mol and $A = 4.0 \times 10^6$ l./(mol sec) at 100° in the reaction of pyridine with MeI in nitrobenzene.[9] Those values in the MeI-initiated polymerization are very close to those of the Menschutkin reaction.

Similar results have already been observed in the polymerization of OZO by MeOTs and MeI initiators.[4] The propagating species of the OZO polymerization was an oxazolinium ion by MeOTs initiator and a covalent-bonded alkyl iodide by MeI initiator.[4] It should be added here, however, that in the present study propagating species of covalent-bonded alkyl iodide was directly observed by nmr spectroscopy for the first time in the MeI-initiated polymerization of PhOZI.

**Phenyl Substituent Effects.** It should be worth while to compare the reactivities and activation parameters between PhOZI and OZI with respect to the effect of 2-phenyl group of OZI monomer (Table III). First, the nucleophilic reactivity of PhOZI is about 16 times decreased by the phenyl group being reflected by $k_i$ value with MeOTs initiator at 35°. Second, the polymerization reactivity ($k_p$) of PhOZI is 44 times less than that of OZI in the MeOTs-initiated system in which both PhOZI and OZI proceeded *via* oxazinium tosylate propagating species. Third, the introduction of phenyl group altered polymerization mechanism in the MeI-initiated polymerization at temperatures higher than 100°. Since $k_p$ was almost the same in nitrobenzene and acetonitrile solvents for the OZI polymerization involving oxazinium propagating species,[1] a $k_p$ value of OZI, $2.5 \times 10^{-2}$ l./(mol sec) at 100° in acetonitrile, was roughly taken to represent that in nitrobenzene. Then, the $k_p$ of PhOZI is about 180 times smaller than that of OZI with MeI initiator in nitrobenzene. Finally, it should be mentioned here that OZI was 43 times less reactive than OZO in $CD_3CN$ by MeOTs initiator.[1] Consequently, PhOZI must be about $1.9 \times 10^3$ times less reactive than unsubstituted five-membered cyclic imino ether of OZO.

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# Plasma Polymerization of Saturated and Unsaturated Hydrocarbons

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ABSTRACT: A series of nine saturated and unsaturated hydrocarbons were polymerized by subjecting them to a radiofrequency glow discharge at reduced pressures. It was found that acetylene polymerizes most rapidly, followed by ethylene and butadiene, then by propylene, *cis*-2-butene and isobutylene. The saturated alkanes: methane, ethane, and propane polymerize most slowly. As shown by previous work, the form of the polymer depends upon the rate of polymer deposition. Thus very high deposition rates produce only a powder, intermediate rates produce either a powder or a film, and low rates produce only a film. It was found from carbon–hydrogen analysis that polymers prepared from the alkanes exhibited a greater loss of hydrogen than did those from olefinic monomers. The polymer prepared from acetylene exhibited the least loss of hydrogen. Infrared spectra of the polymers made of ethane, ethylene, and acetylene showed that with increasing monomer unsaturation the polymer contained more double bonds, fewer methylene groups, and a greater tendency to be oxidized after preparation. An examination of the mechanism of ethylene polymerization led to the conclusion that a significant amount of oligomerization occurs in the gas phase. In addition it is hypothesized that an important initial step is the partial conversion of ethylene to acetylene. This hypothesis can also be extended to the other monomers to explain their relative rates of polymer deposition.

There has recently been an increasing interest in the use of low pressure electric discharges for the polymerization of organic and organometallic compounds.[1-5] The formation of a polymer by this means is a complex process which is initiated by collisions between energetic free electrons, present in the plasma formed by the discharge, and molecules of the monomer. The products of these collisions are ions, excited molecules, and free radicals.[6] Once formed these species can react with themselves as well as with additional ground-state molecules to produce polymers both in the gas phase as well as on solid surfaces placed in the plasma. Because of its complexity, the mechanism of plasma polymerization is not well understood. In our previous publications[7,8] dealing with the plasma polymerization of ethylene, a mechanism was proposed to explain the dependence of polymer deposition rate and the type of polymer formed on the reaction conditions. In the present work, the investigation is broadened to include a number of saturated and unsaturated hydrocarbon gases. On the basis of their relative rates of polymer deposition and the characteristics of the corresponding polymers, additional information has been obtained relating to the plasma polymerization of hydrocarbons.

## Experimental Section

Monomer gases (CP grade) were purchased from Matheson Gas Products, and were used as received. The detailed experimental arrangement for plasma polymerization has been described previously.[7] The apparatus consists of an evacuable bell jar housing a parallel pair of disc electrodes. An International Plasma Corporation Model PM 401 radiofrequency generator was used to sustain the discharge. The generator operates at 13.56 MHz and has a maximum power output of 150 W. The lower electrode was water cooled. The rate of polymer deposition was determined by

