Discharge and film study of plasma polymerization of acetylene, ethane and propane

Steven F. Durrant, Rogério P. Mota*and Mário A. Bica de Moraes
Laboratório de Processos de Plasma
Departamento de Física Aplicada, Instituto de Física Gleb Wataghin
Universidade Estadual de Campinas, 13083-970, Campinas, SP, Brazil

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Films were deposited from acetylene, ethane and propane in a radiofrequency (rf) polymerization system. The influence of two important system parameters, pressure and applied power, on the composition of the plasma and the deposited material was examined. Actinometric optical emission spectroscopy was used to determine trends in the electron density N_e, the electron temperature T_e, and the relative concentration of the radical CH, as a function of the two system parameters. Films grown under various conditions of pressure and applied power were characterized by transmission infrared spectroscopy. Deposition rates were determined by optical interferometry. Plasma CH concentrations, N_e and T_e were found to be directly related to the composition and rate of deposition of the films. These relations indicate why, under the same conditions, acetylene polymerizes at a much higher rate than the other two monomers.

Plasma polymerization is well known and widely used[1], for example, in the production of optical coatings[2] and semi-permeable membranes[3]. A multitude of hydrogenated carbon films has also been produced by this technique[4]. Single[5-8] and multiple monomers[2,9], or monomers mixed with inorganic gases[10-11] may be polymerized in the discharge. In addition, the simultaneous sputtering of a metal cathode with plasma polymerization allows the production of composite metal-polymer films[12].

Despite the usefulness of plasma polymerization, there is inadequate understanding of the processes that occur in the discharge and on the growing polymer film, and this is true even of relatively simple systems, such as those of single monomers. In this work, polymer films were grown in rf plasmas of C_2H_2, C_2H_6 and C_3H_8, and a comparative study of the discharge and film properties made for various pressures and applied powers.

Species present in the discharge were detected by optical emission spectroscopy, and the *actinometric technique* employed. This method, which has been extensively explored[13,14] since its advocation about a decade ago[15], has the great advantage of being simple to carry out and non-intrusive. Thus, we have actinometricaliy determined trends in the concentrations of species of interest as a function of a plasma parameter, in this case either the system pressure or the applied power. Argon and nitrogen were used as probe gases (actinometers) diluted to small proportions in the monomers.

To correlate optical observations and polymer properties, deposition rates were determined by optical interferometry, and film molecular structures studied by infrared spectroscopy.

Experimental

A rf polymerization system (in-house design), with two external aluminum ring electrodes was used. Full details of this system (and of the optical monitoring equipment) are given elsewhere[11]. Briefly, it consists of a Pyrex tubular reactor, diameter 7 cm, pumped by

*Present address: Departamento de Física e Química, FEG, Universidade Estadual Paulista, 12500, Guaratinguetá, SP, Brazil

a two-stage rotary pump. The discharge was sustained by a rf generator (120 MHz, 80 W maximum power) capacitively coupled to the ring electrodes through an impedance matching network and through-line watt meter. Gases were admitted to the reactor through leak valves and the pressure controlled by a thermocouple gauge calibrated against a capacitance manometer (Edwards Barocel 600). The reactor was fitted with a quartz window, and a monochromator spectrometer of 1 m focal length used to monitor the intensities of the species in the plasma. Acetylene (99.5% pure), argon and nitrogen (purity better than 99.95%) were supplied by White Martins, Brazil. Ethane and propane (minimum purity 98%) were supplied by Matheson, USA.

The CH emission, at 431.4 nm, and the emissions from the actinometers N_2 and Ar, at 337.1 and 750.3 nm, respectively, were monitored. As in previous work[11,16], variations in the relative concentrations of CH were obtained by normalization of the CH intensity by the intensity of the N_2 ernission at 337.1 nm. Only one actinometer was used at any one time and was present at only a few percent of the total pressure. Since the actinometers were introduced through needle valves it was generally impossible to employ exactly the same flow rate for separate experiments. Therefore, except in a few cases specified in the text, comparison of relative concentrations is possible only for a particular monomer. Thus, trends in the concentrations are shown, but it is impossible to say, for example, that at a fixed pressure the concentration of CH in a plasma of C_2H_2 is X times as great as that found in a plasma of C_2H_6.

