((<https://doi.org/10.1002/ppap.202000244>))

Article type: Full paper

Unique combination of spatial and temporal control of maleic anhydride plasma polymerization

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The chemical properties of plasma polymers strongly depend on the operating conditions of
plasma polymerization and impact their final application. Low-pressure pulsed plasma
polymerization of maleic anhydride was investigated at different positions from the glow
discharge in a unique 1 m long reactor. Based on a macroscopic approach, the growth kinetics
of maleic anhydride plasma polymerization were investigated and led to the identification of
three growth regimes. The calculation of apparent activation energies associated with each
regime and each position, the chemical characterization of polymer films by XPS and ATR
FTIR as well as OES analyses of plasma species formed during deposition strongly indicate a
combined spatial and temporal influence on the plasma polymerization kinetics.

1 Introduction

During plasma polymerization, film growth is ensured by gas phase dissociation processes and surface growth processes under continuous reactivation and recombination reactions.^[1] Firstly, Yasuda proposed a growth mechanism known as rapid step-growth polymerization (RSGP).^[2] According to this mechanism, free radicals are the most concentrated species and therefore the most likely to react. They can be easily generated by electron impact, excitations or collisional energy transfers. Meanwhile, the deposited film undergoes interactions with the reactive species which may lead to film degradation. The identification of these basic processes at the origin of the crosslinked structure of plasma polymers led to the introduction of the CAP mechanism (Competitive Ablation and Polymerization).^[3] Ablation mainly depends on the power provided to the monomer and its residence time in the plasma. In order to estimate the energy transferred to the gas, Yasuda introduced the reaction parameter W/FM where W is the power provided to the precursor (denoted also as 'monomer' in the following), F its flow rate, and M its molecular weight.^[4] Thus, at low energy input (energy-deficient regime) linear increase of the mass deposition rate is ensured by the large domination of the polymerization while etching phenomena are absent.^[5] At high energy input (monomer-deficient regime), on the contrary, ablation mechanisms are no longer negligible and therefore a decrease in the polymer growth rate can be observed. Thus, the reaction parameter W/F (or W/FM) corresponds to a specific energy that governs reactions within the plasma active zone according to the concept of chemical quasi-equilibrium.^[6] This macroscopic approach allows a less complex and more accessible description of plasma polymerization than molecular studies. In fact, for radical-dominated plasma polymerization, the film deposition rate solely depends on the energy provided per particle of the gas mixture flowing through the plasma phase.^[7] Taking into account geometrical parameters of the reactor, this macroscopic approach has been further developed by Hegemann et al. and led to the correlation of the polymer film deposition rate

with an apparent activation energy associated to a specific state of the precursor, related to dissociation energies or enthalpies of formation.^[6,8,9] While radical-dominated polymerization mechanism were assumed in numerous studies dealing with plasma polymerization,^[10–13] because of the strong presence of radicals within the plasma polymer,^[14] other studies have been focused on the importance of ions contribution^[15,16]. However, these mechanistic studies are still controversial. Many questions are also still open on the location of chain initiation and/or growth, on the substrate or in the plasma phase.^[17,18] All these discussions and studies concerning the mechanisms of plasma polymerization including radical polymerization, ionic polymerization, ion-molecule reactions and even fragmentation- poly-recombination of the precursor are well reported in Friedrich's review^[14] and frequently debated.^[19,20] Despite of these controversial discussions, various authors have agreed on the fact that the polymerization mechanisms can be significantly modified by changing the operating mode of plasma polymerization from continuous to pulsed.^[21–25] Pulsed plasma polymerization is characterized by the duty cycle (DC), defined as $t_{on} / (t_{on} + t_{off})$, t_{on} being the time when the radio frequency excitation is supplied to the electrodes and t_{off} , the time during which it is interrupted. A low duty cycle promotes the retention of chemical functions because it limits the fragmentation of the precursor to short time periods. In this way, a temporal control of plasma polymerization is addressed.^[23,24] In addition, the influence of the position of the sample in the reactor and more precisely in relation to the discharge on the plasma polymer properties was addressed in several studies.^[26–29] Carrying out plasma polymerization in the post-discharge zone (also known as remote plasma deposition) is known to limit the crosslinking of plasma polymers since less ions are found far from the glow discharge, thus leading to a spatial control of plasma polymerization.^[30]

