PLASMA POLYMERIZATION OF ETHYLENE IN AN ATMOSPHERIC PRESSURE DISCHARGE

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ABSTRACT

The polymerization of ethylene in an atmospheric pressure pulsed discharge has been studied. Partial pressures of ethylene up to 4 kN/m^2 were used with helium as a diluent. Deposition rates were the same throughout the discharge and were in the 1-2 Å/sec range. The films were clear, soft, and adhered well to glass substrates. Oligomers that scattered 637.8-nm light were always observed in the gas phase. The results suggest that Brownian diffusion of these oligomers was the rate limiting step in film deposition.

1. INTRODUCTION

At present, most reported plasma processes are carried out at low pressures, usually 300 N/m^2 or less. We describe here a plasma polymerization reactor which operates at atmospheric pressure (101 kN/m^2). The interest in operating at this pressure is based on its potential economic advantages. Also, it was anticipated that operation at high partial pressure of monomer might result in high film deposition rates. Ethylene monomer was chosen because its polymerization has been studied in detail in low pressure discharges.(1,2)

2. EXPERIMENTAL

Discharge Circuit. The circuit and reactor are shown in Fig. 1. The circuit consists of a high voltage 60-Hz power supply which charges the capacitor C in an LC resonant circuit to a voltage determined by the spark gap electrode separation. When the spark gap fires, the circuit resonates with a frequency near $1/\sqrt{LC}$. This excites the secondary of the Tesla transformer and a large ac voltage is applied across the electrodes in the reactor. The rate at which the spark gap fires is controlled by the setting of the variable transformer.

Breakdown waveforms are shown in Fig. 2. Since the circuit and the electrodes are symmetric, the breakdown waveforms do not depend on the initial polarity. The breakdown waveforms show two characteristics: a breakdown voltage, V_b, and an extinction voltage, V_e. V_b is the voltage at which the circuit begins to load down due to current flow through the plasma and V_e is the voltage at which current stops flowing. The current is a pulse which begins at V_b, reaches a maximum, and drops to zero at V_e; it flows for about 100 ns. So, at a spark gap firing rate of 480/sec, a discharge occurs 480 times per second.

The reactor (Fig. 1) consists of a glass pipe cross with a 15.2 cm i.d. in the direction of gas flow and a 10.6 cm i.d. along the electrode axis. The electrodes, which were brass disks 9.5 cm in diameter and 1.25 cm thick with edges of 0.16-cm radii, were potted in polyester casting resin and machined to 11.43-cm diameter with a 0.318-cm-thick polyester coating on each electrode face. This design permits the production of a uniform discharge by limiting but not preventing secondary cathode emission.(3) Secondary emission still occurred at the joint between the resin and the 0.95-cm-diameter stem at the back of each electrode. An electrode gap of 3.81 cm was used.

3. RESULTS

Operation of a uniform glow discharge in pure ethylene was not possible at atmospheric pressure. A discharge in pure ethylene constricted at pressures above 4 kN/m^2. With helium as a diluent, a uniform discharge could be maintained at a partial pressure of ethylene of 8 kN/m^2. This increase in the maximum partial pressure of ethylene is due in part to the high thermal conductivity of helium and to the fact that constriction under these conditions is thermal in nature.(3,4)

Films were deposited on glass microscope slides oriented parallel to the electrode faces. Deposition rates were independent of vertical position and were the same on the lower and upper surfaces of the glass slides. Unless otherwise noted, all of the results discussed below relate to films which were of uniform thickness.

In all cases, the plasma polymerized ethylene films were uncolored, soluble in ethanol, and had an olefinic odor (similar to ethylene) which disappeared after a few weeks of storage in room air.

Infrared transmission spectra of films deposited on cesium iodide windows showed no absorption around 1600 cm^{-1}, indicating the absence of significant amounts of vinyl groups or unsaturation in the polymer films.