The monochromator yielded a typical resolution of about 0.1 nm under the conditions used. Precisions of the emission peak heights were around +/- 3% standard error of the mean ($n = 3$). This would be the typical error in the points of the graphs showing the relative intensities of the actinometers (Figs. 1 (a, b) and Figs. 2(a, b)). The relative CH plasma concentrations, derived by the division of the plasma CH intensity by the intensity of the actinometer, therefore exhibit precisions of about +/- 4%. For the actinometric data, Figs. 1 to 4, the lines are only eye-guides. The accuracy of the applied power and pressure measurements are estimated to be about 3% and 5%, respectively.

Films were grown on glass and KBr substrates placed on a water-cooled circular metal tray located between the electrodes. Transmission infrared measurements were performed using a Jasco IR 700 spectrophotometer. Film thicknesses were determined by the step-height method using an interferometer microscope (Varian, A-scope).

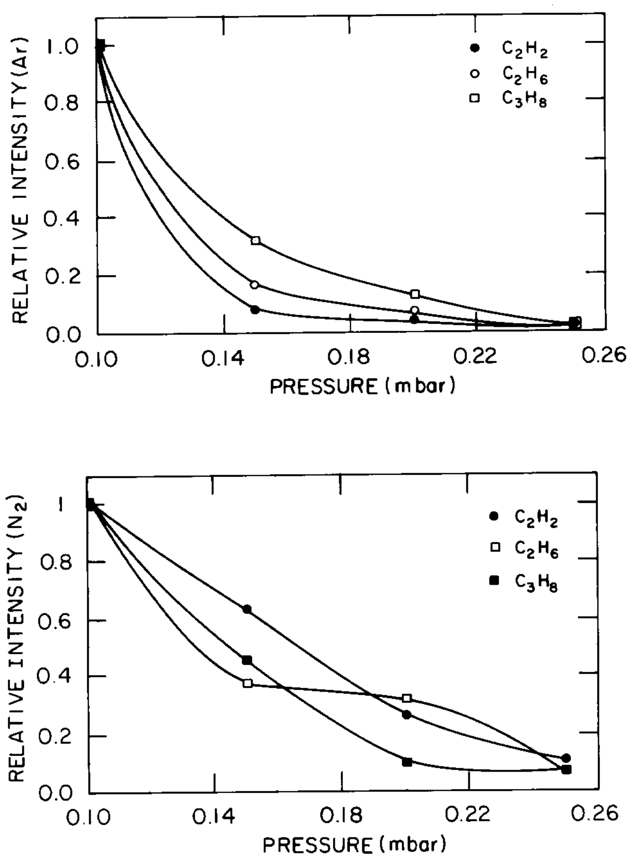

Figure 1. Relative intensities of the actinometers in C_2H_2, C_2H_6 and C_3H_8 as a function of pressure. (a) Ar; (b) N_2. Applied power: 13 W.

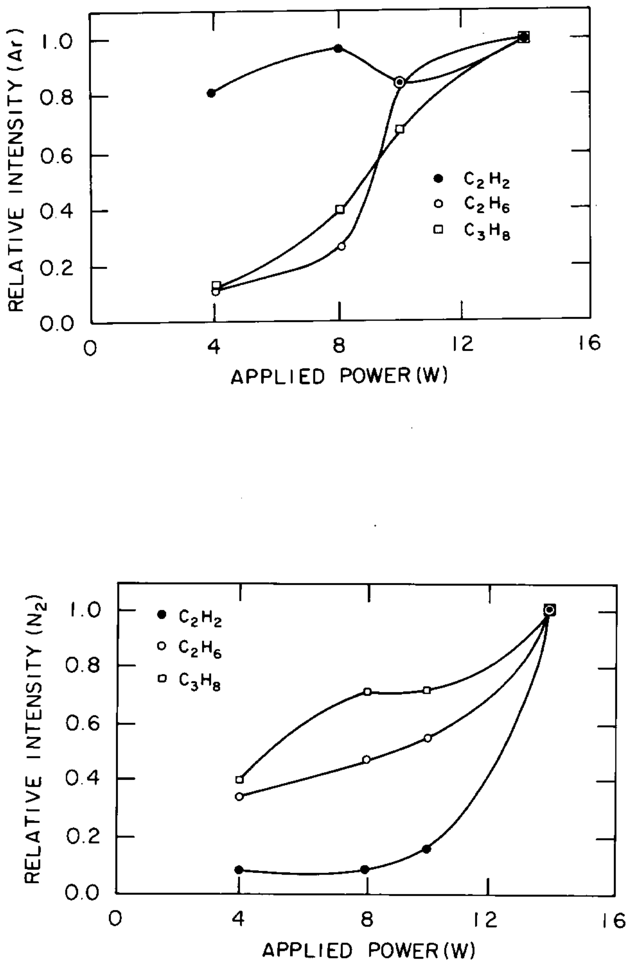

Figure 2. Relative intensities of the actinometers in C_2H_2, C_2H_6 and C_3H_8 as a function of applied power. (a) Ar; (b) N_2. Pressure: 0.2 mbar.