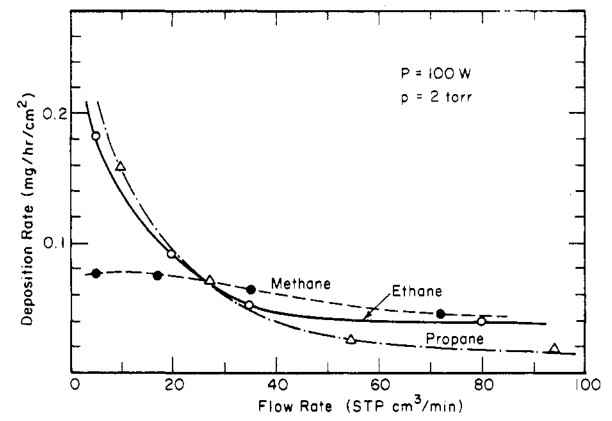

**Figure 1.** Rates of polymer deposition of alkanes as a function of monomer flow rate (pressure 2 Torr; power 100 W).

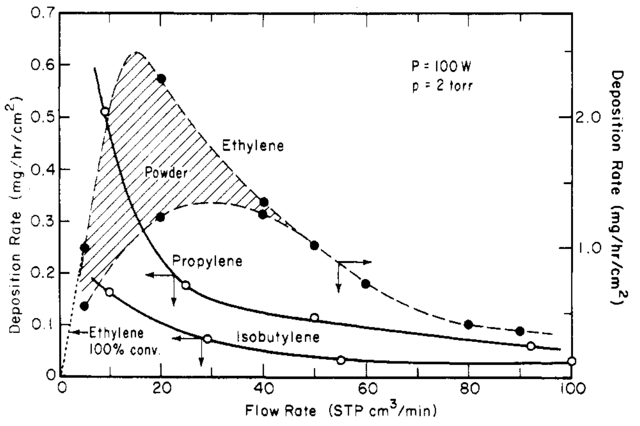

**Figure 2.** Rates of polymer deposition of olefins as a function of monomer flow rate (pressure 2 Torr; power 100 W).

weighing the amount of polymer accumulated on a piece of aluminum foil covering the lower electrode. This quantity is sometimes referred to as the rate of plasma polymerization. Strictly speaking it does not have the same quantitative significance as the rate of polymerization defined in conventional polymerization reactions. However, the deposition rate over the same given area of the electrode can be assumed to bear a direct proportion to the "true" polymerization rate, and thus serves as a meaningful basis for comparison among the several reactions under investigation.

## Results and Discussion

**Rates of Polymer Deposition.** The rates of polymer deposition in a glow discharge at a pressure of 2 Torr and a power of 100 W are compared in Figure 1 for three saturated hydrocarbons. It is seen that at high monomer flow rates the deposition rates are fairly constant with increasing flow rate. Here propane has the lowest deposition rate, ethane has a higher rate, and methane still higher. Note that the rates of deposition are expressed in terms of mg/(hr cm²). If these were expressed on a molar basis, the order of methane > ethane > propane would have been more clearly delineated. This hierarchy is, however, reversed at low flow rates. Of particular interest is the behavior of methane, which has a very gradual increase in deposition rate with decreasing flow rate. In contrast, deposition rates increase dramatically for ethane and propane. This difference is probably a consequence of the unique mechanism of methane polymerization, as shall be discussed later.

The deposition rates of three olefinic hydrocarbons are compared in Figure 2. Here isobutylene polymerizes most slowly, while propylene polymerizes faster throughout the entire range of flow rates. Ethylene, on the other hand, has a deposition rate that is an order of magnitude greater than either isobutylene or propylene (note the enhanced ordinate scale for ethylene in Figure 2). These data appear to indicate that in a given homologous series of hydrocarbons, higher deposition rates are favored by lower molecular weights.

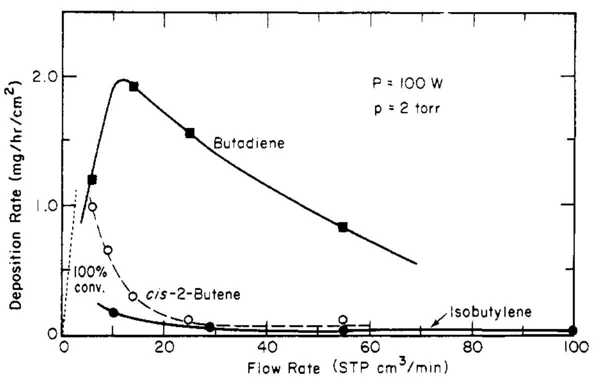

**Figure 3.** Rates of polymer deposition of butadiene, *cis*-2-isobutene, and isobutylene as a function of monomer flow rate (pressure 2 Torr; power 100 W).

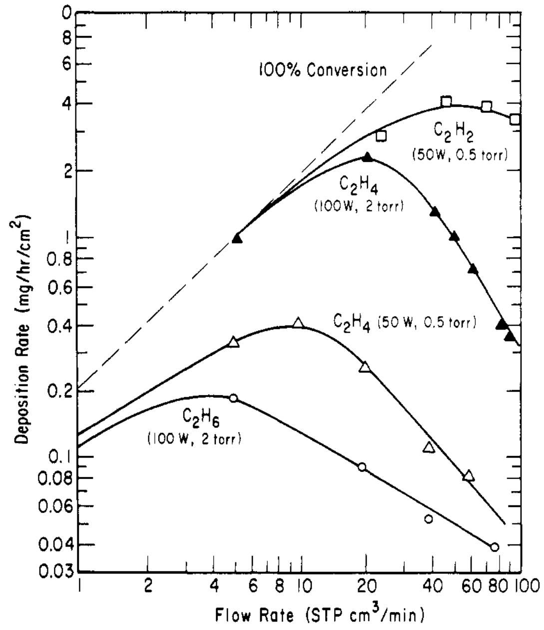

**Figure 4.** Double logarithmic plot of rates of polymer deposition of acetylene and ethylene as a function of monomer flow rate.

