

# Polymerization of Organic Compounds in an Electrodeless Glow Discharge. IX. Flow-Rate Dependence of Properties of Plasma Polymers of Acetylene and Acrylonitrile

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## Synopsis

Properties (free-radical concentration, gas permeabilities, internal stress, and contact angle of water) of plasma polymers of acetylene and of acrylonitrile were investigated as a function of flow rate of monomer in an electrodeless glow discharge. It was found that the monomer flow rate has a strong influence on free-radical concentration, gas permeabilities, and internal stress but little influence on the contact angle of water. The discharge power has little effect on properties when the full glow is maintained in the reactor. Gas permeabilities decrease with increasing concentration of free radicals in plasma polymers.

## INTRODUCTION

Although there are numerous reports on the deposition rate of plasma polymerization as a function of some of the operational parameters, relatively little is known about how properties of plasma polymer depend on the operational parameters. This is probably due to the difficulties involved in such a study. First, plasma polymer is formed in a very thin layer which is generally bonded to a substrate that is much thicker than the coating. The characterization of the thin layer in such a composite structure is extremely difficult. Secondly, some of the operational parameters such as flow rate, pressure, and discharge power are system-dependent parameters, and in some cases they have no significant meaning beyond being a means of controlling the process in a particular apparatus.

The dependence of polymer deposition rate on flow rate, for instance, is rather complicated in a bell-jar-type reactor,<sup>1,2</sup> whereas it is generally linearly proportional to the flow rate in a simple tube reactor in the full glow region.<sup>3,4</sup> Therefore, "flow rate" cannot be correlated with the properties of polymer unless the flow pattern is well defined for a system and polymer properties are uniquely related to the flow rate.

There seems to be, however, a common denominator aspect that can be correlated with polymer properties. That is, "better film" is obtained when a polymer film is formed relatively slowly. In the tail flame portion of glow dis-

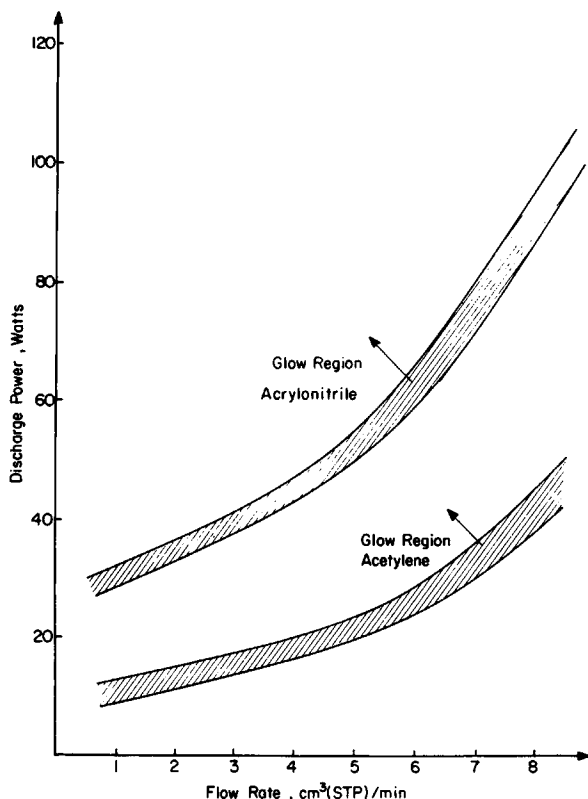


Fig. 1. Dependence of glow on flow rate and discharge power for acrylonitrile and acetylene.

charge used in a series of studies, as reported in the previous report,<sup>4</sup> the flow rate is well defined and the deposition rate is uniquely related to the flow rate. Therefore, the investigation of the flow-rate dependence of polymer seems to be warranted for such a system. A study was carried out using acetylene and acrylonitrile as the monomers. The reasons why those monomers are chosen in this study are as follows: (1) Acrylonitrile and acetylene are monomers which polymerize easily in plasma, which allows us to carry out experiments in wider ranges of conditions. For instance, if a monomer requires a very high discharge power to maintain a full glow, the flow rate cannot be changed much; this will be discussed later. (2) Both monomers yield polymers which have very low characteristic gas permeabilities. Therefore, by depositing plasma polymer onto polyethylene film (which has high gas permeability), the characteristic gas permeability of plasma polymer can be calculated from the overall gas permeability of composite films. If the gas permeability of plasma polymer is not sufficiently low, gas permeabilities of a composite film are controlled mainly by the substrate polymer, which has much larger thickness, and the permeability of a thin deposit cannot be estimated.