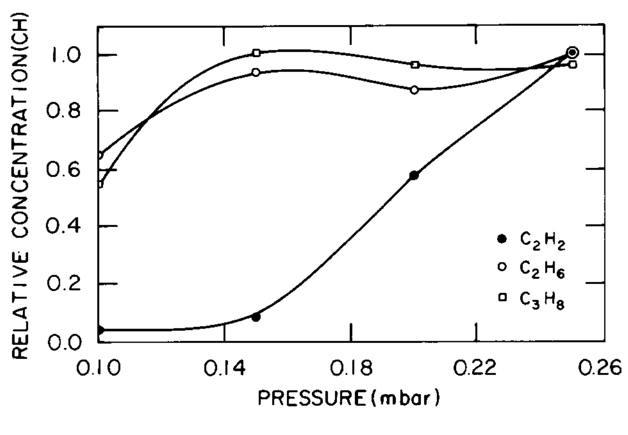

Figure 3. Dependence of the relative plasma concentration of species CH on pressure for C_2H_2, C_2H_6 and C_3H_8. Applied power: 13 W.

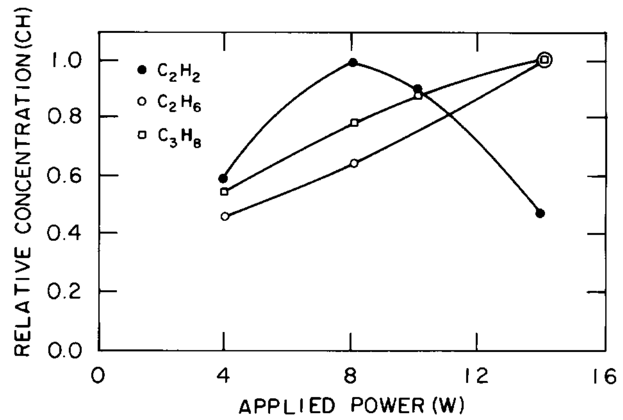

Figure 4. Dependence of the relative plasma concentration of species CH on applied power for C_2H_2, C_2H_6 and C_3H_8. Pressure: 0.2 mbar.

Results and Discussion

Optical spectroscopy of the discharge

Figure 1 shows the behavior of the self-normalized Ar and N_2 emission intensities as a function of the pressure of C_2H_2, C_2H_6 and C_3H_8. The intensities of both actinometers fall rapidly with increasing pressure for all three gases. Thus either the mean electron density N_e, or the mean electron energy E_e is reduced (or both are reduced). In the shorthand notation adopted elsewhere[17], the activity,

$$A = N_e E_e \ , \tag{1}$$

is reduced. It should be noted that the use of A is a convenient shorthand only; we are not concerned here with the exact dependence of the emission intensity on the plasma parameters. If the same flow of the actinometer is maintained in the presence of each of the three gases, it is possible to infer differences in the behavior of the plasma electrons. Argon was used for this purpose and it was found that, at a total pressure of 0.2 mbar and an applied power of 13 W, the Ar emission intensity is about 80 times greater from C_2H_2 than from the other two gases. Thus, at any given pressure the activity in the C_2H_2 plasma is much higher than those of the other two monomers.

The self-normalized emission intensities of Ar and N_2 are plotted in Fig. 2, for the three monomers, as a function of the applied power. Even though the rates of change of the intensities vary widely from one monomer to another, an overall increase in the intensities is observed with increasing power.

An important species to investigate in the plasma is the free radical CH. This species arises from fragmentation of the monomer molecules. The behavior of the relative plasma CH concentration as a function of pressure and applied rf power may provide important information on film growth. Figure 3 shows the relative plasma concentration, n_{CH} for the three monomers as a function of pressure. For the C_2H_6 and C_3H_8 plasmas, a rise in the pressure from 0.10 to 0.15 mbar is seen to significantly increase n_{CH}; for pressures higher than 0.15 mbar, n_{CH} is nearly constant. A contrasting behavior is observed for C_2H_2: the CH concentration is nearly constant between 0.1 and 0.15 mbar, but rises very steeply for pressures higher than 0.15 mbar.

