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Fundamentals of Plasma Polymerization

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ABSTRACT

The plasma polymerization of ethylene is used as an example through which to discuss the elementary steps involved in forming a polymer in an electric discharge. The relationship of the experimentally controlled variables to the rate of formation of first generation active species is discussed. These species are related, in turn, to the overall rate of polymerization through a simple model. Two asymptotic conditions are discussed which correspond to minimal and total conversion of monomer to polymer. The dependence of polymer deposition rate on monomer flow rate predicted by the model is found to correspond very closely to that observed experimentally. The predicted effect of gas pressure on polymer deposition rate also agrees with that found experimentally.

The formation of a polymer in the plasma produced by a low-pressure electric discharge is a complex process involving both homogeneous and heterogeneous steps. Various theories have been proposed to explain this phenomenon [1], but, to date, no generally accepted models have appeared. The purpose of the present paper is twofold. The first is to review some of the elementary reactions expected to occur when an organic monomer is introduced into a plasma. The second purpose is to propose a relationship between the experimentally controlled variables and the rate at which polymer is formed. As a vehicle for this discussion, we shall consider the plasma polymerization of ethylene in a high-frequency discharge.

The geometry of the discharge to be considered is illustrated in Fig. 1. Two parallel planar electrodes are used to sustain the discharge and confine the gas flow. By imposing a sufficiently large electric field across the electrodes, the gas contained in the gap is broken down and made to conduct. The degree of ionization in the plasma produced this way is about one part in 10^5 to 10^6, and the number of free electrons and positive ions is almost equal. Since plasma polymerization is most frequently carried out in the pressure range of 0.1 to 10 Torr, the plasma is maintained in a nonequilibrium state [2] which means that the electron temperature T_e is 10 to 100 times greater than the ion temperature T_+ which, in turn, is nearly equivalent to the gas temperature T_g. Typical values for T_e and T_g are 10^4 and 300°K, respectively.

When ethylene enters the plasma it immediately undergoes a series of reactions with the free electrons. Representative reactions and the energies required to initiate them are:

$$e + C_2H_4 \rightarrow C_2H_2 + H_2 + e \qquad E = 1.8\ \text{eV} \qquad (1)$$

$$e + C_2H_4 \rightarrow C_2H_2 + 2H + e \qquad E = 6.3\ \text{eV} \qquad (2)$$

$$e + C_2H_4 \rightarrow 2CH_2 + e \qquad E = 7.3\ \text{eV} \qquad (3)$$

$$e + C_2H_4 \rightarrow C_2H_4^+ + 2e \qquad E = 10.5\ \text{eV} \qquad (4)$$

$$e + C_2H_4 \rightarrow C_2H_2^+ + H_2 + 2e \qquad E = 13.1\ \text{eV} \qquad (5)$$

$$e + C_2H_4 \rightarrow C_2H_3^+ + H + 2e \qquad E = 13.3\ \text{eV} \qquad (6)$$

The acetylene formed by Reactions (1) and (2) is termed a derivative monomer since it has been found to participate in the polymerization process. The remaining free radicals and ions are referred to as first generation active species.

Subsequent to their formation, the free radicals and ions produced by Reactions (2) through (5) can react with either ethylene or the

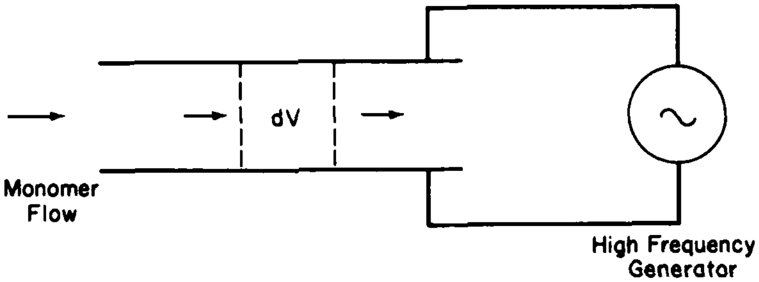

FIG. 1. Schematic of plasma polymerization reactor.

