

# Polymerization of Methane

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## Synopsis

Plasma polymerization of methane in a magnetically enhanced capacitively coupled bell jar reactor operating at a frequency of 10 kHz is reported. Dependence of polymer deposition rate on monomer feed rate ( $F$ ), composite power parameter ( $W/FM$ ), electrode temperature, and electrode cleanliness have been examined. Such functional properties as wettability, adhesion, and thermal stability of the polymer are found to depend on the composite power parameter ( $W/FM$ ) of the plasma. The permeability studies indicate highly crosslinked nature of the polymer. ESCA studies reveal codeposition of electrode material with the polymer under high  $W/FM$  conditions, potential applications of plasma polymer of methane are suggested.

## INTRODUCTION

Methane as we all know is the simplest of all organic compounds. It does not contain any characteristic functional group and therefore cannot be polymerized by conventional means. Methane, however, offers special advantages to plasma polymer chemists. Its low molecular weight allows high levels of  $W/FM$  (an energy transfer parameter, where  $W$  is the electrical wattage,  $F$  monomer feed rate, and  $M$  molecular weight) to be attained. Due to the absence of reactive functional groups, contributions from plasma-induced processes in plasma polymerization are minimized so that highly crosslinked structures are formed. Also for the same reason methane polymerizes slowly in plasma, and other useful mechanisms such as SEAP (sputtering of electrodes by active species of plasma) that lead to codeposition of electrode material in the organic polymer matrix can be activated by increasing  $W/FM$  values. Mechanisms like SEAP have been found to improve the adhesion of plasma polymers to metallic substrates. From the surface modification point of view, methane has the advantage of being a hydrogen-rich monomer. Different levels of crosslink density and surface free energy can be obtained by selective removal of hydrogen during the plasma polymerization process. In addition, methane is a gas, easily available, and easy to work with. The following paper describes plasma polymerization of methane and its applications in many different areas of science and technology. For familiarity with the plasma polymerization process (also called glow discharge polymerization) the reader is referred to one of the recent reviews published on the process in the literature.<sup>1-3</sup> The intermediates involved in methane plasma polymerization have been discussed by Smolinsky et al. (see reference 2).

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## EXPERIMENTAL

The polymerization of methane was conducted in a bell jar reactor using magnetically enhanced plasma. The design of the polymerization reactor and the method of polymer preparation are described elsewhere.<sup>4</sup> The substrates were rotated on a disc in the plasma zone to ensure a uniform coating. The plasma system was equipped with all modern diagnostic instruments. The monomer feed rate was controlled by a Tylan mass flow controller (Model FC-260/RO-14) calibrated for methane. The thickness of the deposited polymer was measured by a Veeco crystal thickness monitor (Model QM-301) with its sensor placed closed to the substrates in the plasma zone. The system pressure was monitored using a MKS Baratron pressure gauge (Model 220B-HS-2AI-B-1). The electric power to the system was supplied from a Crown power amplifier (Model M-600) coupled with a Hewlett-Packard oscillator (Model 209A). All results reported in this paper were obtained at a fixed frequency of 10 KHz.

## RESULTS AND DISCUSSION

### Kinetics of Plasma Polymerization

As we all know plasma polymerization is a system-dependent process. Discussion of the absolute kinetics of the plasma polymerization, therefore, is

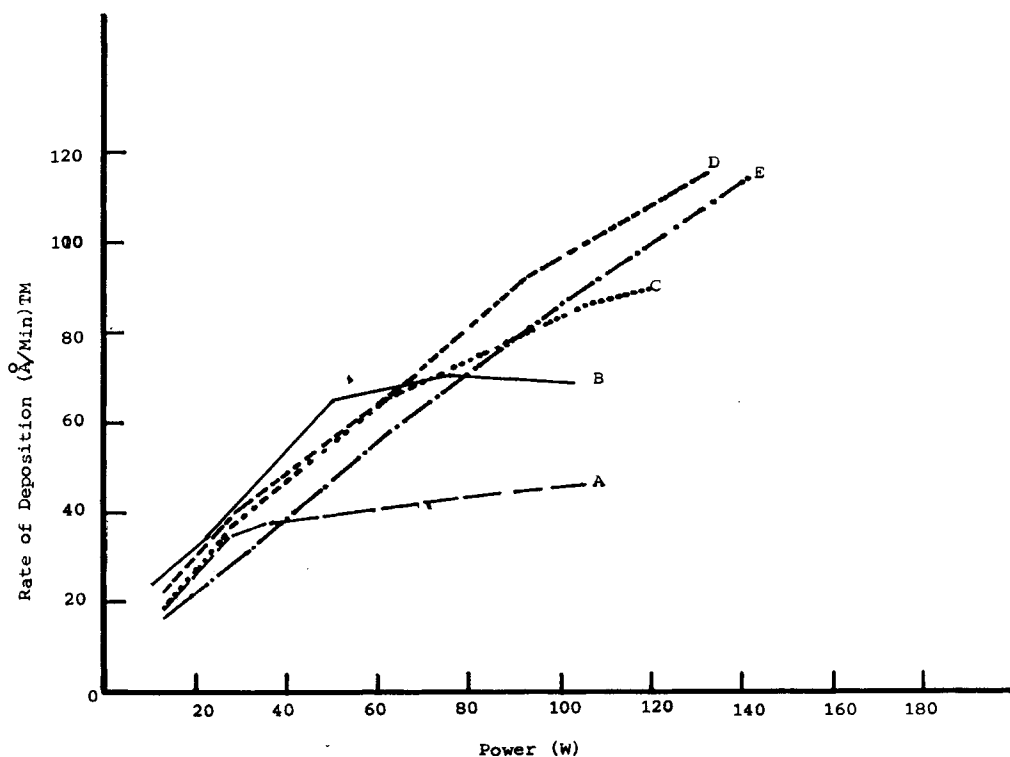


Fig. 1. PPM deposition rate as a function of discharge power at different monomer feed rates (cc/min): (A) 0.25; (B) 0.46; (C) 1.64; (D) 3.40; (E) 6.30.

not possible. The kinetics results indicated in this paper gives a general overview of the process without attaching any significance to the numbers.