The increases in n_{CH} with increasing pressure occur despite the falling electron temperatures of the plasmas, but there are two points to note here. First, there is probably a considerable density of electrons in the high-energy tail of the electron energy distribution function and these electrons are sufficient to maintain production of the CH radical. Second, the supply of CH units (in the form of monomer) increases with increasing pressure.

In a separate experiment, using the same flow of actinometer for each of the three monomers, we found that n_{CH} was about 40 times higher in a discharge of C_2H_2 compared to discharges of C_2H_6 and C_3H_8 (total pressure of 0.2 mbar, applied power 13 W). This may be taken as evidence of the relatively high activity of the C_2H_2 plasma, generating molecular fragments at a higher rate. Such observed differences cannot be attributed to differences in the ionization potentials of the three gases, since they are almost identical[18]. Moreover, the strength in the triple carbon bond in C_2H_2 is greater than that of C-C bonds of C_2H_6 and C_3H_8. The greater plasma activity of the C_2H_2 discharges might be due to the greater ionization cross-section of this gas or to a lower recombination rate. However, recent theoretical and experimental work on the total electron-impact ionization cross-sections, σ, of these gases[19−21] shows both that their functional dependence on electron energy is very similar and that, for any particular electron energy, the absolute values of σ do not differ greatly. Hence, of the two possibilities indicated above only a lower recombination rate for acetylene remains open.

The effect of applied power on the CH plasma concentration was also investigated. A plot of n_{CH} *versus* applied power is shown in Fig. 4. The CH concentration monotonically rises with pressure in plasmas of C_2H_6 and C_3H_8. In the C_2H_2 plasma, however, n_{CH} rises to a maximum at about 8W then declines markedly. Since the plasma activity is not reduced when power is increased from 8 to 15W (cf. Fig. 2), this decline is possibly related to an increase in the rate of recombination of CH compared to that of CH generation from C_2H_2 molecules. However, the cause of such a change in recombination rate is obscure.

Deposition rates

The deposition rates of films of the three monomers are given Fig. 5 as a function of pressure, and in Fig. 6 as a function of the applied power. The data in both figures show that C_2H_2 polymerizes at a far greater rate than the other two gases (note scales). As we can see from Fig. 5, at 0.2 mbar, for example, the deposition rate for C_2H_2 is nearly 230 nm/min, about 20 and 50 times higher than that of C_2H_6 and C_3H_8, respectively. Also, the dependence of the deposition rate, R, on pressure differs widely for the three monomers: with increasing feed pressure R increases for C_2H_2, decreases for C_3H_8, and varies slowly for C_2H_6. On the other hand, the dependencies of R on power (Fig. 6), are somewhat similar for the three gases, but show maxima at different applied powers.

A strong correlation between the deposition rate of plasma polymerized C_2H_2 and the CH plasma concentration can be seen. For C_2H_2 plasmas, a similar dependence of R and n_{CH} on pressure is observable (cf Figs. 5 and 3). Identical behaviors for R and n_{CH} on applied power can be observed by comparison of Figs. 6 and 4. Inspection of the data of Figs. 3 to 6 for C_2H_6 and C_3H_8 reveals no correlation between R and n_{CH}. Probably the species CH_X (x = 1 to 3) are important precursors for film formation. Some plasma polymers, then, grow by continuous adsorption of these "building blocks" onto the polymer surface. In agreement with these ideas, our data indicate that the CH species is very probably the most important precursor for film formation in C_2H_2 discharges. The lack of correlation between R and n_{CH} for C_2H_6 and C_3H_8 indicates that other precursors, such as CH_2 and to some extent CH_3, also contribute to film formation. However, the species CH_2 was not detected optically in any of the discharges.

The relatively high deposition rate of plasma polymerized C_2H_2 is probably related to the greater electron activity of the C_2H_2 discharges compared to the discharges of C_2H_6 and C_3H_8. As noted previously, this may in turn relate to lower recombination rates compared to the other monomers.

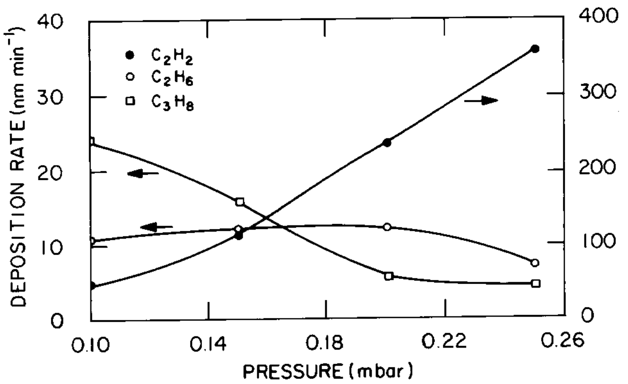

Figure 5. Pressure dependence of the deposition rate of polymers from C_2H_2, C_2H_6 and C_3H_8. Applied power: 13 W.