In this study, the possibility to combine a spatial with a temporal control of plasma polymerization was investigated by performing pulsed plasma polymerization in an original

home-built low-pressure plasma reactor, being 1 m long and enabling the deposition of plasma polymers within or outside the glow discharge. For this purpose, maleic anhydride has been chosen as a precursor since it is very sensitive to the operating conditions in which plasma polymerization is performed^[23,24,31,32] and it is also a good candidate to fabricate functional polymer thin films for various applications. *maleic anhydride* plasma polymers have, for instance, been used to control the interactions between cells/bacteria with a surface,^[33] to get hydrophilic textiles,^[34] to serve as a matrix for the synthesis of nanoparticles^[35] or simply to be an efficient ground layer for subsequent post-modification, especially by vapor phase aminolysis reactions mainly to control adhesion properties.^[36–38] For these applications, preserving reactive anhydride groups is crucial but challenging. Even at relatively low input energies, anhydride groups can be easily fragmented, compromising the final use of the polymer thin film. A macroscopic approach has been chosen in this work to describe the growth kinetics of pulsed plasma polymerization at different locations in the reactor in order to determine the different activation energies involved during deposition. Chemical characterization of maleic anhydride plasma polymer thin films but also of the plasma phase provided interesting results to get more insights into plasma polymerization kinetics, considering polymerization at various specific energies in three different regions of the plasma reactor (pre-discharge, discharge and post-discharge zones).

2 EXPERIMENTAL SECTION

2.1 Deposition of maleic anhydride plasma polymer by plasma polymerization

Maleic anhydride, $C_2H_2(CO)_2O$, (Prolabo, 99.5% purity) was ground into a fine powder and loaded into a stoppered glass gas delivery tube. Then, a degassing step led to vacuum in the tube by performing three freeze–pump–thaw cycles. Maleic anhydride plasma polymer were deposited onto $1 \times 1 \text{ cm}^2$ single side-polished silicon wafers (100, Si-Mat), which were cleaned

with ethanol and acetone before use. Plasma polymerization experiments were carried out in a unique, home-built RF plasma reactor, operating at low pressure. The chamber consists of a quartz tube (100 cm in length and 6 cm in diameter) coupled with an externally wound copper coil. A pirani pressure gauge in series with a two-stage rotary pump (Edwards E2M 18) connected to a liquid nitrogen cold trap completes the reactor. All parts of the equipment are assembled with grease-free Cajon fittings. An L-C matching network (Dressler, VM 1500W-ICP) is used to balance the impedances of the generator (Dressler, Cesar 133, 13.56 MHz) and the reactor by minimizing the standing wave ratio of the transmitted power. Using an oscilloscope, the shape of the pulses during deposition was controlled and the average power W delivered to the system was calculated according to Equation 1, where P_g is the continuous wave power input indicated by the generator, DC the duty cycle, t_{on} the pulse-on time, and t_{off} the pulse-off time:

$$W = P_g \times DC = P_g \times [t_{on} / (t_{on} + t_{off})] \quad (1)$$

Prior to each plasma deposition, the reactor was cleaned for a minimum of 30 min using a high-power air plasma treatment ($P_g = 65$ W) to ensure the elimination of residues in the reactor. The substrates were afterwards introduced into the chamber by placing them onto a glass support in the desired zone of the reactor. Three preferential positions were chosen for this study (Figure 1): P1 in the pre-discharge zone, P3 in the discharge zone, which is located at the middle of the copper coil, and P5 in the post-discharge zone. Position P1 was selected in order to get information at the entrance of the reactor corresponding to the pre-discharge zone. Here, only one position is enough to probe the entire pre-discharge zone. At the opposite, in order to get information in the entire post-discharge zone of the plasma reactor, 6 positions have been well selected, from position P5 to position P10. P5 is located at 45 cm from the monomer entrance of the reactor, P6 at 57 cm, P7 at 67 cm, P8 at 77 cm, P9 at 87 cm and P10 at 97 cm. For the discharge zone, other positions such as P2 and P4 have also been studied and confirmed the

same trends as those obtained at P3. Something very important to underline here was the heterogeneity of the coatings according to the location of the samples. All the coatings obtained in position P5 (and for all the above positions: P1, P2, P3, P4) were uniform (in thickness and chemistry point of view). However, all the coatings obtained beyond position P5 (i.e., at P6, P7, P8, P9 and P10) were non-uniform. They are composed mainly of particles and heterogeneous layers and could not be used in this study. Therefore, P5 could be considered as a spatial border: All the positions above P5 (and including P5) allowed the deposition of uniform coatings, which were the conditions required for this study.

Once a base pressure of approx. 4×10^{-4} mbar was reached, the precursor was introduced into the reaction chamber at a constant pressure of 0.1 mbar (which corresponds to a flow rate of approx. $56 \mu\text{g.s}^{-1}$, corresponding to 0.77 sccm for maleic anhydride). At this stage, the plasma was ignited at different conditions of power input ($P_g = [20\text{-}50 \text{ W}]$) while varying the duty cycle (DC = [2-50%]). The frequency of plasma pulses was kept constant at 816 Hz. Upon completion of deposition, the RF generator was switched off. Prior to venting to atmospheric pressure and retrieving the samples, the monomer feed was kept to flow for 2 min. This step enables the latest created plasma species and living radicals to react and avoids undesirable reaction of residual free radicals with air to take place within the plasma polymer film when the reactor is vented. More details on the experimental setup and experimental conditions are given in Figure S1, Figure S2 and Table S1 in Supporting Information.