Comparison of Figures 1 and 2 shows that for molecules with the same number of carbon atoms, the presence of unsaturation leads to a higher polymer deposition rate. In addition, Figure 3 shows that for three monomers containing four carbon atoms, butadiene with two double bonds polymerizes substantially faster than either *cis*-2-butene or isobutylene each of which contains one double bond. To investigate the role of unsaturation one step further, acetylene was polymerized under the same conditions of 2 Torr and 100 W. In this case, the rate was so high that polymer was formed instantaneously not only on the electrodes, but also throughout the reactor. In order to more reliably determine the deposition rate, the pressure was reduced to 0.5 Torr and the power to 50 W. Figure 4 shows that under these conditions acetylene, which contains a triple bond, polymerizes faster than ethylene, which contains a double bond, by more than an order of magnitude. Figure 4 also shows that for identical conditions ethylene polymerizes faster than ethane by an order of magnitude.

Another interesting feature emerging from the comparison of polymerization behavior of ethane, ethylene, and

**Table I**
**Carbon–Hydrogen Ratios of Plasma Polymerized Hydrocarbons**

| Compound | H/C Ratio Polymer | H/C Ratio Monomer | H/C (Polymer) / H/C (Monomer) |
|---|---|---|---|
| Acetylene | 0.95 | 1.00 | 0.95 |
| Ethylene | 1.49 | 2.00 | 0.75 |
| Propylene | 1.40 | 2.00 | 0.70 |
| Isobutylene | 1.44 | 2.00 | 0.72 |
| *cis*-2-Butene | 1.34 | 2.00 | 0.67 |
| Butadiene | 1.33 | 1.50 | 0.88 |
| Methane | 2.40 | 4.00 | 0.60 |
| Ethane | 1.55 | 3.00 | 0.52 |
| Propane | 1.58 | 2.67 | 0.59 |

acetylene is the existence of maxima in deposition rates of the latter two monomers (Figure 4). In our previous publication,[8,9] we have explained this behavior in terms of the competition between the rate of generation of reactive species and the rate of flow of the monomer feed gas. At very low flow rates, where the residence time of the monomer in the plasma is sufficiently high to establish a steady-state concentration of reactive species, polymerization consumes all of the monomer. As the flow rate is increased, the polymer deposition rate will first increase due to the greater supply of monomer. However, as the flow rate continues to increase, a point is reached where the reactive species are removed so rapidly that the effective residence time for these species is reduced, and the deposition rate decreases. This mechanism should also hold for ethane and a maximum must also exist in its deposition rate *vs.* flow rate curve. The absence of this maximum in Figure 4 is most likely due to the low flow rate at which it occurs. Such a low flow rate could not be obtained with the existing equipment. Finally, it should be noted that the position of the maximum deposition rate for any monomer can be correlated with its relative ease of polymerization. Maxima for the more easily polymerized monomers are located at higher flow rates.

**Polymer Characterization.** The carbon and hydrogen content of each polymer was determined by Pregl's method[10] and the results are summarized in Table I. All samples were made under the condition of 2-Torr pressure, 5-$cm^3$/min (STP) flow rate, and 100-W power. The second column of Table I shows the experimentally determined values of the number of hydrogen atoms per carbon atom in the polymers. For the sake of comparison, H/C ratios for the original monomers are given in the third column. The fourth column lists values of the H/C ratio for each polymer divided by that of the monomer.

The general conclusion one can immediately draw from Table I is that each of the polymers is hydrogen deficient by comparison with its respective monomers. Acetylene, however, has almost the same number of hydrogens per carbon atom as the monomer, and can be considered unique among all the hydrocarbons investigated here. The second group of polymers that are approximately 10–30% hydrogen deficient are produced from double bond containing monomers, with butadiene leading the list. Finally, polymers derived from alkanes are found to be the most hydrogen deficient, with only about half as many hydrogen atoms per carbon atom in the polymer as in the monomer.

The observed hydrogen deficiency suggests that the polymers are very highly cross-linked three-dimensional networks containing significant amounts of unsaturation. Further confirmation of these characteristics was obtained from measurements of solvent swelling and infrared spectra.

It is well known that linear amorphous polymers will dissolve in appropriate solvents but that cross-linked polymers only exhibit swelling. The degree of swelling decreases with increasing degree of cross-linking, until at very high cross-link densities no swelling is detectable. Attempts to dissolve or swell the rigid polymer films and powders made during this study in boiling *m*-xylene, a common solvent for parafins, were unsuccessful. Oily films, however, were soluble because of their very low molecular weight.[8]

