jar-type of reactor. Both reactors contained parallel plate internal electrodes. Experiments with the tubular reactor showed that both the total thickness of the deposit and its distribution in the axial direction were strong functions of the flow rate. At low flow rates the polymer thickness decreased in the flow direction, while at high flow rates the polymer thickness increased. Each of these observations is explained by a simple model of plasma polymerization. Using the bell-jar reactor, different monomer flow distribution configurations were tested to determine their effect on the distribution of polymer thickness. It was found that distribution or diffusion of the monomer inflow provided a more uniform film.

INTRODUCTION

The use of plasma-polymerized films for whatever purpose will undoubtedly require that they be prepared with uniform thickness. To accomplish this it is first necessary to know how the discharge conditions affect the rate of polymer deposition. In previous work [1-3] we have known that flow rate can have a significant influence both on the rate of polymer deposition and the form of the polymer. The purpose of the present study was to carry this work further to explore the effects of flow rate, flow configuration, and reactor geometry on the rate of polymer deposition and the distribution of film thickness in the film produced. Ethylene was used for these studies since the majority of the earlier work had focused on the behavior of this monomer.

EXPERIMENTAL

The two reactors used in this work are illustrated in Figs. 1 and 2. The first (Fig. 1) is built around a glass tube 7.8 cm in diameter and 40 cm long. A pair of copper electrodes 15 cm long are located in the middle of the reactor, and Teflon inserts are placed before and after the electrodes to form a gas passage of uniform cross section. The electrodes are 6 cm wide and are spaced 5 cm apart. Gas is supplied through a circular fritted distributor, 4 cm in diameter, located 15 cm ahead of the discharge zone. The second reactor (Fig. 2) is a glass bell jar containing two 6-in. diameter copper electrodes spaced 5 cm apart. Monomer is fed through a glass tube to the upper part of the reactor and evacuated through a port in the baseplate.

Power for both reactors was supplied by an IPC Model PM401 rf generator which operates at 13.56 MHz and has a maximum output of 150 W. The upper electrode of each reactor is connected to the generator through an impedance matching network. The lower electrode is grounded and maintained at 20°C by water flowing through it.

The flow rate of ethylene (Matheson, CP grade) into each reactor was monitored by a rotameter and controlled by a needle valve. The pressure in the reactor was adjusted by a second valve located between the reactor and the vacuum pump. Pressure was measured with a McLeod gauge.

Either aluminum foil or a chromium-finished steel plate was used as the substrate onto which the polymer was deposited. Before each experiment the substrate surface was cleaned with acetone and then placed on the lower electrode. After the deposition the amount of

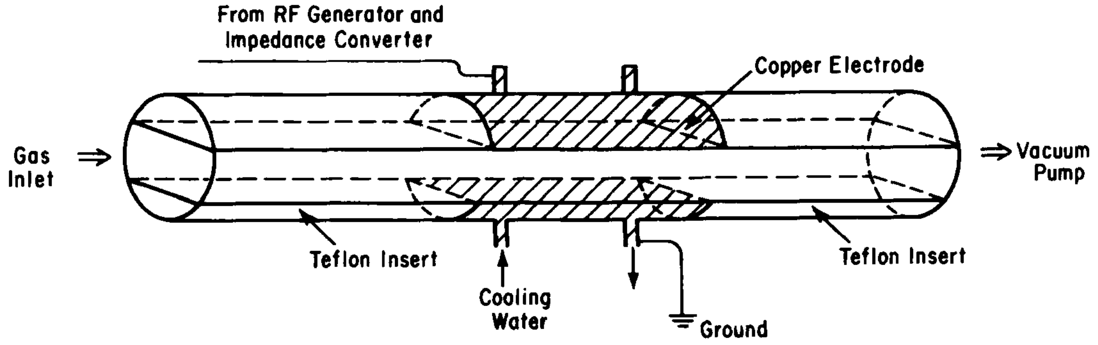

FIG. 1. Schematic of the tubular-type reactor.

