

# Polymerization of Organic Compounds in an Electrodeless Glow Discharge. XI. Pressure in Glow Discharge

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## Synopsis

The pressure of a steady-state flow of monomer,  $p_0$ , changes to a new steady-state flow pressure,  $p_g$ , in glow discharge. The value of  $p_g$  is dependent on the flow rate of monomer, the pumping-out rate of the vacuum system for the product gas (which is hydrogen in many cases of plasma polymerization of hydrocarbons), and the characteristic hydrogen yield of a monomer associated with plasma polymerization. The relationships between these factors were established and examined for plasma polymerizations of acetylene, ethylene, and acrylonitrile.

## INTRODUCTION

In glow discharge of an organic compound, where plasma polymerization of the compound occurs, the total number of molecules in the gas phase changes. Polymerization decreases the total number of molecules in the gas phase, and the splitting of the original monomer molecule (e.g., evolution of hydrogen, or detachment of chemical groups) increases the total number of molecules in the gas phase. Although this is a self-evident aspect of plasma polymerization, the system pressure of polymer-forming plasma has not been dealt with properly in studies of plasma polymerization. In many reports appearing in the literature, no distinction between the system pressure in and before the discharge is made. Some investigators recognize the change in system pressure after the discharge is initiated, but no quantitative analysis regarding the cause of the change and how it is related to other operational parameters has been presented.

In parts II and III of this series of studies,<sup>1,2</sup> it has been shown that the pressure of a steady-state flow in plasma,  $p_g$ , is different from the pressure of the steady-state flow of monomer before plasma is initiated,  $p_0$ , and that the ratio  $\delta = p_g/p_0$  can be correlated to characteristic behavior of an organic compound in plasma.

In parts IV and V of the same series,<sup>3,4</sup> the pressure change observed in a closed system was examined. In a closed system, the original pressure  $p_0$  changes to  $p_g$  within a few seconds in most cases, and the value of  $\gamma^0 = p_g/p_0$  is fairly close to the value of hydrogen yield (number of hydrogen molecules evolved from a molecule of monomer when polymerization occurs) for many hydrocarbons<sup>3</sup> and for amines and nitriles.<sup>4</sup>

The value of  $\gamma^0$  is an important characteristic parameter of a monomer for

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plasma polymerization which can be easily measured. The value of  $\delta$  (in a steady flow system) is not usually identical to the value of  $\gamma^0$  and depends on other factors of plasma polymerization. If we know the relationship between  $p_g$  (in a steady-state flow) and  $\gamma^0$  (in a closed system), the influence of operational factors such as flow rate, discharge power, etc., on the characteristic nature of plasma polymerization of a monomer can be easily monitored by the reading of  $p_g$  in a steady-state flow experiment. The objective of this paper is not to evaluate the value of  $\gamma^0$  from the flow system experiment, but to find quantitative relationship which describes the dependence of the system pressure in the actual glow discharge (where plasma polymerization takes place) to other operational parameters of plasma polymerization. The basic factors that control the value of  $p_g$  are examined in this paper.

## DEPENDENCE OF $p_g$ ON FLOW RATE

### Flow Rate and System Pressure of Flow

The flow of gas in a tube can be related to the pressure as follows:

**Mean Free Path Larger than the Diameter.** For a cylindrical tube of diameter  $d$  and length  $L$ , the number of molecules flowing from side 2 (pressure  $p_2$  and temperature  $T_2$ ) to side 1 (pressure  $p_1$  and temperature  $T_1$ ) is given by<sup>5</sup>

$$F = \frac{Nd^3\pi}{3L\sqrt{2\pi MR}} \left( \frac{p_2}{\sqrt{T_2}} - \frac{p_1}{\sqrt{T_1}} \right)$$

where  $M$  is the molecular weight,  $N$  is Avogadro's number, and  $R$  is the gas constant. In this case, the flow is linearly proportional to the pressure drop ( $p_2 - p_1$ ) if  $T_2 \approx T_1$ .