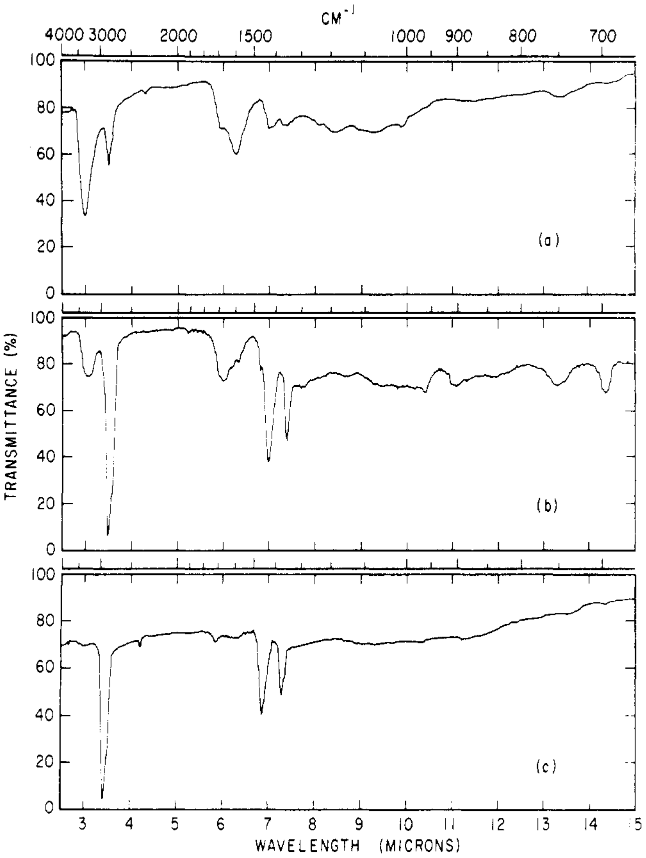

**Figure 5.** Infrared spectra of plasma polymerized hydrocarbons: (a) acetylene, (b) ethylene, and (c) ethane.

Infrared spectra of the polymers produced from acetylene, ethylene, and ethane are shown in Figure 5. The absence of the $CH_2$ rocking band at 730 $cm^{-1}$ normally observed in crystalline parafins indicates that these polymers are amorphous. We have also noted previously that plasma-polymerized ethylene shows no evidence of crystallinity by X-ray diffraction.

The spectrum shown in Figure 5a exhibits a strong peak at 1600 $cm^{-1}$, which is due to vibrations of the C=C bond. This peak is weaker in Figure 5b, and is almost undetectable in Figure 5c. On the other hand, the peak intensities at 2960 $cm^{-1}$ ($CH_2$ stretching), 1463 $cm^{-1}$ ($CH_2$ bending), and 1369 $cm^{-1}$ ($CH_2$ wagging) are very strong in Figures 5b and 5c, but much weaker in Figure 5a. These observations suggest that the plasma-polymerized acetylene contains mainly double bonds in the chain, ethane contains mainly single bonds with a structure not unlike a highly cross-linked polymethylene, while the plasma-polymerized ethylene has an intermediate structure.

Another interesting feature one notes in these spectra is that the peak at 3400 $cm^{-1}$ for OH stretching is very strong for plasma-polymerized acetylene. But the same peak is much weaker for plasma-polymerized ethylene and nearly undetectable for plasma-polymerized ethane. The C=O stretching frequency at 1700 $cm^{-1}$ also follows this

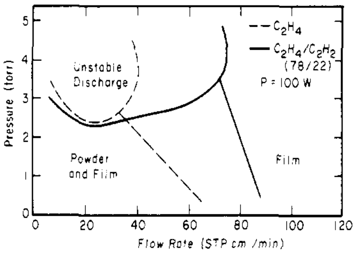

**Figure 6.** Characteristic map for the plasma polymerization of ethylene (broken line), and ethylene mixed with 22 vol % acetylene (full lines) (power 100 W).

trend. The presence of these functional groups is most likely due to a partial oxidation of the polymer surface after its preparation. The reactions with atmospheric oxygen are more extensive for acetylene and ethylene polymers probably because their double bonds are more susceptible than the single bonds in the ethane polymer.

**Powder and Film Formation.** We have already shown in previous publications[7-9] that the form of the polymers produced by the plasma polymerization of ethylene depends strongly on the reaction conditions. Figure 6 illustrates a "characteristic map" for the plasma polymerization of this monomer. It is shown here that the polymer may be a powder at low pressure and low flow rate, a colorless rigid film at low pressure and high flow rate, and an oily film at high pressure and high flow rate. The discharge becomes unstable in the region of high pressure and low flow rate. Also shown in Figure 6 is the characteristic map for the plasma polymerization of ethylene mixed with 22% of acetylene. As we shall see presently, the effect of introducing acetylene is to increase polymer deposition rate. For the more rapidly polymerizing systems, both the regions of powder formation and unstable discharge are enlarged while the film formation region is reduced. The trend appears to hold for all of the hydrocarbon monomers investigated in this work. Thus pure acetylene, which polymerizes extremely vigorously, forms only a powder over the region of pressure and flow rate for which polymerization is possible (Figure 7). Butadiene, which polymerizes at a rate comparable to ethylene, forms a powder at low flow rates and a film at high flow rates, as does ethylene. Propylene, isobutylene, and *cis*-2-butene polymerize more slowly. These monomers form rigid films at high flow rates but oily films at low flow rates. The alkanes which polymerize slowly under all conditions form only rigid films.

