

# Polymerization of Organic Compounds in an Electrodeless Glow Discharge. VII. A Fluid Mechanic Aspect of Plasma and Its Effect on the Polymer Deposition Rate

H. YASUDA and T. HSU, *Research Triangle Institute, Research Triangle Park, North Carolina 27709*

## Synopsis

The deposition rate of polymer from plasma of an organic compound is influenced by the fluid mechanical aspect of plasma. Using cylindrical reactors which have constriction of various size, and utilizing the tail-flame portion of inductively coupled r.f. (13.5 MHz) glow discharge, it is demonstrated that the polymer deposition rate is proportional to the ratio of surface area/volume of the reactor tube, which has been often neglected in studies of polymer deposition rate.

## INTRODUCTION

It is well known that the polymer deposition rate from polymer-forming plasma of an organic vapor is influenced by the conditions of discharge. Factors of discharge such as vapor pressure, discharge wattage, current density in the case of discharge with electrodes, flow rate of monomer, etc., have been reported to play important roles in determining the rate by which the polymer deposits. However, little attention has been paid to the fluid mechanical aspect of plasma, and many elaborate investigations have been reported without even specifying the geometric factor of the reaction vessels used.

Although the deposition of polymer occurs onto the surface exposed to plasma, the deposition rate such as one given by  $g/cm^2 \cdot min$  does not constitute the accurate description of plasma polymerization unless vapor phase from which the solid polymer deposits is specified. For instance, a certain deposition rate observed with large volume reactor cannot be directly compared with the deposition rate observed with a very small volume reactor. This situation becomes crucially important for discharge with electrodes under the conditions where the majority of polymer deposits exclusively onto the surface of electrodes.

In case of inductively coupled glow discharge where polymer deposition occurs on the entire surface exposed to plasma, the situation is much simpler since the ratio of surface area/volume of the reaction vessel can be easily specified.

It is intended to show how important the fluid mechanical aspect of plasma

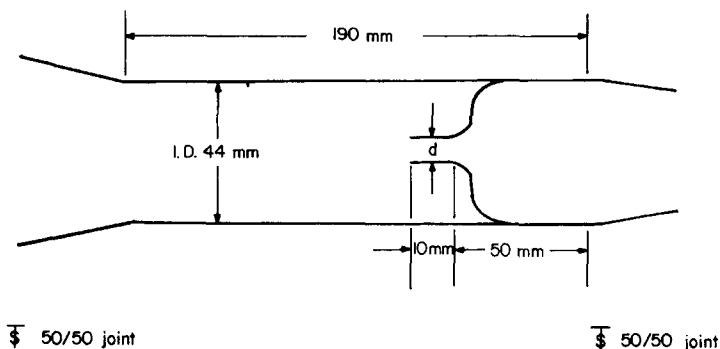


Fig. 1. Schematic representation of a reaction tube with a constriction.

is and to draw attention to the need of a more specific description of the reaction vessels used in the study of polymer deposition rates.

### EXPERIMENTAL

The reaction system used in this study is essentially the same as the one described previously.<sup>1,2</sup> Special reaction tubes are made for this study. Schematic representation of the reaction tube is shown in Figure 1. The total volume of the tubes are made as nearly identical as possible. The size of constriction is varied by using different-sized glass tubes. The total volume of the reaction system including a pressure gauge is approximately 1 liter. A small aluminum foil strip is placed in the small tube, and the weight increase due to polymer deposition is measured. The conditions of discharge are selected so that glow extends to the entire volume of a reaction tube. The glow in the small tube portion is very intense, but glow is maintained also in the downstream side of the constriction. Polymer deposition rates are measured under identical conditions using reaction tubes which have constriction tubes of various size.

### RESULTS AND DISCUSSION

Since a steady-state flow is maintained, the total number of molecules in the gas phase (plasma) passing through in a unit time is identical at the constricted portion with that at the wide tube portion. The surface area exposed to plasma is given by  $S = 2\pi rl$ , where  $r$  is the radius and  $l$  is the length. The volume of plasma in the same tube is given by  $V = \pi r^2 l$ . Therefore, the ratio of surface area/volume is given by  $S/V = 2/r$ .

