Effects of Reaction Conditions on the Plasma Polymerization of Ethylene

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Plasma Polymerization of Ethylene

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ABSTRACT

Ethylene can be polymerized at low pressures in a radio-
frequency glow discharge. The form of the resulting
polymer may be a powder at low pressure (1 to 2 Torr)
and low monomer feed rate (10 to 40 cc/min), a colorless
film at low pressure and high feed rate (70 to 90 cc/min),
or an oil at high pressure (4 to 5 Torr) and high feed rate.
The powder and film forms of plasma-polymerized ethylene
are insoluble in common organic solvents, indicating a
highly cross-linked structure. The oily products, however,
are soluble in acetone and xylene. Chemical evidence in-
dicates that the oil is most likely composed of highly
branched oligomers of ethylene. Mass spectrometric
analysis of the gaseous effluents show that under film-
forming conditions the only hydrocarbon species observable
are those derived from ethylene. The powder- and oil-
forming conditions, on the other hand, yielded oligomeric
species. On the basis of this evidence, a mechanism for
the plasma-polymerization of ethylene is proposed.

INTRODUCTION

The preparation of polymers in a low-pressure electrical dis-
charge is known as plasma polymerization. This technique is now
receiving increasing interest because it offers a method for deposit-
ing thin pinhole-free films starting from a wide class of monomers.
The plasma polymerization process is quite complex and has been
found to be sensitive to the operating conditions. Thus in addition to
forming films it is also possible to form oils and powders. In
previous publications [1, 2] we have reported on the effects of
operating conditions on the type of polymer formed during the plasma
polymerization of ethylene in a radio-frequency discharge. Particu-
lar attention was paid to the physical and chemical characteristics of
the film and powder forms of the product. The present work presents
quantitative data on the rates of formation of these products and their
distribution. Additional data are presented concerning the formation
of a low molecular weight oil and the composition of the gases in the
effluent from the discharge. All of the results are discussed in the
light of a hypothetical model of the polymerization process.

EXPERIMENTAL SECTION

Details of the plasma polymerization reactor have been reported
previously [1]. The central part of this apparatus is an evacuable
bell jar containing a pair of parallel disk electrodes. The gap
between the electrodes is adjustable. The discharge is sustained by
an International Plasma Corporation Model PM 401 Radiofrequency
Generator which operates at 13.56 MHz and is capable of delivering
up to 150 W. The lower electrode on which the substrate is placed
is water cooled. Throughout this study, aluminum foil was used as
the substrate. The electrode gap was fixed at 5 cm unless
otherwise indicated.

RESULTS

Effects of Polymerization Conditions on Product
Characteristics

In a previous publication [1] we have shown that the form of the
polymer produced during the plasma polymerization of ethylene
depends on the pressure in the reactor, the flow rate of the monomer,
and the power supplied to the plasma. As shown in Fig. 1, at low
pressures and low monomer flow rates the polymer is present both
as a powder and a film. At high pressures and high flow rates, the
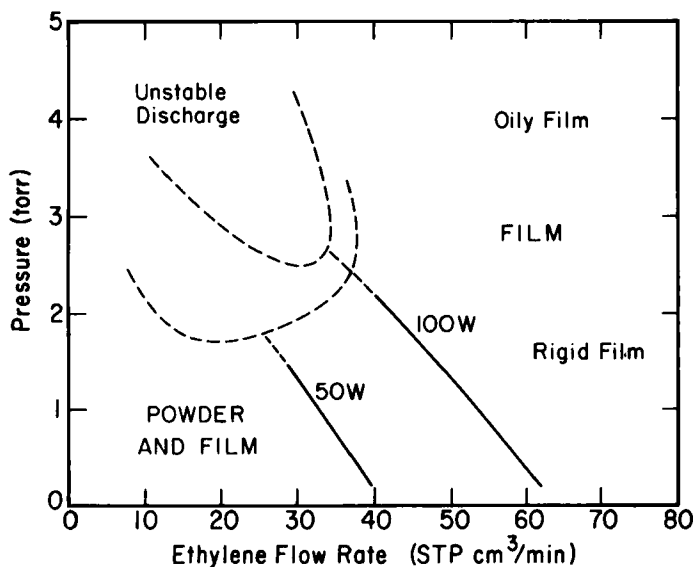
FIG. 1. Dependence of the type of polymer formed on power, pressure, and flow rate.

polymer appears in the form of an oily film. Only at low pressure and high flow rate can a solid, pinhole-free film be obtained. If the pressure in the reactor is high and the flow rate is low, the discharge becomes unstable. Also shown in Fig. 1 is the effect of power input. Decreased power makes it possible to produce a film at lower flow rates. This trend has been confirmed for powers of 25 to 150 W as well. It should be noted that the transitions from powder to film and film to oil regions are gradual and that the lines of demarcation shown in Fig. 1 must be regarded as approximate.