Elemental analysis of a typical film yielded the following empirical formula: $C_2H_{3.26}O_{0.23}$. Typical literature values(5) for n in C_2H_n are in the range of 2.6-3 for rf discharge-produced ethylene films, while for linear conventional polyethylene, $n = 4$. The lower degree of hydrogen abstraction observed here ($n = 3.26$) suggests that less unsaturation or crosslinking is present in the polymer films produced here at atmospheric pressure than at low pressure in an rf discharge.

An important difference between polymerization in this atmospheric pressure pulsed discharge and in low pressure rf discharges is that in the high pressure discharge, oligomers large enough to visibly scatter light from a He-Ne laser (632.8 nm) were always observed in the gas phase. Under conditions in which uniform clear films were produced, these scattering centers were uniformly distributed throughout the discharge volume. Qualitatively, their gas phase density (estimated visually under laser light illumination) was highest under conditions of highest rates of deposition (up to 3 Å/sec). However, the films produced at these high rates were not clear; they were fogged and almost opaque. It has been noted that in low pressure discharges, high deposition rates are also accompanied by powder formation and the production of opaque films.(6) Fogging of films can be caused by surface roughness or by the presence of scattering centers embedded in the bulk film. A prior scanning electron microscope (SEM) study of particle incorporation in plasma polymerized organosilicon films(7) showed that submicrometer diameter spheres were uniformly distributed throughout the polymer films. No such particles were observed with the films produced here (25-nm resolution). Thus, the fogged appearance of these films was apparently caused by surface roughness, and not by the presence of particles embedded in the film.

The magnitude of the surface roughness required to cause fogging can be estimated. Diffuse reflectance begins when the roughness height h is greater than $\lambda/16$ for normal incidence of light of wavelength λ.(8) For visible light (400-700 nm), this corresponds to h between 25 and 44 nm. SEM examination of a fogged film surface revealed the presence of surface roughness on the film surface (Fig. 3). This SEM photograph was taken with the sample at an angle of 45° relative to the electron beam. Particles with 800 to 5000 nm (0.8-5 μm) diameters are evident in the figure, and they appear to protrude from the surface by 400-2500 nm. It is evident from Fig. 3 that the larger particles are agglomerates of smaller ones. SEM examination of a clear film showed absolutely no structure (25-nm resolution). So, under conditions in which clear films are deposited, the gas phase oligomers could be either too small to produce diffuse reflectance on the surface (smaller than 25 nm) or they could incorporate homogeneously into the bulk polymer film.

Effect of Spark Gap Firing Rate. The power in a pulsed discharge can be varied either by the power per pulse or by the pulse repetition rate. With the circuit used here, the power per pulse can be varied by the magnitude of the spark gap electrode separation. The spark gap firing rate can be varied by changing the output of the variable transformer (Fig. 1). Because the voltages and current did not vary with the firing rate (from 60-840/sec), the average power varied directly with the firing rate. This power was 0.5 W at a rate of 480/sec with a peak pulse power of 15 kW.

The effect of varying the firing rate is shown in Fig. 4. The film deposition rate varies linearly with the firing rate up to a rate of 600/sec, suggesting that a constant amount of polymer is formed each time a discharge occurred. For rates greater than 600/sec, the deposition rate increased nonlinearly, indicating that some change in the mechanism(s) of deposition occurred, or that a nonlinear relationship between the production of active species and the firing rate existed. The low average power of 1 W at 600/sec suggests that temperature changes were not responsible for the nonlinear relationship between firing rate and deposition rate.

The ethylene concentration was also measured. A sampling probe and gas chromatograph were used to sample ethylene inside the discharge. Ethylene concentrations were constant in the direction parallel to the electric field and decreased nearly linearly in the flow direction. Therefore, concentrations were measured in the center of the discharge. Figure 4 shows that the extent of reaction $(c_o-c)/c_o$ was proportional to the firing rate even at the high rates for which the deposition rate was not proportional to the firing rate. Here, c is the measured ethylene concentration and c_o is the feed concentration. The linearity of the extent of reaction curve in Fig. 4 and the nonlinearity of the deposition rate curve in the same figure demonstrate that the deposition rate did not vary directly with the amount of ethylene consumed.