**Mean Free Path Smaller than the Diameter.** In this case, the Poiseuille formula for the flow of liquid through a tube is applicable.<sup>5</sup> For a short tube, flow being isothermal, the amount of gas in moles  $\text{sec}^{-1}$  flowing through a tube of length  $L$  cm and diameter  $d$  cm is given by

$$\frac{(d/2)^4\pi(p_2^2 - p_1^2)}{16L\eta RT}$$

where  $p_2$  and  $p_1$  are pressures (dynes/cm<sup>2</sup>) at the two ends of the tube,  $R$  is the gas constant, and  $\eta$  is the viscosity of the gas. When  $p_1$  is maintained at zero (compared to  $p_2$ ), flow in this case is proportional to the square of the pressure  $p_2$ .

In a practical polymerization system, the reactor is not a straight cylindrical tube and the pressure reading is not taken at the inlet and outlet of the gas flow. Therefore, in the pressure range which we use (i.e., 0 to 200  $\mu\text{m Hg}$ ) and under the condition of  $p_1 \approx 0$ , the gas flow is empirically given by

$$F = ap^b \quad (1)$$

and the value of  $b$  lies in the range of  $1 < b < 2$ , where  $p$  is the system pressure of the reactor measured at a fixed point. How well this relationship is obeyed can be seen from the results shown in this paper.

The actual flow rate  $F$  and pressure  $p$  of the flow system of a gas are controlled

by (1) the feed-in rate, which is governed by the opening of a metering valve and by the tank pressure applied at the valve, and (2) the pumping rate, which is governed by the pump capacity, by the distance and size of tubing between the reactor and the pump, by the presence of a trap, and by the condensibility of the gas.

A liquid-nitrogen trap acts as an excellent pump for many condensible organic vapors when the trap is placed close to the outlet of the reaction tube. Typical cases are shown in Figure 1, where flow rate is plotted against pressure of the system with and without the liquid-nitrogen trap. In this case, the liquid-nitrogen trap provides a pumping rate which is six to seven times higher than that of the mechanical pump.

### Change in System Pressure of a Flow Due to Glow Discharge

Experiments carried out in closed systems<sup>3,4</sup> indicate that the total number of organic vapors,  $n$ , changes to  $\gamma n$  when the monomer is subjected to glow discharge. Since pressure is directly proportional to the number of gas molecules in a closed system, the value of  $\gamma^0 = p_g/p_0$  obtained by a closed system can be used as a characteristic parameter of a monomer.

As far as the gas phase is concerned, therefore, plasma polymerization in a closed system can be described by



Let us assume the same reaction (plasma polymerization observed in a closed

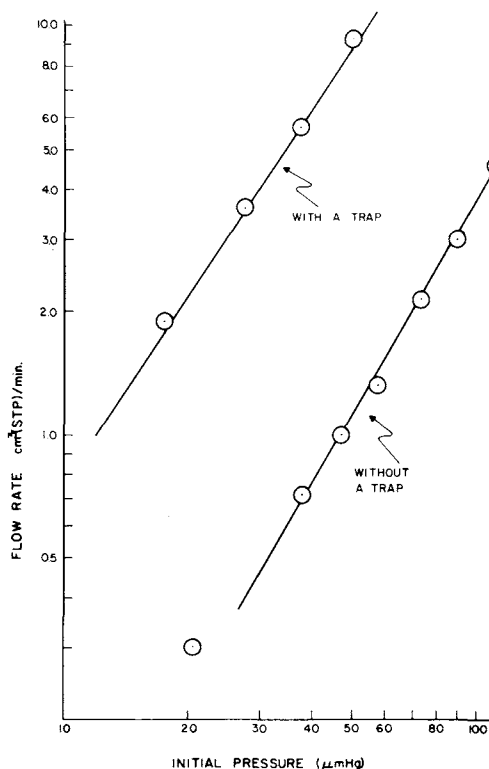


Fig. 1. Flow rate vs pressure for ethylene obtained with and without liquid-nitrogen trap.

system) occurs in a steady-state flow system. In this case, reaction (2) can be written as

$$dn/dt \rightarrow \gamma dn/dt. \quad (3)$$

In a flow system, the plasma polymerization is visualized by a process which changes the flow rate of gas.