## EXPERIMENTAL

The flow of a monomer was determined by the measurement of pressure increase rate when the pumping was abruptly stopped in a steady-state flow.

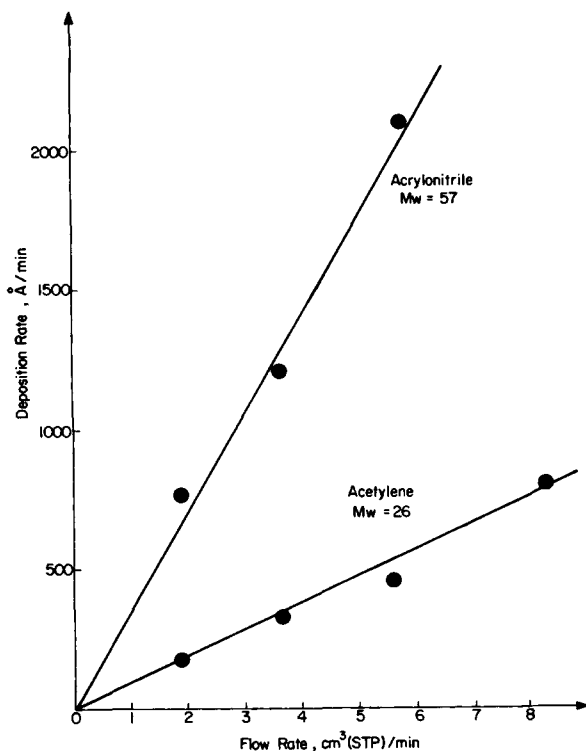


Fig. 2. Dependence of polymer deposition rate on monomer flow rate for acrylonitrile and acetylene.

The detail of the method was described previously.<sup>4</sup> The pressure of the flow system (before discharge) was adjusted to 60  $\mu\text{m Hg}$  by changing the opening of a stopcock leading to the vacuum system.

The deposition rate was estimated by weighing the amount of polymer deposit after a predetermined period of plasma polymerization. The deposition rate is expressed by thickness growth rate in  $\text{\AA}/\text{min}$ , which is calculated from weight increase, assuming the density of the polymer to be unity. Although the density of the polymer may be greater than unity, the deposition rate given in  $\text{\AA}/\text{min}$  seems to be adequate enough for the purpose of this study. The deposition rate in  $\text{mg}/\text{cm}^2\text{-min}$  can be obtained by multiplying  $10^{-5}$  by the value of  $\text{\AA}/\text{min}$ .

Based on the polymer deposition rate, 1000- $\text{\AA}$ -thick plasma polymer was deposited onto a low-density polyethylene film. The plasma polymer-polyethylene composite film was used for the measurement of gas permeabilities ( $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$ ), of internal stress, and of contact angle of water.

The internal stress was calculated from the radius of curl formed by a composite film. The internal stress  $\sigma$  in dynes/cm<sup>2</sup> is given by

$$\sigma = \frac{ED^2}{6Rd}$$

when  $E$  is the modulus of the substrate polymer ( $E = 10^9$  dynes/cm<sup>2</sup> for low-density polyethylene),  $D$  is the thickness of substrate film ( $D = 5 \times 10^{-3}$  cm),  $R$  is the radius of the roll into which a composite film curls up, and  $d$  is the