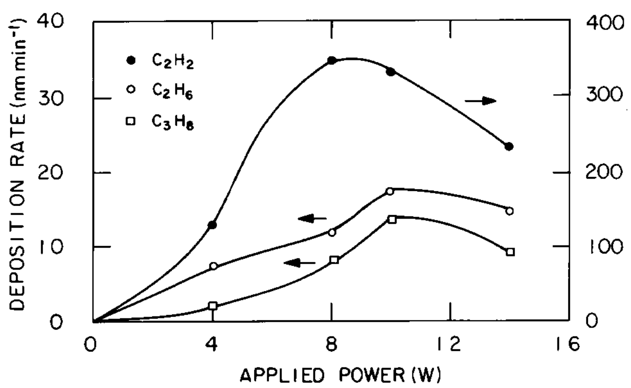

Figure 6. Power dependence of the deposition rate of polymers from C_2H_2, C_2H_6 and C_3H_8. Pressure: 0.2 mbar.

Structure of the polymer films

Representative infrared spectra of plasma polymerized C_2H_2, C_2H_6 and C_3H_8 films are shown in fig. 7. All films were obtained at an applied power of 13W and a pressure of 0.20 mbar. Each spectrum exhibits early the same absorption features. The strong bands around 2900 cm^{-1} are due to C-H stretching vibrations in CH_2 and CH_3 groups. The presence of these groups is confirmed by the bands at 1450 cm^{-1} (bending in CH_2 and CH_3 groups) and at 1375 cm^{-1} (bending in CH_3 group). Owing to the presence of C=C bonds, an absorption at 1620 cm^{-1} is observed most distinctly for plasma-polymerized C_2H_2. However, since recombination of reactive molecular fragments is an important mechanism in film formation, it is possible that C=C bonds are also present in the other polymers, though at comparatively low densities.

Other absorptions are due to hydroxyl and carbonyl groups at 3500 cm^{-1} and 1700 cm^{-1}, respectively. (The latter absorption is weak and partially covered by noise, but is visible in spectrum b). As previously shown by other investigators[22], plasma polymers contain a high concentration of free radicals, trapped in the film from the plasma. Therefore, these groups probably arise from reactions between free radicals and ambient oxygen[23].

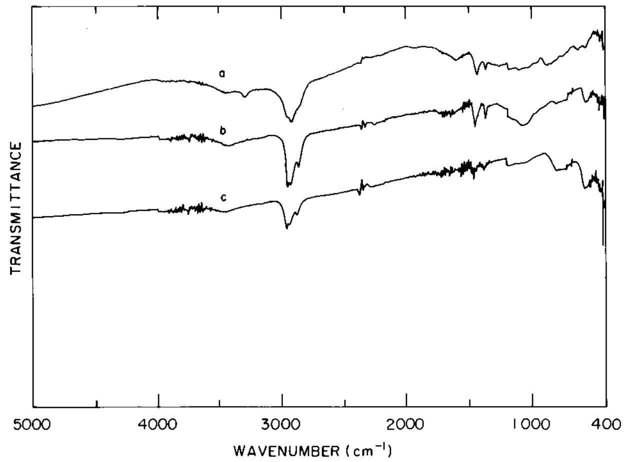

Figure 7. Transmission infrared spectra of plasma polymers from (a) C_2H_2; (b) C_2H_6; (c) C_3H_8. Pressure: 0.2 mbar; applied power: 13 W.

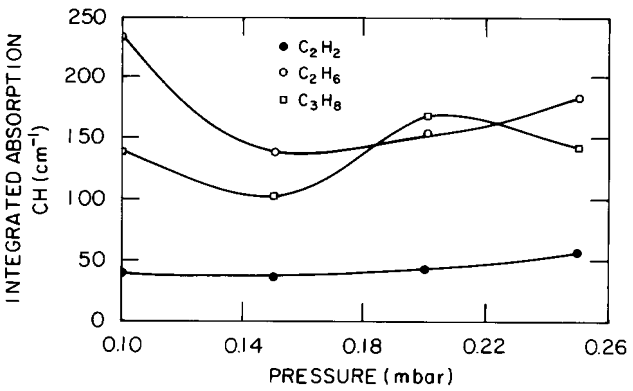

Figure 8. Integrated C-H band absorption of the three polymers as a function of pressure. Applied power: 13 W.