In addition to pressure, flow rate, and power, it has been found that the size of the gap between the electrodes also influences the form of the polymer product. Figure 2 shows the dependence of the deposition rate and the distribution between powder and film on the size of the electrode gap. As the gap narrows the amount of powder produced increases while the amount of film remains the same. For gaps larger than 3 cm the production of powder is no longer observed and only a film is produced.

In order to characterize further the polymer produced at various pressures and flow rates, 12 samples were chosen for detailed analysis. The results are given in Table 1. The following general trends can be deduced from these results.
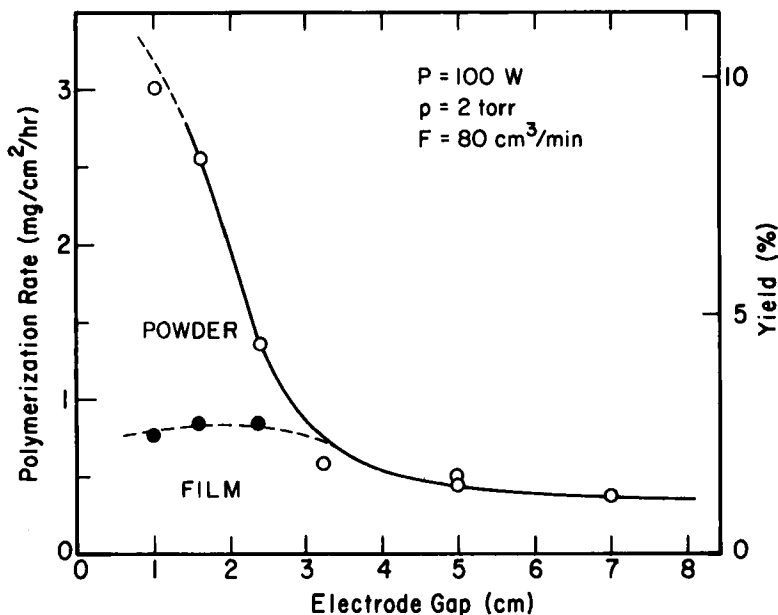
FIG. 2. Dependence of the type of polymer formed on electrode gap.

1. The rate of polymer deposition at a given monomer flow rate in-
creases with increasing pressure and finally approaches a plateau. For
a given pressure the deposition rate first increases with increasing flow
rate, reaches a maximum at an intermediate flow rate, and then de-
creases with further increases in flow rate.

2. The overall yield of polymer decreases rapidly with increasing
flow rate, and more slowly with decreasing pressure.

3. The amount of powder generated is always less than half of the
total yield even at the lowest pressure and flow rate. The other part
of the product is film. At higher pressures and flow rates, there is no
visible production of powder.

4. The chemical composition of the polymer, determined by Pregl's
method of carbon-hydrogen analysis, indicates that the value of n in
the chemical formula of C_2H_n is between 2.6 and 3.0. The higher values
of n correspond to polymers produced at low flow rates. For a given
flow rate and pressure, the chemical compositions of the powder and
the film show no significant difference. In all instances the polymer
is hydrogen-deficient by comparison with conventional polyethylene.

5. Polymers produced at low pressures are insoluble in acetone

TABLE 1. Characteristics of Plasma Polymerized Ethylene[a]

P (Torr)		F (cc/min) 5	F (cc/min) 22	F (cc/min) 42	F (cc/min) 83
5.0	1.			1.73	0.63
	2.			11.8	2.4
	3.			0	0
	4.			2.63 (f)	2.59 (f)
	5.			s; sw; s	sw; s; s
3.1	1.			1.32	0.59
	2.			11.9	2.5
	3.			0	0
	4.			2.67 (f)	2.76 (f)
	5.			sw; s; s	sw; s; s
1.9	1.	1.00	2.30	1.36	0.43
	2.	78.5	39.0	11.8	2.0
	3.	44.9	46.5	0	0
	4.	3.04 (p) 2.99 (f)	2.80 (p) 2.74 (f)	2.59 (f)	2.73 (f)
	5.	sw; sw; sw	sw; sw; sw	sw; s; s	sw; sw; sw
0.7	1.	0.51	1.10	0.38	0.28
	2.	45.8	22.2	4.0	1.4
	3.	23.2	26.5	9.3	0
	4.	2.84 (p) 2.90 (f)	2.72 (p) 2.68 (f)	2.70 (p) 2.65 (f)	2.72 (f)
	5.	i; i; sw	i; i; sw	i; i; sw	i; i; sw

[a] 1 = Deposition rate (mg/hr cm^3). 2 = Overall yield (%). 3 = % Powder (not incorporated into film). 4 = Value of n in C_2H_n (p, powder; f, film). 5 = Solubilities in acetone, cold m-xylene, and boiling m-xylene (i, insoluble; s, soluble; sw, swollen). F = Ethylene flow rate (STP). P = Pressure.

and in cold or boiling m-xylene, although swelling occurs in some in-
stances. This is an excellent indication of a cross-linked structure.
Oily polymers produced at high pressures as well as high flow rates
are either soluble or readily swollen in these solvents. In this in-
stance it may be concluded that the number of cross-links is in-
sufficient to form a gel structure, and that the polymer is most likely
composed of branches oligomers.