The flow rate  $F_1$  of monomer coming into the reactor is given by the pressure of the flow system  $p_1$  of the monomer before discharge according to eq. (1):

$$dn/dt = F_1 = a_1 p_1^{b_1}. \quad (4)$$

As soon as the reaction (plasma polymerization) occurs, the total number of molecules in gas phase changes to  $\gamma(dn/dt)$  and this amount of gas must be pumped out by the vacuum system to maintain a steady-state flow. The pumping-out rate  $F_2$  for the gas to be pumped out is also given by eq. (1):

$$F_2 = a_2 p_2^{b_2}. \quad (5)$$

Therefore,

$$a_2 p_2^{b_2} = \gamma a_1 p_1^{b_1} \quad (6)$$

or

$$a_2 p_2^{b_2} = \gamma F_1. \quad (6')$$

Consequently, the pressure in discharge,  $p_g$ , started from a steady-state flow which had the system pressure  $p_0$  is given by

$$\log p_g = \log c + d \log p_0 \quad (7)$$

where

$$c = (\gamma a_1 / a_2)^{1/b_2} \quad (8)$$

$$d = b_1 / b_2 \quad (9)$$

or

$$\log p_g = \log c' + d' \log F_0 \quad (10)$$

where

$$c' = (\gamma / a_2)^{1/b_2} \quad (11)$$

$$d' = 1/b_2. \quad (12)$$

Subscript 1 denotes the monomer, and subscript 2 denotes the gas to be pumped out from the system (product gases) for eqs. 4–12.

If we know the product gases and parameters  $a_2$  and  $b_2$ , the validity of eqs. (7) and (10) can be examined. From the results of closed-system experiments,<sup>3,4</sup> the major portion of gas products from plasma polymerization of acetylene, ethylene, and acrylonitrile is hydrogen. Therefore, parameters (i.e.,  $a_2$  and  $b_2$ ) for hydrogen can be used for this purpose, and the value of  $\gamma^0$  obtained by closed-system experiments can be compared to the values of  $\gamma$  observed in flow-system experiments to check the validity of eqs. (7) and (10).

## EXPERIMENTAL

The reaction tube used for this study is identical to one previously described.<sup>1,2</sup> Although the vacuum system is slightly different, the essential design of the reactor system remains the same. The pressure of the system is read by a Baratron pressure transducer located just before the valve (outlet valve) that connects the reactor to the vacuum system. Two pumping rates were used, one without and one with the liquid nitrogen trap. *Unless otherwise indicated, experiments were carried out without changing the opening of the outlet valve.* The monomer flow is controlled by the opening of a metering valve while keeping the outlet valve fully open. Once the opening of the metering valve is set under a constant pressure of the monomer reservoir, the monomer flow rate is independent of the system pressure (within the range used in this study).

The flow rate is measured by closing the outlet valve and recording the initial slope of pressure increase as a function of time. Using the  $p$ - $V$  relationship, the flow rate in  $\text{cm}^3(\text{S.T.P.})/\text{min}$  is calculated. After the pressure and flow rate are determined, glow discharge is initiated and the pressure in discharge is recorded. The same procedure was applied to obtain the flow rate-to-pressure relationship for hydrogen, the product gas. High enough discharge power (100 watts) was used to maintain full glow through the reaction tube for all flow rates.

## RESULTS AND DISCUSSION

The relationship between monomer flow rate and system pressure is well represented by the empirical equation given by eq. (1), as seen in a typical example shown in Figure 1 for ethylene. It should be noted that the system pressure  $p_0$ , before the discharge is initiated, is dependent on both flow rate of monomer  $F_0$  and also the pumping rate of the system. Namely, with a liquid-nitrogen trap which acts as an excellent pump for condensible vapors such as ethylene, the system pressure is much lower compared to the case without the trap, even when the monomer flow rate is identical.