Figure 1 shows variation of the rate of methane plasma polymer deposition vs. discharge power at several different monomer feed rates. The discharge power was obtained by multiplying current and voltage components measured at the electrode during polymerization. Figure 2 is a replot of Figure 1, but the composite power parameter  $W/FM$  has been used in place of power. This gives a much clearer picture of the plasma polymerization of methane. Three regions of plasma polymer deposition can be identified in Figure 2. In region 1 plasma polymerization is governed by the available discharge power, and an almost linear dependence of polymer deposition rates with  $W/FM$  is noticed at all monomer feed rates. In region 3 the plasma polymerization is governed by the monomer feed rates and polymer deposition rates saturates with respect to power. In region 2 polymer deposition is governed by both parameters. Yasuda has given a very interesting description of plasma polymer deposition kinetics in his book.<sup>3</sup>

A few other interesting observations were made during plasma polymerization of methane. One of these pertains to the breakdown voltage in the system. The breakdown voltage is defined as the voltage required for initiat-

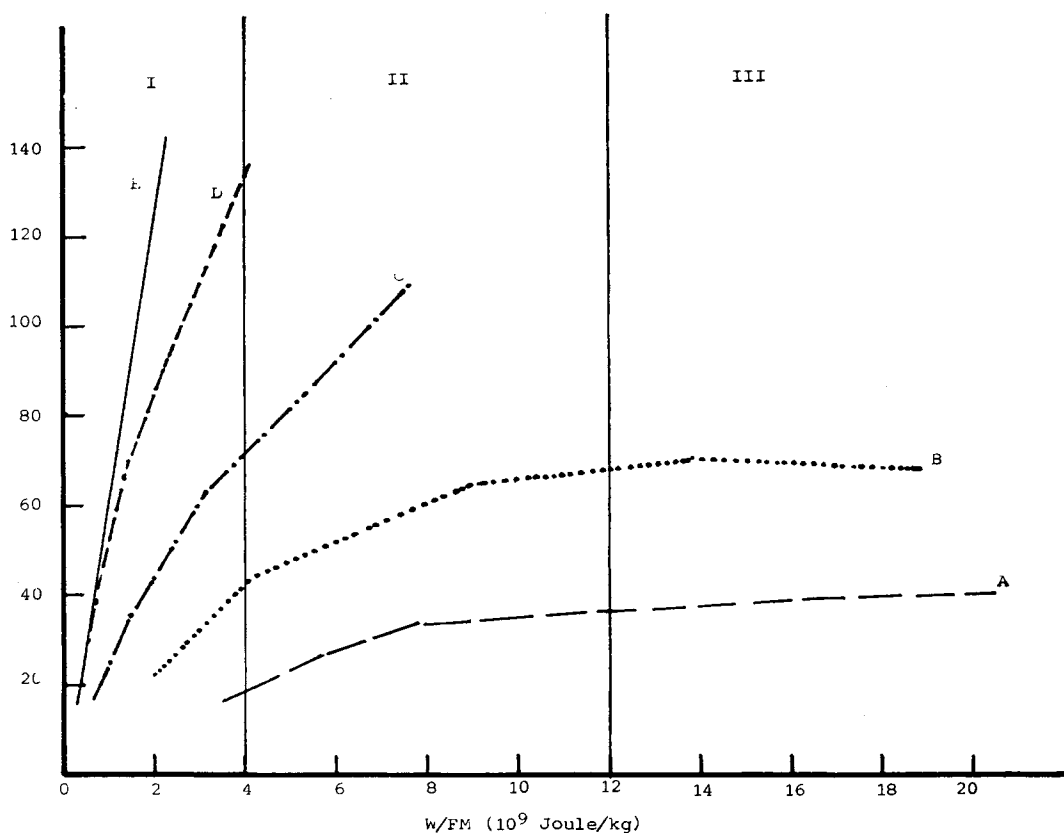


Fig. 2. PPM deposition rate as a function of energy parameter  $W/FM$  at different monomer feed rates (cc/min): (A) 0.25; (B) 0.46; (C) 1.64; (D) 3.40; (E) 6.30.

TABLE I

Monomer feed rate (MFR) [mL (STP)/min]	Pressure ( $P_1$ ) (mtorr)	Breakdown voltage (V)
0.25	7.0	398 $\pm$ 5
0.40	12.0	360 $\pm$ 5
1.64	24.0	300 $\pm$ 5
3.41	40.0	285 $\pm$ 5

ing the glow. Table I lists the breakdown voltages for methane monomer as a function of monomer feed rate and system pressure. As indicated, the breakdown voltage decreases with increasing monomer feed rate. This is true as long as clean electrodes are used. Polymer-coated electrodes (e.g., from previous runs) added their own impedance. This was especially evident at low monomer feed rates where sometimes it was even difficult to initiate glow due to high breakdown voltage required.

The cleanliness of the electrodes also affected the polymer deposition kinetics as is evident from Figure 3. Higher rates of deposition were obtained especially at low monomer feed rates, with clean electrodes. At high monomer feed rates and with successive experiments using uncleaned but cooled electrodes, this difference in kinetics tend to disappear as is evident from Figures 4 and 5. The high rate of polymer deposition with clean electrodes at low monomer feed rate is perhaps due to the codeposition of electrode material with the polymer. This aspect of polymer deposition will be discussed in more detail in the latter part of this paper.

