A Correlation of the Chemistry with the Polymerization Rate in an rf Discharge of Methane

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ABSTRACT

In a 150-V methane discharge, the rate of polymerization
is approximately 3 times greater on the electrodes than
on the walls. The sum of the C_1 and C_2 ions is 2 to 3 times
higher in the dark space adjacent to the electrodes than in
the space adjacent to the walls. Ethylene and acetylene
are present in about equal amounts in all regions of the
discharge. It is concluded that the ions $C_2H_3^+$, $C_2H_2^+$, CH_3^+,
CH_2^+, and CH^+ have the greatest influence on the rate of
polymerization, while the neutrals CH_4, C_2H_2, C_2H_4, and
C_2H_6 have the least influence.

INTRODUCTION

We have been interested in the polymerization process that
occurs when volatile organic compounds are subjected to an rf
discharge [1]. The resulting polymeric films exhibit potentially
useful properties, particularly as passive materials for integrated
optical circuitry [2]. A considerable amount of speculation con-
cerning the mechanism of the polymerization process has been

based mainly on indirect evidence of the chemistry involved [3]. We
have taken a more direct approach by designing and constructing a
mass-spectrometric sampling station [4] which enabled us to
examine the ionic and neutral products formed in the discharge
by mass analyzing the species which effuse through a pinhole in
the discharge zone [5-7]. It was assumed that a knowledge of the
species observed should give some insight into the mechanism of
polymer formation under discharge conditions.

In our most recent work [8] the ionic and neutral species present
in different regions of an rf discharge in methane have been examined.
It was clear that for a capacitively coupled discharge, schematically
represented in Fig. 1, at least three distinct regions of chemical
interest exist: R, the sheath between the rf electrode and the
luminous plasma; G, the sheath between the ground electrode and
the plasma; and W, the sheath between the wall and plasma. High
energy-cost processes occur mainly in region R. The dominant
ions found [8] were C^+, CH^+, CH_2^+, CH_3^+, $C_2H_2^+$, and $C_2H_3^+$, with
practically no ions seen containing more than three carbon atoms.
Region W reflects the chemistry occurring essentially in the bulk
of the plasma [8]. There, the ions CH_3^+, CH_5^+, $C_2H_3^+$, and $C_2H_5^+$
are dominant, with a significant fraction of the total ion flux
consisting of C_4 to C_6 ions. The chemistry of region G closely
resembles that of region R. The dissimilarities observed between
regions R and W were attributed to the differences in energies of
the electrons present as well as the differences in kinetic energies
of the primary ions formed which underwent ion-molecule reactions
to yield secondary ions. Ions containing two or more carbon atoms
were shown to result from ion-molecule reactions rather than from
primary ionization of C_2 neutrals. The neutral gas composition
also differed in the three regions of the discharge and was also
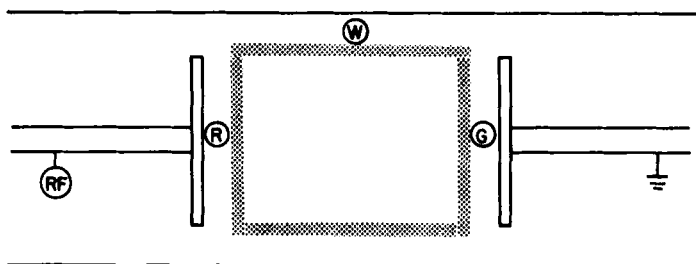a function of the energy available.

FIG. 1. Schematic representation of a capacitively coupled rf
discharge in methane. The letters R, W, and G are labels for the
dark space between the luminous plasma bulk and the rf electrode,
container wall, and ground electrode, respectively.

In this paper we describe an apparatus which enabled us to determine the differences in the rate of polymer deposition in the regions R, W, and G. In addition, we outline some of the chemistry taking place in these regions and discuss the relationship to polymer formation.

EXPERIMENTAL

Analysis of the ionic and neutral species in the discharge was carried out as described previously [8]. Figure 2 shows a schematic representation of the experimental arrangement used to determine the rates of polymer deposition. The glass tube was constructed of 105 mm ID pipe with flattened ends containing grooves which accommodated O-rings. The electrodes were made of 10 × 50 mm OD aluminum disks pressed fit onto aluminum supporting rods which in turn were threaded into a nylon pipe bushing in 10 × 135 mm OD aluminum end-plates. When assembled, the rf and ground electrodes were approximately 20 ± 0.2 mm apart with the face of the electrically floating electrode 30 ± 2 mm from the axis of the other two electrodes. This geometry faithfully reproduces that used in the mass spectrometric measurements [7, 8].

