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Polymerization of Organic Compounds in an Electrodeless Glow Discharge. VIII. Dependence of Plasma Polymerization of Acrylonitrile on Glow Characteristic

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Synopsis

The effects of experimental conditions (i.e., flow rate, pressure, discharge wattage, and glow characteristics) on the plasma polymerization of acrylonitrile were investigated. It was found that the glow characteristic is highly dependent on both flow rate and discharge wattage and that the plasma polymerization depends strongly on the glow characteristic. However, when experimental conditions are selected to maintain a fully developed glow in the tail flame portion of rf discharge, plasma polymerization is independent of discharge wattage and pressure. The polymer deposition rate is linearly proportional to the monomer flow rate. The deviations from this ideal situation are generally attributable to incomplete glow or partial glow under conditions which caused the deviation. The "character" of the glow largely determines the chemistry of the system. Consequently, the properties of polymers formed under different glow characteristics are also different.

INTRODUCTION

In this series of studies on plasma polymerization, we have used the tail flame portion of glow discharge in a relatively simple tube reactor.[1,2] This kind of reactor has a definite advantage in that the accurate flow rate of monomers, which go through the entire volume of the reactor, can be easily measured. In bell-jar-type reactors, on the other hand, the monomer feed-in rate into the reactor does not generally correspond to the monomer flow rate in the plasma region, which is only a small portion of total volume of the apparatus.

In previous studies, 1–3 the discharge power to be used for a monomer was selected so that full glow could be maintained throughout the entire reaction tube at the highest pressure to be used in the experiment. This procedure was chosen based on the observation that the deposition of polymer occurs only on the surface that is exposed to the "glow." Some extent of polymer deposition also occurs onto the surface that is not directly in contact with the "glow;" however, its rate is several orders of magnitude smaller than that in the glow region, and such a polymer deposition is not considered in studies of polymer deposition rate.

Under conditions of full glow in the tail flame portion of an inductively coupled

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rf discharge, the polymer deposition rates for most organic compounds investigated were found to be nearly independent of discharge power and to be linearly proportional to the monomer flow rate (within a range of experimental conditions).

The importance of the extent of glow was also observed in a study which employed a reaction tube that had a constriction.[4] The apparent intensity of glow in the constriction was much higher than that in the wide portion of the tube, and the deposition rate onto the wall of the smaller-diameter portion (constriction) was found to be higher also. This increase was attributed to the increase of the surface/volume ratio in the constriction, indicating that the polymer deposition rate itself is dependent on the surface/volume ratio. This implies that the deposition rate of polymer in a glow discharge is a system-dependent parameter and not a parameter unique to a monomer. Therefore, a deposition rate observed in a reaction system does not necessarily describe the deposition rates which will be observed in a different reactor.

An important aspect also found in the study[4] was that the increase of the deposition rate in the constriction is not due to the increase in the flow rate. Although the linear velocity increases in the constriction, the total number of monomer molecules passing through the constriction was identical to that in the wider portion of the reactor. This indicates that the characteristics of glow may also be an important factor, although the previous studies[1–3] showed that the deposition rate is nearly independent of the intensity of glow in the full glow region.

In this study, the effect of the glow characteristic was examined at various discharge power values and different flow rates. Acrylonitrile happened to be an ideal monomer for this study since the transition of partial glow to full glow could be observed within convenient ranges of both discharge power and flow rate in the standard reactor used in this series of studies.

EXPERIMENTAL

The flow rate of the monomer was determined by the following method. First, the entire system was evacuated to a pressure of <0.1 μm Hg. Then, without changing the opening of the stopcock which connects to the pump system, a steady-state monomer flow was established by adjusting the metering valve opening, and the pressure of the system was recorded. The stopcock in the downstream side of the reactor was then closed, and the increase in pressure was recorded as a function of time. From the initial rate of pressure increase (dp/dt) and the volume of the reactor V, the flow rate in cm^3(S.T.P.)/min was calculated.

After the determination of flow rate, the system pressure of the steady state was adjusted to 60 μm Hg by controlling the opening of the downstream-side stopcock. It was confirmed that the change in steady-state flow pressure did not cause change in the monomer flow rate within the range of conditions employed in this study.