Figure 1: Schematic illustration of the low-pressure plasma reactor used for this study. The different studied positions of the sample are indicated (P1 to P5).

2.2 Characterization of maleic anhydride plasma polymer thin films

2.2.1 Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR FTIR)

ATR FTIR spectroscopy was used to analyze the chemical composition of maleic anhydride plasma polymer thin films. Measurements were performed on a FTIR spectrometer iS50 (Thermo Scientific) equipped with a high sensitive, low noise, MCT detector and coupled with a Grazing angle Germanium ATR accessory (VariGATR, Harrick Scientific Products). The angle of incidence was 65°. Spectra were collected at wavenumbers ranging from 650 to 4000 cm^{-1} , with a resolution of 4 cm^{-1} and a total of 64 scans. A minimum of three spectra were recorded for each sample. The values are mean of two independent experiments. It is worthwhile to notice here that each sample was immediately analyzed after being removed from the plasma chamber.

2.2.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) analyses have been performed to determine outermost surface chemistry of the deposited films using a VG SCIENTA SES 2002 spectrometer operating at 420 W. The instrument was equipped with a concentric hemispherical analyzer. Al anode emitting $\text{K}\alpha_{1,2}$ anode (1486.6 eV) was monochromatized. Emitted photo electrons were collected at a take-off angle of 90 ° from the substrate with electron detection in constant analyzer energy mode. Survey spectrum was recorded with a pass energy of 500 eV and a step size of 0.5 eV whereas for high resolution spectra (C1s and O1s) pass energy was set to 100 eV with a step size of 0.1 eV, selecting a spot size of approximately 4 x 6 mm^2 . Peak fitting was carried out with mixed Gaussian-Lorentzian (30%) components with equal full-width-at-half-maximum (fwhm) values using CASAXPS software (CASA Software Ltd version 2.3.18). The surface composition expressed in at.% was determined using integrated peak areas of each components and takes into account transmission factor of the spectrometer, mean free path and

Scofield sensitivity factors of each atom (C1s: 1.00, O1s: 2.93). Standard deviation has been estimated from measurements performed onto two substrates obtained from two different plasma runs.

2.2.3 Ellipsometry

The coating thickness was estimated using ellipsometry with a phase modulation Multiskop (M-033k001, Physik Instrumente). The sample was placed between the laser source arm and the detector arm so as to be exposed to laser radiation at 532 nm (Nd:YAG laser). The cross section of the laser beam is about 1 mm². Average value of thickness was calculated with at least five measurements performed in air at different positions of the sample by considering a Cauchy model.

2.2.4 Atomic Force Microscopy (AFM)

Surface roughness measurements were performed using a FlexAFM scanning probe microscope running with a Nanosurf C3000 controller (Nanosurf) in air. A silicon cantilever was used for all measurements. The spring constant of the cantilever was 13-77 N m⁻¹. Tapping mode was used and at least five scans were performed using 256 X 256 lines at different sample locations to check the uniformity of the surface. Only 2 µm × 2 µm images, obtained at the center of each sample, are presented in the Supporting Information. Data processing and data analysis were performed using Gwyddion software. In particular, the mean roughness (Sa) has been selected in this study.

2.2.5 Optical Emission Spectroscopy (OES)

The plasma discharge was analyzed by Optical Emission Spectroscopy (OES), which is particularly useful in order to detect the active species formed during the deposition and to understand the large variety of chemical processes occurring within the plasma glow discharge.

Plasma emission spectra were obtained using a Horiba Scientific – IHR 550 spectrophotometer coupled with CDD multichannel detector. The light emission was captured with silicon oxide optical fibers placed at the different locations of the sample (P1 to P5). The spectrophotometer was calibrated using the lab fluorescent tube lamp (atomic mercury line at 485.833 nm). A dark spectrum was subtracted from each spectrum. Spectral integration times were optimized for each plasma condition to obtain a strong signal. Typical integration times varied from 1 to 5 s. All data were processed with Syner Jobin Yvon V35 software. When OES measurements were performed, an additional flow of Ar (2 sccm) was injected in the reactor at the gas inlet (Figure 1).