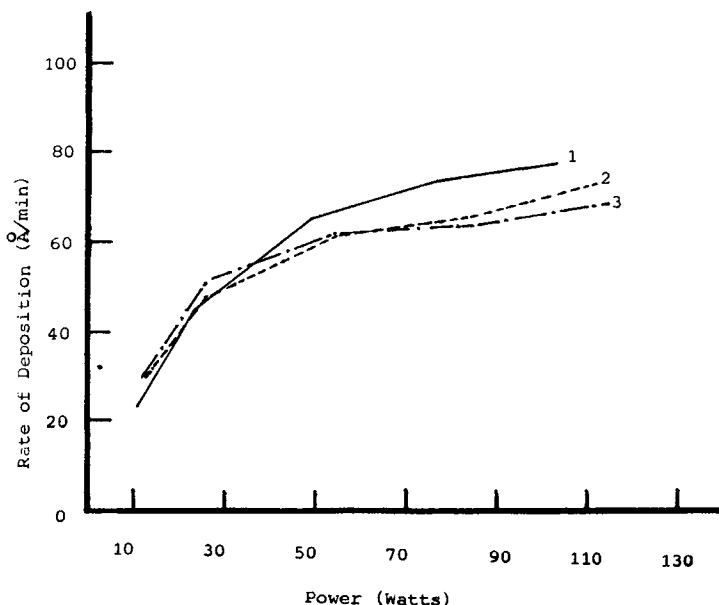


Fig. 3. PPM deposition rate as a function of discharge power—electrode cleanliness effect. 1, 2, and 3 refers to successive experiments at monomer feed rate of 0.46 cc/min. Electrodes were cooled in between.

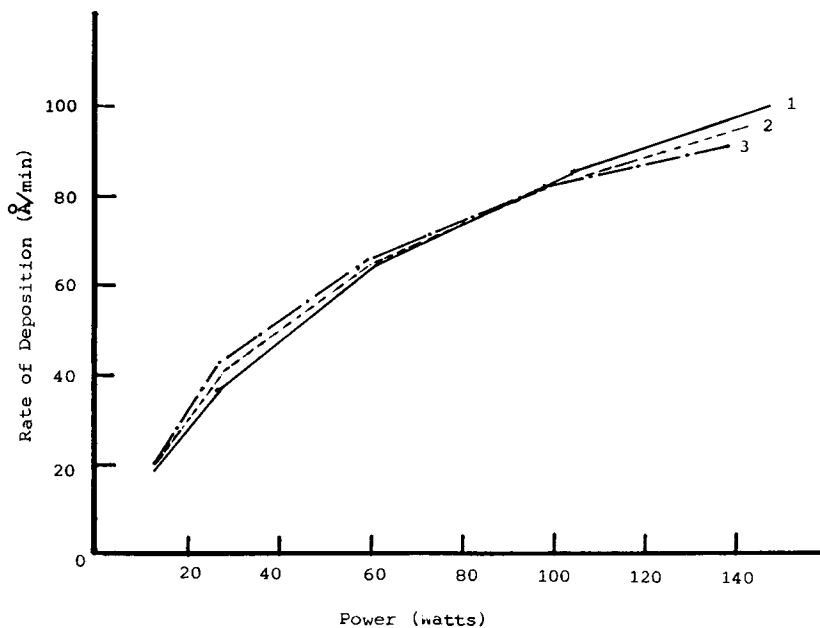


Fig. 4. PPM deposition rate as a function of discharge power—electrode cleanliness effect. 1, 2, and 3 refers to successive experiments at monomer feed rate of 1.64 cc/min. Electrodes were cooled in between.

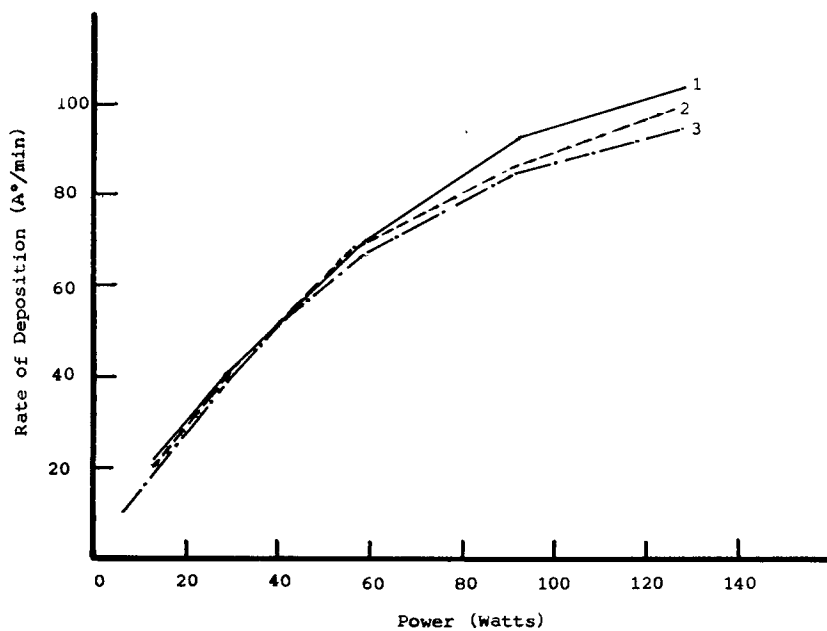


Fig. 5. PPM deposition rate as a function of discharge power—electrode cleanliness effect. 1, 2, and 3 refers to successive experiments at monomer feed rate of 3.40 cc/min.