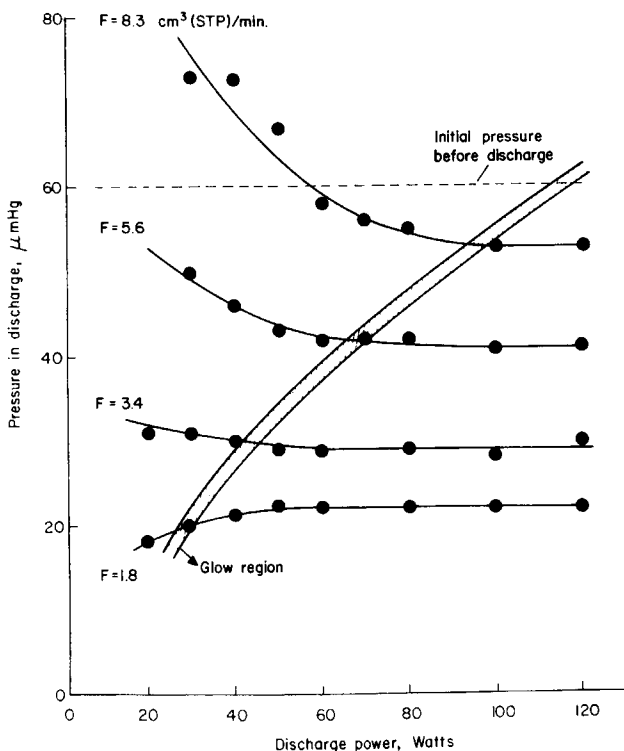


Fig. 3. Dependence of system pressure in discharge of acrylonitrile on discharge power at different flow rates.

thickness of plasma polymer ( $d = 10^{-5}$  cm in this study). The details of the method were presented in a previous report.<sup>5</sup>

The permeability of plasma polymer was calculated from the permeability of a composite film which is given by

$$\frac{l}{P} = \frac{l_1}{P_1} + \frac{l_2}{P_2}$$

where  $P$  and  $l$  are the permeability and thickness, respectively, of a composite film;  $P_1$  and  $l_1$  are the permeability and thickness, respectively, of the substrate polymer; and  $P_2$  and  $l_2$  are the permeability and thickness, respectively, of the plasma polymer. Gas permeabilities were measured by using an isobaric apparatus described previously.<sup>6</sup>

Contact angles of water were measured by a microscope with a goniometer eyepiece by using triple distilled water. Samples for electron spin resonance (ESR) spectroscopy were prepared by depositing a polymer onto a 4-mm-O.D. glass tube according to the method described previously.<sup>7,8</sup>

## RESULTS AND DISCUSSION

Acrylonitrile requires higher wattage to maintain the glow than acetylene, as seen in Figure 1, where the threshold discharge power to maintain full glow is plotted against the flow rate. The deposition rates as a function of flow rate are

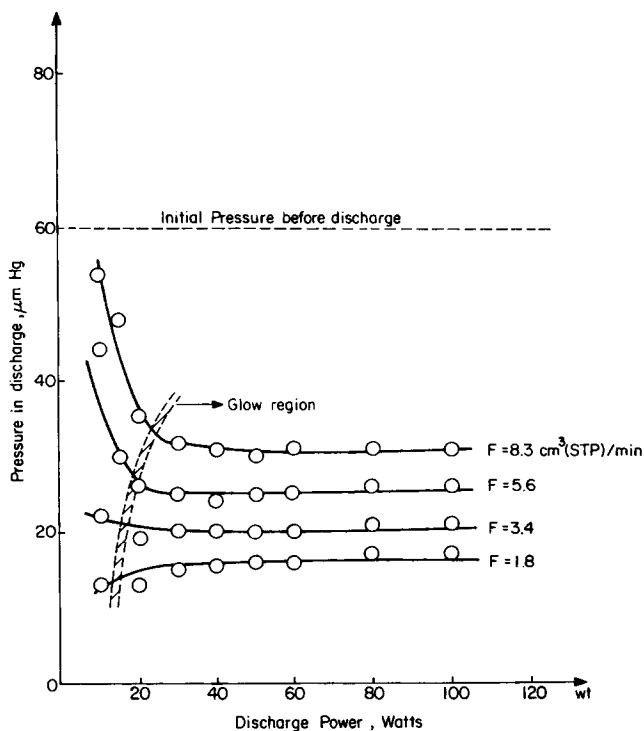


Fig. 4. Dependence of system pressure in discharge of acetylene on discharge power at different flow rates.

shown in Figure 2. The apparent high deposition rate of acrylonitrile compared to that of acetylene is partly due to the difference of molecular weight (i.e., 57 for acrylonitrile and 26 for acetylene). Even after the effect of molecular weight