3 Results and Discussion

3.1 Macroscopic kinetics of maleic anhydride plasma polymerization

To understand and control plasma polymer deposition, Yasuda et al. introduced a methodology consisting of measuring the deposition rate of the plasma polymer as a function of the specific energy provided to the precursor.^[39] The evolution of the deposition rate with the specific energy enabled to distinguish between an energy-deficient regime, where deposition rate increased with specific energy, and energy-excess regimes, where deposition rate remained constant or even decreased by increasing specific energy due to substantial etching processes of the deposited plasma polymer. Derived from Yasuda's formalism based on the concept of quasi-chemical equilibrium, other authors have preferred a so-called macroscopic approach to describe plasma polymerization and comment on the deposition rate of plasma polymer. This second approach, formulated by Hegemann et al., takes into account geometrical parameters of the reactor such as plasma expansion and corresponding absorbed power.^[5] They proposed to follow the evolution of the deposition rate of the plasma polymer at various specific energies

in order to have access to one or more apparent activation energies (E_a) related to a specific state of the precursor, using a modified Arrhenius approach as shown in Equation 2:^[7,25,40,41,42]

$$\left(\frac{R}{F}\right) = G \times \exp\left(\frac{E_a}{W/F}\right) \quad (2)$$

with R the deposition rate of the plasma polymer, F the precursor flow rate, G a factor depending on the operational conditions of the reactor, E_a the apparent activation energy corresponding to a given state of the precursor, and W the average energy delivered by the generator. From Equation 2, an Arrhenius-type plot depicting $\ln(R/F)$ as a function of the inverse of the specific energy given to the system $(W/F)^{-1}$ can be used to identify different polymerization regimes. Indeed, the slope of this curve is equal to the activation energy at the corresponding specific energy regime. This apparent activation energy might then be compared with bonding energies of the precursor to get information on the polymerization mechanism in the different polymerization regimes.^[5] Therefore, knowledge of the real available energy per monomer molecule in the plasma is required depending on absorbed power and plasma expansion. Note that here delivered power is considered instead, which still allows comparison of the different positions and regimes by discussing 'apparent' activation energies.

This formalism has been applied in this work in order to control the deposition of maleic anhydride plasma polymer synthesized by pulsed plasma polymerization performed in a low-pressure RF plasma reactor. As illustrated in Figure 1, a 1 m long plasma reactor enables to conduct simultaneously plasma polymerization in different locations of the plasma discharge: in a pre-discharge zone (position P1), in the discharge zone (position P3) and in the post-discharge zone (position P5).

Figure 2 shows the Arrhenius-type plots representing the natural logarithm of the deposited thickness per flow rate unit versus the inverse specific energy provided by the generator at three relevant positions within the reactor, namely P1 in the pre-discharge zone, P3 in the glow

discharge and P5 in the post-discharge zone. Here, it is worthwhile to notice that all the deposition rates were extracted from graphs depicting the thicknesses as a function of deposition times for all experimental conditions. These graphs are shown in Figure S3 of the Supporting Information.

Figure 2. Arrhenius-type plot describing the deposition of the plasma polymer as a function of the inverse of the specific energy provided to the precursor during pulsed plasma polymerization of maleic anhydride: (a) for the pre-discharge zone (P1) close to the gas inlet, (b) for the discharge zone (P3) and (c) for the post-discharge zone (P5) towards the pump.

Three domains of maleic anhydride plasma polymer growth are clearly observed for any sample position: i) the first regime (I) is observed at low energy input showing typical deposition rates,

e.g., at P3 around 4 nm min^{-1} . From the slope of the linear fits, apparent activation energies can be calculated (Table 1). They are equal to $13 \pm 1 \text{ eV}$, $7 \pm 1 \text{ eV}$ and $16 \pm 2 \text{ eV}$ per precursor molecule respectively for P1 (pre-discharge zone), P3 (discharge zone) and P5 (post-discharge zone). These activation energies are higher than any bond dissociation energy of the precursor, particularly higher than the Π bond of the $\text{C}=\text{C}$ (2.8 eV), which theoretically ensures sufficient energy to initiate plasma polymerization via a radical mechanism. Note, however, that nominal power values were used here, which are likely to be distinctly higher than absorbed power values in the active plasma zone required to properly calculate E_a . Hence, despite of these high values of apparent activation energies, the growth rate of the plasma polymer is limited in this regime by the input power delivered by the generator: the increase in the deposition rate originates from an increase of the specific energy (from the left to the right of the graph). It is worthy to note that differences in terms of apparent activation energy can be observed between the different positions in this first regime. This point will be discussed in more detail later. ii) When the specific energy is increased, a slope change is observed giving rise to a second regime (II) with higher apparent activation energies. This slope change indicates the dissociation of new chemical bonds within maleic anhydride and an increase in the film growth rate. Interestingly, at this energy input level, the values of activation energies corresponding to the different reactor zones are very close: $25 \pm 4 \text{ eV}$, $20 \pm 2 \text{ eV}$ and $22 \pm 2 \text{ eV}$ per molecule respectively for P1, P3 and P5 (Table 1). It can be noted that these activation energies are again overestimated with respect to bond dissociation energies of the precursor, however, indicating a higher degree of precursor fragmentation. iii) With further increasing specific energy, a third growth regime (III) appears. In this regime, different growth behaviors are observed for the three positions. In the pre-discharge zone and the discharge zone a slope deviation appears, indicating an increase in the growth rate with the increase of the energy input reaching $R = 24 \text{ nm min}^{-1}$ for P1. The slope deviation is less pronounced for P3 reaching a lower $R =$

14 nm min⁻¹, probably because competitive mechanisms come into play. These mechanisms include not only a probable polymer etching (e.g. due to enhanced formation of reactive oxygen species by fragmentation) but also a balance between plasma polymerization as the form of thin film and nanoparticles formation. Indeed, powder particles were observed in the post-discharge zone after P5 (see Figure S4 in Supporting Information). This third growth regime, corresponding to a more complex growth mechanism, is mostly highlighted within the post-discharge zone (P5) and leads to a significant decrease in deposition rate from the highest measured value $R = 7 \text{ nm min}^{-1}$ at the II/III transition. More details about this powder formation will be discussed in a forthcoming communication.

