

Pulsed plasma initiated chemical vapor deposition (PiCVD) of polymer layers – A kinetic model for the description of gas phase to surface interactions in pulsed plasma discharges

François Loyer^{ID} | Simon Bulou^{ID} | Patrick Choquet^{ID} | Nicolas D. Boscher^{ID}

Luxembourg Institute of Science and Technology, Materials Research and Technology, 5 Avenue des Hauts-Fourneaux, Esch/Alzette L-4362, Luxembourg

Correspondence

Nicolas D. Boscher, Luxembourg Institute of Science and Technology, Materials Research and Technology, 5 Avenue des Hauts-Fourneaux, Esch/Alzette, L-4362 Luxembourg.
 Email: nicolas.boscher@list.lu

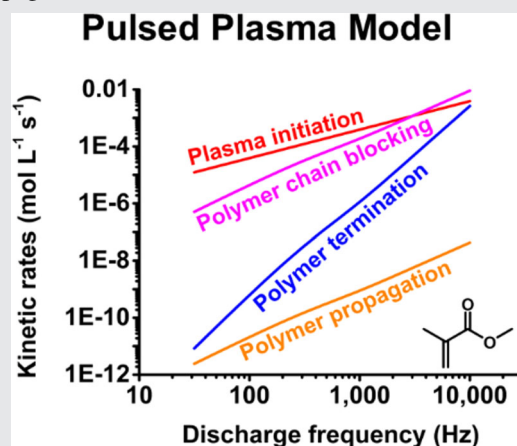
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A new kinetic model for studying the growth mechanisms in ultra-short square pulsed atmospheric-pressure dielectric barrier discharges (AP-DBD) is presented. Interpretation of the deposition rates yields information on the dominant mechanisms along each pulse cycle (i.e., initiation, propagation, chain-transfer, and termination). Further investigations extracted important parameters for the understanding of free-radical kinetics in the plasma deposition processes. Based on the thin films' chemistry, topography, polymeric length and growth rates, the chemical and physical meaning of the calculated parameters and their impacts on the thin films' polymeric structure are discussed.

KEYWORDS

atmospheric-plasma CVD, conventional polymerization, kinetic model, polymerization mechanisms, pulsed plasma



1 | INTRODUCTION

The combination of long plasma off-time (i.e., up to hundreds of milliseconds) together with ultra-short (i.e., tens to hundreds of nanoseconds) plasma pulses are known to efficiently initiate the free-radical polymerization of vinyl monomers while greatly reducing the detrimental plasma

fragmentation.^[1–3] High-resolution mass spectrometry (HRMS) evidenced that the ultra-short plasma pulses cleave a small number of the vinyl monomer units into defined radical and neutral fragments that are able to either initiate or terminate the polymerization.^[4] Subsequently, part of the formed radicals and the vinyl monomers diffuse and adsorb from the vapor phase onto the surface where the free-radical

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polymerization occurs.^[1] As a result, thin films with an unprecedented degree of polymerization for plasma-enhanced chemical vapor deposition (PECVD) processes are synthesized.^[1] Moreover, unlike the current CVD approaches for the growth of conventional polymer coatings such as initiated chemical vapor deposition (iCVD),^[5–9] the use of temporally isolated plasma discharges does not imply to operate under vacuum, nor does imply additional chemical reactants.^[1–3] This process called atmospheric-pressure plasma-initiated chemical vapor deposition (AP-PiCVD) allowed the simultaneous atmospheric-pressure synthesis and deposition of true homopolymer layers^[4] such as poly(diethylallylphosphate)^[3] and poly(glycidyl methacrylate).^[10] The chemical and physical properties of the thin films grown using ultra-short plasma pulses result from a competition between conventional polymerization reactions (initiation, propagation, and termination) and plasma-polymerization reactions (fragmentation and recombination).^[1,2] Such competition is notably expressed by the switch from oxygen integration at low plasma discharges frequencies to the oxygen fragmentation and carbon integration when the frequency of plasma pulses increases.^[4] This transition is accompanied by variations in the morphology of the produced thin films, as a result of a shift from predominant gas phase mechanisms to predominant surface mechanisms.^[1] The prevalence of those proposed reaction pathways is governed by the plasma discharge conditions and gas phase composition. In particular, previous works highlighted that the kinetics of AP-PiCVD are strongly related to the repetition frequency of the ultra-short plasma pulses.^[1,2] The present work aims at providing a model to describe and understand the AP-PiCVD kinetic data. Since the polymerization does not take place under steady-state conditions in AP-PiCVD, a new model called the pulsed plasma method (PPM) is proposed. Unlike other models describing the kinetic of plasma polymerization,^[11–17] the PPM model integrates the non-steady plasma initiation, the polymerization propagation and termination, as well as chain transfer events, allowing an extraction and comparison of the kinetic parameters highlighting the key mechanisms undergone by the monomer under pulsed plasma discharges. Moreover, evidence from the PPM model provides chemical and physical descriptions for previously reported frequency-dependent transitions in AP-PiCVD and the dominant mechanisms for different deposition conditions.

2 | EXPERIMENTAL

2.1 | Plasma-initiated chemical vapor deposition

The thin films displayed in this study were deposited using an atmospheric-pressure dielectric barrier discharge (AP-DBD) setup as previously described (Figure S1).^[18] Ultra-short

TABLE 1 Intrinsic properties of MMA and GMA

Properties	MMA	GMA
MW_M ($\text{g} \cdot \text{mol}^{-1}$)	100.121	142.155
P_{sat} (bar)	0.039	0.0008
$\rho_{\text{vap},M}$ ($\text{g} \cdot \text{L}^{-1}$)	4.464	6.249
$\rho_{\text{poly},M}$ ($\text{g} \cdot \text{L}^{-1}$)	1180	1070
$k_{p,20^\circ\text{C}}$ ($\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	274 ^[19]	494 ^[20]
$k_{p,50^\circ\text{C}}$ ($\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	642 ^[19]	1220 ^[20]

MW_M being the monomer's molecular weight, P_{sat} the monomer's vapor pressure, $\rho_{\text{vap},M}$ the monomer's vapor density, $\rho_{\text{poly},M}$ the conventional polymer's density, and k_p the polymerization propagation rate.

($t_{\text{on}} \approx 100$ ns) and perfectly reproducible plasma discharges were generated by 15 μs square pulses of 6.5 kV using an AHTPB10F generator from Effitech (Figure S2). For every experiment, the discharge gap was maintained at 1 mm and all generator's input parameters were kept identical except for the pulse repetition frequency ranging from 31.6 to 10 000 Hz (i.e., $t_{\text{off}} = 31.6$ to 0.1 ms). Methyl methacrylate (MMA, Sigma–Aldrich 99%) and glycidyl methacrylate (GMA, Sigma–Aldrich 97%) were selected as monomers due to their intrinsic properties (Table 1) yielding to different thin film grown in AP-PiCVD (Figure 1),^[1,4] despite being both methacrylate compounds. The two monomers were used as-supplied and were directly carried to the deposition area using a bubbler setup with argon (Air Liquid 99.998%) as a carrier gas. The carrier gas flow was set to 0.3 and 25.7 $\text{L} \cdot \text{min}^{-1}$ for MMA and GMA, respectively. The total gas flow was completed with argon to 20.0 and 30.0 $\text{L} \cdot \text{min}^{-1}$ for MMA and GMA cases, respectively. These conditions correspond to molar flow rates of 0.44 and 0.49 $\text{mmol} \cdot \text{min}^{-1}$ for the MMA and GMA monomers, respectively. To avoid oxygen and nitrogen contamination from atmosphere, “argon curtains” were added on both sides of the electrodes in order to minimize external gas contaminations. All depositions were carried on polished 4 silicon wafers (Siltronix), which were cleaned using a 95%/5% argon/oxygen plasma for 40 s prior to each experiment.

2.2 | Thin film characterization

Both top-view and cross-section SEM imaging and thickness measurements were carried out on a Hitachi SU-70 FE-SEM (Tokyo, Japan). The samples were coated with a 5 nm platinum coating prior to the measurements in order to avoid charge effects. The thicknesses and deposition rates were determined by a KLA-Tencor P-17 Stylus profiler (Milpitas, CA, USA).