The extent of glow was examined at each flow rate, simply by observing the glow at a given discharge wattage, while gradually increasing the discharge wattage up to 120 W and then while gradually decreasing it again. The threshold wattage which produces the glow that is fully extended in the entire tube was recorded. Below the threshold value, the flow is weakened and it does not fill

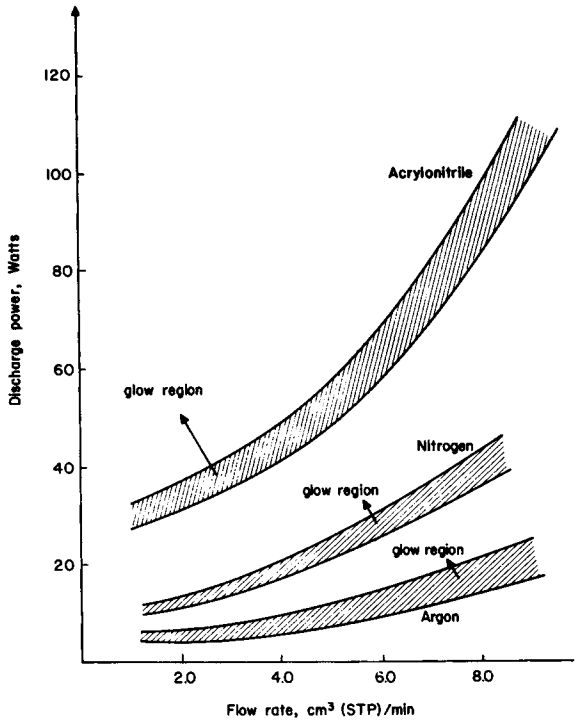

Fig. 1. Dependence of glow on flow rate and discharge power for acrylonitrile, nitrogen, and argon.

the entire volume. The threshold value can be measured only in a rough range; however, it is possible to determine the dependence of glow on the flow rate by using a wide band instead of a line, as shown in Figures 1 and 2.

The polymer deposition rate is determined by measuring the weight increase of small pieces of aluminum foil placed in a fixed position in the reaction tube.

RESULTS AND DISCUSSION

The dependence of glow of acrylonitrile on the flow rate is shown in Figure 1, where the same dependence is compared with nitrogen and argon plasma. With any set of combinations of flow rate and wattage which is located above each line shown by a wide band, the glow covers the entire reaction tube; below the line, the downstream side of the tube is not completely covered by a glow although discharge occurs. The area within a band may be considered as a transient glow region.

Deposition rates were measured under two series of experimental conditions. The wattage dependence was examined at a fixed flow rate of 5.8 cm^3(S.T.P.)/min. This condition was chosen because it was known that in the full glow region the deposition rate is nearly independent of discharge wattage.[1,2] This condition is shown in Figure 2 by the line AB.

The dependence of deposition rate on flow rate was measured at 60, 100, and 130 W. The line CD in Figure 2 corresponds to the condition at 60 W.

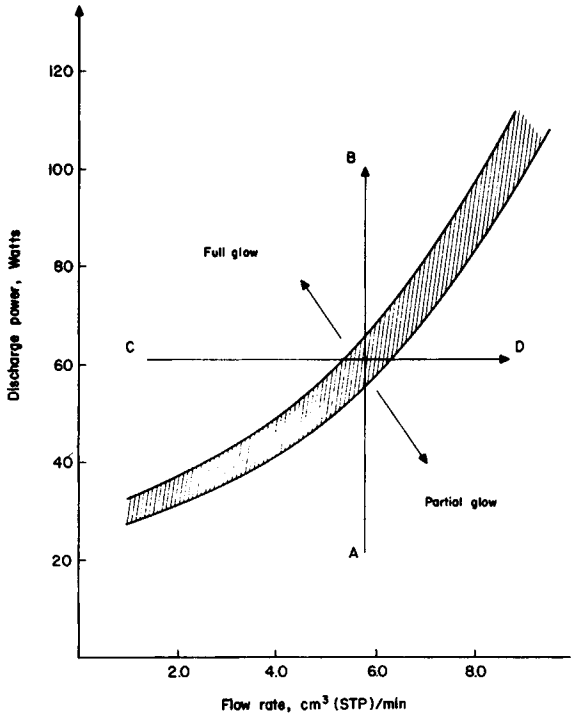

Fig. 2. Influence of glow on experiments: AB, variable discharge power at a fixed flow rate 5.8 cm^3(S.T.P.)/min; CD, variable flow rate at a fixed discharge power (60 W).

