Formation of an Amorphous Powder During the Polymerization of Ethylene in a Radio-Frequency Discharge

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Synopsis

An investigation has been carried out to determine the influence of operating conditions on the character of the final product resulting from the polymerization of ethylene in a radio-frequency discharge.   It has been found that low pressures and high ratios of discharge power to gas flow rate lead to the deposition of a powder as well as a film.   From visual observations of powder deposition, it has been possible to divide the plane formed by the axis of pressure and flow rate into a region in which powder is deposited together with a film and a region in which only a film is deposited.   Numerous physical measurements have been carried out in order to characterize the powder.   From these measurements, it has been concluded that the powder is a relatively dense, amorphous, and highly crosslinked polymer composed of short-chain segments containing no more than two adjacent methylene groups.   Many forms of unsaturation have been observed which, together with the high crosslink density, explain the measured hydrogen-to-carbon ratio of 2.7 to 2.   Evidence of oxidation has been observed through the appearance of hydroxyl and carbonyl bands in the infrared spectrum of the polymer.   A mechanism for the formation of the powder has been proposed which suggests that the polymerization of the powder takes place totally in the gas phase.

INTRODUCTION

The formation of thin polymer films in a high-frequency glow discharge has been demonstrated for a wide variety of monomers and has been discussed in several recent reviews.[1–4]   Under certain circumstances it has been noted that a polymeric powder is formed in addition to the film.[5–7]   With the exception of the work of Neiswender,[6] very little attention has been given to defining the conditions which cause a powder to be formed or to characterizing the powder.   The present communication describes our observations on the deposition of an amorphous powder during the polymerization of ethylene in a radio-frequency discharge.

EXPERIMENTAL

The apparatus which was used is shown in Figure 1.   The discharge chamber consisted of a glass bell jar containing two parallel disc electrodes.
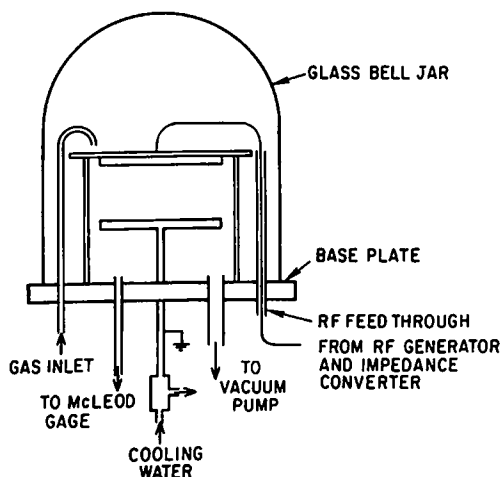
Fig. 1. Schematic of the apparatus.

The diameter of the copper electrodes was 6 in. and the distance between them was adjusted to 5 cm.   A piece of aluminum foil was placed over the lower electrode in order to collect the powder.   Power for the discharge was supplied by an IPC Model PM 401 generator operating at 13.56 MHz. The generator was connected to the upper electrode through an impedance matching network, while the lower electrode was grounded.

Gaseous ethylene was fed to the chamber through a regulator and a needle valve.   The flow rate of gas was measured with a rotameter and the gas pressure was determined by a McLeod gauge.   Using this equipment, it was possible to operate over the range of 0 to 70 cm^3/min at S.T.P. in flow rate and 10^{-2} to 10 torr in pressure.

RESULTS AND DISCUSSION

For a constant power of 100 watts, it was observed that the formation of a polymer powder was a strong function of the gas pressure and flow rate. By visually determining the presence or absence of a powder, it was possible to divide the plane defined by the pressure and flow rate axes into three regions.   These regions are identified in Figure 2.   Although solid curves have been shown between adjacent regions, it should be recognized that the transition from one region to the next is not sharply defined and that some overlap does exist.   From Figure 2, we see that the formation of a powder is favored by low pressures and low flow rates.   By contrast, high pressures and flow rates suppress the deposition of powder and lead to the formation of a film as the sole product.   At low flow rates and pressures above 2.5 torr, the discharge becomes unstable.   Under these circumstances, the glow covers only a portion of the electrode surface and moves about the electrode in an irregular manner.   In the presence of this unstable opera-
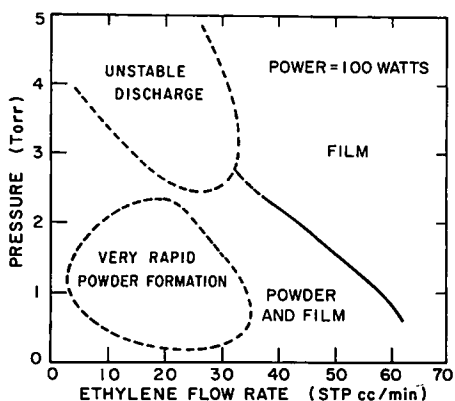
Fig. 2. Illustration of powder and film regions at 100 watts.

tion, the transition between powder and film formation becomes much less distinct, as indicated in Figure 2.