The characteristic map for acetylene in Figure 7 requires further comment. The only conditions under which polymers are produced are those located in the shaded region. At low flow rates the deposition rate is so high that all of the monomer is converted instantaneously and therefore it becomes impossible to maintain the monomer pressure. The broken line indicates the lowest pressures achievable by the pump when unreacted monomer gas is fed at various flow rates. This limit is extended when the discharge is on, since the rapid polymerization reaction acts as an additional pump. At higher pressures, the discharge is unstable. Under these conditions the glow covers only a portion of the electrodes and moves from one position to another in an irregular manner. It is believed that the presence of powder particles in the gas phase is closely connected to the onset of the unstable operation. This connection is based on the observation that a large quantity of particles in the gas can act as an electron sink making it harder to sustain the discharge.[11] Correspondingly, acetylene, which forms powder exclusively, is characterized by a large unstable region. This unstable region is much smaller for ethylene (Figure 6), whose deposition rate of polymer is slower than that of acetylene by an order of magnitude. Finally, the alkanes which polymerize very slowly and do not produce a powder product show no evidence of unstable operation.

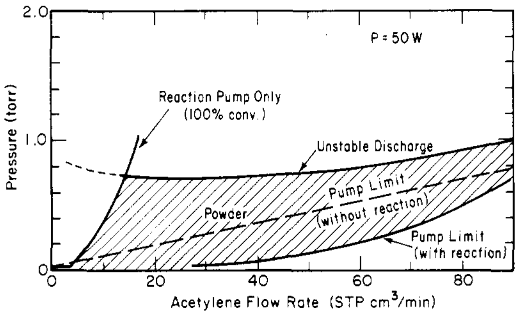

**Figure 7.** Characteristic map for the plasma polymerization of acetylene (power 50 W).

**Polymerization Mechanism.** Since the process of plasma polymerization is quite complex it is not possible to put forth a complete mechanism for any of the monomers under study. Nevertheless some clues as to the key elements in the mechanism can be deduced. To begin with we note that while both ionic and free-radical mechanisms have been proposed to explain plasma polymerization, we believe that only the latter need be considered. The basis for this contention is that the energy required to form free radicals (3-4 eV)[12] is considerably less than that required to form ions (9-13 eV). Since the average electron energy in low pressure discharges is typically 2-5 eV,[13] one anticipates a substantially higher concentration of radicals than ions. Although no experimental figures are available for organic systems it has been shown in inorganic systems that free radicals are present to the extent of $10^{-2}$ to $10^{-1}$ of the neutral species whereas ions are present to the extent of $10^{-6}$ to $10^{-5}$ of the neutrals.[14]

An additional argument against an ionic mechanism is the observation that the ionization potentials for acetylene, ethylene, and ethane are 11.4, 10.5, and 11.65 eV, respectively.[15] If we were to assume an ionic mechanism, the rate limiting step for polymerization would have to be ionization due to the high energy involved in this step relative to all others. As a consequence ethylene would be expected to polymerize faster than acetylene, and acetylene and ethane would be expected to have comparable rates of polymerization. Since neither of these predictions is borne out experimentally we conclude that an ionic mechanism cannot be dominant.

It is well known that considerable amounts of stable radical sites remain on the surface of deposited polymer after its preparation. Denaro[16] showed by titration of plasma polymerized styrene with DPPH (1,1-diphenyl-2-picrylhydrazyl) that one in twenty polymer molecules is a radical. Morita, Mizutani and Ieda[17] found by esr that the spin density of plasma polymerized polyethylene is $\sim 3 \times 10^{19}$ spins/g, which corresponds approximately to one radical in 5-10 polymer molecules. Both estimations were made by taking the molecular weight as 2500.

It has been noted[18] in dc glow discharge that polymerization takes place exclusively on the cathode. However, it is well known that in dc discharges the chemical reactions take place mainly in the negative glow region near the cathode.[19] Thus this observation cannot be taken as evidence that ionic species formed in the plasma are attracted to the cathode and then polymerized there.

In a previous study[8] of the plasma polymerization of ethylene, we proposed that the following three steps were involved in the generation of the primary free radicals in

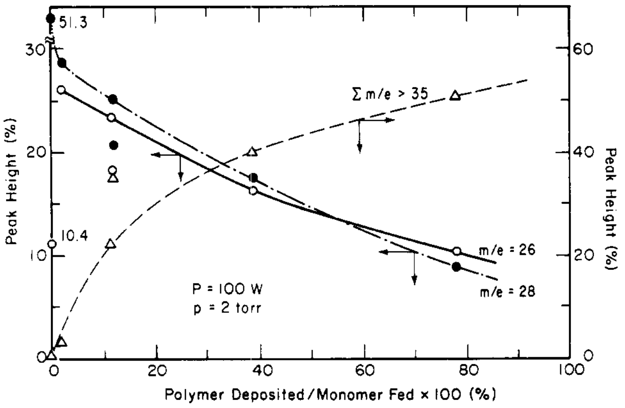

**Figure 8.** Mass spectroscopic data from the reactor effluent gas in the plasma polymerization of ethylene as a function of conversion. Mass number 26 refers to acetylenic species, 28 ethylenic species, and those above 35 polymeric species.

the gas phase.

$$e + C_2H_4 \rightleftarrows C_2H_2 + 2H\cdot \text{ (or } H_2) + e \tag{1}$$

$$H\cdot + C_2H_4 + X \longrightarrow C_2H_5\cdot + X \tag{2}$$

$$H\cdot + C_2H_2 + X \longrightarrow C_2H_3\cdot + X \tag{3}$$

Additional free radicals were assumed to be formed on the surface of the growing polymer film by the impingement of energetic electrons and ions and the adsorption of ultraviolet radiation produced by the discharge. This step is represented by the reaction

$$S - X \longrightarrow S - R_n\cdot + H\cdot \tag{4}$$

where S is a surface site, X is a monomer or a polymer segment, and $R_n\cdot$ is a radical of $n$ units. Both the surface and gas phase free radicals are then assumed to react farther with either ethylene or acetylene *via* reactions 5a and 5b.