The integrated absorptions of the band around 2900 cm^{-1} are proportional to the density of C-H bonds in the film. Figure 8 depicts the integrated absorptions, calculated by a method described by Lanford and Rand[24], as a function of pressure, for films obtained at constant power. The density of C-H bonds N is equal to βI, where I is the integrated absorption. In comparing the values of I for each monomer it is assumed that β, which depends to some extent on film structure, is constant. From Fig. 8 it may be seen that the C-H bond densities in plasma-polymerized C_2H_6 and C_3H_8 show a considerable variation with pressure, while for C_2H_2 this variation is much reduced. Furthermore, plasma-polymerized C_2H_2 contains a lower density of C-H bonds, which is consistent with the lower H/C ratio in the monomer molecule. Indeed, in most of the pressure range, absorptions are in the sequence $C_2H_2 < C_3H_8 < C_2H_6$ and this matches the sequence of H/C in the molecules, namely 1:2.67:3. We may note that for C_2H_2 plasmas the higher plasma [CH] obtained at higher pressures (Fig. 3) leads to higher deposition rates (Fig. 5) rather than higher CH bond densities.

Integrated absorptions of the C-H band, calculated in the same manner as for Fig. 8, for films grown at constant pressure are shown in Fig. 9, as a function of the applied power. As can be seen in the figure, changes in the applied power in the range 4 to 14 W do not change the bond density by more than about 60%. Again, as expected, the curve for C_2H_2 lies below the others. However, in opposition to the data of Fig. 8, the integrated absorptions do not follow the sequence $C_2H_2 < C_3H_8 < C_2H_6$. Rather, the C-H bond density in the polymer from C_3H_8 is now higher than that from C_2H_6. Again, we may note that for C_2H_2 discharges, while the film [CH] is not strongly dependent on applied power, the dependence of the plasma [CH] on applied power (Fig. 4) strongly resembles the functional dependence of the deposition rate on the same parameter (Fig. 6).

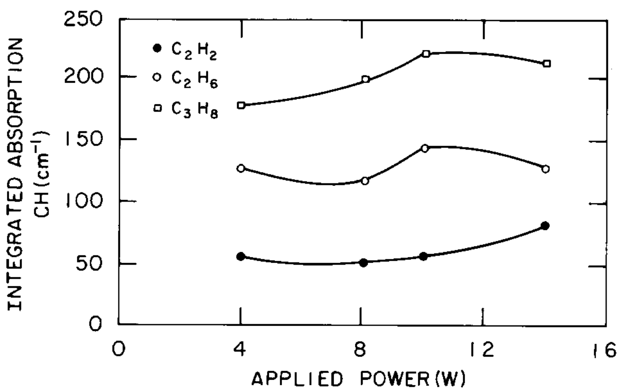

Figure 9. Integrated C-H band absorption of the three polymers as a function of applied power. Pressure: 0.2 mbar.

That the integrated absorptions do not necessarily follow the same H/C sequence of the monomers is related, primarily, to the extensive fragmentation of the monomers in the plasma. A large proportion of these fragments (including H, H_2 and other H-containing species) is pumped away from the reactor during film deposition at a rate that depends on the experimental conditions. Therefore, the H/C ratio in the monomer is not always preserved in the polymerization process.

Conclusions

Actinometric optical emission spectroscopy was used to measure the "plasma activities" and relative CH concentrations in plasmas of C_2H_2, C_2H_6 and C_3H_8 as a function of the system pressure and applied power. Our data indicate that the plasma activity is greater in C_2H_2 plasmas. This may be due to comparatively low electron-ion recombination rates. The H "active" C_2H_2 discharge produces a relatively high fragmentation of the monomer leading to high concentrations of CH, an important building block for polymer formation. For the polymers from C_2H_6 and C_3H_8 no correlation has been found between the deposition rate and CH plasma concentration. Furthermore, consideration of the molecular structure of these monomers shows that the CH species cannot be produced by the breaking of a single bond by an energetic electron. As the CH species was detected in plasmas of these monomers, multiple fragmentation of these molecules must occur. However, actinometry indicates that plasmas of these gases are relatively inactive.

Despite the difference in activity between the acetylene plasmas and those of the other two monomers, infrared spectroscopy of material deposited from each gas showed that the films contained the same functional groups.

Acknowledgments

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