With a decrease in the power to 50 watts, the results shown in Figure 3 were obtained.   The major changes which occurred as a result of the reduction in power were a shift of the line defining the region of powder deposition to lower flow rates and an increase in the area of unstable operation. Similar trends with power were also observed at 25 and 150 watts.   By dividing the power by the gas flow rate, it may be shown that the critical parameter is the energy dissipated per mole of gas.   For a pressure of 2 torr, the appropriate points on the border of the powder deposition region for 50, 100, and 150 watts correspond to dosages of 2.68×10^6, 2.98×10^6, and 2.68×10^6 joule/mole, respectively.   The close agreement of these three values suggests that the borderline can be specified in terms of a critical dosage for each pressure.   Neiswender[6] has reached a similar conclusion for the plasma polymerization of benzene and styrene.

The formation of the polymer powder was accompanied by a number of interesting visual effects.   The first of these was the concentration of the
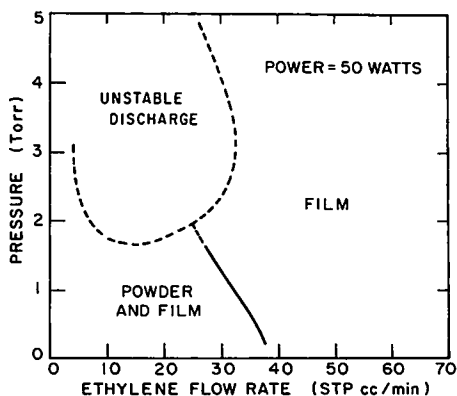

Fig. 3. Illustration of powder and film regions at 50 watts.

powder into thin disc-like zones suspended about $1/2$ cm from each of the electrodes. These zones usually did not cover the surface of the electrode and tended to occur most frequently over that portion of the electrodes closest to the outlet port. Observation of the powder particles through a small telescope showed them to be in very rapid circular motion within each zone. The intensity of the circulation increased with increasing power, and on a number of occasions it was possible to develop a small "tornado" extending down from the zone located above the lower electrode. Other swirling patterns were also observed near the edge of the electrodes. The concentration of the powder into vertical planes has also been noted by Denaro et al.[4] during the polymerization of styrene.

Examination of the powder showed that at low flow rates the particles are needle-like in shape. As the flow rate was increased, the powder became progressively finer. For conditions in the immediate vicinity of the borderline of the powder deposition region, it was noted that the films deposited were not transparent and suggested the incorporation of very fine powder particles. With a further increase in flow rate, a transparent film was formed, indicating that any powder now trapped in the film must be smaller than the wavelength of visible light. These observations are in close agreement with those of Thompson and Smolinsky[7] for polymers prepared from organosilicon monomers.

A sample of the powder prepared at 1.0 torr, 20 cc/min, and 100 watts was removed from the apparatus for further examination. The powder had a yellowish white color and under a microscope was seen to consist of individual particles of irregular shape having an average size of 1 to 2 μ. The density of the powder measured by flotation in a solution of m-xylene and carbon tetrachloride was 1.12 g/cm^3. This value is quite high when compared with 0.92 g/cm^3 for amorphous polyethylene and 1.00 g/cm^3 for crystalline polyethylene. Solubility measurements showed that the polymer particles were essentially insoluble in boiling xylene, which is a common solvent for conventional polyethylene. Chemical analysis gave an overall stoichiometry of $C_2H_{2.7}O_{0.2}$.

In order to examine the powder for any phase transitions, a sample was placed in a differential scanning calorimeter. The DSC results showed that a melting point could not be observed. Conventional polyethylene melts in the range of 120° to 140°C. The polymer was stable up to 330°C, where it began to change color, and vigorous decomposition did not occur until about 380°C.

Figures 4a to 4c show the infrared spectra for a commercial polyethylene film, a discharge deposited film, and a KBr mull containing the powder formed in the discharge. The major absorption bands are identified in Table I, together with their assignment to particular modes of vibration.