acetylene formed by Reactions (1) and (2) to produce additional free radical and ionic species. Examples of the formation of these second and third generation species is represented by [3, 4]:

$$H\cdot + C_2H_4 \rightarrow C_2H_5\cdot \quad (7)$$

$$H\cdot + C_2H_5\cdot \rightarrow 2CH_3\cdot \quad (8)$$

$$H\cdot + C_2H_2 \rightarrow C_2H_3\cdot \quad (9)$$

$$C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3 \quad (10)$$

$$C_3H_5^+ + C_2H_4 \rightarrow C_5H_9^+ \quad (11)$$

The first, second, and third generation free radicals and ions are assumed to react further with either ethylene or acetylene to produce species of increasing molecular weight:

$$R_n\cdot + \begin{Bmatrix} C_2H_4 \\ C_2H_2 \end{Bmatrix} \rightarrow R_{n+1}\cdot \quad (12)$$

$$I_n + \begin{Bmatrix} C_2H_4 \\ C_2H_2 \end{Bmatrix} \rightarrow I_{n+1} \quad (13)$$

Direct evidence for such processes has been reported by Kobayashi et al. [5, 6]. As a part of that work, mass spectrometric analyses were performed of the noncondensible gases effluent from a discharge sustained in ethylene. It was found that hydrocarbon products up through C_7 could be identified and that their concentration increased as the flow rate of ethylene fed to the discharge was decreased.

The occurrence of reactions such as (12) and (13) suggests a pathway for gas-phase polymerization, and the question of whether a free radical or an ionic mechanism predominates has been argued [1]. At present it would appear that the free-radical interpretation more satisfactorily explains the experimental observations. Kobayashi et al. [5] have compared the rates of polymer formation from alkanes, alkenes, and alkynes and have observed a strong positive correlation between rate and degree of unsaturation. Such a correlation would be expected for free-radical reactions since free radicals readily add to double and triple bonds. In a more recent study the same authors have observed [7] that the addition of small amounts of halogen atoms has a catalytic effect on the rate of hydrocarbon polymerization. This effect can readily be explained if it is assumed that the function of the halogen atoms is to abstract hydrogen atoms from the hydrocarbon species, thereby enhancing the concentration of free radicals. In support of this interpretation is the observation that the polymers produced in the presence of a catalyst possess a lower H/C ratio than those produced in the absence of the catalyst.

A fraction of the free radicals and ions formed in the gas phase will diffuse to the surfaces containing the plasma. At these surfaces the following types of reaction can occur:

$$\mathrm{M} + \mathrm{S} \longrightarrow \mathrm{S{-}M} \tag{14}$$

$$\mathrm{R}_n\cdot + \mathrm{S{-}M} \longrightarrow \mathrm{S{-}R}_{n+1}\cdot \tag{15}$$

$$\mathrm{I}_n + \mathrm{S{-}M} \longrightarrow \mathrm{S{-}I}_{n+1} \tag{16}$$

$$\mathrm{R}_n\cdot + \mathrm{S} \longrightarrow \mathrm{S{-}R}_n\cdot \tag{17}$$

$$\mathrm{I}_n + \mathrm{S} \longrightarrow \mathrm{S{-}I}_n \tag{18}$$

$$\mathrm{M} + \mathrm{S{-}R}_n\cdot \longrightarrow \mathrm{S{-}R}_{n+1}\cdot \tag{19}$$

$$\mathrm{M} + \mathrm{S{-}I}_n \longrightarrow \mathrm{S{-}I}_{n+1} \tag{20}$$

$$S{-}R_n\cdot + S{-}M \longrightarrow S{-}R_{n+1}\cdot + S \tag{21}$$

$$S{-}I_n + S{-}M \longrightarrow S{-}I_{n+1} + S \tag{22}$$

where M is a monomer molecule (either ethylene or acetylene), $R_n\cdot$ is a radical of n units, I_n is an ion of n units, and S is a surface site on the polymer. In addition to the adsorption of radicals from the gas phase, surface free radicals can be formed through the release of energy on the surface by electron-ion recombination, bombardment by ions accelerated in the sheath which separates the bulk plasma from the surface, and absorption of UV radiation produced by the plasma. These processes are described by

$$e + I + S{-}P_{n+m} + S \rightarrow S{-}R_n\cdot + S{-}R_m\cdot + N \tag{23}$$

$$I^* + S{-}P_{n+m} + S \rightarrow S{-}R_n\cdot + S{-}R_m\cdot + I \tag{24}$$

$$h\nu + S{-}P_{n+m} + S \rightarrow S{-}R_n\cdot + S{-}R_m\cdot \tag{25}$$

where $S{-}P_{n+m}$ is a segment of the polymer film, I is an ion in the ground state, I* is an energetic ion, and N is the neutralized product of the ion I.