TABLE I  
Characteristics of ESR Spin Signals<sup>a</sup>

Sample	$C_s^0$ , spins/cm <sup>3</sup>	Peak width, gauss	Half-life of decay, min	
			Initial	2nd
<b>Acrylonitrile (100 W)</b>				
$F = 1.8$	$8.0 \times 10^{18}$	19.0	22	110
$F = 3.4$	$4.0 \times 10^{18}$	18.5	30	180
$F = 5.6$	$1.8 \times 10^{18}$	18.0	34	190
$F = 8.3$	$1.1 \times 10^{18}$	17.0	50	270
<b>Acetylene (45 W)</b>				
$F = 1.8$	$1.5 \times 10^{20}$	16.5	70	250
$F = 3.4$	$1.8 \times 10^{20}$	16.0	120	250
$F = 5.6$	$3.6 \times 10^{20}$	15.0	180	280
$F = 8.3$	$4.0 \times 10^{20}$	14.0	210	280
<b>Acetylene (100 W)</b>				
$F = 1.8$	$2.0 \times 10^{20}$	17.5	28	240
$F = 3.4$	$2.2 \times 10^{20}$	17.0	33	240
$F = 5.6$	$2.3 \times 10^{20}$	17.0	35	240
$F = 8.3$	$3.5 \times 10^{20}$	16.0	37	250

<sup>a</sup>  $F$  = Flow rate in cm<sup>3</sup>(S.T.P.)/min;  $C_s^0$  = initial spin concentration.

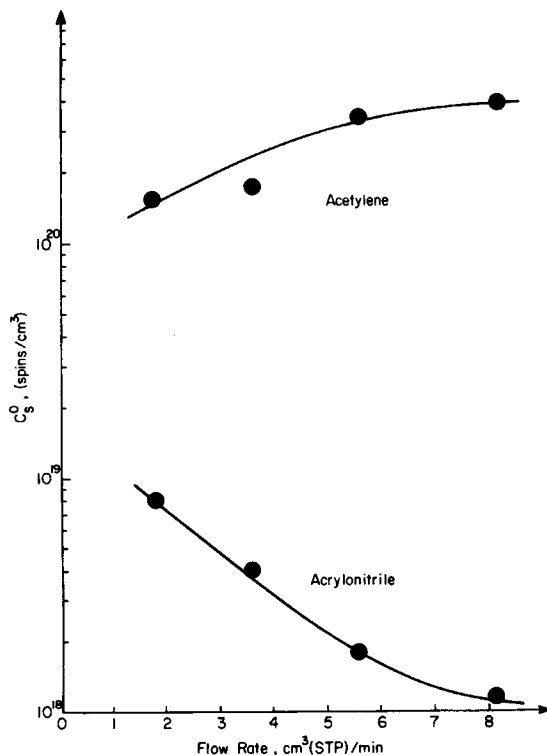


Fig. 5. Dependence of free-radical concentration in plasma polymers of acrylonitrile and acetylene on monomer flow rate (45 W for acetylene and 100 W for acrylonitrile).

is taken into consideration, acrylonitrile has a considerably higher characteristic polymerization rate. The characteristic deposition rate constant  $k$ , which is given by

$$\text{deposition rate in g/cm}^2 \cdot \text{min} = k \frac{M \times \text{flow rate in cm}^3(\text{S.T.P.})/\text{min}}{2.24 \times 10^4}$$

where  $M$  is the molecular weight of the monomer, represents this difference more clearly.<sup>3</sup>

It is interesting to note that the values of  $k$  (i.e.,  $k = 1.36 \times 10^{-3} \text{ cm}^{-2}$  for acrylonitrile and  $k = 8.12 \times 10^{-4} \text{ cm}^{-2}$  for acetylene) are roughly proportional to the total number of bonds which easily participate in plasma polymerization (i.e., three for acrylonitrile and two for acetylene). This is in accordance with observation that acrylonitrile polymerizes by utilizing  $\text{C}\equiv\text{N}$  as well as  $\text{C}=\text{C}$ .<sup>9</sup>

Since plasma polymerization of acetylene allows us to carry out experiments in a wider range of discharge power (>40 watts) without changing glow characteristic, as seen in Figure 1, polymerization was carried out at 100 and 45 watts. No significant difference in deposition rates due to the difference in discharge power was observed. This is in accordance with observations reported previously.<sup>4,10</sup> In Figures 3 and 4, the pressures of steady-state flow in glow discharge are plotted as a function of discharge power for acrylonitrile and for acetylene, respectively. In both cases, results indicate that in the partial glow