2.3 | Polymer characterization

The polymers chain growth was determined by size exclusion chromatography (SEC) using a Thermo Scientific (Sunnyvale, CA, USA) Dionex UltiMate 3000 LC system. Each

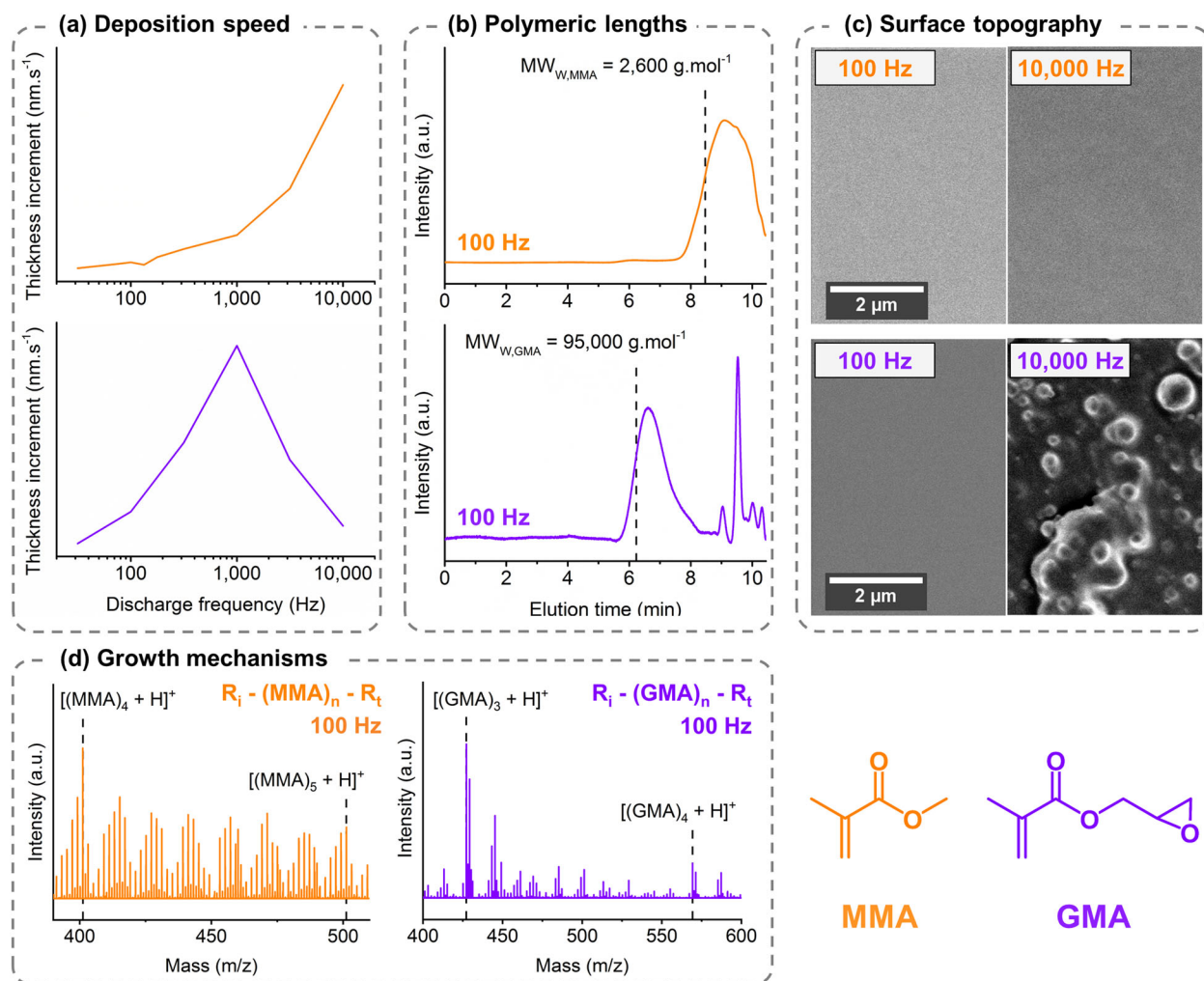


FIGURE 1 Summary of previous experimental data for MMA and GMA-based thin films grown by AP-PiCVD on which the present kinetic study relies on, namely (a) the deposition rate according to the discharge frequency,^[1] (b) the size distribution by size exclusion chromatography (SEC) of thin films grown at 100 Hz,^[1] (c) the surface topography by scanning electron microscopy (SEM) of the thin films grown at 100 and 10 000 Hz,^[1] and (d) the matrix-assisted laser desorption/ionization high-resolution mass spectra (MALDI-HRMS) of the thin films grown at 100 Hz^[4]

measurement corresponds to the soluble fraction of the polymer in THF and not necessarily the entire distribution. The elution times were translated into molecular weights using polystyrene standards ranging from 162 to 364 000 g·mol⁻¹ (Agilent EasiVial PS-M). Matrix-assisted laser desorption/ionization high-resolution mass spectrometry (MALDI-HRMS) measurements were performed on an AP MALDI PDF+ ion source from MassTech Inc. coupled to an LTQ/Orbitrap Elite from Thermo Scientific. Dithranol diluted in THF was selected as the matrix due to its known efficiency for the ionization of PMMA^[21] and methacrylate-based plasma-polymers.^[2] A 0.1 µL of the matrix was then spotted on the thin films to form a co-crystal with the soluble part of the thin film when the THF evaporated.

2.4 | Plasma characterization

Both the ultra-short square-wave high-voltage pulse from Effitech's generator and the current of discharge were

investigated using a Teledyne Lecroy HDO4054A oscilloscope together with Teledyne Lecroy PPE 20 kV high voltage probe and Teledyne Lecroy CP030 current probe respectively. The argon species activated from the plasma discharge were monitored using time-resolved optical emission spectroscopy (TR-OES) using a Princeton Instruments Acton SP2750 spectrometer equipped with a Pi-Max 3 i-CCD. A grating of 150 lines mm⁻¹ blazed at 300 nm was used. TR-OES was achieved on Ar I line at 751.46 nm in order to assess that excited plasma species are only produced during rising and falling time of the square-wave high voltage pulses.^[22,23]

2.5 | Experimental data

The present kinetic study relies on previously reported data highlighting the different behaviors of two series of methacrylate-based thin films deposited by AP-PiCVD.^[1,4] Notably, the deposition rate as a function of the plasma

discharge frequency displays maxima that are dependent on the investigated monomer (i.e., MMA or GMA) (Figure 1a). In the case of GMA, increasing the frequency ultimately leads to a drop of the deposition rate due to excessive fragmentation and depletion of the monomer. On the other hand, lowering the frequency below this transition induces a drop of the deposition rate due to a lack of polymerization initiating species. Such a competition between gas-phase and surface reactions are illustrated by strong changes in the thin films' topography (Figure 1c).^[1] More particularly, in spite of a similar deposition rates, the GMA-based thin films elaborated at 100 and 10 000 Hz exhibit smooth and highly granular morphologies, respectively.^[1] High-resolution mass spectrometry (HRMS) analyses allowed for a global description of the growth mechanisms while employing ultra-short plasma pulses, elucidating the free-radical polymerization initiation and the numerous side-mechanisms that eventually become predominant for very high frequencies (Figure 1d).^[4] The competition between these growth mechanisms also correlated with the strong disparity in average molecular weights between MMA and GMA-based thin film (Figure 1b).^[1] Indeed, MMA is shown to be highly sensitive to plasma fragmentation leading to chain-blocking fragments and consequently yielding low molecular weights, while GMA is protected by the weak epoxy bond preventing a molecular cleavage hence yielding higher molecular weights. In this work, the deposition rate as a function of the plasma discharge frequency (Figure 1a) and the different mechanisms elucidated in our previous works^[1,4] are considered for the description of the growth mechanisms and determination of the kinetic parameters.