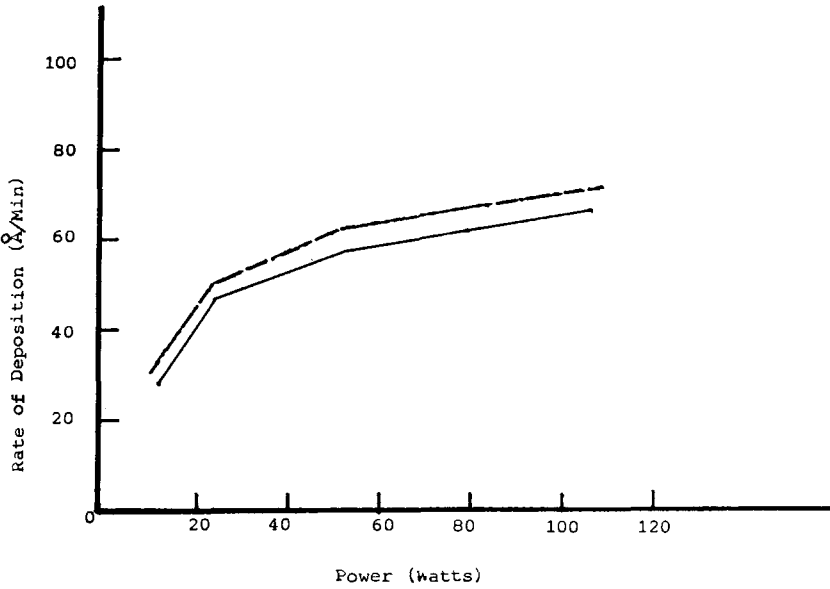


Fig. 6. PPM deposition rate as a function of discharge power—electrode temperature effect. C refers to clean electrodes at ambient temperature (at 25°C), H refers to hot electrodes. Monomer feed rate = 0.46 cc/min.

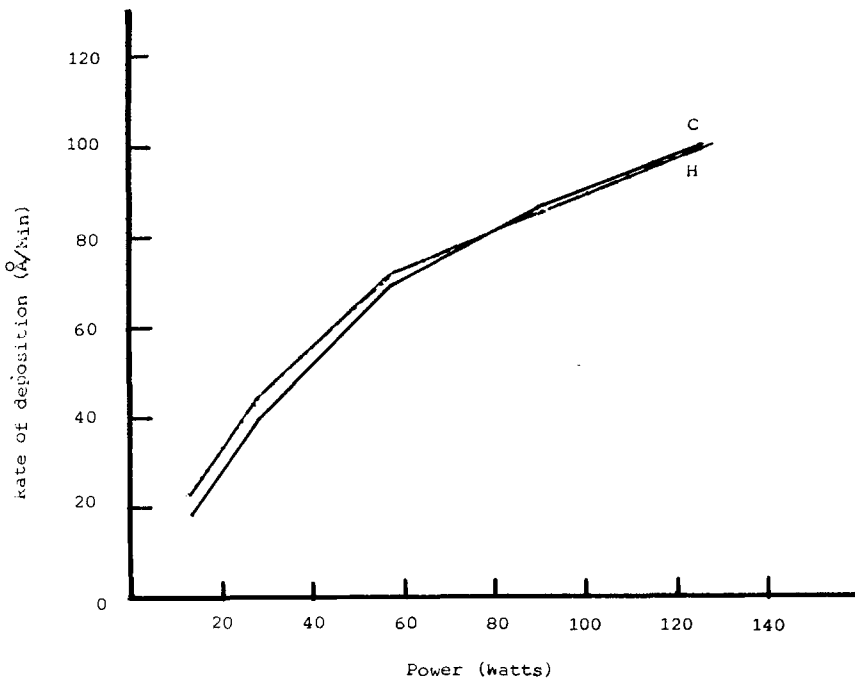


Fig. 7. PPM deposition rate as a function of discharge power—electrode temperature effect. C refers to clean electrodes at ambient temperature (at 25°C), H refers to hot electrodes. Monomer feed rate = 3.40 cc/min.

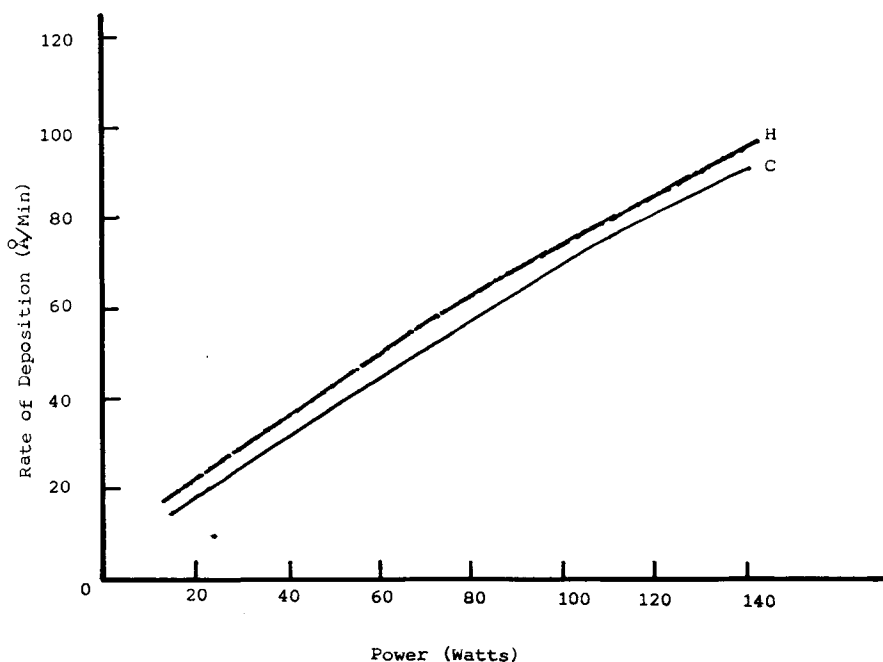


Fig. 8. PPM deposition rate as a function of discharge power—electrode temperature effect. C refers to clean electrodes at ambient temperature (at 25°C), H refers to hot electrodes. Monomer feed rate = 6.29 cc/min.