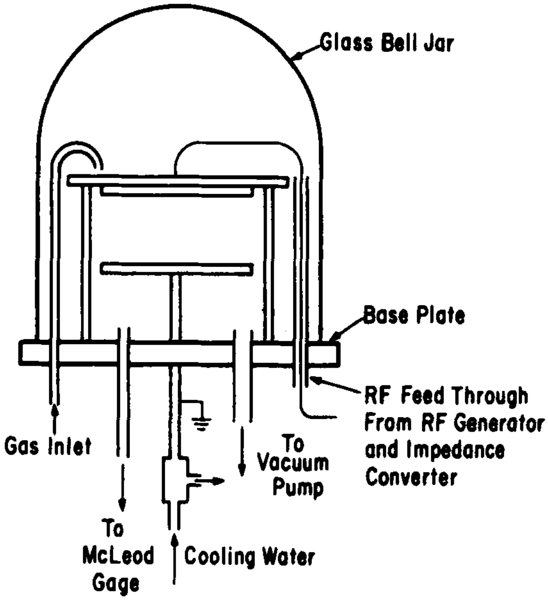

FIG. 2. Schematic of the bell-jar reactor.

polymer deposited was measured as a function of position in the direction of gas flow. When aluminum foil was used as the substrate, the distribution of polymer mass was determined by weighing each of the strips used to cover the electrode surface. The weight of polymer deposited on each strip was confirmed by measuring the sum of the weights of carbon and hydrogen in the film determined by Pregel's method. For deposition on the steel plate, the polymer thickness distribution was measured with a Surfanalyzer (Clevite Corp.). This instrument records film thickness directly through the displacement of a stylus which is traversed across the film.

RESULTS AND DISCUSSION

Figure 3 illustrates the distribution of polymer deposition in the tubular reactor as a function of axial position. The solid lines were obtained by determining the weight of polymer accumulated on 5 cm wide strips of aluminum foil in a fixed interval of time. Since the deposition rate was found to be independent of time, the rate was expressed as the mass of polymer accumulated per unit of time.

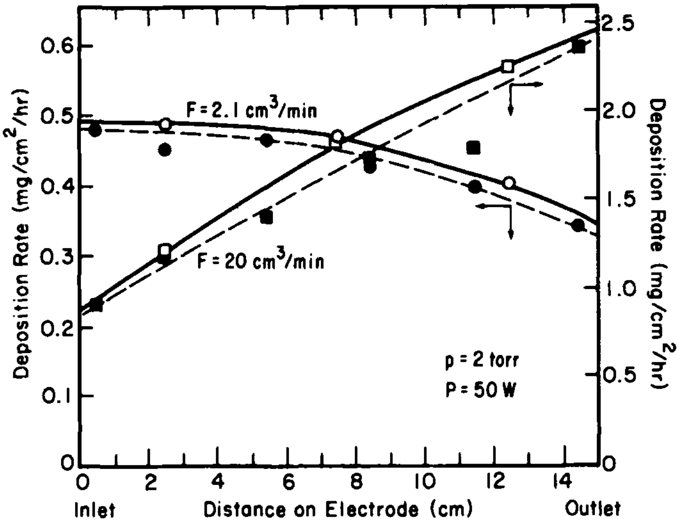

FIG. 3. Effect of monomer flow rate on the deposition rate distribution along the electrode length (pressure 2 Torr, power 50 W).

The dashed curves in Fig. 1 were obtained from the weights of carbon and hydrogen present in a strip 1 cm wide. As may be seen, the deposition rates measured by the two methods agree quite well.

Figure 3 shows that both the level and the distribution of deposition rates depend on the ethylene flow rate to the reactor. It should be noted that the indicated flow rates are at STP. At the lower flow rate the deposition rate decreases in the direction of flow, while at the higher flow rate this trend is reversed.

The effect of flow rate on the total polymer deposition rate for the tubular reactor is shown in Fig. 4. At low flow rates the deposition rate is equivalent to the monomer feed rate, indicating that the monomer is converted to polymer quantitatively. With increasing flow rate the deposition rate at first follows the 100% conversion line but then passes through a maximum, and finally decreases at higher flow rates.