Characterization of the Oily Polymer

As indicated in Table 1, the polymers produced at high pressures
and high flow rates are oily and are soluble in appropriate solvents.
It was therefore of interest to determine the molecular weight of this
polymer. For this purpose a sample prepared at 5 Torrs, 40 cc/min,
and 100 W was dissolved in m-xylene upon removal from the reactor.
The molecular weight of the polymer was determined on a Mechrolab
Model 301 vapor pressure osmometer. It was found that the molecular
weight of this polymer was approximately 450, which is in agreement
with our hypothesis that the oil is a branched oligomer of ethylene.
However, upon storage of the solution at -10°C for 1 week, the
molecular weight was found to have increased to nearly 1500. This
observation suggested that the polymer was "alive" and that polymer-
ization continued during storage. As further evidence of the presence of
long-lived free radicals, an electron spin resonance trace of the oil was
taken on a Varian V5502 ESR Spectrometer which operates in the x-band
at 9.5 GHz. The g-value of this trace is 2.00 and the peak-to-peak width
is 2.63 gauss. After 5 days the same sample still showed radical activity
although its strength had decreased to about half of the original value.

In order to characterize further the structure of the oily polymer,
it was deposited on a sodium chloride substrate. An IR spectrum of
the oil was then taken on a Perkin-Elmer Model 21 Infrared
Spectrophotometer. Figure 3a shows the IR spectrum of the freshly
polymerized oil. This spectrum is fairly similar to those of the
plasma-polymerized film and powder published previously (Fig. 4 of
Ref. 1). The principal differences are that the bands at 3400 and 1600
to 1700 cm^{-1} are much weaker for the oily polymer than they are for
either the film or the powder. An additional characteristic of the
oily polymer is the broad band present between 1000 and 1300 cm^{-1}.
Upon storage under ambient conditions for 4 days, the absorbance in
all three regions increased (Fig. 3b). Very large increases were ob-
served when the sample was heated in an air oven at 100°C for 40
min (Fig. 3c). It is known [3] that the region between 3200 and 3650
cm^{-1} is characteristic of assorted free and associated OH stretching
frequencies, the region between 1540 and 1740 cm^{-1} is attributable
to carbonyl vibrations in various structures of aliphatic compounds,
and the region between 1000 to 1300 cm^{-1} could contain OH deforma-
tions and CO stretching absorptions of alcoholic groups, and vibra-
tions of alkyl ketones. Thus it is likely that changes in the spectra
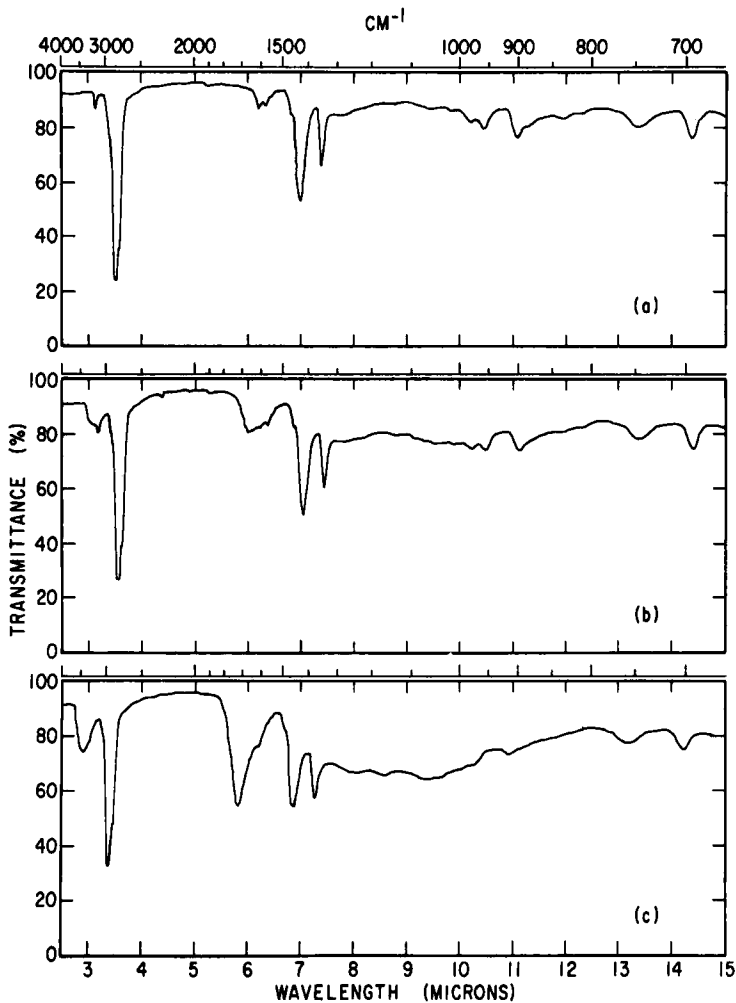
FIG. 3. IR spectra of the oily polymer: (a) 10 min after deposition; (b) 4 days after deposition; and (c) after heating in air at 100°C for 40 min.

upon exposure to air are due to the oxidation of reactive sites in the polymer to hydroxy- or carboxy-type functional groups.