$$R_n\cdot + \begin{Bmatrix} C_2H_4 \\ C_2H_2 \end{Bmatrix} \longrightarrow R_{n+1}\cdot \tag{5a}$$

$$S - R_n\cdot + \begin{Bmatrix} C_2H_4 \\ C_2H_2 \end{Bmatrix} \longrightarrow S - R_{n+1}\cdot \tag{5b}$$

These two reactions are postulated to be the major contributors to the growth of the polymer. The postulate can be justified by the observation that unsaturated monomers are polymerized at substantially higher rates than the saturated ones.

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

$$R_n\cdot + R_m\cdot \longrightarrow X_{n+m} \tag{6a}$$

$$S - R_n\cdot + R_m\cdot \longrightarrow S - X_{n+m} \tag{6b}$$

$$S - R_n\cdot + S - R_m\cdot \longrightarrow S - X_{n+m} + S \tag{6c}$$

these steps do not lead to the cessation of polymerization in the conventional sense. The reason for this is that new radicals can be produced by processes similar to steps 1–4, *i.e.*

$$e + X \longrightarrow R_n\cdot + H\cdot + e \tag{7}$$

$$e + X \longrightarrow R_n\cdot + R_m\cdot + e \tag{8}$$

$$H\cdot + X \longrightarrow R_n\cdot + H_2 \tag{9}$$

$$S - X \longrightarrow S - R_n\cdot + H\cdot \tag{10}$$

Consequently reactions 6a–c can in fact contribute to some extent to the propagation of polymerization, depending on the free radical concentration and the frequency of these reactivation reactions (7–10). All of these reactions (6–10) are responsible for the highly branched and highly cross-linked structure of plasma-polymerized hydrocarbons.

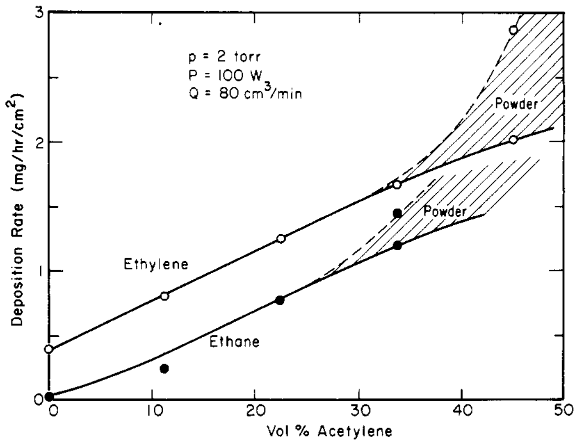

**Figure 9.** Rates of polymer deposition of ethane and ethylene as a function of acetylene addition (power 100 W, monomer flow rate 90 cm³/min, and pressure 2 Torr).

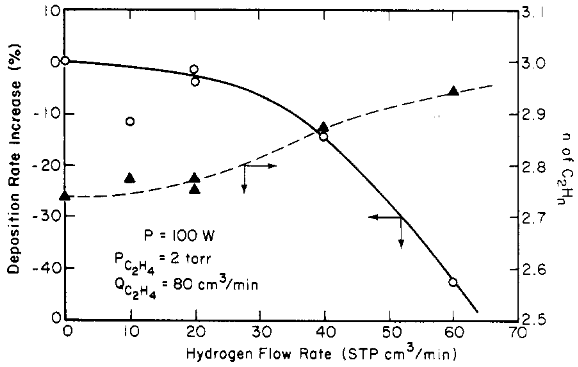

**Figure 10.** Changes in rates of polymer deposition of ethylene and the chemical composition of plasma-polymerized ethylene as a function of hydrogen addition (power 100 W, monomer flow rate 80 cm³/min STP, and monomer partial pressure 2 Torr).

Based upon the steps presented above the rate of monomer consumption is the sum of

$$r_m \text{ (homogeneous)} = \sum_i k_{p,i}[M_i][R\cdot] \tag{11a}$$

$$r_m \text{ (heterogeneous)} = \sum_i k_{p,i}'[M_i][S - R\cdot] \tag{11b}$$

in the conventional manner. In eq 11 $[M_i]$ represents the concentration of active monomer $i$ (*viz.*, ethylene or acetylene in the case of ethylene polymerization). Obviously the rate of monomer consumption bears a direct relation to the rate of polymer deposition. Equation 11 thus illustrates that the concentration of both monomer and free radicals is important in dictating the deposition rate.

As a part of the present investigation a series of experiments were performed aimed at substantiating some of the elements of the mechanism outlined above. The primary emphasis of these experiments was to define the role of acetylene during the plasma polymerization of ethylene and the extent to which gas phase polymerization might occur.