It is an important point that the system pressure  $p_0$  is not a unique function of the flow rate but is highly dependent on the pumping rate. Manipulation of the  $p_0$  value requires change in flow rate and/or change in pumping rate.

How well eqs. (7) and (10) are followed is shown in Figures 2 and 3, respectively, for results obtained with glow discharge of ethylene. The important point here is that the system pressure  $p_g$  in discharge, when the outlet valve is maintained in the same condition, is determined by the monomer flow rate and the characteristic nature of the monomer (represented by the parameter  $\gamma^0$ ), not by the initial system pressure  $p_0$ . Only when the pumping rates of the system are known, for the monomer and for the product gas, can  $p_g$  be related to  $p_0$  by eqs. (7), (8), and (9). The most important relationship to describe  $p_g$  is given by eq. (10).

Flow characteristics (parameters  $a$  and  $b$ ) of monomers and hydrogen are summarized in Table I. Results of  $p_g$  are summarized in terms of parameters  $c$ ,  $d$ ,  $c'$ , and  $d'$ , eqs. (7) and (10), in Table II.

The validity of the relationship is examined by comparing experimental values with corresponding theoretical values in Table III. Results shown in Table III show that the  $p_g$ -versus- $p_0$  and  $p_g$ -versus- $F_0$  relationships are well described by eqs. (7) and (10), respectively.

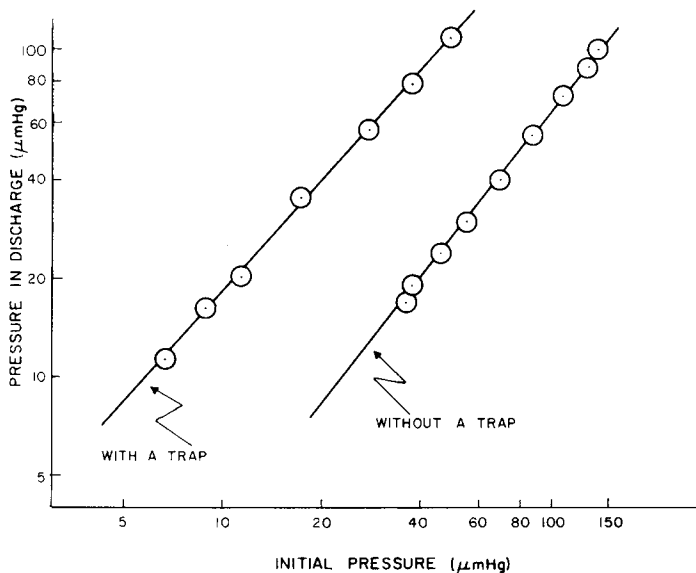


Fig. 2. Pressure in discharge,  $p_g$ , vs initial pressure  $p_0$  for ethylene.

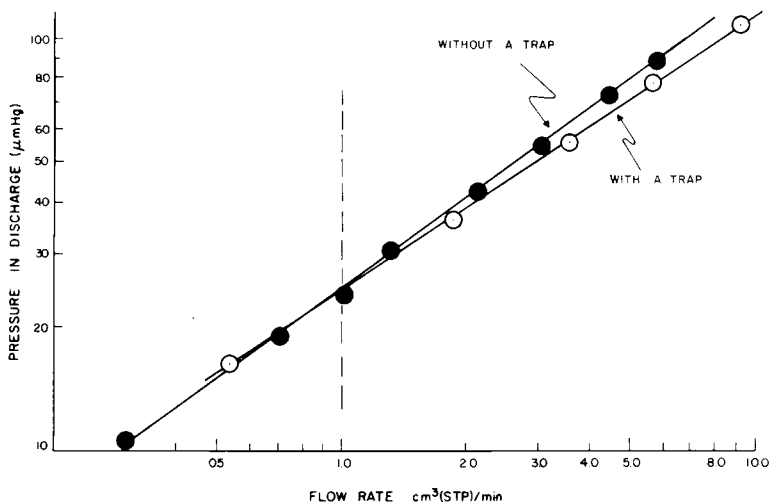


Fig. 3. Pressure in discharge,  $p_g$ , vs flow rate  $F_0$  for ethylene.