3 | RESULTS AND DISCUSSION

3.1 | Model development

Such as depicted in Figure 2, the proposed mechanisms for the AP-PiCVD polymerization start with the monomer's ($M_{(g)}$) homolytic activation by the ultra-short plasma pulses leading to either (i) the creation of radical monomer species ($M\bullet_{(g)}$) out of the vinyl's π -bond opening or (ii) the statistical cleavage of the whole molecule forming radical fragments ($X\bullet_{(g)}$),^[4,24] resulting from low energy (ca. $\epsilon_{(i)} \geq 2$ eV)^[25] and high energy (ca. $\epsilon_{(ii)} \geq 4$ eV)^[26] electronic interactions. Subsequently, the primary radicals ($M\bullet_{(g)}$ and $X\bullet_{(g)}$) may either (iii) recombine ($M_{(g)}$ or $X_{(g)}$) or (iv) diffuse to the surface where they are adsorbed ($M\bullet_{(ad)}$ and $X\bullet_{(ad)}$) allowing (v) the polymerization to propagate freely. Additionally, neutral fragments ($X_{(ad)}$, and contributions from the atmosphere) may also interact during the polymeric growth by chain transfer reactions (vi), consequently ending the growing chain by an X_j termination and producing a free-radical $X_{jj}\bullet$. In an opposite manner, the fragmented radical species ($X\bullet$ and $X_{jj}\bullet$) are also able to activate a monomer or polymer chain (vi) by abstraction of an atom or

group of atoms. Finally, the polymerization may also be conventionally terminated by disproportionation or coupling reactions with primary radicals or other growing chains (vii).

In light of the proposed mechanisms (Figure 2) and of the specific limitations arising from AP-DBD systems, the common methods used to solve the free-radical polymerization's kinetics cannot be applied to the AP-PiCVD process, as its overall setup and layer's growth mechanisms differ from wet chemistry or iCVD methods (Table 2). Notably, the generation of reactive species in a partially passivated open air system implies a different knowledge of the initial parameters such as the monomer concentration [$M_{(g)}$], the concentration of radical species [$M\bullet_{(g)}$] over time, the amount of radical species participating to the polymerization reaction [$M\bullet_{(g)}$]_{reacted}/[$M\bullet_{(g)}$]_{created}, the propagation rate and the actual reaction volume. Consequently, the polymerization mechanisms need to be adapted to the medium, especially to take into account the chain transfer reactions which usually maintain the global concentration of radicals in closed systems, have to be reconsidered. Indeed, within AP-PiCVD's continuously renewed gas phase, the number of reacted transfer agents $X_{jj}\bullet$ – from neutral fragmented X reacting by chain transfer with free-radicals – that would be able to participate in the polymerization a second time can be considered as statistically low unless they are already adsorbed on the surface. As such, chain transfer mechanisms must be treated as a termination process resulting from the plasma fragmentation, therefore lowering the effective concentration of free-radicals as well as blocking the chains' terminal reactive ends in the operation. Moreover, due to their comparable reactivity and the lack of information on the plasma-dependent kinetic rate of fragmentation R_f , $M\bullet$, and $X\bullet$ cannot be individually discerned from each other and will be considered as a unique radical concentration [$M\bullet$] resulting from the initiation mechanism, R_i . Specifically, while the ratio of fragmented reactive species $X\bullet$ compared to the conventional free-radicals $M\bullet$ would not change the initiation mechanisms, they would strongly affect the molecular chain length through non-propagating termination potentially inducing cross-linking phenomena, and therefore will be monitored through the chain transfer mechanisms. Finally, the use of ultra-short plasma pulses prevent the application of the well-known steady-state approximation (i.e., $d[M\bullet]/dt = 0$ at any time, or $R_i = R_t$)^[27] since the concentration of radicals cannot be considered constant during each plasma pulse unlike low-pressure iCVD processes or conventional wet chemistry approaches.

3.2 | Pulsed plasma method – Mathematical model for non-steady-state conditions

Some AP-PiCVD parameters such as the constant concentration of monomer in the gas phase [$M_{(g)}$] can easily be calculated (Eq. S1) using the monomers' intrinsic properties

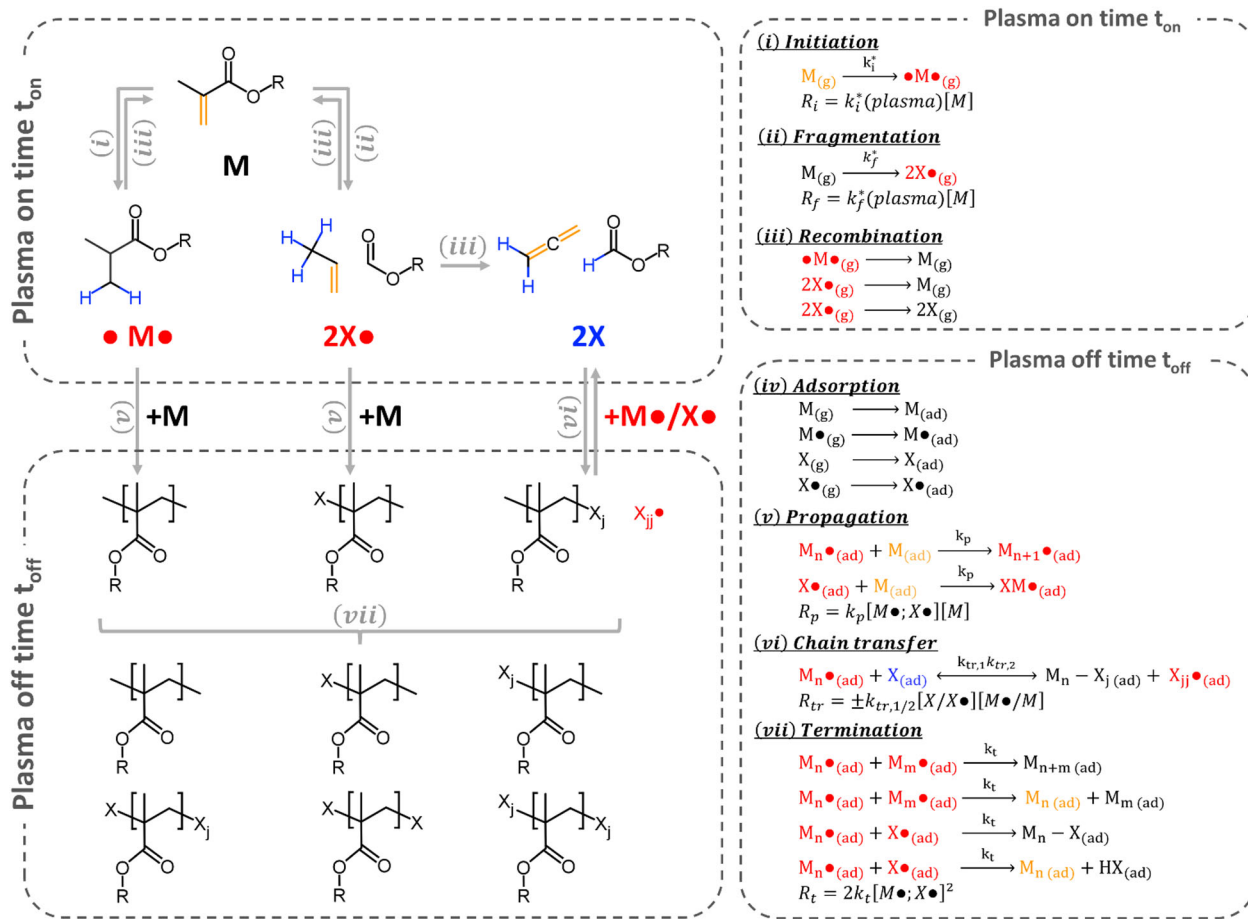


FIGURE 2 Example of the possible species resulting from the interactions between the plasma reactive species and the methacrylates ($R = CH_3$ and $CH_2-CH(O)CH$ for MMA and GMA, respectively). The global reactions and the kinetic rate equations are provided, with the significant chemical functions for the considered polymerization mechanism(s) associated to a color. Namely, the vinyl's initiation in yellow, the free-radical polymerization in red and the neutral species (from recombined fragments or the atmosphere) in blue