Examination of the spectra shown in Figures 4a to 4c reveals that the plasma polymerized polymers have a number of absorption bands in common with conventional polyethylene. These bands are the CH$_2$ stretching vibrations in the region of 3000 to 2850 cm^{-1}, a CH$_2$ bending vibration at
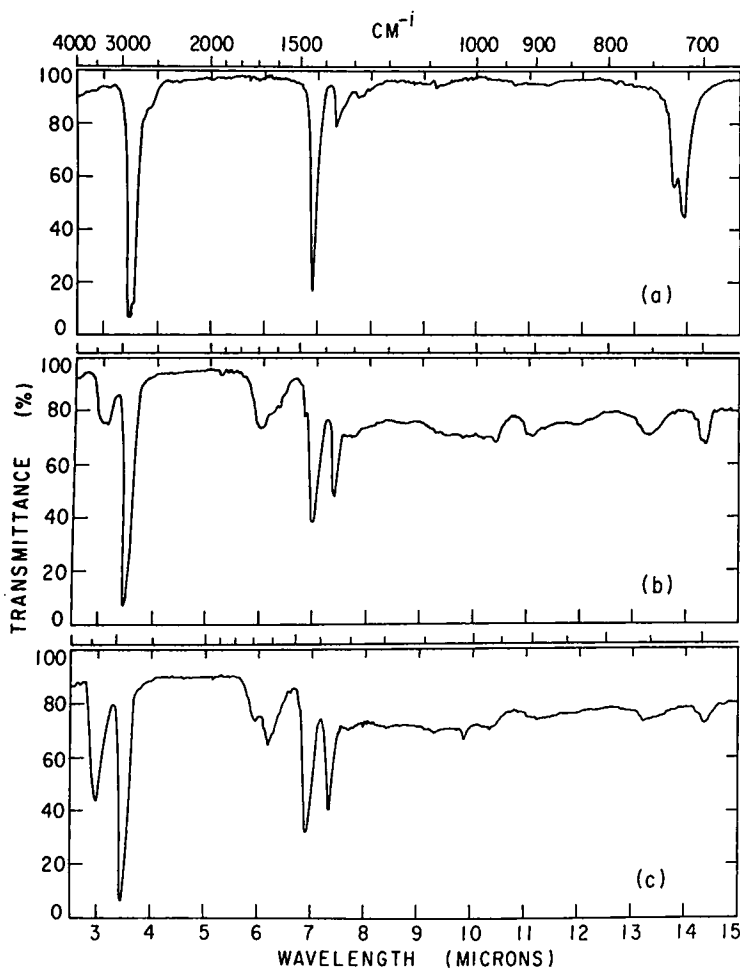
Fig. 4. Infrared spectra of (a) low-density polyethylene film, (b) plasma-polymerized film, (c) plasma-polymerized powder.

1463 cm^{-1}, and a CH$_2$ wagging vibration at 1369 cm^{-1}. The remaining features of the spectra, shown in Figures 4b and 4c, indicate notable differences from the spectrum in Figure 4a. One example is the absence of bands at 1353 and 1303 cm^{-1} characteristic of amorphous polyethylene and the absence of bands at 730 and 720 cm^{-1} characteristic of CH$_2$ rocking vibrations in a long chain of methylene groups. By contrast, Figures 4b and 4c show a strong band at 750 cm^{-1} related to the vibration of $+$CH$_2+_2$. The presence of various forms of unsaturation is a second feature which distinguishes the plasma polymerized materials from conventional polyethylene. The bands in Figures 4b and 4c indicative of unsaturation appear at 1600, 960, 890, and 700 cm^{-1}. Finally, the presence of bands at 3400, 1700, and 1680 cm^{-1} shows that the plasma polymerized polymers rapidly react with atmospheric oxygen to produce hydroxyl and carbonyl

TABLE I
Assignment of Infrared Absorption Bands

Low-density polyethylene film, cm⁻¹	Plasma-polymerized film, cm⁻¹	Plasma-polymerized powder, cm⁻¹	Assignment	Ref.
—	3400	3400	OH stretch	8
2924	3000	3000 ⎞		
2899	2960	2960 ⎟	CH₂ stretch	9
2857	2900	2900 ⎟		
2850	—	— ⎠		
—	1700	1700	CO stretch in $$\begin{array}{c} O \\ \parallel \\ -CH_2-C-CH_2- \end{array}$$	8
—	1680	—	CO stretch in $$\begin{array}{c} O \\ \parallel \\ -CH=CH-C- \end{array}$$	8
—	1600	1600	C=C stretch	8
1473	—	— ⎫	CH₂ bend	9
1463	1463	1463 ⎬		
1369	1369	1369 ⎫	CH₂ wag	9
1353	—	— ⎬		
1303	—	—	CH₂ twist	9
—	960	960	CH out of plane deformation in —CH=CH—(trans)	8
—	900	890	CH out of plane deformation in CRR'=CH₂ or CHR=CHR' or CH₃ rock in a chain of 3 to 4 C atoms	8, 10
—	750	750	CH₂ rock in $-(CH_2)_2-$	9, 11
730	—	—	CH₂ rock in $-(CH_2)_3-$	9, 11
720	—	—	CH₂ rock in $-(CH_2)_{n \geq 5}-$	9, 11
—	700	700	CH out of plane deformation in —CH=CH— (cis)	8