The plots of  $\log p_g$  versus  $\log F_0$  for different monomers which produce the same gas (e.g.,  $H_2$ ) yield parallel straight lines which intercept  $F_0 = 1$  at different values depending on value of  $\gamma$  for the monomer, as shown in Figure 4 for acetylene and ethylene. The value of  $p_g$  is dependent on  $\gamma$  and  $F_0$ . In case of closed-system experiments,  $p_g$  is dependent on  $\gamma$  and  $p_0$ . Good agreement between  $\gamma$  calculated from data obtained by a flow-system experiment with that obtained in a closed-system experiment indicates that the basic reaction involved (i.e.,  $n \rightarrow \gamma n$ ) is identical in both experiments and confirms the validity of relationship given by eq. (10).

Since  $p_g$  is a function of  $\gamma$ ,  $F_0$ , and the pumping rate, under certain experimental conditions where no change in flow rate and pumping rate is involved,

TABLE I  
Flow Characteristics of Monomers and Hydrogen<sup>a</sup>

	With trap	Without trap
H <sub>2</sub>	$a_2 = 1.23 \times 10^{-2}$ $b_2 = 1.32$	$a_2 = 1.00 \times 10^{-2}$ $b_2 = 1.30$
Acetylene	$a_1 = 4.88 \times 10^{-2}$ $b_1 = 1.35$	$a_1 = 0.34 \times 10^{-2}$ $b_1 = 1.50$
Ethylene	$a_1 = 2.56 \times 10^{-2}$ $b_1 = 1.50$	$a_1 = 0.189 \times 10^{-2}$ $b_1 = 1.64$
Acrylonitrile	$a_1 = 12.3 \times 10^{-2}$ $b_1 = 1.73$	$a_1 = 0.11 \times 10^{-2}$ $b_1 = 1.79$

<sup>a</sup>  $F = ap^b$ , where  $F$  is flow rate in  $\text{cm}^3(\text{S.T.P.})/\text{min}$  and  $p$  is the flow pressure in  $\mu\text{m Hg}$ . H<sub>2</sub> is considered as the product gas, and subscript 2 is used for H<sub>2</sub>.

TABLE II  
Dependence of  $p_g$  on Flow Rate and Initial Pressure<sup>a</sup>

	With trap	Without trap
Acetylene	$c = 0.56$	$c = 0.064$
	$d = 1.03$	$d = 1.20$
	$c' = 4.0$	$c' = 4.5$
	$d' = 0.68$	$d' = 0.93$
Ethylene	$c = 1.29$	$c = 0.179$
	$d = 1.14$	$d = 1.28$
	$c' = 24$	$c' = 24$
	$d' = 0.69$	$d' = 0.73$
Acrylonitrile	$c = 0.220$	$c = 0.119$
	$d = 1.29$	$d = 1.22$
	$c' = 4.0$	$c' = 10$
	$d' = 0.95$	$d' = 0.74$

<sup>a</sup>  $\log p_g = \log c + d \log p_0$ ;  $\log p_g = \log c' + d' \log F_0$ .

the change in  $p_g$  directly indicates the change in  $\gamma$ . An example is shown in Figure 5, where changes in  $p_g$ , due to discharge power at fixed flow rates (and a fixed initial pressure  $p_0$ ), are shown for plasma polymerization of ethylene. (In order to adjust  $p_0$  to a constant value, the pumping rate is changed by adjusting the outlet value.) As indicated in Figure 5, above a threshold value of discharge power, which is characterized by fully developed glow,  $p_g$  is independent of discharge wattage. The constancy of  $p_g$  means that plasma polymerization is independent of discharge power in this region. By the same token, the conspicuously high  $p_g$  values at lower discharge wattages and high flow rates (in partial glow region) indicate that the basic chemical reaction, i.e.,  $n \rightarrow \gamma n$ , is different in this region.