(Table 1) – such as its saturation pressure P_{sat} , its molecular weight MW_M and its vapor density $\rho_{vap,M}$ – and the deposition parameters (Eq. 1) – such as the flux of carrier gas $F_{carrier}$, the total flux F_{tot} , the total pressure P_{tot} , the temperature T , and the gas constant R . Still, a new mathematical model is required to address the non-steady-state kinetic of open volume pulsed plasmas (Figure S2).

$$[M] = \frac{P_{tot} P_{sat} F_{carrier} MW_M}{F_{tot} R^2 T^2 \rho_{vap,M}} \quad (1)$$

The model developed in the present work, called pulsed plasma method (PPM), is based on the same principle as the traditional non-steady models – rotating sector method (RSM)^[28–30] and pulsed-laser polymerization (PLP)^[31–33] – using light pulse energy sources with various illumination times (t_{on}) and dark times (t_{off}) (Figure 3a). Unlike the more recent PLP model which requires low and highly resolved energy outputs,^[27] the RSM model only needs the experimental growth parameters (Table 3) to mathematically describe the free-radicals' concentration in non-steady

kinetics. Therefore, adapting the RSM equations to our ultra-short plasma on time ($t_{on} \approx 100$ ns) and adaptable plasma off-times ($t_{off} = 31.6$ – 0.1 ms) constructed the basis for the PPM model, allowing further data extraction of the kinetic parameters defining the surface/gas phase mechanisms of pulsed plasma polymerization.

In the traditional RSM approach, one would simply plot the ratio between the propagation rate R_p and the propagation rate in steady-state conditions $R_{p,s}$ (i.e., under constant illumination, $DC_s = 1$), versus the logarithm of the on-time $\log_{10}(t_{on})$ (Eq. 2). Comparing the shift between the experimental plot and the model plot it is possible to estimate $\log_{10}(\tau_s)$ and, subsequently, the kinetic ratio k_p/k_t (Eq. 3).^[27]

$$\frac{R_p}{R_{p,s}} = \frac{[M \bullet]_s}{[M \bullet]_s} = DC \left[1 + \frac{\tau_{qs}}{t_{on}} \ln \left(\frac{[M \bullet]_{max}/[M \bullet]_{min} + [M \bullet]_{max}/[M \bullet]_s}{1 + [M \bullet]_{max}/[M \bullet]_s} \right) \right] \quad (2)$$

$$\tau_s = \frac{[M \bullet]_s}{R_t} = \frac{k_p[M]}{k_t R_{p,s}} \quad (3)$$

TABLE 2 Comparison between different free-radical polymerization approaches (i.e., wet chemistry, iCVD, and AP-PiCVD) based on the system initial informations and the resulting kinetic equations

Parameters	Wet chemistry	iCVD	AP-PiCVD
$[M]$	Initially known, decrease over polymerization	Constant flux of monomer	Constant flux of monomer
$[M\bullet]$	Controlled through the amount of initiator $[I]$ and the polymerization conditions	Constant flux of initiator $[I]$ activated by hot filaments	Renewed in a constant uncontrolled amount with each discharge, mixed with side-species from fragmentation
$[M\bullet]_{\text{reacted}}/[M\bullet]_{\text{created}}$	Almost all of the radical initiators react	Unknown number of radicals initiators react	Unknown number of radicals initiators react
Medium volume	Known closed volume	Closed chamber under renewed vacuum	Open air volume with gradients of reactivity partially passivated by argon barriers
Initiation	$R_i = k_i [I] = k_t [M\bullet]^2$	$R_i = k_i [I] = k_t [M\bullet]^2$	$R_i^* = k_i^* (\text{plasma}) [M_{(g)}]$
Propagation	$R_p = k_p [M][M\bullet]$	$R_p = k_p [M][M\bullet]$	$R_p = k_p [M_{(g)}][M_{(g)}\bullet]$
Chain transfer	$R_{tr} = k_{tr} [X][M\bullet]$	$R_{tr} = k_{tr} [X][M\bullet]$	$R_{tr} = \pm k_{tr} [X/X\bullet][M\bullet/M]$
Termination	$R_t = k_t [M\bullet]^2 = k_i [I]$	$R_t = k_t [M\bullet]^2 = k_i [I]$	$R_t = k_t [M_{(g)}\bullet]^2$
Fragmentation	–	–	$R_f^* = k_f^* (\text{plasma}) [M_{(g)}]$

The plasma-induced initiation R_i^* and fragmentation R_f^* equations are developed for the sake of coherence, however, their plasma-kinetic constants (i.e., k_i^* and k_f^*) will not be addressed in this kinetic study.

Unfortunately, this convenient determination of τ_s cannot be applied to our AP-PiCVD approach, since the RSM model requires the on-time (t_{on}) to be an independent variable and the off-time (t_{off}) a constant (Figure 3b), compelling a complete fitting of the function. Additionally, the RSM model is based on the experimental measurement of a steady-state mode (i.e., $\text{DC}_s = 1$), which is intrinsically incompatible with an AP-DBD set-up since the electrons need to accumulate on the surface before reaching a breakdown potential to generate the discharge. In order to be as close as possible to the steady-

state, one can work a sine wave plasma ignition source to determine the deposition rate that would correspond to quasi-steady-state conditions, denoted as “qs” further in the text. Simple electrical measurements give the ratio between the plasma on and off-times (i.e., the DC_{qs}), ca. 50% in the present case (Figure 3c). The average ratio of radical conversion $[M\bullet]/[M\bullet]_{\text{qs}}$ requires pre-calculations of its inner terms to fit this function with our plasma off-time-dependent experimental data. Notably, solving the RSM equations (Eq. S2) as linear systems with two variables (Eq. S3), the

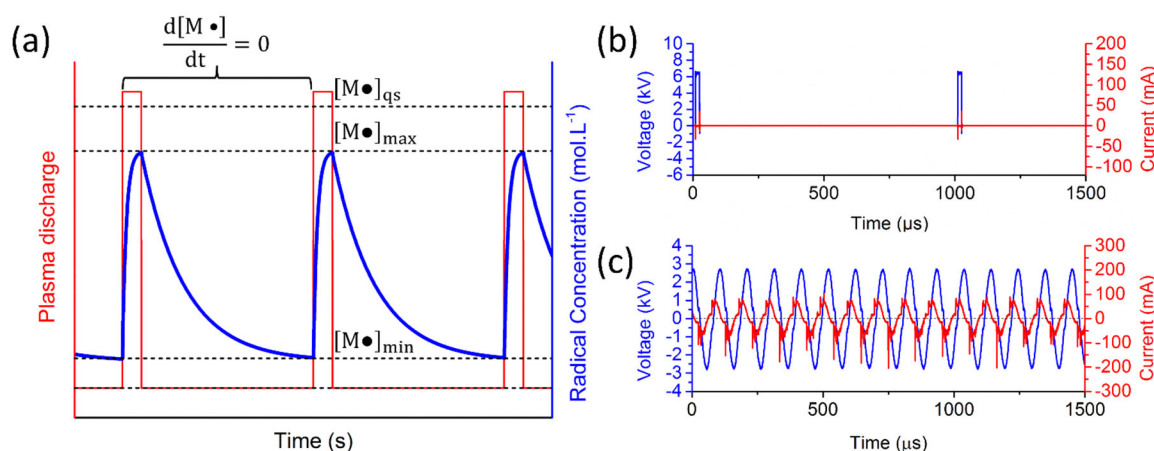
**FIGURE 3** (a) Scheme of the approximated square-wave plasma discharge displaying the radicals concentrations following the plasma discharge over time, for the sake of the discussion the two current discharges (Figure S2) are approximated as a single one. Both the calculated initiated $[M\bullet]_{\text{max}}$ and the remaining $[M\bullet]_{\text{min}}$ radical concentration are displayed as well as the radical concentration $[M\bullet]_{\text{qs}}$ corresponding to a continuous discharge mode (i.e., quasi-steady-state mode). Traces of the applied voltage and the corresponding current discharges for (b) the ultra-short AP-DBD pulses at a frequency of 1000 Hz ($t_{\text{off}} = 1$ ms) and (c) the sine wave-excited AP-DBD (i.e., quasi-steady-state mode)