Composition of the Gas Phase

A determination of the composition of the gas leaving the reactor was undertaken to identify the presence of partially polymerized species.

TABLE 2. Mass Spectra of Gaseous Products[a]

m/e	Monomer ethylene	2 Torrs, 5 cm³/min, 78% yield of polymer	2 Torrs, 20 cm³/min, 39% yield of polymer	2 Torrs, 40 cm³/min, 12% yield of polymer	2 Torrs, 80 cm³/min, 2% yield of polymer	5 Torrs, 40 cm³/min, 12% yield of polymer
10						
11						
12		0.1	0.1		0.9	0.2
13		0.1	0.2		1.4	0.4
14	3.5	0.6	0.3	0.1	2.1	0.7
15		2.3	1.3	0.1	0.8	0.4
16	1.2	2.9	1.3	0.1	1.1	0.6
17	3.8	.5	0.7	0.2	2.6	0.2
18	14.5	2.8	3.0	1.0	9.8	0.9
19		.1				t
20		.1				
21						
22						
23						
24	0.6	0.6	0.9	0.9	1.5	1.4
25	2.0	2.4	3.3	3.9	4.9	4.6
26	10.4	10.3	16.3	18.1	26.0	23.3
27	11.3	7.4	8.8	12.4	18.0	16.4
28	51.3	8.9	17.5	21.5	28.0	25.1
29	0.9	7.9	4.6	3.8	2.1	2.7
30	0.6	2.4	1.5	0.6	0.6	0.5
31		0.1	0.1	0.1		
32						
33				0.1		
34						t

35	0.1	0.2	0.1		t
36	0.6	0.6	0.4		0.2
37	0.9	0.7	0.3		0.3
38	4.1	2.7	2.9	0.7	1.6
39	1.3	1.1	0.9	0.3	0.1
40	6.2	3.6	4.1	1.1	2.4
41	3.4	2.2	2.2	0.3	1.4
42	8.5	4.6	5.3	1.0	2.8
43	2.1	1.7	1.2	0.7	0.7
44	0.2	0.1	0.1		0.1
45			t		
46					
47					
48	0.2	0.1	0.1		0.1
49	0.5	0.5	0.4		0.3
50	1.0	1.4	1.8		1.1
51	0.4	0.7	0.9		0.7
52	0.5	0.7	1.3		0.7
53	0.6	0.6	0.7		0.4
54	0.5	0.5	0.5		0.3
55	1.3	1.1	1.1		0.9
56	2.2	1.0	1.0		0.6
57	3.8	1.4	1.0		0.6
58	0.7	0.3	0.3		0.5
59	0.1	0.1	t		
60	0.1	t	t		0.1
61		0.1	t		t
62	0.2	0.1	0.1		0.1
63		0.2	0.2		0.1
64		0.1	0.1		
65	0.2	0.2	0.3		0.1
66	0.4	0.2	0.3		0.1

(continued)

Table 2 (continued)

m/e	Monomer ethylene	2 Torrs, 5 cm³/min, 78% yield of polymer	2 Torrs, 20 cm³/min, 39% yield of polymer	2 Torrs, 40 cm³/min, 12% yield of polymer	2 Torrs, 80 cm³/min, 2% yield of polymer	5 Torrs, 40 cm³/min, 12% yield of polymer
67		0.8	0.6	0.9		0.6
68		0.3	0.3	0.3		0.2
69		0.8	0.4	0.6		0.4
70		0.9	0.4	0.4		0.3
71		1.1	0.3	0.3		0.3
72		0.1	0.1	0.1		0.1
73		0.1	t	0.1		0.1
74		0.2	0.1	0.2		0.1
75		0.1	0.1	0.1		t
76		0.1	0.1	0.1		t
77		0.2	0.2	0.4		0.3
78		0.4	0.6	0.6		0.5
79		0.3	0.3	0.4		0.4
80		0.2	0.1	0.2		0.1
81		0.6	0.3	0.4		0.3
82		0.2	0.2	0.2		0.1
83		0.3	0.2	0.2		0.1
84		0.4	0.2	0.3		0.1
85		0.5	0.2	0.1		0.1
86		0.2	t	0.1		0.1
87		0.1	t	t		t
88			t	t		
89			0.1	t		t
90						t