To investigate the degree to which gas phase polymerization of ethylene does occur, the composition of the effluent gas from the reactor was analyzed by a mass spectrometer. For this work an evacuated ampoule was attached to the line between the reactor and the vacuum pump. Fifteen minutes after the discharge was turned on

### Table II

A. Mass Spectra of Effluent Gas

| $m/e$ | $C_2H_2$ monomer | $C_2H_2$ 0.5 Torr 40 cm$^3$/min 50 W | $C_2H_4$ Monomer | $C_2H_4$ 2.0 Torr 40 cm$^3$/min 100 W | $C_2H_6$ Monomer | $C_2H_6$ 2.0 Torr 40 cm$^3$/min 100 W | $C_4H_6$ Monomer | $C_4H_6$ 2.0 Torr 40 cm$^3$/min 100 W |
|---|---|---|---|---|---|---|---|---|
| 22 | | | | | | | | |
| 23 | | | | | | | | |
| 24 | 4.0 | 3.2 | 0.6 | 0.9 | 0.3 | 0.3 | 0.1 | 0.3 |
| 25 | 13.8 | 11.0 | 2.0 | 3.9 | 1.5 | 1.4 | 0.9 | 0.9 |
| 26 | 65.5 | 59.8 | 10.4 | 18.1 | 9.3 | 9.1 | 4.9 | 6.6 |
| 27 | 1.5 | 1.6 | 11.3 | 12.4 | 13.3 | 12.4 | 11.0 | 7.9 |
| 28 | 0.2 | 0.5 | 51.3 | 21.5 | 44.8 | 41.7 | 9.6 | 4.8 |
| 29 | 0.2 | 0.2 | 0.9 | 3.8 | 11.4 | 12.4 | 0.2 | 1.5 |
| 30 | 0.1 | 0.1 | 0.6 | 0.6 | 15.9 | 14.9 | | 0.4 |
| 31 | 0.1 | | | 0.1 | 0.4 | 0.4 | | 0.1 |
| 32 | | | | | | | | |
| 33 | | | | | | | | 0.1 |
| 34 | | | | 0.1 | | | | |
| 35 | | | | | | | | |
| 36–47 | 1.4 | 2.9 | | 17.6 | 1.1 | 4.6 | 24.7 | 23.7 |
| | | | | | | | 46.8 | 42.5 |
| 48–59 | 1.2 | 10.5 | | 9.1 | | 0.7 | 18.6[a] | 13.6[a] |
| >60 | | 3.2 | | 8.4 | | 0.4 | | 10.5 |

B. Comparison of $C_2H_2$ Mass Spectra Intensities and Polymer Deposition Rates

| | $C_2H_2$ | $C_2H_4$ | $C_2H_6$ | $C_4H_6$ |
|---|---|---|---|---|
| $C_2H_2$ content[b] (%) | 59.8 | 13.7 | 0.4 | 3.1 |
| Deposition rate (mg/cm$^2$ per hr) | 3.95 | 1.29 | 0.053 | 1.14 |
| Polymer deposited/monomer fed × 100 | 51 | 15 | 0.6 | 7.2 |

[a] $m/e = 54$. [b] Defined as $I_{C_2H_2}$ for $C_2H_2$ and $I_{C_2H_2} - I_{mon}(I_{C_2H_2}{}^0/I_{mon}{}^0)$ for all other monomers, where $I$ designates the intensity of the mass spectral peak in the effluent gas and $I^0$ the peak intensity for the monomer.

the ampoule was filled with the effluent gas and sealed. The contents of the ampoule were subsequently analyzed on a CEC-110B high-resolution mass spectrometer.

Figure 8 illustrates the mass spectroscopy results as a function of the fraction of the ethylene monomer converted to deposited polymer, where the peak heights are expressed as a percentage of the sum over all peaks whose mass number is greater than 10. Three curves are shown, one for ethylene (mass number 28), a second for acetylene (mass number 26), and a third representing all species whose mass to charge ratio is greater than 35. We note at once that acetylene is present even at low degrees of conversion and to an extent which is greater than that observed in the cracking pattern of ethylene alone. As the extent of conversion increases the concentrations of ethylene and acetylene both fall while bearing a nearly constant ratio to each other. By contrast, the concentrations of higher molecular weight species increase with increasing monomer conversion. The implication of these results is that part of the ethylene is rapidly converted to acetylene and that both ethylene and acetylene can lead to the appearance of higher molecular weight species in the gas phase.

In as much as it had been observed that acetylene polymerizes much more rapidly than ethylene under identical conditions (see Figure 4), it was of interest to determine whether the principal source of polymer obtained during the polymerization of ethylene might not be the acetylene derived *via* reaction 1. To examine this point further the rate of polymer deposition was measured for premixed mixtures of ethylene and acetylene. During these experiments the total flow rate was maintained constant thereby producing a constant residence time for both ethylene and acetylene. As may be seen from Figure 9, initially the rate of deposition increases linearly with increasing content of acetylene in the monomer mixture and the only product formed is a film. Above 30 vol % of acetylene, the rate rises more rapidly and powder is formed in addition to the film. A similar pattern is observed if ethane is substituted for ethylene. A significant observation is that the slopes of the linear portions of the curves in Figure 9 are nearly identical for ethane and ethylene, about 0.3–0.4 mg/(cm$^2$ hr) per 10 vol % of acetylene. This corresponds to about a 20% conversion of the acetylene in the monomer mixture. Based upon this evidence we may hypothesize that the added acetylene polymerizes independently of the comonomer (*i.e.*, ethylene or ethane) and that when ethylene alone is used as the monomer its deposition rate is governed by the amount of acetylene formed *via* processes such as reaction 1.