By using the macroscopic kinetics approach for plasma polymerization of maleic anhydride, such different growth regimes could be identified depending on the energy input into the active plasma zone and the position of the sample in the reactor. Consequently, different activation energy values were determined for each regime. Now, in order to explain the obtained results and to study in particular the spatio-temporal effect on the polymer qualitative variations in the surface chemistry, chemical characterizations of thin films as well as plasma species analysis were performed and discussed in the next part.

Table 1. Apparent activation energies involved during pulsed plasma polymerization of maleic anhydride for the different reactor zones in the different growth regimes with increasing energy input from I to III.

Positions	P5 (post-discharge)			P3 (discharge)			P1 (pre-discharge)		
Regimes	III	II	I	III	II	I	III	II	I
E_a (eV)	Competitive mechanisms	22 ± 2	16 ± 2	Competitive mechanisms	20 ± 2	7 ± 1	150 ± 22	25 ± 4	13 ± 1

3.2 Chemical characterization of maleic anhydride plasma polymer thin films deposited in various growth regimes and various positions

Complementary to the kinetics study based on the evolution of the polymer growth rates as a function of the specific energy and the position of the sample in the reactor, ~~poly~~ maleic anhydride plasma polymer thin films have been chemically characterized in order to identify qualitative variations in the chemical fingerprint of the plasma coatings (resulting from differences in fragmentation of the precursor molecule) according to the growth regime and also to the location from the plasma discharge. Systematically, samples corresponding to the inverse specific energy $2.14 \cdot 10^{-2} [\text{J cm}^{-3}]^{-1}$ ($P_g=30 \text{ W}$, DC=2%), $0.43 \cdot 10^{-2} [\text{J cm}^{-3}]^{-1}$ ($P_g=30 \text{ W}$, DC=10%) and $0.09 \cdot 10^{-2} [\text{J cm}^{-3}]^{-1}$ ($P_g=30 \text{ W}$, DC=50%) for each position were analyzed to represent the chemical composition of maleic anhydride) plasma polymer synthesized in regimes I, II and III, respectively. The thickness of the plasma polymer thin films was set to 50 nm. It should be noted that the morphology of the polymer thin films will not be discussed in this paper, since AFM images obtained at different locations on the surface of each sample proved the existence of a homogenous, smooth polymer thin film regardless of its position from P1 to P5 and of the growth regime (see Figure S5 in Supporting Information).

Typical high resolution XPS spectra of the C1s for maleic anhydride plasma polymer indicate hydrocarbon ($\underline{\text{C}}\text{-C}$, $\underline{\text{C}}\text{H}_x$ at 285.0 eV), carbon in alpha position of anhydride/carboxylic acid/ester groups ($\underline{\text{C}}\text{-C=O}$ at 285.6 eV), carbon singly bonded to oxygen ($\underline{\text{C}}\text{-OR}$ at 286.5 eV), carbon doubly bonded to oxygen ($\underline{\text{C}}\text{=O}$ at 287.9 eV) and anhydride groups/carboxylic acid/ester groups ($\text{O}=\underline{\text{C}}\text{-O-}\underline{\text{C}}\text{=O/O-}\underline{\text{C}}\text{=O}$ at 289.5 eV) (see Figure S6 in Supporting Information).

Figure 3 shows the relative areas of three relevant peaks for samples fabricated in the different growth regimes and at different positions: the $\text{O}=\underline{\text{C}}\text{-O-}\underline{\text{C}}\text{=O/O-}\underline{\text{C}}\text{=O}$ peak representative of anhydride, carboxylic and ester groups and the $\underline{\text{C}}\text{-C}$, $\underline{\text{C}}\text{H}_x$ or $\underline{\text{C}}\text{-OR}$ peak representative of

328 monomer fragmentation. As expected, moving from regime I to III leads to the decrease in the
329 concentration of anhydride, carboxylic and ester groups, especially from the regime I to II, and
330 an increase in the concentration of C-OR related to the creation of new types of oxygenated
331 functionalities due to high fragmentation degree of the precursor. It should be noted that the
332 possible ring opening of the anhydride to form the acid is not visible by XPS since the binding
333 energies of the two carbons are the same. The increase in the hydrocarbon group content from
334 regime I to II indicates a probable rise in the crosslinking of the plasma polymer matrix when
335 the energy input increases. The drop in this relative area in the third regime could be explained
336 by the presence of many residual free radicals on the surface at the end of the polymerization,
337 which can instantly react with atmospheric oxygen when the samples were recovered.