m/e				
91	0.6	0.4	0.5	0.3
92	0.2	0.1	0.2	0.1
93	0.1	0.1	0.1	t
94	0.1	0.1	0.1	0.1
95	0.3	0.2	0.2	0.1
96	0.2	0.1	0.1	0.1
97	0.3	0.1	0.1	0.1
98	0.2	0.1	0.1	t
99	0.1	t	t	
100	t	t	t	
101	t	t	t	t
102	0.1	0.1	0.1	t
103	t	t	0.1	0.1
104		t	0.1	t
105	0.1	0.1	0.2	t
106	0.1	0.1	0.1	t
107		t	t	t
108	t	t	t	t
109	0.2	0.1	t	t
110		0.1	0.1	t
111	0.1	t	t	t
112	0.1	t	t	
113		t	t	
114	t	t	0.1	t
115	t	0.1	t	0.1
116		t	t	0.1
117	0.1	t	t	t
118	0.1	0.1	t	t
119		t		t
120	t	t	t	t

^{a}t = Trace.

For this purpose an evacuated ampule was attached to the line leading from the reactor to the vacuum pump. Fifteen minutes after the discharge was turned on the ampule was filled with the effluent gas and sealed. The contents of the ampule were then analyzed on a CEC-110B high resolution mass spectrometer.

The results of the mass spectrometric analyses are tabulated in Table 2. For each set of conditions the peak heights are expressed as a percentage of the sum over all peaks greater than m/e = 10.

The effects of flow rate on gas composition for a fixed pressure and power are immediately evident from Table 2. As the flow rate is increased from 5 to 80 cc/min, the intensity of the mass 28 peak due to C_2H_4 rises. Correspondingly, the peaks associated with values of m/e greater than 28 decrease in intensity with increasing flow rate. These results indicate that at high residence times a significant portion of the ethylene fed to the reactor is converted to higher molecular weight hydrocarbons. The peak at mass 26, which is most likely due to C_2H_2, also grows with increased flow rate. This suggests that C_2H_4 is rapidly converted to C_2H_2 due to electron bombardment in the plasma and that C_2H_2 is then capable of reacting further to form products of higher molecular weight.

Also shown in Table 2 is the effect of a change in pressure at constant flow rate. In this case the intensity of the peak at mass 28 is enhanced with increased pressure while the peaks at higher molecular weights are attenuated. The peak at mass 26 is also enhanced at higher pressures. It should be borne in mind that the change in pressure from 2 to 5 Torrs causes an increase in the residence time by a factor of 2.5. Since the observed effects do not follow the pattern for changes in the residence time, they must be ascribed totally to the gas phase pressure and its influence on the plasma characteristics and the rates of homogeneous reactions.

DISCUSSION

Plasma polymerization is an extremely complex process involving both homogeneous and heterogeneous reactions which lead to the production of the various forms of polymer noted in the previous section. A quantitative interpretation of the polymerization kinetics is virtually impossible at present because of the complexity of the problem and the lack of sufficient elementary data. Nevertheless, recent work by Bell and his co-workers [4, 5, 6] has shown that simpler plasma reactions can be understood and interpreted in terms of the physical characteristics describing the plasma. In view of this work, an attempt will be made to apply some of the concepts developed there in order to develop a qualitative picture of plasma polymerization and its dependence on the discharge operating conditions.

The principal energy carriers in a glow discharge are the free electrons produced through a partial ionization of the supporting gas. These electrons are characterized by a distribution of energies and an average energy of a few electron volts. The population of electrons possessing energies above the average rapidly decreases with increasing energy. Nevertheless, a small number of electrons can have energies as high as 10 to 20 eV.
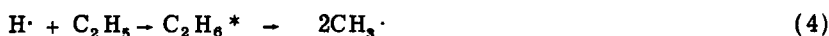
Collisions between the free electrons and the molecules of the parent gas produce a variety of products such as excited molecules, free radicals, and ions. Many of these species are chemically active and are able to react further to produce stable products. Since the concentration of free radicals in a plasma is usually five to six orders of magnitude higher than that of the ions [6], the former species is considered to be the primary precursor to stable products.

It therefore seems reasonable to assume that the process of plasma polymerization follows a free radical mechanism. The first stages of this mechanism are assumed to be

$$e + C_2H_4 \rightarrow C_2H_2 + H_2 + e \qquad (1)$$

$$e + C_2H_4 \rightarrow C_2H_2 + 2H\cdot + e \qquad (2)$$

by analogy with the photolysis of ethylene [7, 8] and the polymerization of ethylene by gamma radiation [9]. Reactions (1) and (2) would also explain the large amounts of acetylene observed in the gaseous products listed in Table 2 and noted earlier by Vastola and Wightman [10] and Paciorek and Kratzer [11].