All measurements reported are for pure methane discharges. Gas pressure in the tube was measured with a calibrated capacitance manometer. The gas flow was such as to give residence
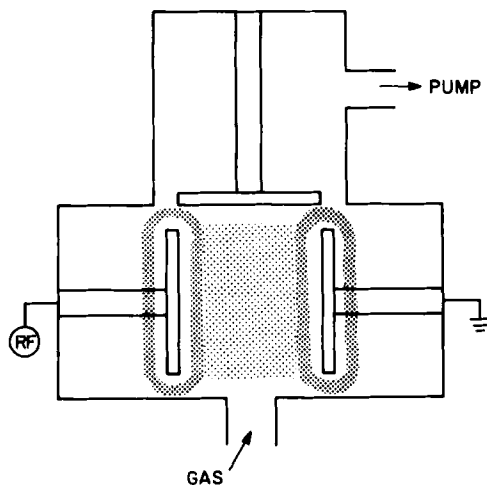
FIG. 2. Schematic of the reactor used to determine polymer deposition rates.

times of from 3 to 5 sec in the interelectrode region. The peak-to-peak rf potential was measured on a 10-MHz oscilloscope while the power input was measured by an rf power meter on the generator. Rate studies were made at 150 V peak-to-peak rf potential at three pressures, 0.3, 0.5, and 0.8 Torr. Polymer was deposited on a polished silicon wafer (0.025 × 31 mm OD) which was held firmly against the face of the electrode by round-head screws. A scanning electron microscope examination of the fractured edge of the wafer gave a picture of the deposited film from which its thickness and thus rate of deposition could be accurately determined. Polymer deposition occurred simultaneously at each location.

RESULTS

The rate monitoring experiment, schematically shown in Fig. 2 and described in the experimental section, was constructed so as to duplicate as closely as possible the dimensions of our radial mass-spectrometric sampling experiment [8]. Power input and flow rate were also reproduced. The floating electrode shown in Fig. 2 is electrically equivalent to the discharge tube wall. Table 1 shows the rate of methane-polymer deposition on the electrode faces for relatively high (0.8 Torr), low (0.3 Torr), and intermediate (0.5 Torr) pressure settings in a 150-V peak-to-peak discharge. We see from the data that polymer deposits essentially at the same rate on the rf and ground electrodes at each pressure setting, but that the rates, going from low to high pressure, are 2.6, 3.2, and 3.6 times slower on the wall electrode, respectively. In addition, we find that the rate of deposition decreases by approximately a factor of 2 as the pressure increases.

TABLE 1. Comparison of the Rate of Methane Polymer Deposition on the Electrodes and Walls in a 150-V p-p rf Discharge [8] at Several Pressures

Pressure (Torr)	Deposition rate (Å/min) for region[a]		
	R	G	W
0.8	11	11	3
0.5	16	16	5
0.3	31	26	11

[a]See Fig. 1 for explanation of symbols
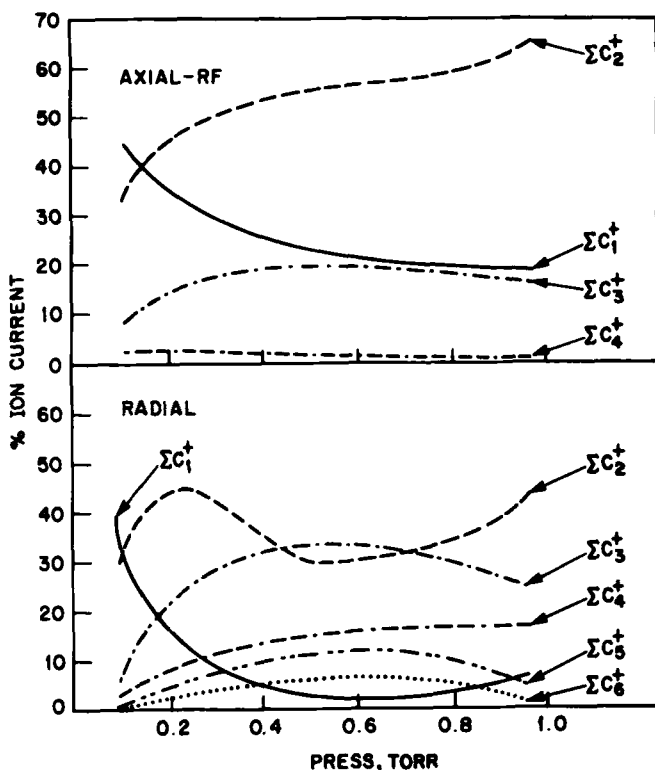
FIG. 3. Percent ion current as a function of pressure for a 150-V p-p methane discharge. Upper half shows data for axial sampling [8] through an orifice in the rf electrode. Lower half shows data for radial sampling [8] through an electrically floating orifice.