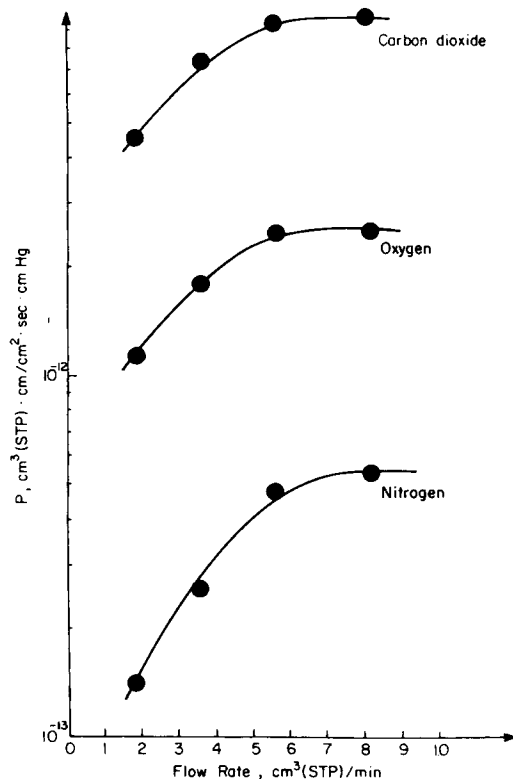


Fig. 6. Dependence of gas permeabilities of plasma polymer of acrylonitrile on monomer flow rate.

region, different chemical reactions occur compared to that in the full glow region. The details of this aspect are discussed in a separate paper.<sup>4</sup> The significance of glow characteristic and the plasma polymerization which is independent of wattage in the full glow region are clearly evident in these results.

Results of ESR study are summarized in Table I. The concentration of trapped free radicals in a plasma polymer is dependent on the flow rate of monomer. As shown in Figure 5, the dependence of free-radical concentration on the monomer flow rate is different for plasma polymerization of acetylene and acrylonitrile. Namely, the concentration of free radicals in plasma polymer of acetylene increases with flow rate, whereas that in plasma polymer of acrylonitrile decreases with increasing flow rate.

A similar discrepancy in the dependence on flow rate is also observed in gas permeabilities. In case of permeabilities, permeability of plasma polymer of acrylonitrile increases with flow rate, as shown in Figure 6, and that of acetylene decreases with increasing flow rate, as shown in Figure 7. Very small differences are observed in gas permeabilities of plasma polymer of acetylene polymerized at 45 and 100 watts, indicating that flow rate has more significant effect than the discharge power on the properties of the polymers.

Although the dependence of gas permeability on the monomer flow rate is opposite in the cases of acetylene and of acrylonitrile, the gas permeabilities

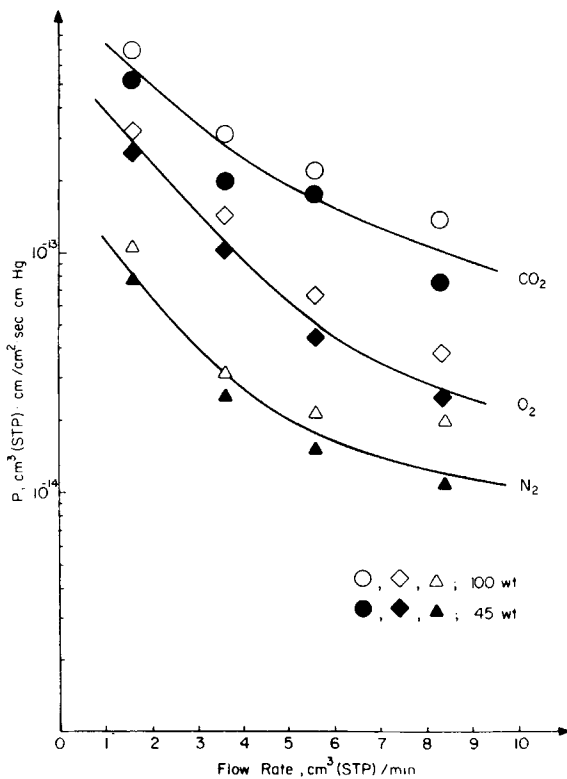


Fig. 7. Dependence of gas permeabilities of plasma polymer of acetylene on monomer flow rate.