The atomic hydrogen produced by reaction (2) could be converted to ethyl, methyl, and vinyl radicals by the following reactions [12, 13]:

$$H\cdot + C_2H_4 \rightarrow C_2H_5 *\cdot \xrightarrow{\text{M}} C_2H_5\cdot \qquad (3)$$

$$H\cdot + C_2H_5 \rightarrow C_2H_6 * \rightarrow 2CH_3\cdot \qquad (4)$$

$$H\cdot + C_2H_2 \rightleftharpoons C_2H_3 *\cdot \xrightarrow{\text{M}} C_2H_3\cdot \qquad (5)$$

These radicals could then react further with either ethylene or acetylene to produce larger radicals. The continued growth of the free radicals would then represent a gas phase polymerization process. It has been proposed [1, 2] that the powder particles produced during the vigorous polymerization of ethylene are formed in this way. At any stage of their growth the radicals might be terminated by reaction with another radical or an atom of hydrogen. Processes such as this would give rise to the presence of the various hydrocarbon species observed in the mass spectra of the gaseous reaction products.

At the low pressures used for plasma polymerization it is expected that a fraction of the free radicals created in the gas phase diffuse to the surfaces containing the plasma. At these surfaces reactions of the following type might occur:

$$M + S \rightleftarrows S-M \tag{6}$$

$$R_n^{\cdot} + S-M \rightarrow S-R_{n+1}^{\cdot} \tag{7}$$

$$R_n^{\cdot} + S \rightarrow S-R_n^{\cdot} \tag{8}$$

$$M + S-R_n^{\cdot} \rightarrow S-R_{n+1}^{\cdot} \tag{9}$$

$$S-M + S-R_n^{\cdot} \rightarrow S-R_{n+1}^{\cdot} + S \tag{10}$$

$$S-R_m^{\cdot} + S-R_n^{\cdot} \rightarrow S-P_{m+n} + S \tag{11}$$

$$R_m^{\cdot} + S-P_n \rightarrow S-P_{m+n} \tag{12}$$

where M is a monomer molecule (either ethylene or acetylene), $R_n^{\cdot}$ is a radical of n units, S is a surface site, and P_n is a terminated polymer chain. In addition to the radicals diffusing to the surface, a certain number may also be formed through the impingement of energetic ions and the adsorption of UV radiation produced by the plasma. These processes would be described by the reactions

$$I^* + S-M \rightarrow S-R^{\cdot} + H^{\cdot} + I \tag{13}$$

$$h\nu + S-M \rightarrow S-R^{\cdot} + H^{\cdot} \tag{14}$$

where I^* and I are ions in the activated and deactivated states, respectively. The growth of a polymer film is expected to proceed through reactions such as (6) through (14).

As noted earlier, the H/C ratio of both the film and the powder lie between 1.3 and 1.5. Similar values have been reported by Vastola and Wightman [10] and by McTaggart [14]. The observed H/C ratio might be explained by the polymerization of roughly equivalent amounts of ethylene and acetylene. Alternatively, we may postulate that the polymer is first formed with a H/C ratio close to 2 which is then reduced through the removal of hydrogen from the polymer by the adsorption of UV radiation and collisions with energetic species. The

first of these two explanations is preferred since it is observed that the H/C ratio is the same for both film and powder products and is relatively insensitive to the polymerization conditions.

Since both the homogeneous and the heterogeneous polymerization processes depend upon free radicals as initiators, it is possible to postulate that the overall rate of polymerization will be related to the gas phase concentration of these radicals. Inasmuch as the radicals are formed by reactions requiring atomic hydrogen, it is anticipated that high free radical concentrations will correlate with high concentrations of atomic hydrogen. The concentration of the latter species depends in turn upon the rate of its formation by Reaction (2) and the rate of its disappearance by convective transport, reaction, and recombination.

In order to proceed with an interpretation of the polymerization kinetics, it is first necessary to examine the relationship between the discharge operating conditions and the rate of atomic hydrogen formation. Based upon Reaction (2), we may express the rate of atomic hydrogen formation by

$$r_2 = k_2 [e][C_2H_4] \tag{1}$$

where $[e]$ and $[C_2H_4]$ are the concentrations of electrons and ethylene, respectively. The reaction rate constant k_2 is dependent upon the average electron energy which is characterized by E/p [15], the ratio of the electric field strength required to sustain the discharge to the gas pressure. An illustration of the relationship between k_2 and E/p is shown in Fig. 4. The principles of discharge physics can be used to show that E/p is related to $p\Lambda$, where $\Lambda = d/\pi$ and d is the electrode separation [15]. An example of this relationship is shown in Fig. 5. Furthermore it can be demonstrated that the quantity $[e]/\overline{P}d$, in which $\overline{P}$ is the power density, can also be expressed as a function of $p\Lambda$ as illustrated in Fig. 5. Thus, once p, d, and $\overline{P}$ are specified, k_2 and $[e]$ can be determined.