The temperature of the electrodes also seems to play a role in the polymer deposition kinetics. Although no quantitative measure of the electrodes temperature was made during this study, we found that higher rates of polymer deposition were obtained when successive runs under identical conditions of monomer feed rate, discharge power, and system pressure were done without intermittent cooling of electrodes. This is evident in Figures 6–8. Since electrode temperature as high as 80°C was observed after 1 h of plasma polymerization at low monomer feed rates and high discharge power, this study also indicated that, so far as kinetics of methane plasma polymerization is concerned, these extraneous factors do not play a very big role.

#### PROPERTIES OF PLASMA-POLYMERIZED METHANE (PPM)

The major thrust of this paper, as we said earlier, is not to discuss the kinetics of methane plasma polymerization, but to draw a relationship between the controllable kinetics parameters and the properties of the polymer. A few important properties of the PPM polymer are discussed below.

##### Contact Angle with Water

As we know, the contact angle of a polymer is indicative of polymer surface free energy and determines how a surface would behave in contact with polar and nonpolar liquids. This property, which is also termed as the wettability of the polymer, is of special interest when considering a surface for adhesive bonding. Table II lists the contact angles with water of PPM polymers deposited on nylon 6 substrate under different polymerizing conditions. A

TABLE II

Polymerization conditions			
MFR [mL (STP)/min]	<i>W</i> (W)	<i>W/FM</i> (J/kg)	Contact angle $\theta_{H_2O} \pm 2^\circ$
0.47	75	$1.3 \times 10^{10}$	73°
0.73	73	$0.84 \times 10^{10}$	77°
3.27	76	$0.19 \times 10^{10}$	82°
8.21	74	$0.075 \times 10^{10}$	90°

NRL contact angle goniometer was used for this purpose. Since PPM polymer has good adhesion with nylon 6 polymer, the uncertainty involved in contact angle measurements as a result of water permeation through the PPM polymer to the substrate was avoided. The results provided an interesting relationship between the composite parameter  $W/FM$  (or monomer feed rate) and the contact angle of water with the polymer. The contact angle increased with an increase in  $W/FM$ .

There were two important implications of the above findings. First, discovery of a simple method for altering substrate surface free energy without affecting its bulk properties. This is of great significance in adhesive applications where the substrate involved is incompatible with the adhesive due to its low surface energy (such as Teflon). The PPM polymer provided a hydrocarbon-rich surface which allowed for better wetting by the adhesive, thus increasing the bonding strength. Second, since PPM polymer is highly crosslinked (as also indicated by the elemental analysis of the polymer; C/H  $\sim 1$  was found), one would expect that the surface characteristics provided by a coating of PPM polymer would be permanent and not decay with time. This second aspect of the PPM polymer was further utilized by oxidizing the PPM polymer with oxygen plasma treatment to give a highly water wettable surface (contact angle with water LT 20°C). Unlike the oxygen-plasma-oxidized conventional polypropylene surface, the PPM polymer surface did not show any significant change in contact angle even after 6 months of room temperature storage. Based on these observations, we later advanced the concept of molecular overturning in polymers which had been published elsewhere.<sup>5</sup>

### Polymer Adhesion

For a plasma polymer to be of practical use, it must adhere tightly to the underlying substrate. It is evident from the fact that most of the early failures of plasma polymers have been due to the lack of sufficient polymer-substrate adhesion. It was later discovered that plasma polymer adhesion, like any other plasma polymer property, is polymerization condition dependent.<sup>6</sup> Major breakthroughs have since been made and a new concept of polymer adhesion to metal substrate (called the concept of Atomic Interfacial Mixing or AIM) has been advanced.<sup>7</sup>

It was considered, perhaps due to the nature of methane monomer, that the adhesion of PPM polymer to plastic substrates should not be much of a problem. This was confirmed by coating thin layers of PPM polymer, under different polymerization conditions, on nylon 6 substrate. The adhesion was



TABLE III

Polymerization conditions			$\theta_{\text{H}_2\text{O}}$	$\theta_{\text{H}_2\text{O}}$
MFR	$W$	$W/FM$	(before)	(after)
[mL (STP)/min]	(W)	(J/kg)	$\pm 2^\circ$	$\pm 2^\circ$
— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>	69°	68°
0.73	73	$0.84 \times 10^{10}$	77°	79°
3.27	76	$0.19 \times 10^{10}$	82°	81°
8.21	74	$0.075 \times 10^{10}$	90°	91°

<sup>a</sup>Untreated nylon 6 substrate.

judged by tape test,<sup>8</sup> and by the measurement of contact angle of coated substrate before and after an ultrasonic cleaning process. The latter involved successive cleaning in a detergent solution and water at 60°C. The result of these tests are presented in Table III. As is evident from the results, PPM polymer adheres very tenaciously to the nylon 6 substrate.