Figure 3. Relative areas of different functionalities present in the high resolution C1s peak (measured by XPS) for maleic anhydride plasma polymer prepared in various growth regimes at different positions (error bars correspond to the standard deviation).

Moreover, the inhibition of the polymerization occurred due to the production of oxygen-rich plasma species coming from monomer fragmentation at high energies, in accordance with the high oxygen content for the samples obtained in this regime (Figure 4). In fact, the stoichiometric ratio calculated from the wide scan XPS spectra increases from $O/C = 0.25$ to 0.43 from regime II to III, i.e. with increasing energy input.

Figure 4. O/C stoichiometric ratios in maleic anhydride plasma polymer determined by wide scan XPS analyses in the different growth regimes at various positions (error bars correspond to the standard deviation).

To complete these XPS results, ATR FTIR analyses were performed on the plasma polymers prepared in the three regimes and the three positions. In accordance with the literature, the characteristic vibration bands of maleic anhydride plasma polymer were identified: asymmetric C=O stretching (1860 cm^{-1}), symmetric C=O stretching (1780 cm^{-1}), cyclic conjugated anhydride group stretching ($1230\text{ cm}^{-1} - 1170\text{ cm}^{-1}$), C-O-C stretching ($1082\text{ cm}^{-1} - 1061\text{ cm}^{-1}$) and cyclic unconjugated anhydride group stretching ($923\text{ cm}^{-1} - 908\text{ cm}^{-1}$).^[24,31] In addition, the formation of carboxylic acid groups due to cyclic anhydride ring opening for some operating conditions induces a peak at 1730 cm^{-1} (C=O stretching). The evaluation of the fragmentation rate of anhydride groups has been performed by calculating the intensity ratio between the intensity of the peak of C=O stretching originating from carboxylic acid groups (I_{acid} , at 1730 cm^{-1}) and the intensity of the peak of symmetric C=O stretching coming from anhydride groups (I_{anh} , at 1780 cm^{-1}) (all relevant information can be found in Supporting Information, Figure S7). However, it should be noted that this ratio is not an absolute value but a relative one since no internal reference has been used to calculate this ratio. Figure 5 summarizes the results of these calculations since it depicts the evolution of the ratio $I_{\text{acid}}/I_{\text{anh}}$ for the different regimes for each reactor zone.

Figure 5. Evolution of the ratio between the intensity of the peak at 1730 cm^{-1} and the intensity of the peak at 1780 cm^{-1} ($I_{\text{acid}}/I_{\text{anh}}$) measured by ATR FTIR for maleic anhydride plasma polymer synthesized in various growth regimes in the three reactor zones (P1, P3 and P5) (Error bars correspond to the standard deviation).

Whatever the position is, no difference is observed between the different samples prepared in the regimes I and II, indicating position-independent film growth mechanisms. Therefore, despite a difference in term of analysis thickness between XPS and ATR FTIR, one can consider that going from regime I to II entails a lack of anhydride (and corresponding acid) groups within the plasma polymer, namely a higher precursor fragmentation. Indeed, the XPS analyses showed that there were less anhydride (and corresponding acid/ester) groups in the regime II in comparison to the first regime, while no difference appeared in the ratio $I_{\text{acid}}/I_{\text{anh}}$ by ATR FTIR. On the contrary, significant differences in anhydride versus acid content can be observed for the samples prepared in the third regime (at high specific energy) for the three positions. $I_{\text{acid}}/I_{\text{anh}}$ ratios were much higher than the ones calculated in the other regimes, especially for P5. Regarding the influence of the position, more acid formation occurred when the sample was prepared in the discharge zone and even more in the post-discharge zone compared to the pre-discharge zone. This result may originate from higher fragmentation of the precursor along the precursor flow within the reactor.

To try to summarize and interpret the results provided by the Arrhenius-type plots describing the polymer growth kinetics as well as the surface characterizations by XPS and FTIR, three growth regimes can be observed when the specific energy increases:

i) A first regime is identified at low specific energy, where the energy provided to the precursor is limited and enables a low fragmentation of the monomer, whatever the position is. In this regime, it also seems that the energy provided by the generator is not fully transmitted to the precursor vapor according to the location in the reactor. Indeed, different activation energies were calculated depending on the position whereas the surface chemistry was similar. The existence of an experimental factor (S_{exp}) which probably takes into account power losses, the spatial dimensions of the reactor and of the plasma may explain these results, as previously reported by Hegemann et al.^[1,43,44] We can thus presume that the calculated activation energy $E_{a(measured)}$ is a result of the multiplication of the real activation energy $E_{a(real)}$ by an experimental factor S_{exp} as shown in Equation 3.