Recent work by Bell and his co-workers [4-6] has shown that the relationships exhibited in Figs. 4 and 5 can be used to describe successfully the dissociation of hydrogen and oxygen, the oxidation of carbon monoxide, and the decomposition of carbon dioxide. Unfortunately, there is insufficient data at present from which to construct Figs. 4 and 5 for ethylene. Consequently, the quantitative modeling of an ethylene discharge is precluded. It is possible, however, to use the shapes of the curves shown in Figs. 4 and 5 to qualitatively interpret the dependence of the overall polymerization rate on the operating conditions.

For a fixed pressure and power it has been shown in Table 1 that the overall rate of polymerization passes through a maximum as the flow rate of ethylene is increased from 5 to 80 cm³/min. This
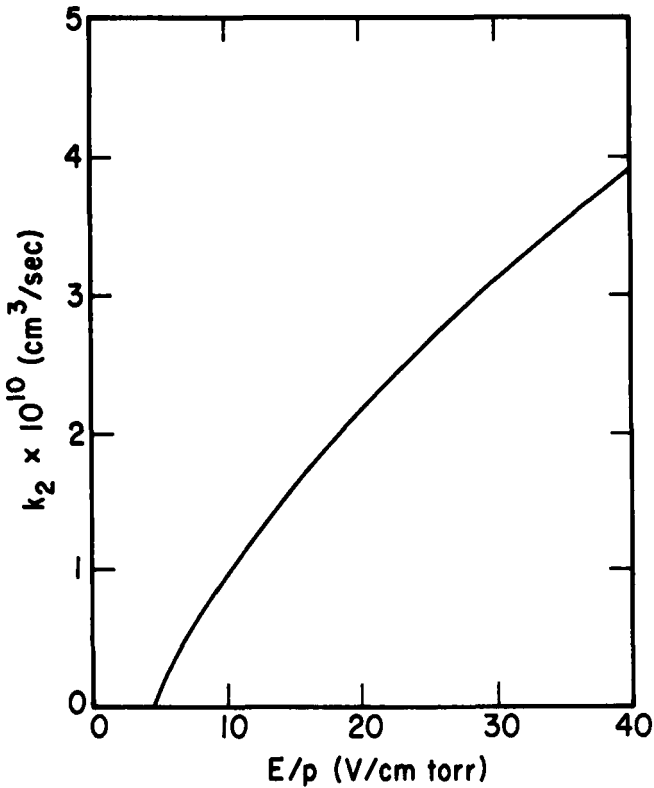
FIG. 4. An example of the dependence of k_2 on E/p.

observation can be explained in the following way. At very low flow
rates the residence time of the gas in the discharge is high enough
for a steady-state free radical concentration to be established which
is independent of the gas flow rate   These radicals then initiate
both homogeneous and heterogeneous polymerization via the mechanisms
discussed above. For sufficiently long residence times essentially all
of the ethylene fed to the discharge will be converted to polymer. As
the flow rate is raised the polymerization rate at first increases due
to the greater supply of monomer. Finally a point is reached at which
the flow rate begins to perturb the free radical concentration. When
this occurs the radical concentration is reduced. This change, to-
gether with the decreased residence time, leads to a situation in which
only a fraction of the ethylene feed can be converted. Figure 6 sum-
marizes this sequence of events. It should be noted that the observed
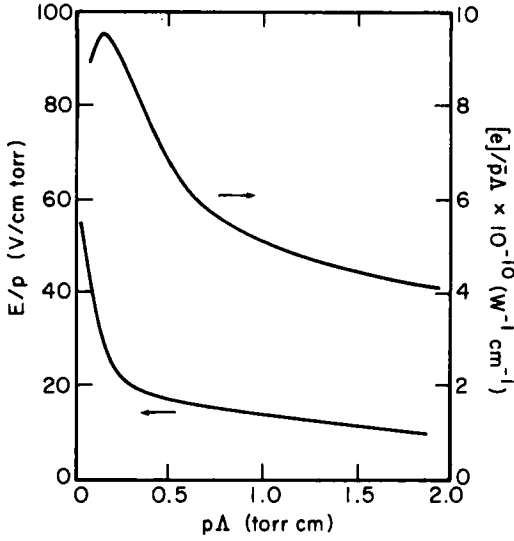influence of flow rate on both film and powder deposition strongly