The wattage dependence is shown in Figure 3, which shows clearly that (1) the apparent dependence of deposition rate on wattage observed at a fixed flow rate (without considering the effect of glow characteristic) may include the effect due to the character of glow, and (2) in fully developed glow the deposition rate is independent of the discharge wattage as previously reported.[1,2]

The flow rate dependence is shown in Figure 4. The results shown in the figure confirm that the deposition rate is proportional to the flow rate, as previously reported.[2] The deviation from this linear dependence on flow rate at higher flow rates is caused by the change from full glow (at low flow rates) to the incomplete glow at higher flow rates as the increase of flow rate crosses the line shown in Figure 2. When the discharge wattage is increased, the increase of flow rate no longer crosses the line within the limits of the experiment, and the deposition rate dependence on flow rate becomes normal.

The properties of polymers that are formed in both the normal glow and weak glow regions are also different. It is observed that the polymer formed in the normal glow region [5.6 cm^3(S.T.P.)/min] is brown and insoluble in any solvent, but the polymer formed in the weak glow is light yellow and soluble in polar solvents such as acetone and dimethylformamide.

The dependence of plasma polymerization on the glow characteristic is also reflected in the pressure in the discharge. The system pressure of steady-state flow of the monomer, p_m, changes to a new system pressure of steady-state flow in the discharge, p_g, and the value of $\delta = p_g/p_m$ was taken as an important parameter related to the plasma polymerization.[2,3] In Figure 5, the p_g values are

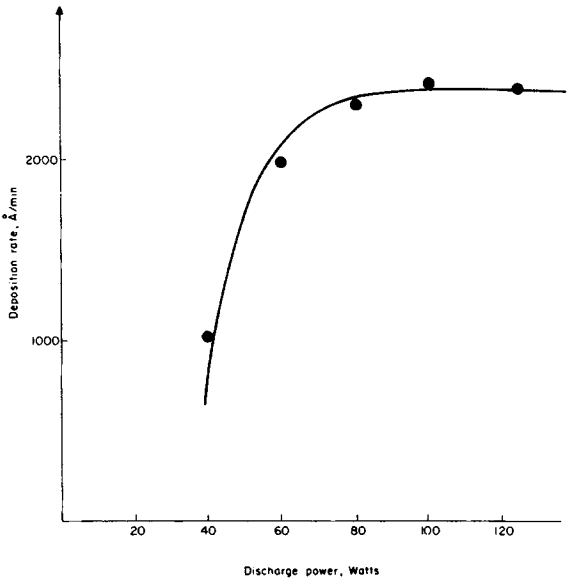

Fig. 3. Dependence of polymer deposition rate on discharge power at a fixed flow rate 5.8 cm^3(S.T.P.)/min.

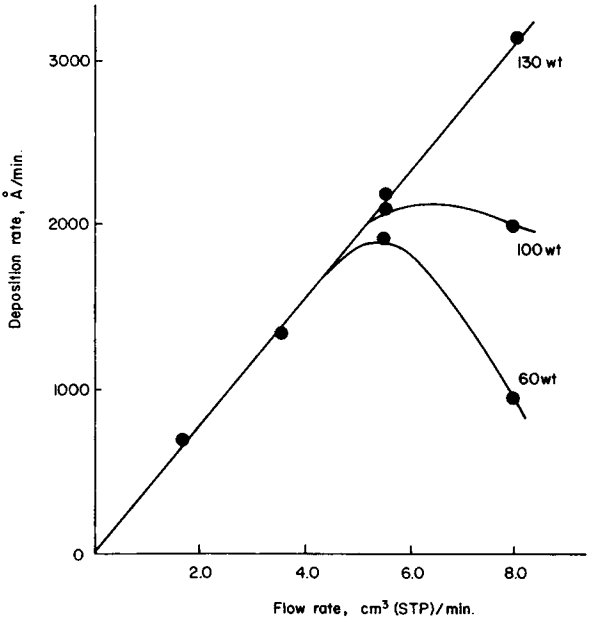

Fig. 4. Dependence of polymer deposition rate on monomer flow rate observed at a fixed discharge power (60 W).