TABLE 3 Description of the significant parameters used in PPM calculations

Parameters	Description	Parameters	Description
t_{on} (s)	Plasma on-time, fixed around 100 ns	$[M\bullet]_{\text{max}}$ (mol · L ⁻¹)	Radical concentration at the end of the plasma on-time (t_{on})
t_{off} (s)	Plasma off-time, variable between 100 μs and 100 ms	$[M\bullet]_{\text{min}}$ (mol · L ⁻¹)	Radical concentration at the end of the plasma off-time (t_{off})
τ (s)	Average lifetime of a growing radical	R_p (mol · L ⁻¹ · s ⁻¹)	Molecular propagation rate
DC	Duty cycle of the pulse	DR (m · s ⁻¹)	Deposition rate

radical ratios $[M\bullet]_{\text{max}}/[M\bullet]_{\text{qs}}$ (Eq. 4) and $[M\bullet]_{\text{min}}/[M\bullet]_{\text{qs}}$ (Eq. 5) can be individually developed.

adjusting τ_{qs} , providing information on the radical lifetime, the radical conversion ratios for both the MMA (Figure 4a)

$$\frac{[M\bullet]_{\text{max}}}{[M\bullet]_{\text{qs}}} = \frac{-\left[\frac{t_{\text{off}}}{\tau_s} (1 - e^{2t_{\text{on}}/\tau_s}) \pm \sqrt{\left[\frac{t_{\text{off}}}{\tau_s} (1 - e^{2t_{\text{on}}/\tau_s})\right]^2 - 4\left(\left[e^{2t_{\text{on}}/\tau_{s-1}}\right] + \frac{t_{\text{off}}}{\tau_s} (e^{2t_{\text{on}}/\tau_s + 1})\right) * (1 - e^{2t_{\text{on}}/\tau_s})}\right]}{2\left[\left(e^{2t_{\text{on}}/\tau_{s-1}}\right) + \frac{t_{\text{off}}}{\tau_s} (e^{2t_{\text{on}}/\tau_s + 1})\right]} \quad (4)$$

$$\frac{[M\bullet]_{\text{min}}}{[M\bullet]_{\text{qs}}} = \frac{-\left[\frac{t_{\text{off}}}{\tau_s} (1 - e^{2t_{\text{on}}/\tau_{s-1}}) \pm \sqrt{\left[\frac{t_{\text{off}}}{\tau_s} (e^{2t_{\text{on}}/\tau_{s-1}})\right]^2 - 4\left(\left[e^{2t_{\text{on}}/\tau_{s-1}}\right] - \frac{t_{\text{off}}}{\tau_s} (e^{2t_{\text{on}}/\tau_s + 1})\right) * (1 - e^{2t_{\text{on}}/\tau_s})}\right]}{2\left[\left(e^{2t_{\text{on}}/\tau_{s-1}}\right) + \frac{t_{\text{off}}}{\tau_s} (e^{2t_{\text{on}}/\tau_s + 1})\right]} \quad (5)$$

Assuming that the thin films' density does not change too significantly from low to high frequencies, the $R_p/R_{p,\text{qs}}$ ratio can be correlated to the deposition rate ratio $\text{DR}/\text{DR}_{\text{qs}}$. This ratio can be theoretically evaluated from Eq. (2) at a given τ_{qs} and experimentally calculated from the measured thin film deposition rates according to the frequency. Although, one has to be cautious before making any comparison, as the model ratio $(\text{DR}/\text{DR}_{\text{qs}})_{\text{PPM}}$ needs to take into account the τ_{qs} , which is dependent on the conversion ratios (Eq. 6) and the experimental ratio $(\text{DR}/\text{DR}_{\text{qs}})_{\text{exp}}$ has to be reduced to one pulse for both terms of the division (Eq. 7).

and GMA cases (Figure 4b) as well as the kinetic ratio k_p/k_t from Eq. (3). The data extracted from the application of the PPM to MMA and GMA are summarized in Table 4.

As expected from the studied frequency range, the maximum conversion rates from monomer to radical with the ultra-short plasma discharge is quite high (ca. 5 and 20% for MMA and GMA, respectively, for $t_{\text{on}} \approx 100$ ns), highlighting the potential of ultrashort plasma pulses to effectively initiate a free-radical polymerization of vinyl monomer even for low DCs. When these data are normalized to the time, this range of value is comparable to PLP experiments (ca. 2–3% at $t_{\text{on}} \approx 10$ ns),^[34] hinting on a linear influence of the activation time on the conversion

$$\left(\frac{\text{DR}}{\text{DR}_{\text{qs}}}\right)_{\text{PPM}} = \frac{[M\bullet]_{\text{max}} - [M\bullet]_{\text{min}}}{[M\bullet]_{\text{qs}}} \text{DC} \left[1 + \frac{\tau_{\text{qs}}}{t_{\text{on}}} \ln \left(\frac{[M\bullet]_{\text{max}}/[M\bullet]_{\text{min}} + [M\bullet]_{\text{max}}/[M\bullet]_{\text{qs}}}{1 + [M\bullet]_{\text{max}}/[M\bullet]_{\text{qs}}} \right)\right] \quad (6)$$

$$\left(\frac{\text{DR}}{\text{DR}_{\text{qs}}}\right)_{\text{exp}} = \frac{\text{DC}}{\text{DC}_{\text{qs}}} * \frac{\text{DR}}{\text{DR}_{\text{qs}}} \quad (7)$$

Ultimately, the converted experimental data (Eq. 7) can be fitted with the proposed theoretical function (Eq. 6) by

ratio. In addition, the strong effect of the plasma off-time on the radical species concentration after each cycle (Table 4) is coherent with the assumption that a suitable t_{off} is not only important but essential. Interestingly, expanding the range of the theoretical calculations for ultra-short pulses (ca. 100 ns) shows that both $[M\bullet]_{\text{min}}/[M\bullet]_{\text{qs}}$ and $[M\bullet]_{\text{max}}/[M\bullet]_{\text{qs}}$ steadily increase with the discharge frequency, until

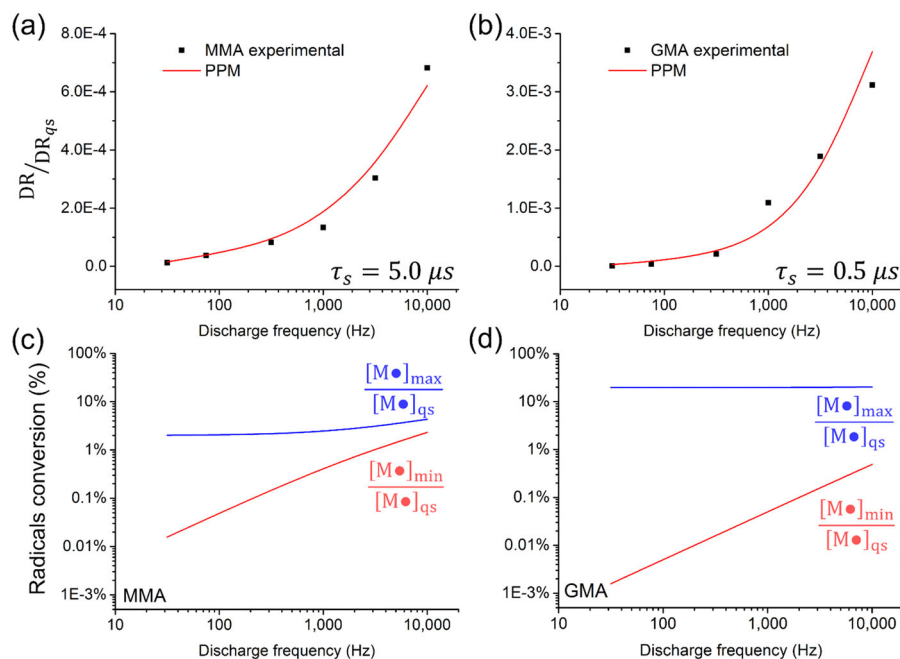


FIGURE 4 (a,b) Experimental DR/DR_{qs} data for the MMA and GMA thin films grown at various pulsed plasma frequencies ($t_{on} = 100$ ns) and their fitting with the PPM model. The calculated steady-state radical lifetime τ_s is provided for each monomer for the conditions investigated, along with (c,d) their theoretical radical conversion ratios $[M\bullet]_{max}/[M\bullet]_{qs}$ and $[M\bullet]_{min}/[M\bullet]_{qs}$ following each plasma discharge and each pulse cycle, respectively