Adhering PPM polymer to metal substrates was a difficult proposition. A test protocol was first developed keeping in mind the forthcoming bioengineering applications of the PPM polymer. We will describe here the results of only one such test developed by our group. This test is referred to as "boiling test" and is described in detail elsewhere.<sup>9</sup> The test is particularly useful for large flat substrates, such as a micro glass slide, where polymer coating can be visually inspected. The results of the boiling test are graded 0B–5B where 0B corresponds to lifting of the entire polymer film almost immediately and 5B corresponds to "not lifting" of polymer film even after three cycles each of 8 h boiling and 16 h room temperature soaking in 0.9% saline solution. It is estimated that 1 week of boiling is approximately equal to 3 years at 37°C. For miniature substrates, such as thin Pt wires, the boiling test was coupled with scanning electron microscopy.

Table IV lists the results of these tests as a function of polymerizing conditions. PPM polymer synthesized by using high  $W/FM$  values (low monomer feed rates) adhered best to glass as well as Pt substrate. A poorly adhering coating on Pt wire, when looked at in an electron microscope at  $1000\times$ , was found to be either wrinkled or ruptured after the test. When a comparison of different metallic substrate was done by depositing same PPM polymer on identical substrates (not morphology), the following trend was evident:

$$\text{Ta} > \text{Pt} > \text{Ag} > \text{Ni} > \text{Ti}$$

TABLE IV

Composite parameter $W/FM$ (J/kg)	Adhesion	
	Glass	Pt
$1.87 \times 10^{10}$	5B	Excellent
$1.11 \times 10^{10}$	4B	Excellent
$0.59 \times 10^{10}$	3B	Good
$0.32 \times 10^{10}$	1B	Poor
$0.16 \times 10^{10}$	1B	Poor
$1.16 \times 10^{10\text{a}}$	0B	Poor

<sup>a</sup>Electrodes coated with polymer from a previous high MFR (low  $W/FM$ ) run.

It was also noticed that electrode material plays an important role in PPM-metal substrate adhesion. Under identical polymerizing conditions Al electrodes were found to provide better adhesion than steel electrodes.

Electrode cleanliness also influenced PPM-metal substrate adhesion. For example it was noticed that if polymer-coated electrodes from a previous low  $W/FM$  run were used, the adhesion of PPM polymer was poor under all polymerizing conditions.

In order to ascertain that it was the overall energy conditions ( $W/FM$ ) and not merely the monomer feed rate that governed PPM polymer adhesion to metallic substrates, experiments were conducted by increasing  $W/FM$  (in effect  $W$ ) at monomer feed rates that originally gave poor adhesion. A substantial improvement in adhesion was noticed confirming our hypothesis of high  $W/FM$  requirement (approximately  $10^{10}$  J/kg) for obtaining good adhesion of PPM polymer to metal and glass substrates.

One immediate application of PPM polymer that was realized as a result of discovering polymerizing conditions for good adhesion of PPM polymer to metal substrates was in improving adhesion of Parylene (polyparaxylylene) polymer to metal substrates. This work has been reported separately.<sup>10</sup> Up to a 300% improvement in pull strength of Parylene polymer was observed when the latter was applied to a platinized brass substrate carrying an ultrathin (300A) primary coating of PPM polymer. The improvement is supposed to have been caused by increased physical interactions between the PPM polymer and the Parylene polymer and by the formation of covalent bonds between the residual free radicals of PPM polymer with the growing radicals of Parylene polymer during its deposition. Plasma polymers are known to contain free radical activity for extended periods of time.<sup>11</sup>

### Permeability of PPM Polymer

Although direct measurements of the permeability of PPM polymer are difficult to conduct due to the ultrathin nature of the film, indirect measurements obtained from study of the composite structures (e.g., a PPM polymer film coated on polypropylene film) revealed that PPM polymer's air and water vapor permeability are comparable to those of metals. The following values were obtained for a 1000A PPM polymer film coated on polypropylene substrate:

$$\begin{array}{l} \text{Water:} \quad 7.57 \times 10^{-13} \\ \text{Air:} \quad 9.70 \times 10^{-14} \end{array} \left[ \text{cm}^3 \text{ (STP) cm/cm}^2 \text{ s cm (Hg)} \right]$$

Several interesting applications have emerged as a result of the low permeability of PPM polymer. In one such application ultrathin coating of PPM polymer were applied to a magnetic substrate for providing environmental protection.<sup>12</sup> Accelerated tests in  $\text{SO}_2/\text{NO}_x$  atmosphere indicated that substantial improvement in corrosion resistance was obtained. In another experimental application, silicon contact lenses were coated with an ultrathin film of PPM polymer to prevent diffusion of active dyes in lense material. The results of these experiments were very encouraging.

TABLE V

Composite parameter $W/FM$ (J/kg)	Relative atomic concentration							
	On surface				After 1 min argon etching			
	C <sub>1s</sub>	O <sub>1s</sub>	N <sub>1s</sub>	Al <sub>2p</sub>	C <sub>1s</sub>	O <sub>1s</sub>	N <sub>1s</sub>	Al <sub>2p</sub>
$1.34 \times 10^{10}$ <sup>a</sup>	1.0	0.29	0.05	0.24	1.0	0.20	0.04	0.28
$0.84 \times 10^{10}$	1.0	0.30	0.05	0.06	1.0	0.26	0.03	0.18
$0.19 \times 10^{10}$	1.0	0.19	0.03	—	1.0	0.05	0.01	—
$0.075 \times 10^{10}$	1.0	0.15	0.02	—	1.0	0.04	0.008	—
$1.16 \times 10^{10}$ <sup>a,b</sup>	1.0	0.08	0.13	0.06	1.0	0.03	0.069	0.06

<sup>a</sup>Result from Auger spectroscopy.

<sup>b</sup>Dirty electrodes, coated with polymer from low  $W/FM$  run.