Figure 3 shows the percentage of total ion current for the C_1 through C_6 ions as a function of pressure as detected mass-spectrometrically in a 150-V methane discharge [8]. The upper set of curves gives data for the case of axial sampling through an orifice located in the rf electrode, while the lower set gives data for radial sampling through an electrically floating orifice [8]. Data for axial sampling through a grounded electrode are very similar to those for axial-rf sampling shown in the upper half of Fig. 3. The obvious major difference between the sets of curves in Fig. 3 is the far greater abundance over the entire pressure range of C_4, C_5, and C_6 ions found near the walls

than adjacent to the electrodes. A second major difference between axial and radial sampling which is not shown by Fig. 3 is the composition of the C_1 and C_2 ions.

Tables 2 and 3 list the percentage compositions of the C_1 and C_2 ions, respectively, adjacent to the electrodes and walls in a 150-V methane discharge [8] at pressures of 0.8, 0.5, and 0.3 Torr. We see in Table 2 that the ions CH^+ and CH_2^+ are found only near the electrodes and along with CH_3^+ account for the major portion of the C_1 ions in these regions. In contrast, the ions CH_3^+ and CH_5^+ account for essentially all the C_1 ions near the walls. Note also that the total percentage of C_1 ions is 2.5 to 7.7 times greater near the electrodes than near the walls. In Table 3, we see that $C_2H_2^+$ and $C_2H_3^+$ are the preponderate ions found next to the electrodes, with $C_2H_5^+$, on the average, accounting for only 9% of the C_2 ions. On the other hand, the major C_2 ions near the walls are $C_2H_3^+$ and $C_2H_5^+$, with each, on the average, comprising 43 and 47%, respectively, of the total C_2 ions.

Table 4 gives the mole fraction of neutral species found near the electrodes and walls in a 150-V methane discharge [8] at the three pressures 0.8, 0.5, and 0.3 Torr. In all cases the sum of the hydrogen and methane is at least 90 mole % of the neutral

TABLE 2. Percent of the C_1 Ions Present in Different Regions of a 150-V p-p Methane Discharge [8] at Several Pressures

Pressure (Torr)	Region[a]	Ions (%)					
		CH^+	CH_2^+	CH_3^+	CH_4^+	CH_5^+	ΣC_1^+
0.8	R	0.9	2.2	15.1	0.3	1.6	20.1
	G	-	0.3	10.3	-	6.3	16.9
	W	-	-	0.75	-	1.8	2.6
0.5	R	2.6	5.5	15.8	0.25	1	25.2
	G	0.45	1.3	14	0.2	2.7	18.7
	W	-	-	3.1	-	1.8	4.9
0.3	R	3.7	7.8	18.4	0.5	1	31.4
	G	0.9	2.6	16.2	0.3	1.9	21
	W	-	-	5	0.5	2.9	8.4

[a]See Fig. 1 for explanation of symbols.

TABLE 3. Percent of the C_2 Ions Present in Different Regions of a 150-V p-p Methane Discharge [8] at Several Pressures

Pressure (Torr)	Region[a]	Ions (%)				
		$C_2H_2^+$	$C_2H_3^+$	$C_2H_4^+$	$C_2H_5^+$	ΣC_2^+
0.8	R	11.5	40	2.2	5.8	59.5
	G	3.8	49	2.1	11	65.9
	W	0.4	3.1	1.9	16.5	33.3
0.5	R	17	34.7	2.1	3.4	57.2
	G	9	3.3	2.5	6	2.7
	W	0.5	12.5	1.8	14.3	29.1
0.3	R	15.5	28.5	2.1	2.8	48.9
	G	10.9	38.6	2.3	5.1	56.9
	W	1	1.9	4.9	17.6	40.9

[a]See Fig. 1 for explanation of symbols.

species. The sum of unsaturated molecules ethylene and acetylene varies from region to region in the range 1.9 to 3.8 mole %. For each of the three pressures, this sum remains nearly constant at a value of 3.6 mole % near the ground electrode; it decreases with decreasing pressure from a value of 3.8 to 1.9 mole % near the rf electrode and increases with decreasing pressure from 2.6 to 3.9 mole % near the walls. We see also in Table 4 that the ratio of hydrogen to methane in all cases decreases with pressure, but the value of this ratio has a spread of about an order of magnitude.