they reach a quasi-steady-state at 10 MHz when the DC_{qs} tend toward 1 (Figure S4a). On the other hand, the discharges' duration in AP-DBD ignited using a sinusoidal excitation (ca. $10 \mu s$ per sinusoid) yields a constant amount of initiation $[M\bullet]_{max}$, independently of the plasma off-time, suggesting a complete conversion of the gas phase for each plasma discharge (Figure S4b). This correlates with the ratios of conversion being highly affected by the time of discharge, hence the necessity to reduce the plasma on-time to prevent the excessive and detrimental alteration and depletion of the monomer. Furthermore, using a $10 \mu s$ long discharge, $[M_{(g)}\bullet]_{qs,max}$ is independent of the considered plasma off-time indicating a conversion ratio per discharge of 100%. Following that assumption, the radical ratios become conversion percentages and may be used to describe our system's non-steady kinetic at any frequency.

3.3 | Non-steady kinetic of open-volume pulsed plasma discharges

If the steady-state assumption cannot be verified at any given time for pulsed plasmas, it is still valid when the mechanisms are considered over a full discharge cycle (Figure 3a). As such, taking in consideration the contribution of each mechanism to the total amount of radicals (Table 2), the kinetic rates over the time span of one cycle can be related to each other (Eq. 8). Using the propagation rate equation ($R_p = k_p[M_{(g)}][M_{(g)}\bullet]$), Eq. (8) can be expressed as a second-order polynomial function of the propagation rate R_p versus the initiation rate R_i (Eq. 9), independently of the radical concentration $[M\bullet]$. As such, based on the PPM model, it is possible to mathematically express the theoretical rate of initiation during one discharge $R_{i,gas}$ (Eq. 10) as well as the converted experimental radical consumption per discharge

TABLE 4 Pulsed Plasma Model parameters extracted from the experimental fitting

Parameters	MMA		GMA	
$[M_{(g)}]$ ($\text{mol} \cdot \text{L}^{-1}$)	$1.95 \cdot 10^{-5}$		$1.31 \cdot 10^{-5}$	
τ_s (μs)	5.00		0.50	
k_p/k_t	$3.36 \cdot 10^{-6}$		$1.92 \cdot 10^{-7}$	
$[M\bullet]_{max}/[M\bullet]_{qs}$	$f = 31.6 \text{ Hz } 2.02\%$	$f = 10\,000 \text{ Hz } 4.31\%$	$f = 31.6 \text{ Hz } 19.74\%$	$f = 10\,000 \text{ Hz } 20.21\%$
$[M\bullet]_{min}/[M\bullet]_{qs}$	$f = 31.6 \text{ Hz } 1.57 \cdot 10^{-4}\%$	$f = 10\,000 \text{ Hz } 2.32\%$	$f = 31.6 \text{ Hz } 1.58 \cdot 10^{-5}\%$	$f = 10\,000 \text{ Hz } 0.49\%$

$R_{p,surface}$ (Eq. 11), relating the gas phase mechanisms to the surface reactivity.

$$\frac{d[M\bullet]}{dt} = R_i^* - R_t - R_{tr} = R_i^* - k_t[M\bullet]^2 \pm k_{tr}[AX][M\bullet] = 0 \quad (8)$$

$$R_i^* = \frac{k_t}{k_p^2} \frac{1}{[M_{(g)}]^2} R_p^2 \pm \frac{k_{tr}}{k_p} \frac{[AX_{(g)}]}{[M_{(g)}]} R_p \quad (9)$$

$$R_{i,gas} = \frac{DC}{t_{on}} * \frac{[M\bullet]_{max} - [M\bullet]_{min}}{[M\bullet]_{qs}} * [M_{(g)}] \quad (10)$$

$$R_{p,surface} = DC * \frac{DR * \rho_{poly,M}}{h_{medium} * \rho_{vap,M}} * [M_{(g)}] \quad (11)$$

From Eqs. (10 and 11), the plot of $R_{i,gas}$ versus $R_{p,surface}$ can be fitted with a simple quadratic function (Figure 5) and the kinetic constants (i.e., k_t/k_p^2 and $k_{tr}/k_p * [X]$) extracted from the fitting. Although, one should be careful of the working frequency range, as fitting the kinetic rates below the transition frequency from predominant gas phase mechanisms to predominant surface mechanisms (Figure 1a) yielded for both monomers a negative value for the second-

degree parameter of the polynomial (i.e., related to the conventional termination rate R_t) (Figure 5). This can be explained by the fact that surface mechanisms and the kinetic of adsorption are preponderant below this threshold and, since the PPM model describes the gas phase polymerization mechanisms, it leads to a global deviation of the curve tendency. However, the effect on the kinetic parameters' absolute values is globally quite low (ca. two times higher or lower) compared to the orders of magnitude considered, as confirmed by a third methacrylate monomer (butyl methacrylate) (Figure S5). Therefore, MMA's second degree fit parameter will be considered as positive in further discussions. No assumption will be made on the sign of the polynomial's first-degree parameter since both initiation and termination are possible by chain transfer depending on who is acting as the transfer agent.

Using the k_t/k_p values obtained from the PPM calculations and the quadratic fit parameters, all kinetic constants can be calculated for both MMA and GMA, aside from the fragmentation and initiation constants k_f and k_i^* , which depend on the plasma power output. Interestingly, when the electrode gap is considered as the reaction medium (i.e., $h_{medium} = 1$ mm), the constant of propagation k_p is much lower than the ones known in wet chemistry (Table 1), 0.015 and $0.052 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for MMA and GMA respectively. This is

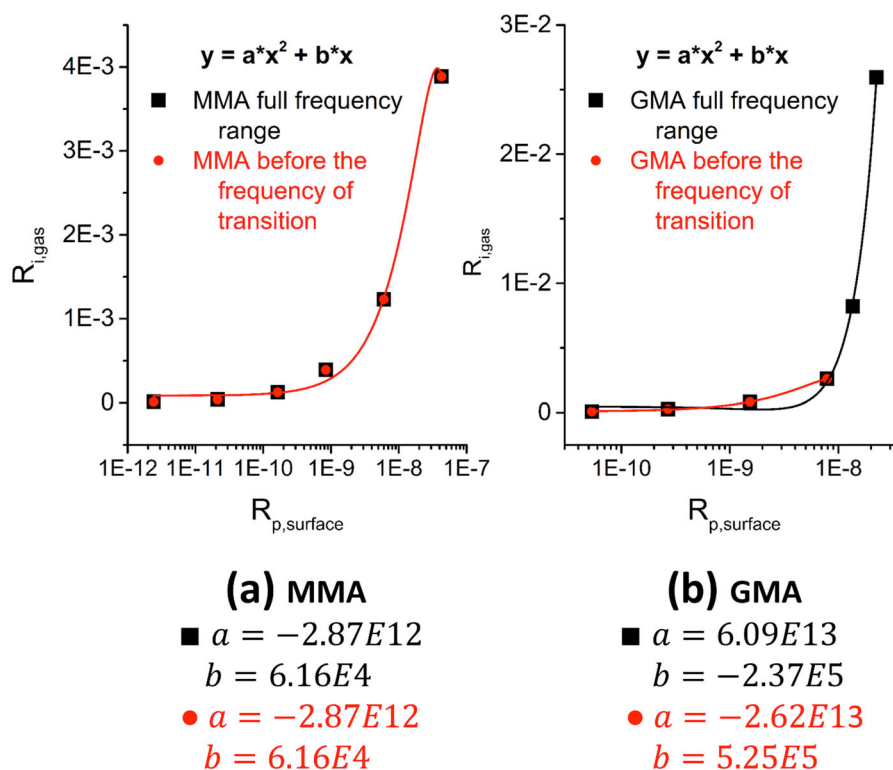


FIGURE 5 Second order polynomial fitting of the theoretical initiation rate $R_{i,gas}$ according to the experimental propagation rate $R_{p,surface}$ for (a) MMA and (b) GMA. The black solid curves are fitted over the complete range of frequency, while the red solid curves are fits realized before the frequency transition (i.e., $f \leq 10\,000$ Hz for MMA and $f \leq 1000$ Hz for GMA). The quadratic fit parameters are given in every case