Effect of Gas Flow Rate. Figure 5 shows the film deposition rate vs. the flow rate of feed for two feed concentrations. The range of flows corresponds to mean residence times from 60 sec to 1290 sec (the flow rates are at NPT). The characteristic time for diffusion of ethylene across the discharge zone is 7 sec. Hence, the reactor was operated at flow rates for which diffusion was fast compared to convection. In Fig. 5, the deposition rate is seen to be virtually independent of flow rate for flows greater than 5 cm^3/sec. Below 5 cm^3/sec the rate increases to a maximum and then decreases. At the low flow rates, the deposition rate is limited by the supply of monomer. As the flow rate is increased, a point is reached at which the gas residence time becomes insufficient for large gas phase free radical concentrations to be attained and consequently the deposition rate declines as the flow rate is further increased. The plateau in deposition rate suggests that at high monomer flow rates deposition is controlled not by gas phase processes but rather by processes occurring at the plasma-substrate interface. Thus, the free radicals necessary for polymer formation might be formed via the impact of ions and electrons with the growing polymer film. It is likely that deposition is controlled by radical formation both at the surface and in the gas phase for low monomer flow rates and at the surface alone for high monomer flow rates.

Gaseous Discharge Products. Gas chromatographic analyses of the gas in the discharge showed that acetylene was the major volatile product. Ethane was also produced but in a much lower concentration than acetylene: the ratio of ethane to acetylene concentration was typically in the 0.02-0.07 range. No other gaseous products were observed (within the detection limits of the chromatograph). These results are similar to those obtained by others(5) in a mass spectrometric analysis of the effluent from a low pressure rf discharge in ethylene.

4. DISCUSSION

The most obvious difference between films that were produced under different conditions in this work was their surface morphology. Because light-scattering oligomers were always observed in the gas phase when film deposition occurred, it is likely that the observed micrometer-sized particles in the fogged film surfaces were individual oligomers or aggregates of oligomers. The difference between the oligomers which form when fogged or clear films were deposited is likely to have been the size to which they grow in the gas phase before reaching the growing film surface. It is also possible that they differed chemically and that the oligomers present under conditions in which fogged films were formed were not reactive enough to form a smooth surface. In both cases, the oligomers may have been oils or polyradicals.

The following discussion includes a description of the motion of these oligomers in the gas phase and a description of the proposed gas phase chemical reactions.

Chemical Reactions in the Gas Phase. Chromatographic analysis of the gas in the discharge showed that the rate of disappearance of ethylene did not vary directly with the film deposition rate. It also revealed that acetylene was the principal gaseous product of the ethylene-helium discharge and only traces of higher molecular weight hydrocarbons were present. The appearance of acetylene is consistent with a free radical mechanism for polymerization similar to the one proposed(5) to describe the low pressure polymerization of ethylene in an rf discharge. In this mechanism, initiation is by electron impact on C_2H_4, propagation is by radical addition to C_2H_4, and termination occurs by the reaction between two radicals.

Oligomer Motion in the Gas Phase. The observation that the film deposition rate was nearly independent of feed concentration, flow rate, and extent of ethylene reaction over wide ranges of these variables, suggested that some mass transfer process limited the deposition rate. Therefore, an attempt was made to relate the motion of the oligomers in the gas phase to the observed deposition rates.

The motion of micrometer- and submicrometer-sized particles in the gas phase can be due to convection, Brownian motion, and sedimentation. Convection occurred perpendicular to the direction of the mass flux that produces deposition and was considered unimportant under conditions of uniform deposition. In helium at NPT, the Brownian displacement of a particle in 1 sec equals the sedimentation displacement for particles of the order of 500-nm diameter and unit density.(9) For particles smaller than 500-nm diameter, Brownian motion dominates sedimentation. This can explain why the deposition rate of clear films was observed to be the same on the top and bottom of glass cover slips positioned between the electrodes.