It is important to note that while chain termination will occur by processes such as

$$R_n\cdot + R_m\cdot \rightarrow P_{n+m} \tag{26}$$

$$S{-}R_n\cdot + R_m\cdot \rightarrow S{-}P_{n+m} \tag{27}$$

$$S{-}R_n\cdot + S{-}R_m\cdot \rightarrow S{-}P_{n+m} + S \tag{28}$$

these steps do not lead to the cessation of polymerization in the conventional sense. The reason for this is that new radicals and ions can be produced by processes similar to Steps (1) through (7) or (23) through (25).

The relationship of the plasma operating conditions to the rate of polymer deposition can now be considered. We begin by noting that the plasma can be characterized by an average electron density n and an average electron energy $\bar{\epsilon}$. The relationship of n and $\bar{\epsilon}$ to the gas pressure p, the interelectrode gap spacing L, and the volume averaged power density $\bar{P}$ are illustrated in Fig. 2. These curves, which are based on elementary laws of discharge physics [2], show that $\bar{\epsilon}$ and the group $n/\bar{P}L$ are uniquely defined by the product pL. For a given value of PL, n is proportional to $\bar{P}$ and hence to the total power P.

Before considering the rates at which Reactions (1) through (6) proceed, it is necessary to determine the rate constants for these reactions. This parameter can be defined by

$$k_j = \int_0^\infty \sqrt{\frac{\epsilon}{2m_e}}\,\sigma_j(\epsilon)f(\epsilon)\,d\epsilon \qquad (29)$$

in which ϵ is the electron energy, m is the electron mass, $\sigma_j(\epsilon)$ is the cross-section for reaction j, and $f(\epsilon)$ is the electron energy

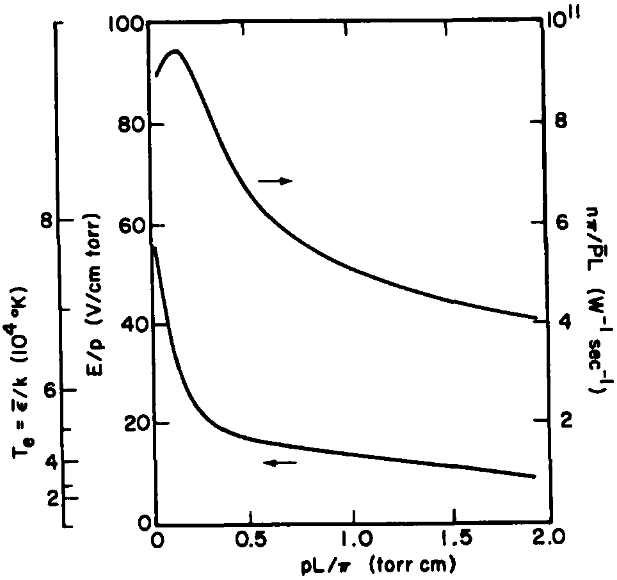

FIG. 2. The effect of pL on T_e and $n/\bar{P}L$.

distribution function. Thus to calculate k_j, both $\sigma_j(\epsilon)$ and $f(\epsilon)$ must be known. While the exact form of $\sigma_j(\epsilon)$ and $f(\epsilon)$ is not known generally, several conclusions can be drawn regarding k_j by examining the qualitative features of these two functions as illustrated in Fig 3. The critical points to bear in mind are that $\sigma_j(\epsilon)$ has a threshold located near the threshold energy of the reaction, and that the threshold energy occurs in the tail of $f(\epsilon)$. As $\bar{\epsilon}$ is increased, the maximum in the distribution shifts slowly to the right and the number of electrons in the tail of $f(\epsilon)$ increases. Because of this, and the form of Eq. (29), it can be deduced that k_j will increase monotonically with increasing $\bar{\epsilon}$ as illustrated in Fig. 4.