coherent with the fact that not all the radical species formed within the discharge gap will contribute to the thin film growth as most of the formed reactive species will deactivate into the gas phase and be flushed away. Moreover, rather short radical lifetimes (ca. $\tau_s = 1 \mu\text{s}$) were calculated for steady-state conditions, in accordance with the lifetime of the argon species as determined by time-resolved optical emission spectroscopy (TR-OES) measurements (Figure S6).^[35] Then, in order to estimate the effective volume contributing to the thin film's growth, one can reverse the calculation using the theoretical value of the kinetic constant of propagation $k_{p,\text{theo}}$ reported in the literature (Table 1). This reactive volume h_{reactive} was shown to be rather similar between MMA and GMA, yielding distances in the range of several hundreds of nanometers (i.e., 0.5 and 0.2 μm , respectively). Interestingly, these distances do not match with obvious physical constants related to the plasma discharge, such as the mean free path of the molecules ($\leq 0.05 \mu\text{m}$) or the plasma sheath ($\geq 100 \mu\text{m}$), which only represents a small fraction of the deposition. Still, calculating the time necessary for a molecule to diffuse through this reactive volume based on MMA's and GMA's molecular flux yields, which is approximately 60 μs , it can be observed that this value matches with the investigated range of plasma off-times. More interestingly, it can also be correlated with the

frequency threshold corresponding to the transition from conventional polymer to plasma-polymer determined from the evolution of the apparent molecular mass in weight obtained by size exclusion chromatography (Figure 6a)^[1] and supported by HRMS investigations (Figure S7).^[4] Very reasonably with plasma physic considerations, and in accordance with a previous mass spectrometry study on methacrylate thin films grown by PiCVD, the PPM model suggests that the shift from conventional free-radical polymerization growth to plasma-polymerization mechanisms is largely dependent of the monomer's exposure to several discharges (i.e., fragmentation) within the volume defined by h_{reactive} . Indeed, the amount of monomer species suffering several plasma-induced fragmentations during their traveling time increase exponentially with the discharge frequency (Figure 6b), stressing the requirement to temporally isolate the discharge and use appropriate plasma off-times.

While a quantitative solution of the kinetic parameters is possible but difficult to obtain based only on the SEC measurements (i.e., not being applicable to all monomers and requiring a very high number of points to find the exact transition frequency), the correlation between the experimental and theory suggests that qualitative information can be obtained on the different polymerization mechanisms. Therefore, every kinetic constants were calculated according to the exact reaction volume h_{reactive} previously determined from the theoretical propagation constant, $k_{p,\text{theo}}$ (Table 5). Consequently, the corresponding kinetic parameters give access to the complete kinetic rates R_i , R_p , R_t , and R_{tr} (Figure S8) and to the reactive concentration of species participating to each of the polymerization mechanisms during one discharge cycle (Figure 7). Each of the calculated concentrations is associated to its respective mechanism's lifetime (i.e., t_{on} for the initiation R_i , τ_{qs} for the fragment's transfer R_{tr} , and $t_{\text{on}} + t_{\text{off}}$ for the conventional propagation R_p and termination R_t rates) and taking into account that the MMA's and GMA's growing chains are fully deactivated after 10^[1] and 100 ms,^[2] respectively (Figure S9). The prevalence of transfer mechanisms for MMA and conventional terminations for GMA is strongly linked to the monomer fragmentation upon plasma exposure. A previous study showed that the MMA molecule was statistically broken down by the high energy species (Figure 1d), generating

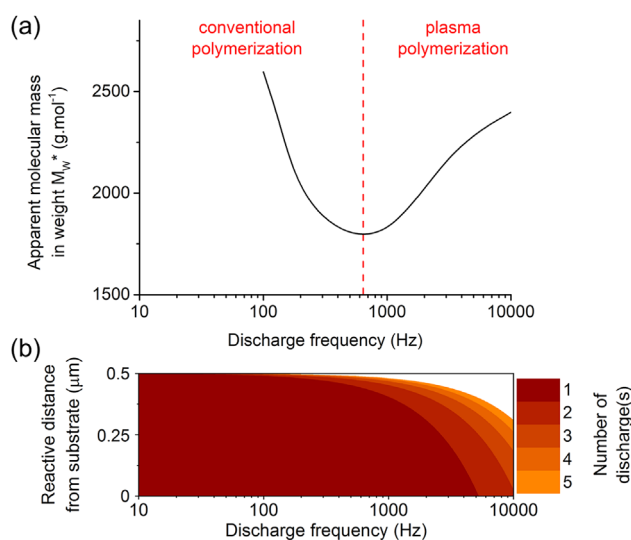


FIGURE 6 (a) MMA's apparent molecular mass in weight M_w^* from SEC measurements. Below the predominant mechanism transition frequency, decrease of the ultra-short plasma pulses frequency yields higher molecular mass due to a strongly favored free-radical polymerization pathway such as evidenced by HRMS (Figure S7).^[4] On the other hand, increase of the frequency above the transition frequency favors dissociation and recombination reactions that form crosslinked plasma-polymers that exhibit increasing apparent molecular masses due to the shorter elution time of these three-dimensional structures.^[1] (b) Spatial distribution of the number of discharge(s) per molecule depending on its position within the reactive volume h_{reactive} and the discharge frequency

TABLE 5 Kinetic parameters calculated from the PPM model and experimental data using a reactive volume (h_{reactive}) of 0.5 and 0.2 μm for MMA and GMA, respectively, calculated from the theoretical kinetic constant of propagation $k_{p,\text{theo}}$

Parameters	MMA	GMA
$k_{p,\text{theo}}^{[19]} (\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$	$2.74 \cdot 10^2$	$4.94 \cdot 10^2$
$k_t (\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$	$4.08 \cdot 10^7$	$1.29 \cdot 10^9$
$k_{tr}^*[\text{AX}] (\text{s}^{-1})$	$1.13 \cdot 10^3$	$1.54 \cdot 10^3$

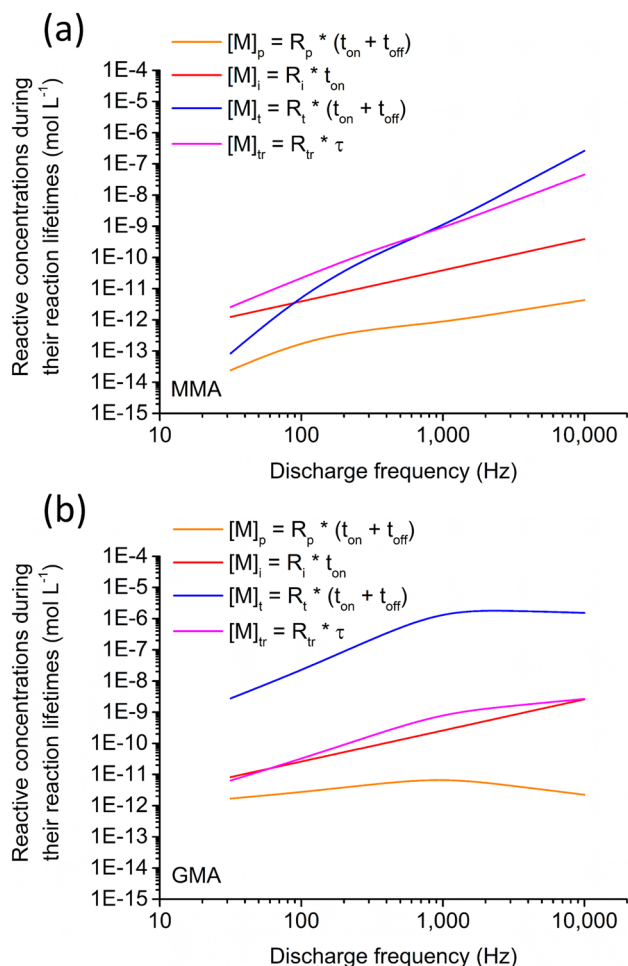


FIGURE 7 Calculated reactive concentrations for each of the polymerization mechanisms (i.e., propagation, initiation, termination, and chain-transfer) for (a) MMA and (b) GMA, derived from their kinetic rate and lifetime over one discharge cycle