The shape of the curve in Fig. 4 has been interpreted [4] on the basis of a simple model of plasma polymerization. At low flow rates the monomer residence time in the discharge is sufficient to allow for the production of a high concentration of polymer precursors, which are assumed to be free radicals caused by electron-monomer collisions. The rate of polymer formation is so rapid

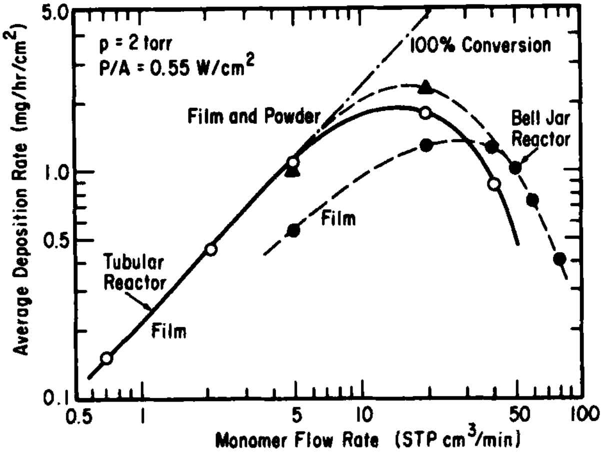

FIG. 4. Overall deposition rate as a function of monomer flow rate for the bell-jar-type and tubular-type reactor (pressure 2 Torr, power 0.55 W/cm^2).

under this condition that essentially all of the monomer is converted to polymer. At very high flow rates the monomer residence time is reduced so that fewer free radicals are formed and the polymer formation rate is therefore reduced.

The effect of residence time can be seen more clearly in Fig. 5. Here the solid curves indicate the deposition rate for a fixed flow rate as a function of the residence time θ. The definition for θ is given by

$$\theta = A\ell/F \tag{1}$$

where A is the cross-sectional area for flow, ℓ is the axial distance measured from the leading edge of the electrode, and F is the volumetric flow rate of ethylene at STP. The dashed curves connect the points of common axial position.

At low residence times, which correspond to a high flow rate, the deposition rate increases with ℓ for a fixed value of F. As the residence time is increased by decreasing F, the slope of the solid curves decreases and finally becomes negative. This pattern can be explained in terms of the model outlined above. At high flow rates the extent of monomer conversion is limited by the gas-phase concentration of free radicals (see Fig. 4). Under this condition the longer the gas spends in the discharge, the greater will be the

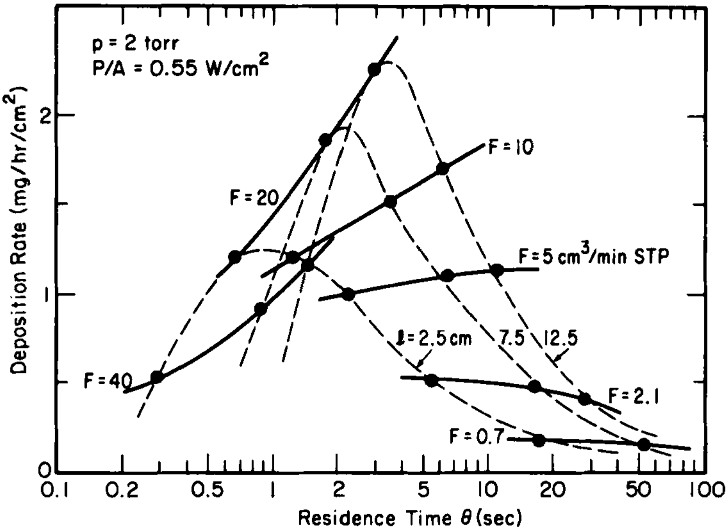

FIG. 5. Effect of residence time on polymer deposition rate.

concentration of free radicals and hence the polymer deposition rate. Hence it is expected that the deposition rate will increase with ℓ as is seen in Fig. 5. At the other extreme, when F is low, the rate of polymer deposition is limited by the availability of monomer. In this case we expect the deposition rate to decrease as the residence time increases due to the depletion of monomer. Reference to Fig. 5 shows that this is exactly what happens.

The dashed curves in Fig. 5 are essentially the same as the curve in Fig. 4. Thus we see that at a fixed axial position the polymer deposition rate passes through a maximum as the residence time is increased by decreasing the flow rate. The interpretation of these curves is the same as that for Fig. 4. It should be noted, however, that at a fixed residence time the dashed curves do not overlap. This signifies that the simple model, while capable of giving a qualitative interpretation of the data, is not sufficiently detailed to give a complete description of the data.