The results shown in Figure 5 also indicate the following important aspect associated with the system pressure in discharge. Namely, the change of  $p_g$  from  $p_0$ , recognized as increase or decrease of the system pressure, is dependent on the value of  $p_0$ , which varies depending on the pumping rate of the monomer at a fixed flow rate. Therefore, in a flow system, the value of  $\delta = p_g/p_0$  is not a parameter to describe the characteristics of a monomer in glow discharge. In a closed system,  $\gamma^0 = p_g/p_0$  is the characteristic parameter of a monomer, as discussed in the previous section.

TABLE III  
 Comparison of Data with Theoretical Values<sup>a</sup>

Parameter	Monomer					
	Acetylene		Ethylene		Acrylonitrile	
	WT	WOT	WT	WOT	WT	WOT
$d'$	0.68	0.93	0.69	0.73	0.95	0.61
$d'$ (theor.)	(0.76)	(0.87)	(0.76)	(0.77)	(0.76)	(0.77)
$\gamma$ from $C'$	0.07	0.07	0.62	0.62	0.08	0.20
$\gamma$ (theor.)	(0.10)	(0.10)	(0.65)	(0.65)	(0.07)	(0.07)
$\gamma$ from $C$	0.12	0.08	0.67	0.57	0.01	0.21
$d$	1.03	1.20	1.14	1.28	1.29	1.38
$d$ (theor.)	(1.02)	(1.16)	(1.14)	(1.26)	(1.31)	(1.38)

<sup>a</sup> WT = With liquid-nitrogen trap; WOT = without liquid-nitrogen trap;  $\log p_g = \log c + d \log p_0$ ;  $\log p_g = \log c' + d' \log F_0$ ;  $d'$  (theor.) obtained from eq. (12);  $d$  (theor.) obtained from eq. (9);  $\gamma$  (theor.) obtained from closed-system experiments.

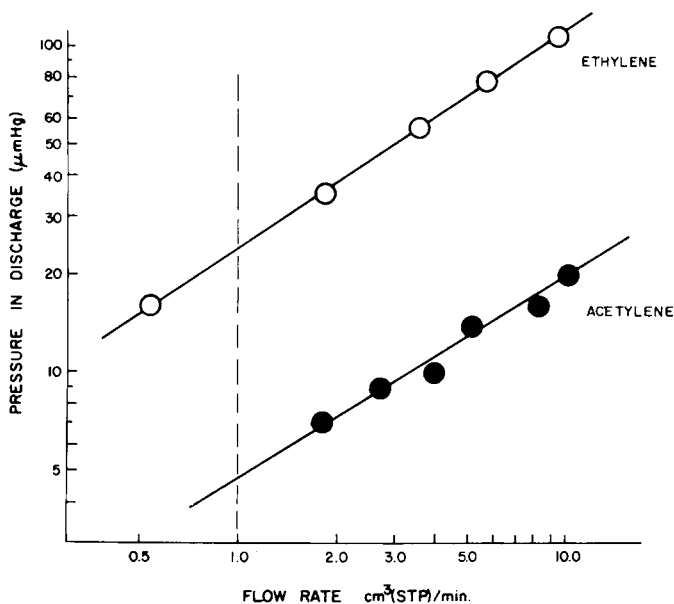


Fig. 4. Pressure in discharge,  $p_g$ , vs flow rate for acetylene and ethylene.