$$E_{a(measured)} = E_{a(real)} \times S_{exp} \quad (3)$$

The complexity of maleic anhydride plasma polymerization as well as other factors, that will be discussed later, make the determination of this experimental factor very difficult, which, however, should enable a $E_{a(real)}$ in accordance with a partial fragmentation of the monomer (see section 3.3). Anyhow, at this level of specific energy, the experimental factor seems to depend highly on the geometrical characteristics of the reactor and the plasma discharge, which leads to different $E_{a(measured)}$ values depending on the position in the reactor. It can be also noted that the activation energies obtained at P1 and P5 are very close and can reflect probably the presence of a symmetric plasma discharge within the reactor, P3 being a central position with respect to specific energies as used in regime I.

ii) A second regime at moderate specific energy is observed, where activation energies are higher, which is in accordance with more fragmentation of the precursor, as revealed by XPS analyses. The activation energy values again appear to be too high supporting the presence of the discussed experimental factor. However, in this regime, similar values of activation energy and similar surface chemistries, whatever the position is, suggest a film growth rate irrespective of a geometrical parameter, probably due to a uniform plasma expansion ranging to both sides, i.e. P1 and P5. Therefore, the experimental factor S_{exp} seems to be dependent on geometrical parameters mostly at low specific energy but also on the input power, which seems to prevail here. Indeed, reaching a certain value of input power, the distance of the sample from the plasma discharge, at least close to the plasma glow discharge, does not seem to influence much the chemical nature of the plasma species and thus leads to a constant value of the activation energy whatever the position. The existence of this energy threshold from which the experimental factor becomes independent of geometrical parameters will be confirmed later.

iii) Finally, a third regime of plasma polymer growth can be identified at high specific energy, where fragmentation of the precursor and/or simultaneous degradation of the growing polymer occurs (more C-OR groups in XPS spectra, more acid formation observed in ATR FTIR spectra). In this regime, the influence of the position of the sample within the reactor is no longer negligible, according to FTIR analyses. Therefore, it is not meaningful to discuss the activation energies, especially for the P3 and P5 positions. In fact, a complex polymer growth mechanism occurred, with a competition of plasma polymerization and degradation of the precursor and the growing plasma polymer.

3.3 Characterization of the plasma phase produced during plasma polymerization of maleic anhydride using optical emission spectroscopy

432 In order to validate the previous conclusions made based on the kinetics study and the
433 characterization of maleic anhydride plasma polymer synthesized in various operating
434 conditions, the analysis of the chemical composition of the plasma phase at different reactor
435 zones and for different deposition conditions was performed by Optical Emission Spectroscopy
436 (OES). In this study, a qualitative analysis of the plasma phase was carried out to identify
437 relevant bands present in the obtained spectra in order to try to correlate the properties of plasma
438 polymer thin films with the presence of specific species in the plasma phase. All spectra
439 correspond to plasma species emitting in a spectral range from 200 nm to 800 nm obtained
440 during plasma polymerization of maleic anhydride. As shown in Figure 6, OES showed that the
441 plasma phase mainly contains CO species but also CH species and atomic hydrogen (H α).
442 According to the literature,^[45–47] the following systems have been identified within the range of
443 the wavelengths considered in this work: the 4th Positive System CO ($A^1\Pi \rightarrow \Sigma^1X^+$) and the
444 1st Negative System CO⁺ ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) between 200 nm and 260 nm, whose lines intensities
445 were very weak. The most intensive emission lines correspond to the 3rd Positive and 5B
446 Systems of CO ($b^3\Sigma^+ \rightarrow a^3\Pi$, from 260 to 350 nm) as well as the Angström System CO ($B^1\Sigma^+$
447 $\rightarrow A^1\Pi$ from 400 to 570 nm). More details about the lines identification are given in Table S2
448 in Supporting Information. By comparing the spectra obtained at different polymerization times,
449 specific energies and positions in the reactor, no new line was observed by changing the
450 operating conditions, only the intensities of the peaks were slightly changing (see Figure S8 in
451 Supporting Information). The emitting species were thus the same but their relative content
452 slightly changed from one condition to the other. It can also be noted that a steady state was
453 reached in less than 20 s, since no difference was observed between spectra recorded at various
454 polymerization times. Lines corresponding to atomic elements such as atomic carbon eg. C(I)
455 at 247.9 nm,^[48] ionic carbon C(II) at 251.2 nm, 392.0 nm, 426.7 nm^[48,49] or atomic oxygen eg.

456 O (I) at 777.0 nm^[50] were not visible, which indicates that the total fragmentation of the
457 monomer was not achieved in the studied operating conditions. This result is noteworthy since
458 very high activation energies were calculated (based on generator power values) by the
459 macroscopic approach used to describe the growth rate of the plasma polymer as a function of
460 the specific energy. Hence, the OES results also support the existence of an experimental factor
461 (S_{exp}) in the calculation of apparent activation energies, as described before. Additional analyses
462 are still necessary to fully interpret OES spectra and relate them to a precise polymerization
463 mechanism.