An additional conclusion, which can be drawn from Fig. 5, is that uniform film thickness can be achieved through the proper selection of flow rate. The flow rate at which uniform film thickness is achieved will probably depend on both the pressure and power selected. However, for each pressure and power there should be a flow rate which yields uniform film thickness.

The effect of flow rate on the total polymer deposition rate for the bell-jar reactor is also illustrated in Fig. 4. The pattern observed is essentially the same as that for the tubular reactor. The overlap of the curves for the two reactors is rather surprising considering that the volumes of the two reactors, and hence the residence times for a given flow rate, differ greatly. An explanation for this observation is not available at this time. Nevertheless, the similarity of the curves indicates that the basic physical phenomena occurring in the two reactors are the same.

To identify the effects of gas flow pattern in the bell-jar reactor on the distribution of film thickness, a series of experiments were performed using the inlet and outlet configurations shown in Fig. 6a. The corresponding curves of thickness distribution are shown in Fig. 6b.

Configurations A and D give similar dome-shaped thickness profile for which the thickest point is at the electrode center. Configuration C gives a similar profile but the total thickness is reduced somewhat. When the monomer inlet is positioned, as in configuration B, the thickness profile is skewed in the direction of flow. A similar effect is seen for configuration E. In this instance the thinnest point in the film is at the electrode center. Finally, configuration F, which is a superposition of configurations A and E, shows a pattern which appears to be a cross between those for configurations A and E.

It is evident from these results that the flow configuration can have a very strong influence on the thickness distribution of the deposited film. Placing the monomer inlet in close proximity to the discharge zone, as in configurations B and E, leads to a thinning out of the film in the immediate vicinity of the inlet. This is most likely due to the high velocity, and hence low residence time of the monomer in this region which, as we have seen in Figs. 4 and 5, leads to low polymer deposition rates. Distribution or diffusion of the monomer inflow aids in providing a more uniform film (see configurations A, C, D, and F).

It should be noted that for all of the flow configurations the film thickness near the perimeter of the electrode is low. It is possible to explain this observation in terms of the electron density distribution, which is highest near the electrode center and falls off with increasing radius. Consequently, the rate of electron-monomer collisions, which are required to initiate the polymerization process [4], is lowest near the perimeter.

CONCLUSIONS

The present work has shown that monomer flow rate and the inlet flow configuration have a strong influence on both the rate

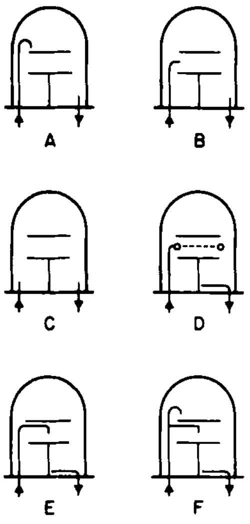

FIG. 6a. Schematic of inlet-outlet configuration of the bell-jar-type reactor.

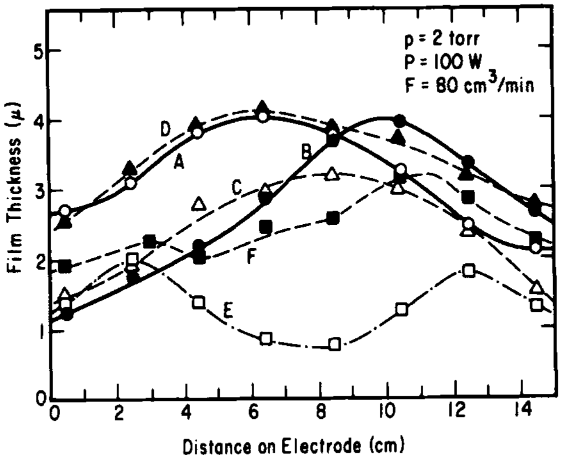

FIG. 6b. Effect of reactor configurations (refer to Fig. 6a for configurations) on the distribution of film thickness on the electrode. (Bell-jar-type reactor; in the flow direction; pressure 2 Torr, power 100 W, ethylene flow rate 80 cm^3/min STP, discharge time 60 min.)

of polymer deposition and the uniformity of the deposited film. Through the use of a simple model of plasma polymerization, it has been possible to explain most of the effects of flow rate on the polymer deposition rate and its distribution in the direction of flow. Finally, it has been shown that, through a proper selection of flow rate and inlet configuration, it is possible to deposit uniform polymer films.

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