It is of interest to note that limited agglomeration of the oligomers would have a relatively small effect on the Brownian motion of the agglomerates because the Brownian diffusion coefficient varies with the reciprocal of the particle radius. For example, a twofold increase in the particle radius requires an eightfold increase in its mass. This means that eight particles would have to combine to decrease the Brownian diffusion rate by a factor of 2. This relatively insensitive response of the diffusion coefficient to agglomeration is a likely explanation for the fact that the deposition rate is independent of gas flow rate over such a large range of flow rates.

5. SUMMARY AND CONCLUSIONS

Plasma polymerization of ethylene has been studied in a pulsed electrical discharge which operated at atmospheric pressure. Films produced in this discharge were soft, uncolored, soluble in ethanol, and passed the cellophane tape pull test for adhesion to a glass substrate. These observations, coupled with the infrared spectra and elemental analysis of the polymer, indicated that the degree of unsaturation and/or crosslinking was low. The low degree of hydrogen abstraction and lack of crosslinking is consistent with the low average electron energies (due to the low electric field-to-pressure ratio) present in the high pressure discharge.

A free radical chain reaction scheme(5) to explain the polymerization is consistent with the results obtained in this work. Gas chromatographic analysis of the gas in the plasma revealed that acetylene was the principal gaseous product of the ethylene-helium discharge and only traces of higher molecular weight hydrocarbons were present. Brownian diffusion of the oligomers formed in the gas phase is suggested to be the rate-limiting step in the film deposition process under the conditions of constant firing rate and low duty cycle.

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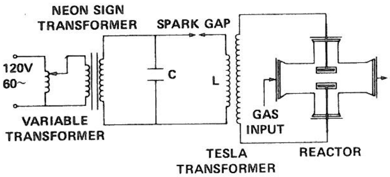

Fig. 1. Schematic of the discharge circuit and reactor.

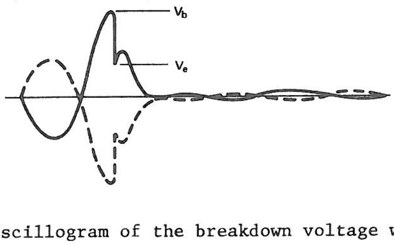

Fig. 2. Oscillogram of the breakdown voltage waveforms.

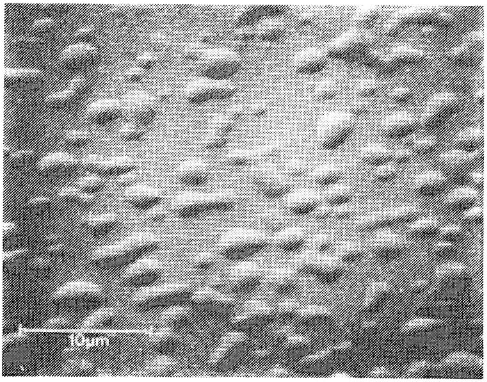

Fig. 3. SEM photograph of a fogged film with the sample at an angle of 45° relative to the electron beam.

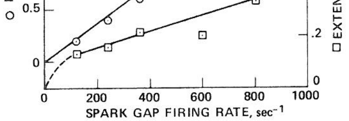

Fig. 4. Film deposition rate (○) and extent of ethylene reaction (□) vs. spark gap firing rate.

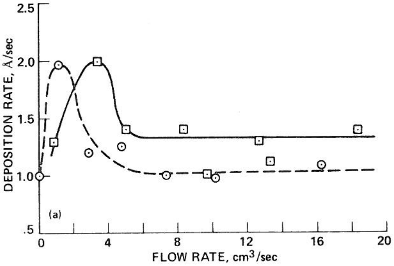

Fig. 5. Film deposition rate vs. gas flow rate (NPT). ○ - 1% C_2H_4 in feed, □ - 2% C_2H_4 in feed. Firing rate: 480 s^{-1}.