### ESCA Studies

In order to understand the complexity of the PPM polymer structure, extensive ESCA studies were performed on polymer deposited under different polymerization conditions. The results are summarized in Table V, nylon 6 was used as the substrate. The relative atomic concentration at the surface were computed from the heights of the peaks and the elemental sensitivity factors of the pure elements and compounds (4B).

A depth profile was determined in selected cases. The most interesting feature of this study was the discovery of Al in the PPM polymer deposited at high  $W/FM$  values and its absence in PPM polymers deposited at low  $W/FM$  values or deposited using polymer coated electrodes. Since good adhesion of PPM polymer to metal substrate was obtained at high  $W/FM$  values, ESCA studies provided an important evidence for the concept of AIM referred earlier. The amount of oxygen in the polymer, which is believed to result from the interaction of residual free radicals of polymer with atmospheric air, was also found to be highest in the polymer synthesized at the highest  $W/FM$  value and increased with increased Al concentration in the coating.

ESCA analysis thus confirmed that electrodes participates in a rather strong manner in the plasma polymerization of methane under high  $W/FM$  conditions and results in the codeposition of electrode material. These studies also emphasized the need of electrode cleanliness for obtaining good polymer-metal substrate adhesion. When the electrodes were precoated with polymer, sputtering the electrode material was forbidden, as is indicated by the results in Table V, and good polymer adhesion was not obtained even at high  $W/FM$  values.

### Thermal Analysis

The thermal analysis of PPM polymer was performed using a Perkin-Elmer thermal analyzer and gave very interesting results. Typical weight loss curves of PPM polymers synthesized under different polymerizing conditions are depicted in Figures 9–12. Aluminum oxide was used as the DTA reference standard. Heating rate was controlled at 10°C/min. Experiments were conducted in both argon as well as air atmosphere.

As the weight loss curves in Figures 9–12 indicate, the thermal stability of PPM polymers is also polymerization-condition-dependent. For PPM polymer

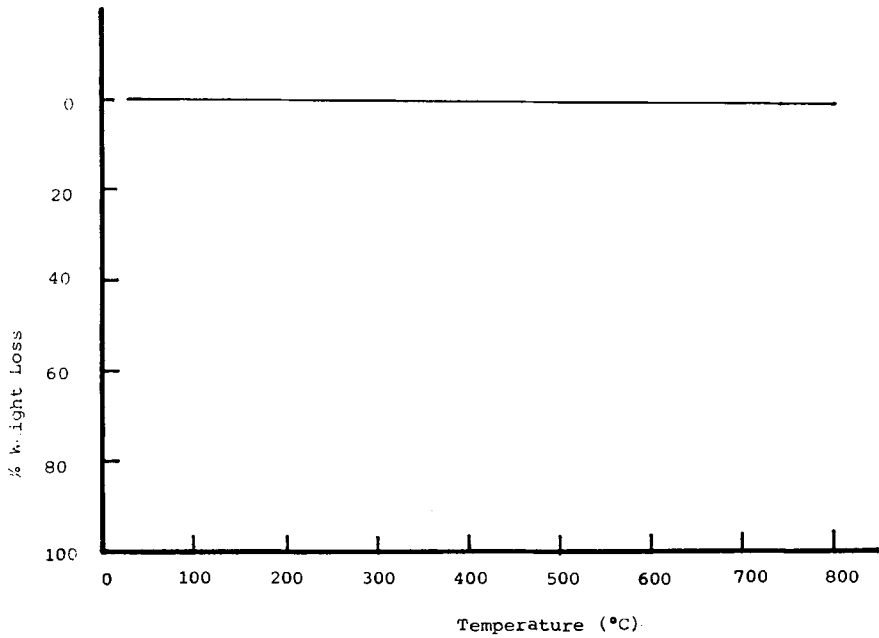


Fig. 9. TGA curve for PPM polymer deposition at 0.66 cc/min, 82 W, in flowing argon.

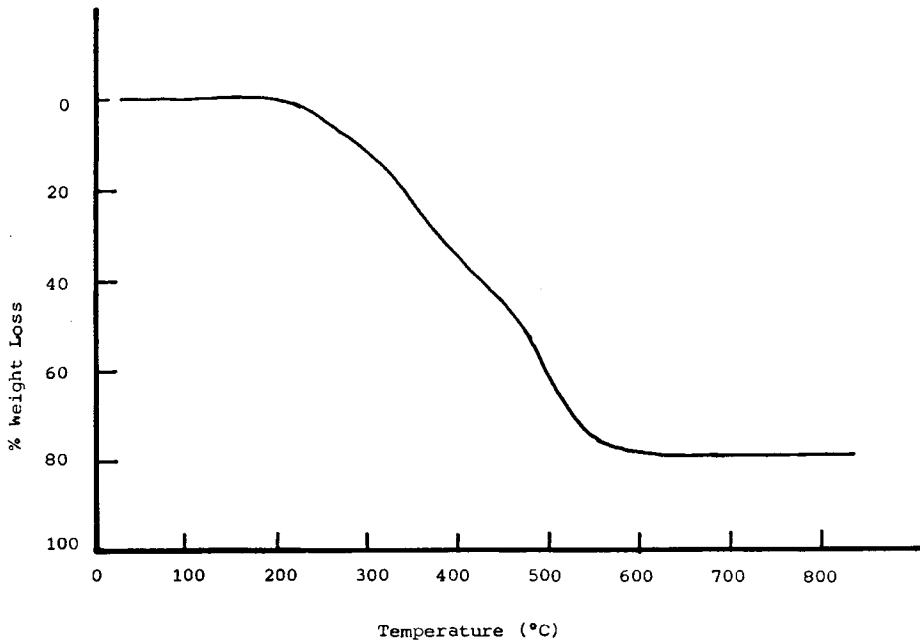


Fig. 10. TGA curve for PPM polymer deposition at 0.66 cc/min, 82 W, in flowing air.