If the polymer deposition rate is independent of the fluid mechanical aspect of plasma, the same rate should be observed regardless of the size of the constriction, since the total number of molecules involved is identical, and also the process of generating plasma takes place at the identical distance away in the upstream side.

Whether plasma phase reaction or wall surface reaction plays the predominant role in polymer deposition has been a subject of interest and of debate in recent years. However, this question cannot be wholly answered without

specifying the detail of the system used, since the ratio of gas phase reaction to the reaction at the wall surface is dependent on geometric factors of the system. Because this question is also related to the subject of this study, it may be worth examining the situations.

For simplicity of discussion, let us consider a simple monomer system and treat the monomer as an ideal gas. From the kinetic theory of gases, the number of collisions between like molecules per unit volume and per unit time,  $Z(AA)$ , is given by

$$Z(AA) = (4\pi RT/M_A)^{1/2} \sigma_{AA}^2 n_A^2$$

where  $M_A$  is the mass of molecule  $A$ ,  $n_A$  is the number of molecules per  $\text{cm}^3$ , and  $\sigma_{AA}$  is the collision diameter, which equals the molecular diameter for collisions between the like molecules. Substituting the known numerical values, one obtains

$$Z(AA) = 3.23 \times 10^4 (T/M_A)^{1/2} \sigma_{AA}^2 n_A^2.$$

Since the number of molecules per  $\text{cm}^3$  at a pressure of  $p$  mm Hg and temperature  $T$  °K is given by

$$n_A = 9.652 \times 10^{18} p/T$$

$Z(AA)$  can be written as a function of  $p$  and  $T$  as

$$Z(AA) = 3.01 \times 10^{42} p^2 T^{-3/2} M_A^{-1/2} \sigma_{AA}^2.$$

The number  $\dot{n}$  molecules striking a unit area per second is given by the kinetic theory of gases as

$$\dot{n} = n_A (RT/2\pi M_A)^{1/2}$$

and, therefore,

$$\dot{n} = 3.51 \times 10^{22} p M^{-1/2} T^{-1/2}.$$

The ratio  $\phi$  of gas-wall collision/gas-gas collision in the total system is given by

$$\phi = \frac{S\dot{n}}{VZ(AA)} = \frac{S}{V} 1.17 \times 10^{-20} \frac{T}{p\sigma_{AA}^2}.$$

This equation indicates that the ratio  $\phi$  is dependent on the surface-volume ratio ( $S/V$ ), temperature, pressure, and the size of the gas molecule. For a given monomer at fixed pressure and temperature, the ratio  $\phi$  is directly proportional to the surface-volume ratio ( $S/V$ ) of the system.

It is interesting to examine if the polymer decomposition rate is dependent on the ratio  $\phi$ . Under the conditions employed in this study,  $S/V$  is given by  $2/r$ , where  $r$  is the radius of the tube in the constriction. Therefore, the dependence of polymer deposition rate on the ratio  $\phi$  can be obtained by the plot of deposition rates versus  $1/d$ , where  $d$  is the inner diameter of the constriction. Such plots are shown in Figure 2 for the plasma polymerization of tetramethyldisiloxane.

The solid circles in Figure 2 represent the deposition rate obtained at a vapor pressure of 60  $\mu\text{m}$  Hg (initial pressure before plasma is initiated), and the open circle, at a vapor pressure of 40  $\mu\text{m}$  Hg. At a vapor pressure of 40