numerous compounds able to initiate or terminate the polymerization reaction.^[4] On the other hand, GMA was effectively protected from this random fragmentation by the low energy epoxy function acting as a chemical buffer (Figure 1d).^[4] As a result, their difference in chain transfer reactions is certainly related to the amount of chain transfer agents (i.e., $[AX]_{MMA} \gg [AX]_{GMA}$), resulting from the molecular breakdown and affecting in inverse proportion both methacrylates' conventional terminations. Moreover, as one would expect, the concentrations of conventional initiators are increasing with the duty cycle, consistently with the amount of species remaining at the end of each pulse $[M\bullet]_{min}$ (Figure 4c,d).

Ultimately, both the initiation rate derived from the PPM model and the propagation rate extracted from the experimental deposition rate relate to the reactions occurring in the gas phase and on the surface (i.e., in the $h_{reactive}$ volume). In order to compare the two, it is possible to calculate the radical concentrations from the kinetic rate equations in the reactive volume (Eq. 12) and in the thin film (Eq. 13), which correspond to the amount of radical species available in the reactive volume and the amount of radical species having reacted, respectively.

$$[M\bullet]_{reactive} = \sqrt{\frac{R_i}{k_t}} = \sqrt{\frac{R_i + R_{tr}}{k_t}} \quad (12)$$

$$[M\bullet]_{reacted} = \frac{R_p}{k_p[M]_g} \quad (13)$$

To gain a better understanding of the reactivity in the thin film's reactive volume, the ratio between radicals reacted (Eq. 13) (i.e., that adsorb and polymerize on the surface) and radicals created (Eq. 12) can be plotted according to the ultra-short plasma pulses frequency (Figure 8b). Strikingly,

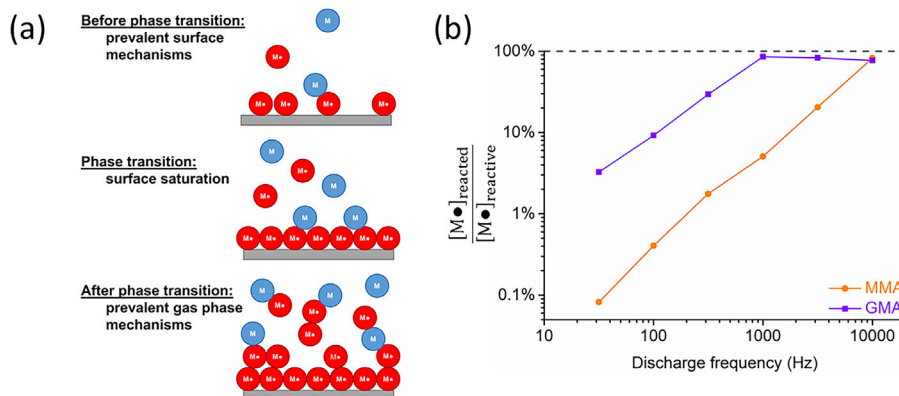


FIGURE 8 (a) Scheme of the transition between surface and gas phase mechanisms due to an excess of reactive species adsorbed on the substrate. (b) Ratio between the concentration of radical reacted $[M\bullet]_{surface}$ over the concentration of radical created $[M\bullet]_{reactive}$ according to the frequency for MMA and GMA

GMA's percentage of radical reactivity steadily increases with the frequency until it saturates at 1000 Hz, while MMA is saturating at 10 000 Hz. Those behaviors perfectly correlate with the deposition rates tendencies and the topographic observations done by SEM (Figure 1a,c), highlighting the transition from preponderant surface mechanisms to preponderant gas phase mechanisms. This additional information based on both experimental and theoretical data confirms the nature of this transition as a saturation of the reactive species on the surface when the radicals cannot adsorb anymore and the reactivity reaches 100% (Figure 8a). Indeed, GMA's low vapor pressure implies that the surface would be more prone to saturate from an excess of reactive species from the gas phase. On the other hand, MMA does not reach its saturation level for the investigated deposition conditions, since it has low adsorption due to its high vapor pressure. Ultimately, due to the apparent linear evolution of the reactivity percentage compared to the discharge frequency plotted in $\log_{10}$ in both axes (Figure 8b), one does not need to reach or even get close to the saturation threshold to extract this information by a simple linear extrapolation.

4 | CONCLUSION

From deposition rate measurements, chemical analyses and morphological characterizations of two methacrylate thin films grown using ultra-short plasma pulses, a kinetic model called pulsed plasma model (PPM) describing the competition between the various mechanisms implied in the growth of thin films using ultra-short plasma pulses was developed. Notably, the investigations confirm the significance of using ultra-short plasma pulses to effectively initiate the free-radical polymerization of vinyl monomers, while considerably minimizing the drawbacks related to the use of plasma. In addition, interpretation of the experimental data with the PPM model have highlighted the strong discrepancies between the two investigated methacrylate monomers in term of termination mechanisms. Such an observation also correlated with the behaviors previously highlighted from experimental investigations^[1] and theoretical studies.^[4] Indeed, MMA displayed a pronounced level of fragmentation during the ultra-short plasma discharge ($t_{on} = 100$ ns), resulting in a high amount of fragmented chemical species than can act as terminating chain-transfer elements and rapidly passivate the growing oligomer chains. Consequently, this mechanism has a strong influence on the growth of the polymer thin film because it interrupts the free-radical polymerization mechanism and limits the polymeric length of the MMA-based thin films (Figure 1b). On the other hand, GMA displayed a low level of monomer fragmentation during the pulse discharge, which yielded an extremely high degree of conventional termination mechanisms directly reflected on its physico-chemical properties (Figure 1). Furthermore, the PPM model allowed to determine

a reactive distance h_{reactive} around 0.35 μm for both methacrylate monomers, highlighting the real volume participating to the thin film's polymerization under the studied conditions. Also, by associating the molar fluxes to this calculated distance, a molecular transit time has been estimated which matches with the experimental frequency threshold corresponding to the transition between conventional free-radical polymerization and plasma-polymerization mechanisms.^[1] Finally, the saturation of reactive species on the surface could be evidenced based on the PPM model calculations and the experimental growth rate of the monomers, highlighting the key role of adsorption mechanisms in the PiCVD process and the necessity to optimize the P_M/P_{sat} ratio. Ultimately, the development of a non-steady kinetic model for pulsed plasma processes highlighted the need of using temporally isolated plasma on-times (i.e., tens to hundreds of nanoseconds) in combination with plasma off-times in accordance with the adsorbed free-radicals lifetime (i.e., tens or hundreds of milliseconds) to promote the growth of conventional polymers in thin film form. The thin film growth, driven by the creation of free-radical by ultra-short plasma pulses and their subsequent adsorption and polymerization with unaltered monomers on the substrate surface, yields the formation of smooth and conformal polymer thin films that retain the properties and functionalities of their counterparts synthesized by solution-based approaches. The AP-PiCVD approach, which was notably already successfully employed for the growth of char-forming polymer layers^[31] or the growth of water-stable thermoresponsive layers,^[36] is currently investigated in a broad range of applications of polymers.

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ORCID

François Loyer  <http://orcid.org/0000-0002-5636-3885>
 Simon Bulou  <http://orcid.org/0000-0003-3750-6235>
 Patrick Choquet  <http://orcid.org/0000-0001-8696-5812>
 Nicolas D. Boscher  <http://orcid.org/0000-0003-3693-6866>

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