The rates at which the first generation active species are produced by Reactions (1) through (5) are given by

$$r_j = k_j nN \tag{30}$$

where N is the concentration of ethylene. The effects of p, L, and $\overline{P}$ on r_j can be determined by combining the curves shown in Figs. 2 and 4 to yield the curve shown in Fig. 5. From Fig. 5 we conclude that r_j increases linearly with $\overline{P}$ and increases with pL up to a broad plateau.

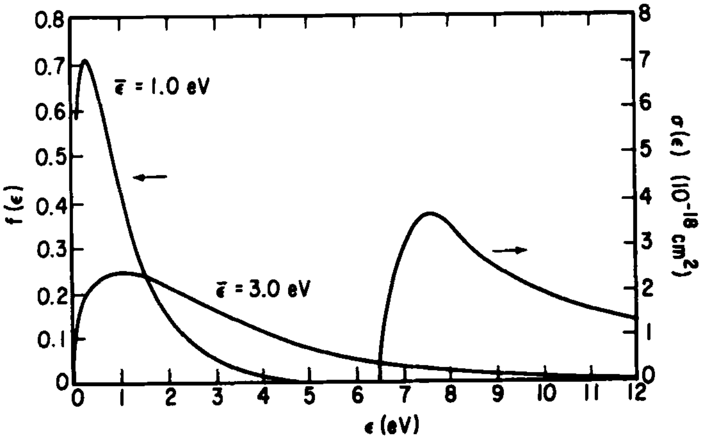

FIG. 3. The effect of ε on f(ε) and σ(ε).

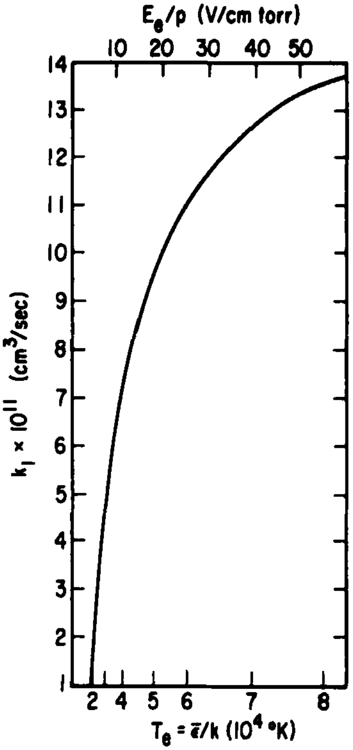

FIG. 4. The effect of T_e on k_1.

To develop a relationship between the rate at which first generation active species are formed and the overall rate of polymer deposition requires a more complete understanding of the intervening elementary reactions that is presently available. We may proceed, however, to explore the dependence of the polymer deposition rate on the experimentally controlled variables by making a number of simplifying assumptions. The principle assumption is that polymerization proceeds by a free-radical mechanism and that the rate of polymer deposition on the electrode surfaces shown in Fig. 1 can be given by

$$r_p = k_p N_R N_M \tag{31}$$

where N_R and N_M are the gas phase concentrations of first generation radicals and monomer, respectively, and k_p is the polymerization

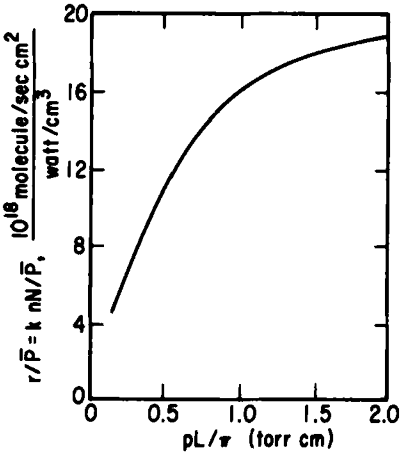

FIG. 5. The effect of pL on $r/\bar{P}$.