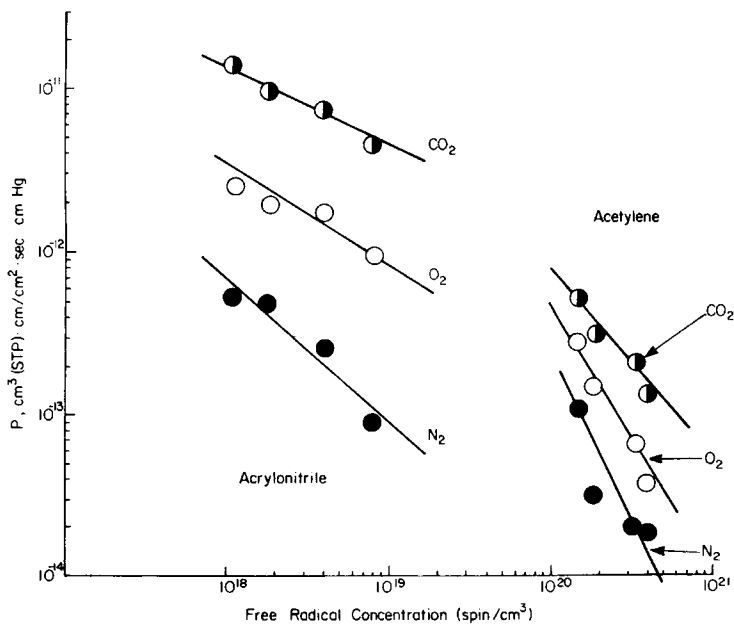


Fig. 8. Correlation between gas permeabilities and free-radical concentration in plasma polymers.



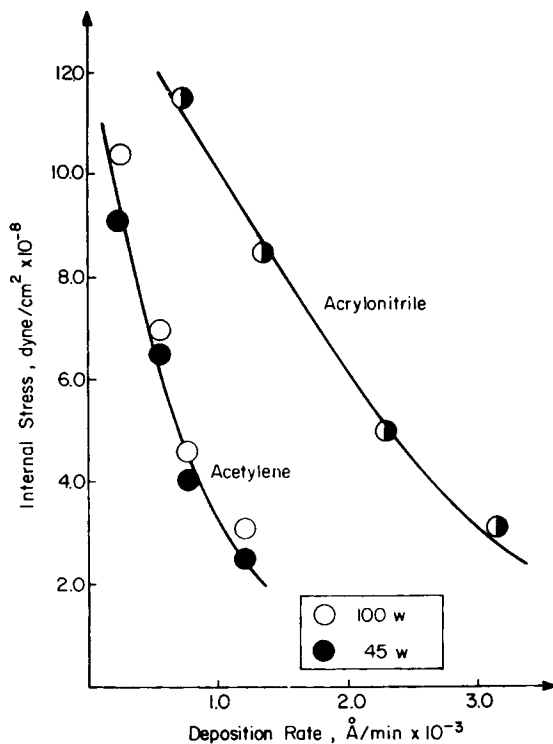


Fig. 9. Dependence of internal stress on the deposition rate.

decrease as the concentration of trapped free radicals increases, as shown in Figure 8. It has been postulated that free radicals in plasma polymers are the consequence of imbalance between the rate of free-radical production by electric discharge and the rate of consumption mainly due to polymer formation<sup>7,11</sup> rather than creation of free radicals on already formed plasma polymer by UV irradiation. Therefore, it is probable that the monomer which yields a more tightly crosslinked polymer will have also higher numbers of free radicals trapped in the polymer. This trend is clearly seen in Figure 8.

The internal stress in plasma polymer of acrylonitrile and acetylene is highly dependent on the monomer flow rate and decreases with increasing deposition rate in both cases, as shown in Figure 9. Here again, the effect of discharge wattage (acetylene) is insignificant compared to the effect of flow rate. In these plasma polymers, there is no simple correlation between the internal stress and the concentration of free radicals in plasma polymers. Although further investigations are needed for elucidation of the internal stress in plasma polymers, the results clearly indicate that the stress built in a plasma polymer is largely determined by how quickly the polymer is formed.