464 Moreover, it is known that inductively coupled plasma (ICP) is subject to a mode transition
465 between capacitively coupled or electrostatic mode (called E mode) and inductively coupled or
466 electromagnetic mode (called H mode) to sustain the plasma discharge.⁵¹ This E→H mode
467 transition occurs above a certain threshold value of input RF power when a sudden jump in the
468 electron density and light emission is observed.⁵² In order to illustrate this mode transition, the
469 intensities of argon lines observed in OES spectra at 738.3, 750.4, 751.5 and 811.5 nm (Figure
470 6) were used here as a probe of the density of atoms in a metastable state.⁵³ The evolution of
471 the Ar line intensity at 738.3 nm as a function of the inverse specific energy (Figure S9 in
472 Supporting Information) for the three reactor zones shows a transition point from E to H mode
473 at the beginning of the second regime. This critical value of $1/(W/F)$ can be estimated around
474 $1.3 \cdot 10^{-2} [J \text{ cm}^{-3}]^{-1}$. When specific energy increases beyond this critical value, or energy
475 threshold, (from the right to the left in Figure S9), the electron density n_e is enhanced, but no
476 significant jump in the deposition rate is observed and the deposition rates even become very
477 similar whatever the reactor zone. The E→H transition is typically accompanied by a drastic
478 change in the electron energy distribution function (*eedf*), that is, an increase in n_e and a
479 decrease in electron temperature T_e .^[54] Hence, the apparent low dependency of deposition rates

on changes in $eedf$ in this regime corroborates the used macroscopic approach indicating that the specific energy delivered per monomer molecule is indeed a key factor in plasma polymerization. Conditions might apply, where the plasma expands rather uniformly to positions P1 and P5 at sufficiently high T_e resulting in the observed comparable activation energies and geometrical factors G (in Equation 2).^[5] Lower plasma expansion in regime I (E mode), on the contrary, requires that different S_{exp} values (in Equation 3) need to be applied for the different positions.

Figure 6. Optical emission spectrum of maleic anhydride during plasma polymerization in regime II, in the discharge zone (P3)

4 Conclusions

Pulsed plasma polymerization of maleic anhydride has been investigated in an original 1 m long RF plasma reactor, operating at low pressure. By using a macroscopic approach to describe film growth kinetics as a function of the specific energy provided to the precursor by the plasma, we were able to identify different growth regimes during plasma polymerization of maleic anhydride. The apparent activation energies were derived corresponding to each regime for the

different reactor zones (pre-discharge, discharge, post-discharge): (i) a first regime at low input energy was observed. In this regime, the calculated activation energy is a result of the multiplication of the real activation energy by an experimental factor (S_{exp}) taking account of (undetermined) power losses and plasma expansion. The existence of this experimental factor (S_{exp}) is consistent with the low fragmentation of the precursor as observed in XPS and ATR FTIR spectra. Noteworthy, S_{exp} is strongly dependent on geometrical parameters of the reactor and the plasma discharge since different activation energy values were determined depending on the position in the reactor; (ii) a second regime at moderate specific energy corresponds to higher activation energies and stronger precursor fragmentation during deposition. Herein, the experimental factor (S_{exp}) still exists but no longer depends on the examined positions, probably due to a transition from E to H mode as identified by OES; (iii) a last regime was obtained at high specific energy, where different polymer chemistries and different growth behaviors were observed depending on the position. Deposition rates were found to decrease along the gas flow in the reactor. A complex growth mechanism including polymer deposition, particles formation but also etching was likely to take place. As a conclusion, this study in an original reactor allowed us to gain insights into the kinetics of plasma polymerization of maleic anhydride by combining a temporal control of the polymerization, using the pulsed mode, and a spatial control of the polymerization, exploiting the unique configuration of the 1 m long reactor. This evidence of a possible spatio-temporal control of plasma polymerization paves the way to get further understanding of complex polymer deposition that may be observed when functional polymer coatings with diverse surface properties are fabricated according to their location in the plasma discharge.

Acknowledgments

The authors are grateful for the financial supports provided by the Institut Carnot MICA and the ANRT (Grant n° 2017/0966). They also would like to thank Philippe Fioux and Simon Gree for their help with surface characterizations and access to the XPS and IR spectroscopy platforms. This manuscript is in honor of the 50 year anniversary of the French Polymer Group (Groupe Français des Polymères - GFP).

Received: ((will be filled in by the editorial staff)); Revised: ((will be filled in by the editorial staff)); Published online: ((please add journal code and manuscript number, e.g., DOI: 10.1002/ppap.201100001))

Keywords: Activation energy; Macroscopic approach; Maleic Anhydride; OES; PECVD

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