FIG. 5. Typical curves of E/p and $[e]/\bar{P}\Lambda$ vs $p\Lambda$ for an rf discharge.
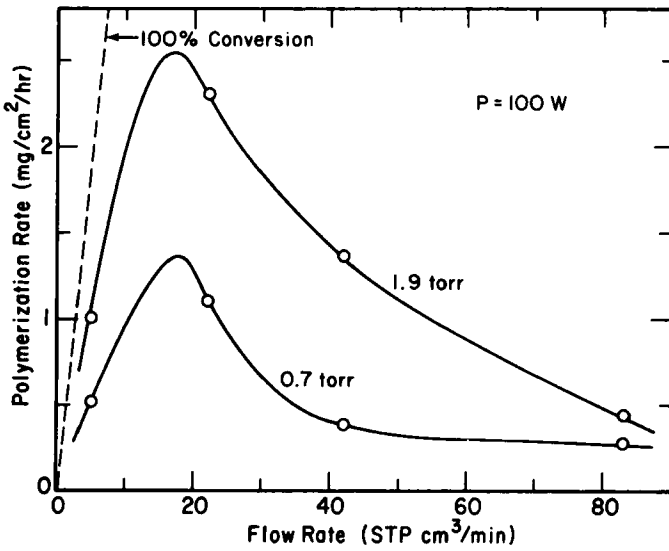
FIG. 6. Effect of flow rate on the overall polymerization rate.

supports the proposal that polymerization proceeds by a free radical mechanism.

The effect of pressure on the polymerization rate is the most difficult to interpret because of the large number of parameters affected. As the pressure increases E/p decreases, causing a reduction in the value of k_2. The value of $[e]$ also decreases, as may be seen from Fig. 4. While the reductions in k_2 and $[e]$ operate to decrease the rate of atomic hydrogen formation, they are partly offset by the increase in ethylene concentration. Although it is not possible to determine the net effect of pressure on r_2 without knowing the exact shape of the curves in Figs. 4 and 5, one may reason by analogy with other systems [4, 5] that r_2 will increase. The increased value of r_2 will cause the free radical production rate to rise. This trend will be enhanced by the fact that for a fixed STP flow rate into the reactor, the residence time increases with pressure. The increased rate of free radical formation is opposed by processes which consume free radicals and are also enhanced by increases in the pressure of ethylene. As a result of these two processes, one anticipates that the free radical concentration will increase with pressure but at a decreasing rate.

The concentration of monomer present on those surfaces where a film is deposited will also increase with increasing ethylene pressure. Since the number of adsorption sites is fixed the surface concentration of adsorbed monomer will approach a maximum equivalent to monolayer coverage.

The observed dependence of the rates of film and powder formation on pressure can now be explained in terms of the anticipated responses of gas phase free radical concentration and the surface concentrations of adsorbed monomer. As the pressure is increased from very low values, the free radical concentration, the monomer concentration, and the concentration of adsorbed monomer all increase. Over this range of pressure the rates of both film and powder formation will increase. When the pressure is increased further, the gas phase polymerization process will begin to decline as a result of chain termination reactions which are second order in free radical concentration. The rate of heterogeneous polymerization will approach a maximum due to a saturation of the surface with adsorbed monomer.

The proposed model can also be used to explain the dependence of the rate of polymerization on the size of the electrode gap. As the value of d is decreased for a fixed power and pressure, the values of E/p and $[e]$ both increase. As a result of the increase in E/p, k_2 increases. The net effect of these changes is to cause the free radical production rate to increase, which in turn brings about an increase in the polymerization rate. The results shown in Fig. 2 agree with this conclusion.

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REFERENCES

[1] H. Kobayashi, A. T. Bell, and M. Shen, J. Appl. Polym. Sci., 18, 885 (1973).
[2] M. Niinomi, H. Kobayashi, A. T. Bell, and M. Shen, J. Appl. Phys., 44, 4317 (1973).
[3] L. J. Bellamy, Infrared Spectra of Complex Molecules, 2nd ed., Wiley, New York, 1958.
[4] A. T. Bell, Ind. Eng. Chem., Fundam., 11, 209 (1972).
[5] A. T. Bell and K. Kwong, Ibid., 12, 90 (1973).
[6] L. C. Brown and A. T. Bell, submitted to Ind. Eng. Chem., Fundam.
[7] Y. Inel, A. Siddigi, and G. G. Meisel, J. Phys. Chem., 75, 1317 (1971).
[8] P. Borell, A. Cervenka, and J. W. Turner, J. Chem. Soc., B, 1971, 2293.
[9] H. Mitsue, S. Machi, M. Hagiwara, and T. Kagiya, J. Polym. Sci., A-1, 5, 1073 (1967).
[10] F. J. Vastola and J. P. Wightman, J. Appl. Chem., 14, 69 (1964).
[11] R. L. Paciorek and R. H. Kratzer, Can. J. Chem., 48, 1777 (1970).
[12] J. M. Brown, P. B. Coates, and B. H. Thrush, Chem. Commun., 1966, 884.
[13] J. V. Michael and H. Niki, J. Chem. Phys., 46, 4965 (1967).
[14] F. K. McTaggart, Plasma Chemistry in Electrical Discharges, Elsevier, New York, 1967.
[15] S. C. Brown, Introduction to Electrical Discharges in Gases, Wiley, New York, 1966.