The contact angles of water on these two kinds of plasma polymers are not sensitive to the flow rate, though a slight decrease in  $\cos \theta$  is observed with increasing flow rate, as shown in Figure 10. This may indicate that by conditions of plasma polymerization. The facts that the internal stress and gas permeabilities are strongly dependent on the flow rate indicate that the flow rate is an important factor to control how these building blocks are assembled in the polymers.

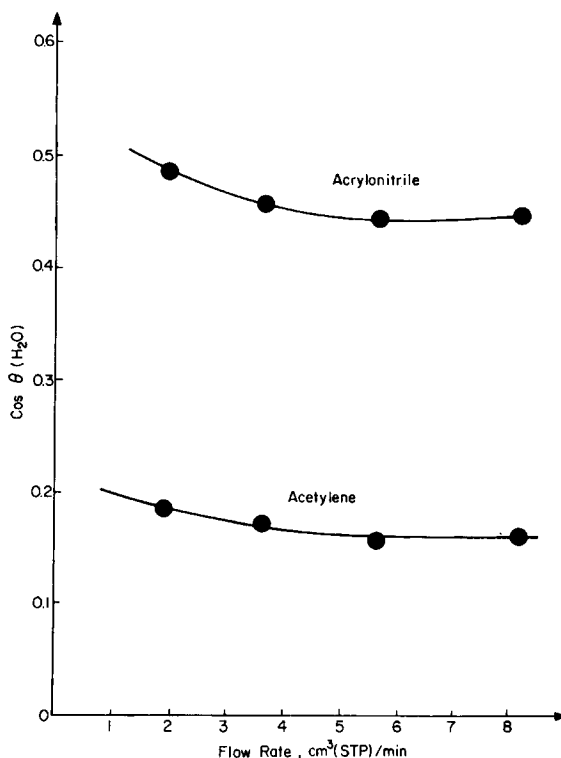


Fig. 10. Dependence of  $\cos \theta$  of contact angle of water on monomer flow rate.

The reason why the effects of flow rate on free-radical concentration and gas permeabilities are different for acetylene and for acrylonitrile is not clear. However, recent studies in progress seems to indicate that acetylene behaves differently from saturated and C=C containing compounds; i.e., results with most other organic compounds follow the trends observed with acrylonitrile.

It has been postulated that overall mechanisms of polymer formation can be represented by repeated stepwise reactions:

Initiation



Propagation



where  $i$  and  $k$  are numbers of repeating units (i.e.,  $i = k = 1$  for the monomer) and  $M^*$  is a reactive species which can be ion of either charge, an excited molecule, and a free radical.

In the case of acrylonitrile (and many other organic compounds), which requires relatively high discharge power to maintain full glow, the propagation by the reaction of a reactive specie with a monomer, reaction (2), may be favored at high flow rate. In the case of acetylene, on the other hand, which requires very

low discharge power to maintain full glow, the propagation by the recombination of two reactive species; reaction (1) may prevail at high flow rate.

If free radicals are the predominant reactive specie, the increase of trapped free radicals in plasma polymer of acetylene with increasing flow rate can be reasonably explained. Namely, the opening of triple bond produces excessive free radicals which cannot be consumed by the coupling reaction.

## CONCLUSIONS

In the full glow region of the tail flame of an inductively coupled rf discharge, the flow rate of monomer is the most important factor which influences the properties of plasma polymers of acetylene and of acrylonitrile. It was found that trapped free-radical concentration, internal stress, and gas permeabilities are highly dependent on the monomer flow rate. Gas permeabilities of these two polymers are correlated to the concentration of free radicals, although the flow rate dependences of gas permeabilities and free-radical concentration are opposite in cases of acetylene and acrylonitrile. The internal stress in both plasma polymer decreases with increasing monomer flow rate. No correlation is found between gas permeabilities and the internal stress. The effects of discharge wattage, observed with plasma polymerization of acetylene, on those properties were found to be small. Very small changes in contact angles of water due to the difference in flow rates and discharge wattages were observed.

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