groups. Upon comparison of the spectra in Figures 4b and 4c, only small differences can be found, suggesting that the film is somewhat more unsaturated than the powder and that the powder is more highly oxidized, probably due to its higher surface area.

To examine the powder for any crystallinity, a KBr disc was prepared containing a large amount of powder. The infrared spectrum of this sample did not exhibit a band at 1894 cm⁻¹, which is indicative of crystalline polyethylene.[11] The absence of any crystalline character was further supported by the total lack of peaks in the x-ray diffraction pattern taken of the powder.

Based on the evidence given above it is possible to attempt an explanation of the polymerization mechanism. One of the primary observations for this discussion is the fact that powder formation is favored by low pressures and high ratios of power to flow rate. It is known from the physics

of electric discharges that a low pressure in a discharge gap requires a high value of E/p, the ratio of electric field strength to pressure, to sustain the discharge. It is also known that the average electron energy is increased with increasing E/p. An increase in the average electron energy will in turn cause the rate constants for electron–molecule collisions to increase. For a fixed pressure and flow rate, the principal effect of an increase in power is to increase the electron density. As a result, we may conclude that both of the conditions required for powder formation are also conducive to high rates of reaction between the free electrons of the plasma and the molecules of ethylene gas. Some of these reactions lead to the formation of free radicals and ions, both of which are highly reactive species. Given a sufficient residence time, these species can further react with each other as well as with the remaining molecules of ethylene. By this means short oligomer chains are formed in the gas phase. During the growth of the chain, it is continually subjected to the bombardment of electrons and ions and radiation of various wavelengths produced by the plasma. These sources of energy can cause the chain to lose hydrogen. A similar process has been described by Hansen and Schonhorn[12] to account for the crosslinking of polymers placed in the discharge of an inert gas.

An important consequence of the loss of hydrogen is the formation of free radicals trapped within the growing chain. These free radicals can serve as branch points for the growth of chains in a new direction, contributing ultimately to the creation of a highly crosslinked structure. If the free radicals are on adjacent carbon atoms, they can react together to form a double bond. Once the polymerization has been initiated in the gas phase, two alternatives are available to the growing polymer. Either it can continue to grow until a visible powder particle is finally created or it can diffuse to the electrode surface to become incorporated in a film. The ultimate fate of the growing polymer will depend on the rate of polymerization in the gas phase. If the polymerization rate is high, it would seem that the formation of a powder would be more likely; and on the contrary if the polymerization rate is low, the deposition of a film should be favored.

CONCLUSIONS

In the course of the present investigation, it has been observed that plasma polymerization of ethylene can lead to the deposition of a powder as well as a film. For a given power, it is possible to divide the plane defined by the axis of pressure and flow rate into a region in which powder is deposited together with a film and a second region in which only a film is formed. Powder formation is found to be favored by a low gas pressure and a high ratio of power to gas flow rate. The transition between the two regions is gradual, the powder particles becoming smaller as one moves toward the region in which only a film is formed.

From the physical measurements made on the powder, it is possible to conclude that the powder is a relatively dense, amorphous, and highly cross-linked polymer composed of short-chain segments containing no more than two adjacent methylene groups. The infrared spectrum of the powder reveals that it contains significant unsaturation which together with the high crosslink density should account for the observed hydrogen to carbon ratio of 2.7 to 2. It is postulated that the free radicals trapped in the freshly formed polymer react with atmospheric oxygen to yield the hydroxyl and carbonyl bands observed in the infrared spectrum.

Finally, a mechanism for the powder formation has been proposed which suggests that the polymerization proceeds in the gas phase. If the polymerization proceeds at a sufficiently rapid rate, a powder particle is formed. At lower polymerization rates, it is speculated that the growing polymer chain diffuses to the electrode surface and becomes incorporated into a film.

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