rate constant. The concentration of free radicals is established by the solution to a species balance written on a differential volume, dV, of the plasma (see Fig. 1). When $N_R \ll N_M$, the balance on free radicals is given by

$$Q_M \frac{dN_R}{dV} = k_1 nN_M - \left(k_2 N_M + 4\frac{D_R}{L^2}\right) N_R \tag{32}$$

where Q_M is the monomer flow rate, k_1 is the rate constant for radical formation via electron-monomer collisions, k_2 is the rate constant for radical reaction with the monomer, and D_R is the diffusion coefficient for radicals. Solving Eq. (32) and introducing the result into Eq. (31) yields

$$r_p = \frac{k_p k_1 nN_M}{k_2'} \left[1 - \exp(-k_2' N_M V/Q_M)\right] \tag{33}$$

where $k_2' = k_2 + 4D_R/N_M L^2$. When the term appearing in the exponent of Eq. (33) is small, Eq. (33) can be simplified to give

$$r_p = k_p (k_1 nN_M) \left(\frac{V}{Q_M}\right) N_M \tag{34}$$

The quantity in the first set of parentheses is the rate of formation of first generation free radicals, and the term in the second set of parentheses is the residence time of the monomer in the discharge.

A plot of r_p vs Q_M corrected to STP is shown in Fig. 6. To prepare this plot it was assumed that the relationship between r_p and Q_M could be described by Eq. (34) over most of the flow rate range. As a result, r_p is shown to be inversely proportional to Q_M. The decrease in r_p is a direct result of the decrease in free-radical concentration caused by the reduced residence time of the monomer in the plasma. For an increase in power, Eq. (33) together with Fig. 5 predict that r_p will increase. Likewise, it is predicted that an increase in pressure will cause r_p to increase.

At low flow rates Eq. (33) can no longer characterize r_p properly since its formulation fails to account for the reduction in monomer

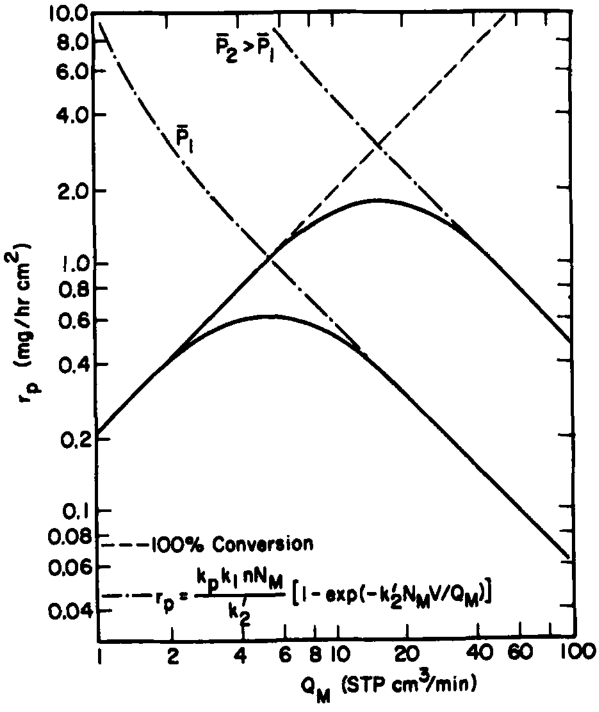

FIG. 6. The effects of Q_M and $\overline{P}$ on r_p, theoretical prediction.

concentration expected at high rates of polymerization. In the extreme it may be assumed that at very low flow rates the rate of polymerization is equivalent to the monomer feed rate, viz., that the monomer is completely converted to polymer. This limiting condition is represented by the straight line in Fig. 6.

In the light of the discussion just presented, it is expected that the curve of r_p will be asymptotic to the 100% conversion line at low flow rates and asymptotic to the curve represented by Eq. (33) at high flow rates. As indicated in Fig. 6, the complete curve will exhibit a maximum. The flow rate at which the maximum occurs is expected to shift upscale as either the power or the pressure is increased.