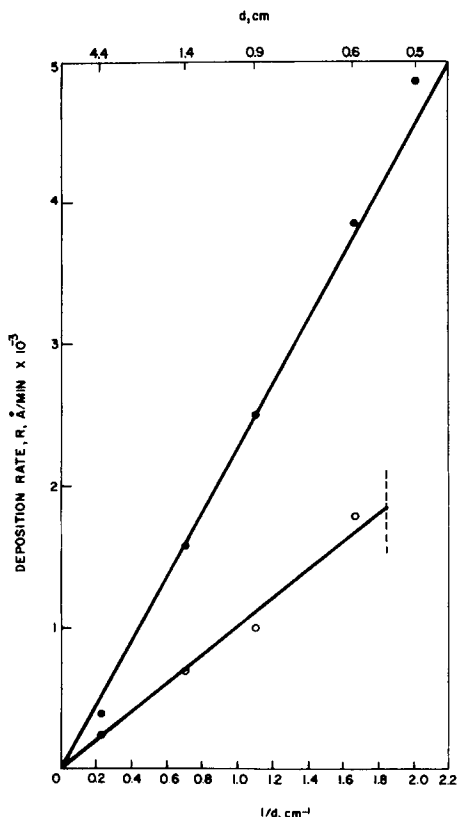


Fig. 2. Dependence of polymer deposition rate on the diameter  $d$  of the constriction.

$\mu\text{m Hg}$ , glow does not penetrate into the 5-mm constriction, and no polymer deposition occurs in the tube. This may probably be due to the factor that low pressure (longer mean free path) does not favor the penetration of plasma into a small tube. The quantitative examination of this factor may require further examinations at various flow rates. At a fixed flow rate of the equipment used, the slopes of two straight lines are in good agreement with the dependence of the deposition rate being approximately proportional to the square of the initial pressure, as previously reported.<sup>1</sup>

The results show that the polymer deposition rate is indeed directly proportional to the surface-to-volume ratio and consequently to the ratio  $\phi$ . It means that neither gas-phase reaction nor the surface reaction is the predominant factor in the plasma polymerization dealt with in this study. For this interpretation, the following important aspects of conditions selected for this study should be noted. (a) The monomer used is not a conventional monomer, and the possibility of plasma-induced polymerization is virtually eliminated. (b) The polymer-collecting surface is a distance away from the inductive coil, and it is expected that the initial process of ionization (e.g., impact of electron and the consequent thermal effect) is largely decoupled in the tail-flame portion of the plasma.

If a vinyl monomer of high condensibility is used, or if the capacitively coupled discharge is used and polymer is collected on a electrode surface, consid-

erably different results might be obtained due to the additional complicated factors. Nevertheless, the results of this experiment clearly indicate that the polymer-forming plasma can be dealt with as a uniform plasma phase and the polymer deposition rate (exclusive of plasma-induced conventional polymerization of condensed monomer) is influenced by the surface-to-volume ratio of the reactor.

This fluid mechanical aspect of plasma is also evident with nonpolymer-forming plasma. It has been observed<sup>3</sup> that the degradation of polymer exposed to N<sub>2</sub> plasma is very severe in the constricted portion, and that polyethylene film inserted in the constricted portion suffered a permanent deformation due to partial melting, whereas the same polyethylene films placed in the wider portions of the tube (before and after the constriction) did not show any visible difference after they were exposed to N<sub>2</sub> plasma simultaneously.

The apparent intensity of glow also follows the same trend, i.e., plasma is much more intense in the pinched portion; and the smaller the diameter of constriction, the more intense is the apparent intensity of the glow.

It has been generally observed that polymer deposition occurs only to a surface that is exposed to glow. More precisely, the deposition rate of polymer onto a surface which does not contact with glow is several orders of magnitude smaller than that onto a surface which contacts glow.

Results shown in this paper clearly demonstrate the deposition rate of polymer onto a surface which contact glow is dependent on the ratio of surface/volume of the glow. This factor seems to have important implications in the application of plasma polymerization which may involve various sizes and shapes of substrates.

This study was supported by the National Heart and Lung Institute, NIH, U.S. Department of Health, Education and Welfare, Contract No. NO1-HB-3-2913.

### 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, M. O. Bumgarner, and N. Morosoff, Annual Report (1973), NO1-HB-2918-1, Biomaterial Program, National Heart and Lung Institute, NIH, U.S. Department of Health, Education, and Welfare; National Technical Information Service, PB-239 097, 1974.

Received July 29, 1975

Revised September 4, 1975