It should also be noted here that the definition of  $\gamma$  is given by eq. (2) for a closed system and by eq. (3) for a flow system. These equations describe the gas phase of the system where plasma polymerization occurs, and they are applicable to any system. In this paper, we have chosen the systems where nearly 100% conversion of monomer to polymer occurs in order to compare the value of  $\gamma^0$  obtained in a closed system and that obtained by a flow system. However, the validity of the equation, i.e., eq. (3), does not require the quantitative high conversion. If the conversion is low (e.g., at extremely low discharge power and/or monomer bypasses the electrodes in a capacitive discharge), the value of  $\gamma$  obtained in a flow system differs from the value of  $\gamma^0$  obtained in a closed system. The value of  $p_g$  is dependent on the value of  $F_0$  as given in eq. (10). Consequently, the higher the flow rate, the higher is the value of  $p_g$ . However,



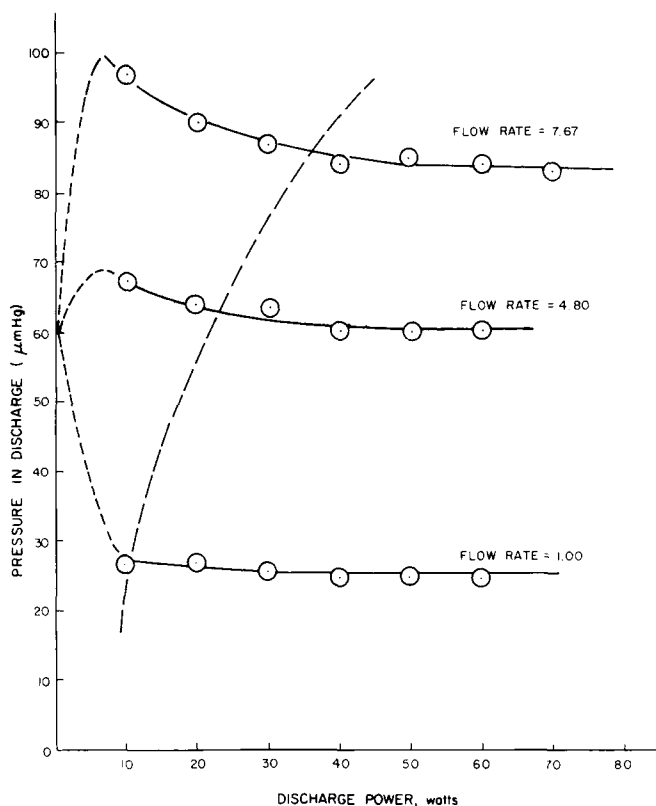


Fig. 5. Pressure in discharge,  $p_g$ , vs discharge power at fixed flow rate  $p_0$  and initial pressure for ethylene (different pumping rates are used to adjust  $p_0$  to 60  $\mu\text{m Hg}$ ).

whether the value of  $p_g$  is higher or lower than the value of  $p_0$  is dependent on the pumping rate, particularly on the preferential pumping of condensible monomer by a cold trap. For instance, at a fixed flow rate of a monomer (ethylene) in a system with a liquid-nitrogen trap,  $p_0$  is low, and the increase in  $p_g$  in most cases is due to the fact that the liquid nitrogen trap does not act as a pump for  $\text{H}_2$  (product gas). However, if the same plasma polymerization is carried out without a liquid-nitrogen trap, the decrease in system pressure (although  $p_g$  is the same as the previous case) is due to the higher  $p_0$  value compared to the case with the trap and a  $\gamma^0$  value for ethylene less than unity.

The examples shown in Figure 5 were obtained at different pumping rates in order to adjust  $p_0$  to a constant value. Therefore, in these cases, both decrease and increase in system pressure from the  $p_0$  value are observed depending on the monomer flow rate. This also implies that  $p_0$  (which is the only parameter observed in many reports appearing in the literature) is not as important as heretofore considered. As far as plasma polymerization is concerned,  $p_g$  is a much more important parameter than  $p_0$ .

The system and the conditions used in this study are ideal cases to demonstrate the relationship between  $p_g$  and other operational parameters, since the entire flow passes through the glow region, and consequently nearly 100% conversion of monomer to polymer occurs. This ideal situation does not always exist in many reactors with capacitive discharge with internal electrodes. Only a portion

of monomer flow passes through the glow region (usually between electrodes) where plasma polymerization predominantly occurs. Consequently, the bypass ratio largely determines the conversion ratio of monomer to polymer in such a system. In such a case, the bypass ratio of flow and/or the conversion ratio of monomer to polymer will cause a great deviation in the  $\gamma$  value from the characteristic value  $\gamma^0$  that is obtained in a closed-system experiment. Even in such a case, however, the meaning of  $\gamma$  defined by eq. (3) does not change, and, consequently, the subsequent equations describing the relationship between  $p_g$  and other operational parameters are valid. The parameters describing the pumping rate (i.e.,  $a_2$  and  $b_2$ ) in such a case are for the mixture of unreacted monomer and product gases, and  $a_2$  and  $b_2$  may not be considered constants.