Additional substantiation of the proposed reaction scheme was obtained by the addition of hydrogen to a constant supply of ethylene maintained at a partial pressure of 2 Torr. The effects of hydrogen on both the deposition rate and the hydrogen content of the polymer are shown in Figure 10. That the deposition rate decreases with increasing hydrogen flow rate leads us to the hypothesis that the added hydrogen causes the acetylene formed by reaction 1 to be reconverted to ethylene. A partial conversion of ethylene to ethane is also expected. The net decrease in the level of unsaturation of the gas phase brought about by these changes would explain the decrease in deposition rate and the increased hydrogen content of the polymer.

The insights into the mechanism of ethylene polymerization developed above also provide an understanding for the relative rates of polymer deposition of the other monomers. As was noted in the discussion of Figures 1–4 the rate of deposition can clearly be correlated with the degree of unsaturation present in the monomer molecule. If one again assumes that in order to obtain polymerization it is favorable to first convert a part of the monomer into acetylene, then the greater the unsaturation of the monomer, the easier it will be to obtain acetylene from it.

**Table III**
**Mechanisms for the Formation of Acetylene**

| Monomer | Mechanism | Ref |
|---|---|---|
| Ethylene | $e + C_2H_4 \rightarrow C_2H_2 + 2H\cdot$ or $H_2 + e$ | 20, 21 |
| Butadiene | $e + C_4H_6 \rightarrow 2C_2H_3\cdot + e$ | 22 |
| | $C_2H_3\cdot \rightarrow C_2H_2 + H\cdot$ | |
| | or | |
| | $e + C_4H_6 \rightarrow C_2H_2 + C_2H_4{}^* + e$ | |
| | $C_2H_4{}^* \rightarrow C_2H_2 + 2H\cdot$ or $H_2$ | |
| *cis*-2-Butene | $e + CH_3CHCHCH_3 \rightarrow C_2H_2 + C_2H_6 + e$ | |
| Propylene | $e + C_3H_6 \rightarrow C_2H_3\cdot + CH_3\cdot + e$ | 21, 23 |
| | $C_2H_3\cdot \rightarrow C_2H_2 + H\cdot$ | |
| Isobutylene | $e + (CH_3)_2CCH_2 \rightarrow CH_3\dot{C}CH_2 + CH_3\cdot + e$ | |
| | $CH_3\dot{C}CH_2 \rightarrow CH_3CH\dot{C}H$ | |
| | $e + CH_3CH\dot{C}H \rightarrow C_2H_2 + CH_3\cdot + e$ | |
| Methane | $e + CH_4 \rightarrow CH_2{:} + H_2 + e$ | 24–26 |
| | $CH_2{:} + CH_4 \rightarrow C_2H_6{}^*$ | |
| | $C_2H_6{}^* \rightarrow CH_3CH_2\cdot + H\cdot$ | |
| | $CH_3CH_2\cdot + H\cdot \rightarrow C_2H_4{}^* + H_2$ | |
| | $C_2H_4{}^* \rightarrow C_2H_2 + H_2$ | |
| Ethane | $e + C_2H_6 \rightarrow C_2H_4 + H_2 + e$ | 27, 28 |
| | $e + C_2H_4 \rightarrow C_2H_2 + H_2 + e$ | |
| Propane | $e + C_3H_8 \rightarrow C_2H_4 + CH_4 + e$ | 27, 29 |
| | $e + C_2H_4 \rightarrow C_2H_2 + H_2 + e$ | |

Table II compares the mass spectra of the monomer and the gaseous effluent for discharges sustained in acetylene, ethylene, ethane, and butadiene. Two points can be made based upon this table. The first is that the spectrum of the effluent gas in every case shows the presence of substantial amounts of species with values of $m/e$ between 35 and 100 which are negligible in the spectrum of the monomer. This is further evidence in support of the assumption that a certain extent of the polymerization occurs in the gas phase. The second point is that the intensity of the acetylene peak in the mass spectrum of the effluent gas, corrected for cracking of the monomer in the mass spectrometer, correlates qualitatively with the observed polymer deposition rates. This observation supports the original proposition.

Going on the proposition that the initial decomposition of the monomer by electron impact to form free radicals and the eventual formation of acetylene are the key steps in defining the rates of plasma polymerization, we can attempt to establish the most probable paths for these two processes. Table III summarizes the relevant elementary steps for each monomer. Wherever possible the mechanism for the formation of acetylene has been based on that proposed for the photolysis of the monomer and references are given to the sources. From Table III it is seen that ethylene should form acetylene by direct electron collision. In the case of butadiene, *cis*-2-butene, and propylene the product of electron collision is a free radical which can rearrange to form acetylene. Isobutylene is also expected to form a free radical upon initial electron collision but the structure of this radical is such that acetylene cannot be formed from it directly. Instead a second electron collision is required. Ethane and propane are both capable of forming acetylene by a process requiring two electron collisions. The conversion of methane into acetylene is unique in that the product of the first step is a diradical. This diradical in turn reacts with a second molecule of methane to form an excited ethane molecule which decomposes to give a free radical. This last radical then rearranges to give acetylene. Here again it can be observed that the ease with which acetylene can be derived from the monomer correlates very closely with the relative rates of polymer deposition.

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