The qualitative predictions of the model just described are now compared with the experimental data shown in Figs. 7 and 8. These data were obtained using an rf discharge sustained between two parallel disk electrodes [5], a geometry essentially identical to that shown in Fig. 1. As may be seen in Fig. 7, for a given pressure and

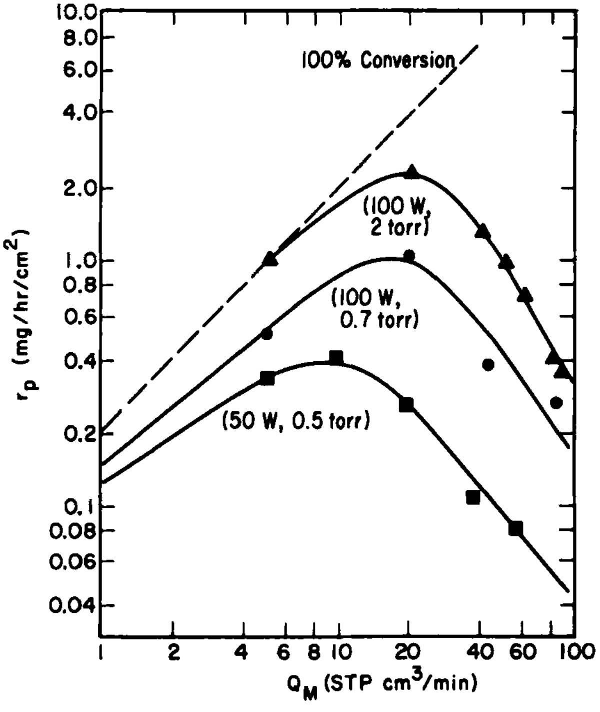

FIG. 7. The effects of Q_M, p, and $\overline{P}$ on r_p, experimental results.

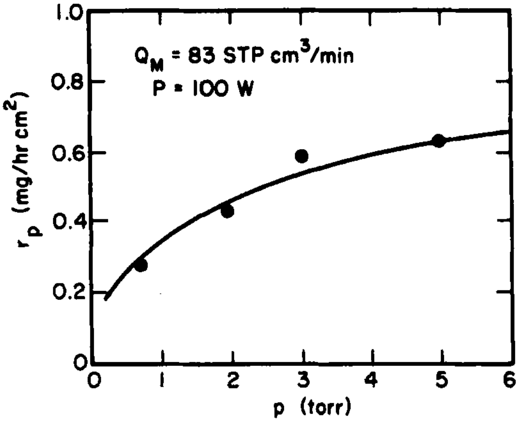

FIG. 8. The effects of p on r_p, experimental results.

power the polymer deposition rate first increases with flow rate and then passes through a maximum. At low flow rates the deposition rate asymptotically approaches the line for complete monomer conversion, and at high flow rates the deposition rate falls inversely with flow rate. When either the power or the pressure is increased, the deposition rate curve is shifted upwards and the maximum in the curve moves to higher flow rates. Each of these observations is qualitatively consistent with the model represented in Fig. 6.

Figure 8 shows the experimental dependence of the deposition rate on pressure for a fixed power and flow rate. Notice that the rate increases with pressure but approaches a plateau. A similar behavior is predicted by combining Eq. (33) with the curve given in Fig. 5.

In summary, the present discussion has outlined the nature and variety of elementary processes which take place during plasma polymerization. A simple model for describing the rate of polymer deposition has been proposed and the qualitative dependence of the deposition rate on pressure, power, and flow rate has been deduced. Finally, a comparison of the predictions of the model with experimental data shows that the model properly predicts the experimentally observed trends.

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REFERENCES

[1] M. Millard, "Synthesis of Organic Polymer Films in Plasmas," in *Techniques and Applications of Plasma Chemistry* (J. R. Hollahan and A. T. Bell, eds.), Wiley, New York, 1974.

[2] A. T. Bell, "Fundamentals of Plasma Chemistry," in *Techniques and Applications of Plasma Chemistry* (J. R. Hollahan and A. T. Bell, eds.), Wiley, New York, 1974.

[3] L. Teng and W. E. Jones, *J. Chem. Soc., Trans. Faraday Soc.*, *1972*, 1267.

[4] V. P. Warneck, *Ber. Bunsenges. Phys. Chem.*, *76*, 428 (1972).

[5] H. Kobayashi, A. T. Bell, and M. Shen, *Macromolecules*, *7*, 277 (1974).

[6] H. Kobayashi, M. Shen, and A. T. Bell, *J. Macromol. Sci.—Chem.*, *A8*, 373 (1974).

[7] H. Kobayashi, M. Shen, and A. T. Bell, *Ibid.*, *A8*, 1345 (1974).