### CONCLUSIONS

The important aspects described in this paper may be summarized as follows:

(1) The flow rate of a monomer is determined by the opening of the metering valve and the applied pressure of the monomer. The system pressure of a flow is dependent on the flow rate (feed-in rate) and the pumping rate. At a fixed flow rate, the system pressure is low when the pumping rate is high.

(2) The pressure in glow discharge,  $p_g$ , is dependent on (a) flow rate of monomer,  $F_0$ ; (b) characteristic  $\gamma^0$  value of the monomer; (c) pumping rate of the product gas which is not the original monomer, see eq. (6) in the text; and (d) the bypass ratio and/or conversion ratio of monomer to polymer.

(3) For monomers that yield a gas (e.g., hydrogen) as the main product gas, the plot of  $\log p_g$  versus  $\log F_0$  yields a straight line with a constant slope when a constant pumping rate is used, and the conversion ratios are the same (e.g.,  $\approx 100\%$ ). The intercept of the straight line at  $F_0 = 1$  is related to the value of  $\gamma$  by

$$(\log p_g)_{F_0=1} = (\gamma/a_2)^{1/b_2}$$

where  $a_2$  and  $b_2$  are parameters that relate flow rate  $F_2$  and pressure  $p_2$  of the product gas in the system by  $F = a_2 p_2^{b_2}$  at the same pumping rate.

(4) When nearly 100% conversion of monomer to polymer occurs by identical mechanism, the value of  $\gamma$  obtained by the above-mentioned relationship is identical to  $\gamma^0$  that is obtained in a closed-system experiment. However, if conversion is not close to 100% and/or the bypass ratio of monomer flow is high, the value of  $\gamma$  in a flow system is not identical to the characteristic value  $\gamma^0$  obtained in a closed-system experiment.

(5) At a fixed monomer flow rate,  $p_g$  is a unique function of the parameter  $\gamma$  which describes the change in the total number of molecules in the gas phase under the conditions of plasma polymerization.

(6) Monomer flow rate  $F_0$  and the system pressure of a steady-state flow,  $p_0$ , before plasma polymerization can be independently adjusted by manipulating the inlet valve (for  $F_0$ ) and the outlet valve openings (for  $p_0$ ). However, the system pressure in glow discharge  $p_g$  is generally considerably different from  $p_0$  (depending on the  $\gamma^0$  value of the monomer and  $F_0$ ), and controlling of  $p_g$  by manipulating the outlet valve, without changing  $F_0$ , is not always possible. For instance, with monomers, which have low  $\gamma^0$  values, the  $p_g$  of the system cannot

be adjusted unless a very high flow rate is employed to increase the bypass ratio and/or to decrease the conversion ratio.

(7) The discussion of the effect of pressure on plasma polymerization requires the distinction between  $p_0$  and  $p_g$  and also measurement of both pressures. The initial pressure of the system,  $p_0$ , is not as important a parameter of plasma polymerization as has been considered heretofore.

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### References

1. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **17**, 1519 (1973).
2. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **17**, 1533 (1973).
3. H. Yasuda, M. O. Bumgarner, and J. J. Hillman, *J. Appl. Polym. Sci.*, **19**, 531 (1975).
4. H. Yasuda, M. O. Bumgarner, and J. J. Hillman, *J. Appl. Polym. Sci.*, **19**, 1403 (1975).
5. H. Melville and B. G. Gowenlock, *Experimental Methods in Gas Reactions*, MacMillan, London, 1964.

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