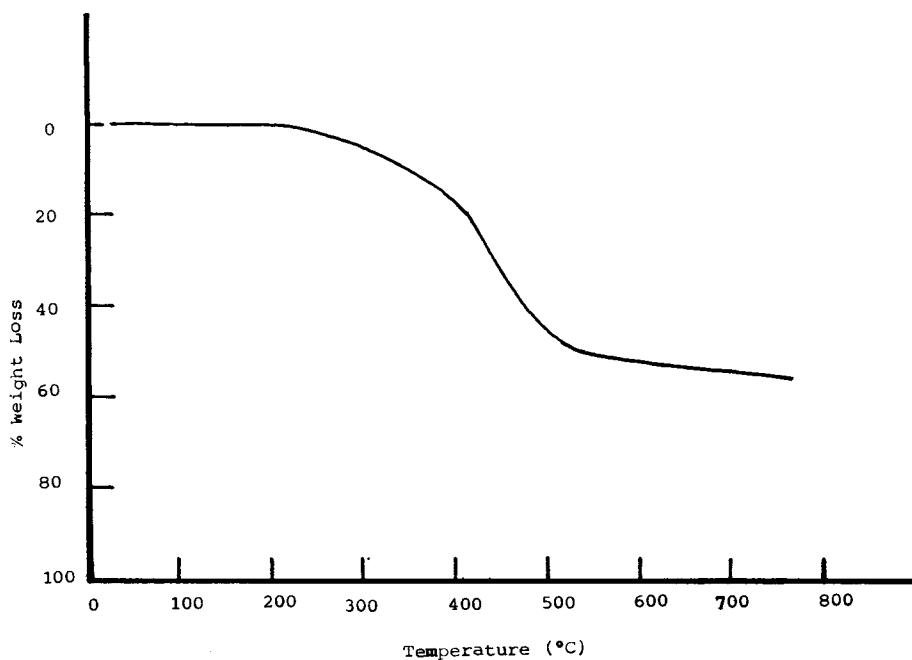


Fig. 11. TGA curve for PPM polymer deposition at 4.2 cc/min, 80 W, in flowing argon.

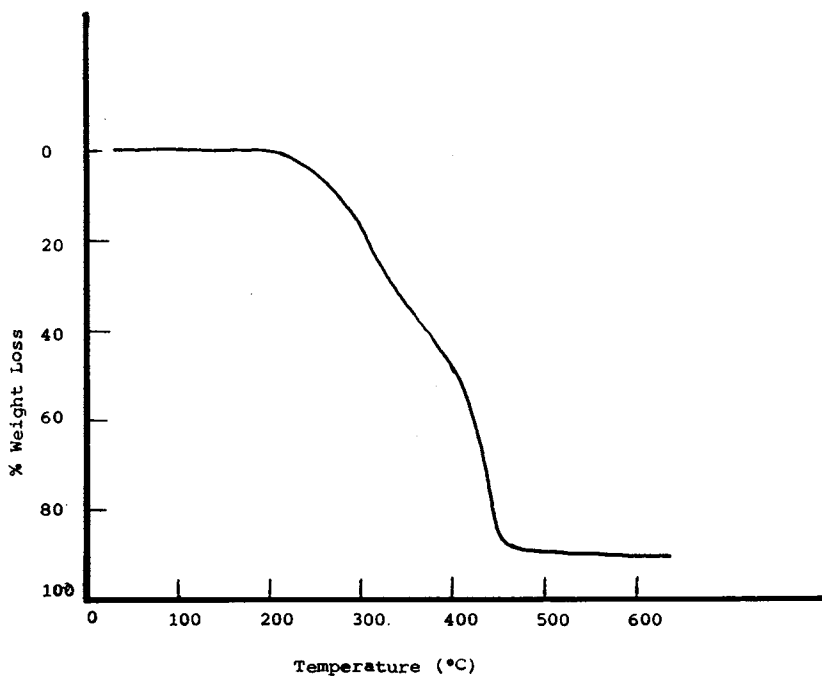


Fig. 12. TGA curve for PPM polymer deposition at 4.2 cc/min, 80 W, in flowing air.

synthesized at low monomer feed rate (high  $W/FM$  value), no weight loss was observed in argon atmosphere even up to a temperature of 800°C, and no characteristic peak was observed in DTA. In air atmosphere this polymer lost 79% weight at 800°C and also gave two exothermic peaks at 320 and 492°C, respectively, in DTA. Analysis of the white residue left at 800°C by X-ray fluorescence spectroscopy confirmed the presence of Al in the polymer. The PPM polymer obtained at a higher monomer feed rate (low  $W/FM$ ), on the other hand, showed weight loss even in argon atmosphere but like the polymer from low monomer feed rate did not give any characteristic DTA peak. In air this latter polymer lost 90% of its weight at 600°C and gave two exothermic peaks at 320 and 440°C, respectively, in DTA. Although interpretation of thermal analysis results of PPM polymer is beyond the scope of this paper, the above study confirmed that the PPM polymer synthesized at high  $W/FM$  value is more crosslinked than the polymer synthesized at low  $W/FM$  value and does not decompose up to a temperature of 800°C in an inert atmosphere.

### CONCLUSION

Thus methane can be polymerized by plasma (or glow discharge process) to yield very versatile polymers that find applications in surface modification, adhesive bonding, and substrate surface protection. The kinetics of methane polymer deposition revealed many interesting facts regarding the plasma polymerization process. The results indicate that functional properties of the methane polymer can be varied by simple variation of plasma polymerization parameters.

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