plotted against the discharge wattage for various flow rates. In this figure, the full glow region is below the line shown by a shaded band. The results indicate that the value of δ is also dependent on the state of glow but becomes constant (independent of wattage) in the full glow region, although the value of δ itself is dependent on the flow rate. The fact that δ is independent of wattage in the

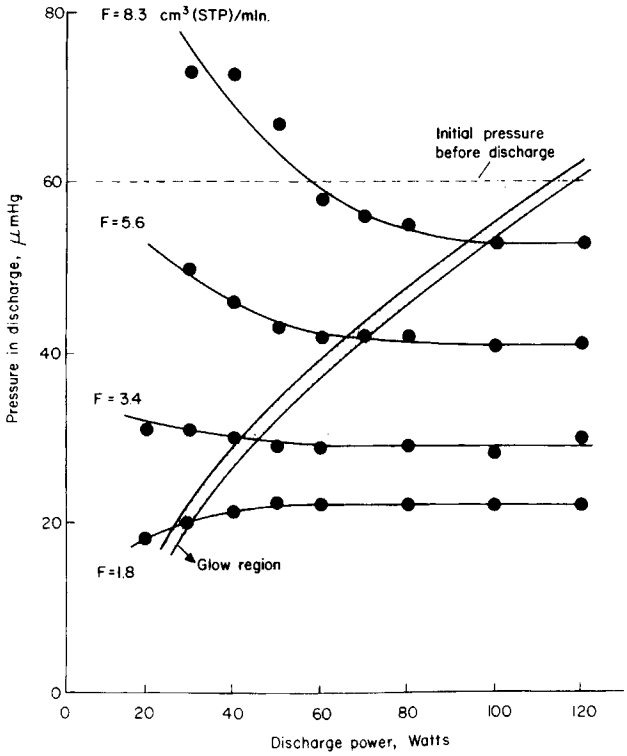

Fig. 5. Dependence of system pressure (of flow) in discharge of acrylonitrile on discharge power at different flow rates.

full glow region is consistent with the wattage-independent deposition rate in this (full glow) region.

The fact that the discharge pressures of acrylonitrile at $F = 8.5$ cm³(S.T.P.)/min at low discharge powers (see Fig. 5) are above the initial pressure before discharge, p_m, indicates that the mechanism of polymer formation or chemistry involved in the partial glow is different from that in the full glow region. If the partial glow is the same glow as the full glow that occupies only a portion of the reactor, the pressure in the discharge should not increase from the initial pressure (p_m) in the case of acrylonitrile, which has a low δ value.[2] This discussion implies that polymer in the partial glow condition is formed by mechanisms different from those in the full glow region. The difference in properties mentioned above may be reflecting the difference in polymerization mechanisms.

CONCLUSIONS

Results shown in this study indicate that glow characteristic is an important factor to be considered in the study of plasma polymerization. The "character" of the glow largely determines the chemistry of the system. The glow itself is dependent on the combined factor of flow rate of monomer and discharge power. If the flow rate is increased, higher wattage is necessary in some cases to maintain the same glow characteristic. Therefore, the true dependence of polymer deposition rate as well as properties of polymers on operational parameters such

as discharge power, flow rate of monomer, and the pressure of the system should be examined without changing the glow characteristic.

Any set of experimental conditions such as that shown by line AB or line CD in Figure 2, which crosses the glow characteristic line, involves an additional change of a parameter "glow characteristic," i.e., from "full glow" to "partial glow" or vice versa. For instance, if the change of glow characteristic is not taken into consideration, we might have reached an erroneous conclusion that the deposition rate of acrylonitrile decreases after passing the maximum as the flow rate increases, based on the experiments carried out at low discharge powers (e.g., 40 W).

The chemistry involved in the partial glow, at least with certain types of monomers, seems to be completely different from that which occurs under full glow conditions. Consequently, the properties of polymers formed in the "full glow" region and in the "incomplete glow" region are also different.

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References

1. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **15**, 2277 (1971).
2. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **17**, 1519 (1973).
3. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **17**, 1533 (1973).
4. H. Yasuda and T. Hsu, *J. Appl. Polym. Sci.*, **20**, 1769 (1976).

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