DISCUSSION

We now have detailed knowledge of the ionic and neutral composition of the different regions of the discharge and the rates of polymer formation in those regions. It is appropriate to consider which of the variables observed controls the polymer deposition process. Polymerization in this system takes place on surfaces rather than in the gas phase; therefore we assume that the chemical species arriving at the surface determine the polymerization

TABLE 4. Mole Fraction of Neutral Species Present in Different Regions of a 150–V Methane Discharge at Several Pressures

Pressure (Torr)	Region[a]	Mole fraction					Ratio $H_2:CH_4$
		H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	
0.8	R	0.55	0.37	0.021	0.017	0.050	1.5
	G	0.34	0.56	0.022	0.015	0.063	0.61
	W	0.14	0.78	0.012	0.014	0.047	0.18
0.5	R	0.63	0.30	0.018	0.013	0.040	2.1
	G	0.41	0.49	0.023	0.012	0.061	0.84
	W	0.22	0.69	0.017	0.017	0.058	0.32
0.3	R	0.80	0.17	0.011	0.008	0.018	4.7
	G	0.54	0.38	0.022	0.014	0.040	1.4
	W	0.46	0.44	0.023	0.016	0.062	1.0

[a]See Fig. 1 for explanation of symbols.

process. First, let us consider the neutrals: These overwhelmingly consist of molecular hydrogen and methane, along with small amounts of ethane, ethylene, and acetylene (Table 2). Plainly, we can dismiss hydrogen as a progenitor of polymer. Molecular methane that impinges on a surface is likely to encounter only radical species, and reactions with radicals would not lead to higher homologs. Thus molecular methane, and for similar reasons ethane, can be excused from direct implication in the polymerization process. The two remaining neutral molecules, ethylene and acetylene, both possess π-bonds and are capable of functioning as polymer building blocks. However, the concentrations of these two unsaturated compounds found in the regions R, W, and G (Table 4) of the discharge do not correlate with the observed polymerization rates (Table 1). Therefore, our first conclusion is that the neutral species CH_4, C_2H_6, C_2H_4, and C_2H_2 do not determine the rate of rf discharge polymerization of methane.

Now consider the ions. Intuitively, one might have expected the buildup of multicarbon-containing ions in the gas phase to be an important early step in the polymerization process. In reality, this proved not to be the case. For example, mass-spectrometric ion sampling near the walls revealed that at 0.5 Torr the C_3 through C_6 ions account for 64% of the current (lower portion of Fig. 3) while near the electrodes these same ions account for only 22% of the current (upper portion of Fig. 3), yet the rate of polymer formation is about 3 times faster on the electrodes than on the walls. We therefore reach the second conclusion that the C_1 and C_2 ions play the primary role in the polymerization process. In addition, we conclude that in the case of the C_1 ions, CH^+, CH_2^+, and CH_3^+ are far more important than CH_4^+ and CH_5^+ in forming polymer (see Table 2). Furthermore, we conclude from Table 3 that $C_2H_3^+$ and to a lesser extent $C_2H_2^+$ play predominate roles while $C_2H_5^+$ plays little if any role in the polymerization process. An interesting result is obtained from a comparison of the ratios of the average values for the percent $C_2H_3^+$ found near the electrodes to that near the walls with the ratios of the rates of polymerization near the electrodes to that near the walls: at 0.8 Torr, the values are 3.1 and 3.7, respectively; at 0.5 Torr, 3.3 and 3.2, respectively; and at 0.3 Torr, 1.9 and 2.6, respectively.

A major source of radicals results from the neutralization at surfaces of such ions as $C_3H_3^+$, $C_2H_3^+$, CH_3^+, CH_2^+, and CH^+. Certainly the resulting radicals C_3H_3, C_2H_3, CH_2, and CH would be very reactive toward other radicals and unsaturated molecules. It is reasonable to postulate that the polymerization process in the methane rf discharge proceeds by the reaction of these unsaturated radicals. Since the radicals result from the neutralization of the corresponding positive ions, the rate of polymer formation is

ultimately controlled by the rate of arrival of these particular
ions.

CONCLUSION

Glow discharge produced methane–polymer deposits more
rapidly on the electrodes than on the walls because in the dark
space adjacent to the electrodes there are a greater number of
one and two carbon ions, especially $C_2H_3^+$, $C_2H_2^+$, CH_3^+, CH_2^+,
and CH^+, than in the space adjacent to the walls. The neutral
molecules ethylene and acetylene do not influence the rate. Ions
arriving on a surface are more important than neutrals in terms
of the rate of polymerization.

ACKNOWLEDGMENT

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